

**Environmentally Friendly Packaging Materials from
Renewable Resources as Alternatives for
Oil-based Polymers**

by

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ABSTRACT

Nearly 60 m tonnes of waste is produced annually in Europe from “plastic packaging” engendering significant challenges for legislative controls and minimisation of environmental impact. There is an increasing demand for biodegradable packaging, which can be disposed of with minimum environmental impact, but the growing market is still in its infancy predominantly due to a lack of materials having environmental, practical and economic suitability. This research project dealt with some processing challenges of environmentally friendly packaging materials from renewable resources, as a long term solution to mitigate some issues associated with oil based plastic packaging.

In this work, novel Polylactic acid (PLA) and starch based composites were developed with the requisite technical properties to fill the gap in the food packaging and cosmetic packaging industry. It was found that starch can be incorporated in a PLA matrix at the 10% level without difficulty in processing in the presence of 2% methyldiphenyl diisocyanate. The blend shows properties similar to pure PLA. It was also found that the elongation at break and impact properties of PLA can be increased remarkably by the addition of a biostrength impact modifier. Furthermore, mixing of PLA and starch in the blend is efficient when the PLA particle size is reduced. It was also found that flexible and tougher PLA/starch blend pellets, that can be injection moulded, can be produced by an extrusion process with a range of additives. Each additive has a maximum level that exhibits optimum properties. The blends also established that 15% starch can be incorporated into the PLA matrix to reduce the cost without any processing difficulties.

Encouragingly, the presence of an impact modifier in the PLA/starch blends has shown more desirable properties. Furthermore, the mechanical properties of the pellets exposed to increased residence time in the injection moulding barrel and of the test specimens stored for 9 months at 21⁰C were also satisfactory for the new blend. The overall results exhibited some attractive properties in the tri blend system, which can be easily adopted by the plastics industry for development of an injection moulded product within the scope of applications such as dry food packaging or cosmetic packaging. A further finding of this project is that biodegradation under a home composting environment can be improved by incorporating starch and certain other modifiers into PLA.

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LIST OF ABBREVIATIONS

Abbreviation	Explanation
AA	Adipic Acid
ABS	Acrylonitrile Butadiene Styrene
ATC	Acetyl triethyl citrate
DOM	Diethyl maleate
DIH	1,6 diisocyanato hexane
EU	European Union
FTIR	Fourier Transform Infra-Red Spectroscopy
GMO	Genetically modified organisms
IM	Impact modifier
MA	Maleic anhydride
MBS	Methylene-Butadiene-Styrene
MDI	Methylenediphenyl diisocyanate
MS	Melt strength
MSDS	Material Safety Data Sheet
PB	Polybutadiene
PC	Polycarbonate
PCL	Poly-caprolactone
PDLA	Poly-D-Lactic acid
PE	Polyethylene
PEG	Polyethylene glycol
PET	Polyethylene Terephthalate
PHB	Poly-hydroxybutyrate
PLA	Polylactic acid
PLE 005=PLAn	GMO free PLA
PLLA	Poly-L-Lactic acid
PNS	Pitachio Nut Shell
PP	Polypropylene
PPG	Polypropylene glycol
PS	Polystyrene
PVC	Polyvinyl chloride
PVA	Polyvinyl alcohol
PVOH	Polyvinyl alcohol
PU	Polyurethane
SA	Stearic Acid
SBR	Styrene butadiene rubber
TC	Triethyl citrate
TDI	Toluene diisocyanate
UV	Ultra violet radiation

Executive summary

The following section of the current research communication is an executive summary of the Doctor of Philosophy (PhD) research project '**Environmentally Friendly Packaging Materials from Renewable Resources as Alternatives for Oil-based Polymers**' conducted in the Wolfson Centre - Centre of Materials and Centre for Phosphors and Display Materials.

1. Background of the PhD Programme in the Wolfson Centre

This section provides a brief introduction to the PhD Programme and describes the overall structure of the research work included in the current thesis.

The Doctor of Philosophy programme (PhD) at the Wolfson Centre is a three year research degree awarded for a research topic of industrial and/or academic interest, based in the Brunel University and also supported by research meeting presentations and an optional programme of core skills development workshops conducted by the graduate school of the Brunel University. The professional development is further extended with undergraduate and foundation degree teaching assistance with programmes of Academic Practice Development Courses accredited by Higher Education Academy (HEA).

Core skills development workshops are mainly focusing on the key areas of Communication, Organisation, Research and Enterprise. The workshops also aim to:

- Provide information to fill any gaps in the knowledge required to undertake the research
- Provide professional development in key management skills and competencies.

The Core skills development workshops successfully taken during this research are as follows.

1. First stage research module
2. Mid stage research module
3. Final stage research module
4. Poster presentations
5. Thesis writing stage 1-4
6. Referencing with Refworks
7. Poster and oral presentations
8. Management skills for researchers
9. Preparing for viva
10. Influencing and leadership skills
11. Writing successful research grant proposals
12. Developing an academic career
13. Project Management
14. Getting Published in the Sciences

Academic Practice Development Courses successfully completed during this research are as follows.

1. Graduate Teaching Assistants' workshop
2. Making a successful research grant proposal
3. Developing a research career
4. A module designing

5. Brunel Associate Practitioners Pathway (BAPP) in Learning and Teaching in Higher Education course- 1 year part time

- Sessions attended

From Syllabus to session

Effective large group teaching

Small group teaching

Blended learning and U-Link

Presentation skills

The student experience

Assessments for learning

Feedback for learning

Student supervision (Supervising projects and dissertations)

Managing student teamwork

Monitoring and evaluation

- Oral presentation to a knowledgeable audience on a given academic practice topic
- A written assignment including teaching observation and self reflection of the teaching

The successful completion of BAPP course grants Associate Fellow Status of the Higher Education Academy (HEA).

The PhD researchers also present their research at the annual conferences, which are attended by all PhD researchers, supervisors, academics and invited delegates. Presenting at the conferences offers opportunity to raise awareness, understanding and prospect of discussing with other academics with issues and possible alternative paths of the research

topic. Based on the research conducted in the presented thesis, the following paper and posters were written, published and presented.

Manjula Silva, Karnik Tarverdi, Robert Withnall, Jack Silver, *Renewable materials for biodegradable packaging (Poster)*, Bioplastic conference in UK, Society of Chemistry and Industry and Loughborough University, 9th April 2009

Vice Chancellors Prize 2009

Manjula Silva, Karnik Tarverdi, Robert Withnall, Jack Silver, *Processing and properties of materials from renewable and sustainable resources (Poster)*, Graduate school poster conference, Brunel University, 6-7 May 2009.

K. Manjula D Silva, Karnik Tarverdi, Robert Withnall, Jack Silver, *Materials from renewable resources for packaging applications: Polylactic acid and starch(Paper)*, Rescon 09, Brunel University, 22-24 June 2009

Vice Chancellors Prize 2010 and 3rd place at the Rescon 2010

Manjula Silva, K.Tarverdi, R.Withnall, J.Silver, *Solution for pollution: biodegradable and renewable materials for plastic packaging (Poster)*, Graduate school poster conference, Brunel University, 5-6 May 2010.

The PhD candidates also present their research at the annual international conferences. From the research conducted in this thesis, following posters were written and presented.

2nd Place

Kodikara Manjula Dilkushi Silva, *A bio-based polymer composite from renewable and sustainable resources(Poster)*, Global Plastic Environmental Conference, Society of Plastic Engineers, Florida, USA, 8-10 March 2010.

Kodikara Manjula Dilkushi Silva, R. Withnall, K Tarverdi, *Fututre plastics beyond petroleum based polymers(Poster)*, Annual Technical Conference (ANTEC), Society of Plastic Engineers, Boston, USA, 1-5 May 2011

2. Introduction to the research topic

This section summarises the PhD project and the objectives. A more meticulous clarification of the research can be found in chapters 1 and 2.

The food packaging industry is growing at a rate of 12 % per year and is a global industry having a market share of nearly 40% of the packaging market, and increasingly favouring polymer based materials by replacing most conventional packaging materials. Consequently, production of extensive amount of waste annually from “plastic packaging” raises significant challenges for legislative constraint and the management of environmental impact. The packaging industry must look at solutions such as reduce and reuse concepts to reduce environmental impact by waste reduction during processing and production of petroleum based or non petroleum based packaging, as an immediate short term solution. Meanwhile, green campaigners, government, and most food retailers are all now demanding biodegradable packaging, which can be disposed of with a minimum of environmental impact. This drive challenges the research and development community to find a sustainable solution using alternative materials from renewable resources, to oil-based polymers that meet environmental and functional requirements whilst being economically viable.

This PhD research aims to deal with the problems associated in the context of processing of biodegradable material and aims to find potential solutions for the production of biodegradable composite material for the packaging industry.

Although there are a number of biodegradable polymers available on the market, the industry is still in its early stage. The market has yet to move forward with commercially and environmentally feasible materials that are used for food and cosmetic packaging and therefore, more research and development is necessary.

3. Research objectives

There were seven prime aims of the research carried out during PhD.

- To perform experimental extrusion and injection moulding trials within current processes and principally study how the incorporation of starch into the polylactic acid (PLA) matrix affects its processing, thermal behaviour, and mechanical properties.
- To understand and investigate how the addition of different additives to PLA and starch blends influences the current extrusion and injection moulding processes, as well as their thermal and mechanical properties.
- To study how starch and additive concentrations influence the blend properties.
- To identify minimum or optimum levels of additives within investigated limits that could confer substantially good properties to the blend systems.
- To reduce waste by improving material utilization within the current injection moulding process by experimentally investigating how the residence time of the material in the injection moulding barrel has an effect on its mechanical properties.
- To investigate mechanical properties upon physical ageing and the extent of biodegradation that may occur when various blended material are disposed of

under domestic (home) composting conditions. Studies were conducted on test samples and assessed by visual observation.

- To develop an alternative material for oil based polymers that can be made from PLA and renewable resource such as starch, with the following properties: high impact strength, high elongation, biodegradable and compostable and are suitable for injection moulding and dry foodstuff or cosmetic packaging.

4. Research methodology

This research project focused on six paths of investigations, all of which are bounded with the initial objective to develop a novel PLA-starch based composite that would provide satisfactory processing needs and improved properties together with environmental requirements to reduce pollution and economic requirements for the material cost.

Current manufacturing equipments were utilised for the process and the investigation of the required specifications and properties for food packaging materials were examined. A literature review of existing research on biodegradable polymers and PLA/starch blends was conducted. A thorough knowledge and understanding and practical insight into the feasibility of suggested future biodegradable polymers was obtained from the literature and a deep understanding based on the following important areas was also obtained.

Environmental impact of plastics

Biopolymers

Plastics from renewable resources

Starch based biopolymers

Starch derived biopolymers

PLA and starch composites

From the literature, the most successful research development of PLA and starch blend with 0.5% methyldipheny diisocyanate (MDI) processed by compression moulding,

conducted by H. Wang and co-authors were laid as the foundation for further extension of the research. Six sub-projects were developed within a defined methodology.

The function of different additives on the properties of the PLA and wheat starch blends (Chapter 4)

Conventional processes were assessed with PLA and starch blends with a higher MDI level.

- Development of PLA and wheat starch blends with different starch levels by incorporating a fixed 2% MDI concentration on a laboratory scale
- Blends were prepared by extrusion and the pellets were injection moulded
- Characterization of the blend properties such as physical properties, mechanical properties and morphology
- PLA/starch/MDI and different glycerol levels were extruded to examine the physical behaviour, appearance and morphology and predominantly the processing.
- Material safety data (MSDS) investigation of MDI
- PLA/starch/SA blends were extruded to examine the processing, physical behaviour, appearance and morphology

The role of biostrength modifier materials on property variation of the blends (Chapter 5)

- A literature review of additives for biopolymers
- Evaluation of suitability of biomodifiers for PLA
- Development of PLA and wheat starch blend with 30% starch content in the presence of biomodifier materials by extrusion.
- Characterization of the blend properties

The effect of glycerol on the properties of PLA and wheat starch blends (Chapter 6)

- Established the baseline formulation of the materials based on PLA and starch blend with a plasticiser
- Carefully mastered the mixing and processing conditions to obtain optimum mechanical and physical properties

- Continuous extrusion to make pellets of the tri-blend system and injection moulding of pellets
- Characterisation of the blend properties and home composting trials

The influence of natural rubber latex on PLA and wheat starch processing and their blend properties (Chapter 7)

- A literature review of the natural rubber latex properties
- Baseline formulations of the PLA and starch blend in the presence of natural rubber phase were identified.
- Mixing and processing conditions were investigated to acquire optimum mechanical and physical properties by careful selection of the additive
- Extrusion and pelletization and injection moulding of the developed pellets
- Effect of residence time on mechanical properties and investigation of the other tri-blend properties

The consequence of adipic acid on the properties of PLA and wheat starch blends (Chapter 8)

- A literature review of the acid hydrolysis of starch
- Development of the formulations of PLA and starch blend with a mild organic acid.
- Optimised physical and mechanical properties by careful selection of the processing conditions and the acid concentrations
- Investigation of materials stability upon increased residence times in the moulding barrel
- Studies of the effect of the key additive on the mechanical and physical properties by extrusion trials, injection moulding trials and characterization of the materials.

The bioimpact modifier and pistachio nutshell with PLA and wheat starch blends (Chapter 9)

- Established the baseline formulation of the materials based on PLA and starch with a biomodifier
- Development of a novel PLA and starch based packaging material on a laboratory scale

- Optimisation of the physical and mechanical properties by careful selection of the processing conditions
- Investigation of material stability upon increased residence time in the moulding barrel
- Study of the effect of the modifier and PNS addition on mechanical and physical properties and home composting on the extruded and injection moulded pellets

5. Findings of the research

- The environmental impact of the conventional polymer based food packaging is of great concern to the consumers, green campaigners and importantly to the government. Beside the challenges of oil based polymer properties that are superior, the environmentally benign biodegradable material market is slowly developing due to the demand. However, it is in its infancy, with insufficient supply, primarily due to deficiency in materials that meet comparable performances and properties upon processing together with environmental and economical requirements.
- An extensive research work on packaging materials exist with new thoughts, direction, guidance but the use of biodegradable polymer materials are not clearly understood. Some important information such as mixing, processing is not available in the literature and research is still ongoing and therefore needs to be published with the wider access to the research community.
- Some previous publications show a few improvements in the properties of biodegradable materials, though they can not be easily adopted by an industry for a commercial application.
- Novel PLA and starch based composites with desirable physical and mechanical properties were manufactured on the laboratory scale with a range of additives. However, further studies needed to be carried out to optimise mechanical properties with some additives.

- A novel, very flexible and tougher composite based on PLA and starch in the presence of impact modifier with suitable physical and mechanical properties was manufactured on laboratory scale. The injection moulding trials and thermoforming trials of actual products can be conducted on the pellets to investigate suitability for real life applications.
- Material stability of the established formulations has been investigated and the effect of residence time of the pellets in the injection moulding barrel on the mechanical properties was established.
- The majority of published materials have focused into industrial composting due to the nature of the base matrix, which needs high temperature for biodegradation. Low temperature home composting environment trials of PLA and starch blend manufactured with glycerol have exhibited very positive degradation upon 12 weeks exposure even with 4 mm thick test samples.

6. Original contribution to knowledge

Of all the work of the current research, the particular aspects that are original contribution to the knowledge include:

- Processing of low cost composite based on starch and PLA materials by extrusion and injection moulding processes in the presence of higher MDI levels and glycerol, stearic acid and investigation of thermal and mechanical properties on a laboratory scale.
- Processing of low cost composite of PLA and starch materials by extrusion and injection moulding processes with the addition of biostrength modifiers at a laboratory scale and explore their thermal behaviour and mechanical properties.

- Incorporation of natural rubber latex into PLA and starch composite and processing of the resultant blends by conventional extruder and injection moulding machine to produce low cost composite with desirable properties.
- Blending of low cost starch material with PLA in the presence of adipic acid and processing under laboratory scale extrusion and injection moulding followed by examination of thermal and mechanical behaviour, rheology, ageing upon mechanical properties.
- Biobased materials are very sensitive to temperature and properties are vastly differing, leading to degradation. Therefore isothermal conditions were devised at processing temperatures. This showed any weight losses of the blends at the investigated process temperatures. As such, percentage weight loss upon temperatures can be assessed prior to actual injection moulding process.
- Some mitigating circumstances during actual mass scale production conditions lead the materials to remain in the injection moulding barrel for a longer period of time than expected, thus some delays in the actual injection moulding process may occur. These extended exposures of material at the elevated temperatures could dramatically influence the mechanical properties of the final product. The consequence is fundamentally and technically very important and therefore, tensile properties of the same blends were performed after the material was subjected to an increased residence time in the injection moulding machine. As such, the feasibility of the mechanical property loss of the material can be evaluated and the maximum time the material can be retained without any property loss can be identified.

7. List of publications

The initial experimental work of the research carried out during the current PhD programme has been published in a peer-reviewed journal.

K. Manjula Dilkushi Silva, K. Tarverdi, R. Withnall and J. Silver, *Incorporation of wheat starch and coupling agents into poly(lactic acid) to develop biodegradable composite*
Plastics, Rubber and Composites: Macromolecular Engineering, 2011, 40(1), 17-24

8. Structure of thesis

Executive summary

- Background to the project
- Research topic and objectives
- Research methodology
- Findings of the research
- Contribution to knowledge
- Publications

Chapter 1: Introduction

- Background motivation
- Research aims

Chapter 2: Literature review

- Environmental impact of plastics
- Introduction to biopolymers
- Plastics from renewable resources
- Starch based biopolymers
- Starch derived biopolymers
- PLA and the packaging industry
- PLA and starch composites
- Introduction to extrusion and injection moulding

Chapter 3: Experimental work

Experimental summary and materials
Preparation of PLA and wheat starch blends
Twin screw extrusion processing
Injection moulding of materials
Physical ageing
Differential scanning calorimetry
Thermogravimetric analysis
Determination of morphology
Water absorption
Fourier Transform Infra-Red Spectroscopy
Parallel plate rheometry
Degradation of the material
Domestic (home) composting

Chapter 4: The function of different additives on the properties of the PLA and wheat starch blends

Thermal behaviour
Dumbbell specimen appearance
Mechanical properties
Morphology
Water absorption
Chapter synopsis

Chapter 5: The role of biostrength modifier materials on property variation of the blends

Thermal behaviour
Investigation of phase transitions
Mechanical properties
The microstructure
Effect of physical aging on mechanical properties

Water absorption
Chapter summary

Chapter 6: The effects of glycerol on the properties of PLA and wheat starch blends

Decomposition by thermogravimetric analysis
Thermal behaviour
Mechanical properties
Micro structure
Fourier Transform Infrared Spectroscopic analysis
Home composting investigations
Chapter summary

Chapter 7: The influence of natural rubber latex on PLA and wheat starch processing and their blend properties

Analysis of thermal stability
Differential scanning calorimetric analysis
Rheological properties
Measurements of mechanical properties
Effect of storage on mechanical properties
Analysing microstructure
Vibration pattern
Chapter summary

Chapter 8: The consequence of adipic acid on the properties of PLA and wheat starch blends

Investigation of thermal behaviour and stability
Flow behaviour
Mechanical properties
Concept of physical ageing on mechanical properties
Morphology of the blends
FTIR spectra
Chapter synopsis

Chapter 9: The bioimpact modifier and pistachio nutshell with PLA and wheat starch blends

Thermal behaviour and material stability

Rheology of the blends

Mechanical properties of the blends

Measurements of ageing studies

Vibration pattern in the IR region

Scanning electron microscopic analysis

Water absorption measurements

Home composting trials

Chapter summary

Chapter 10: Conclusion and future directions

Conclusions of the overall results

Potential biodegradable blend from renewable resources to oil based polymers

Development of novel PLA-starch based composites

Recommendations for future directions

Contribution to knowledge

1 *CHAPTER ONE*

INTRODUCTION

1.1 Background motivation

Human life has been extensively and inseparably linked with plastic materials from the cradle due to the beneficial features of plastic and its products. The UK produces and consumes plastics for public requirements and it is estimated that approximately 2500 ktonnes of plastics produces in the UK annually, but UK's plastic processors consumes double the amount produce and remains of the top 5 processors of plastics in the EU with some 4.8 million tonnes of materials processed in the UK. Figure 1.1 presents how plastic consumption in the UK breaks down by application area. The food packaging industry, which is expanding at a rate of 12 % per year, is a global industry having a market share of approximately 40% of the total packaging market.

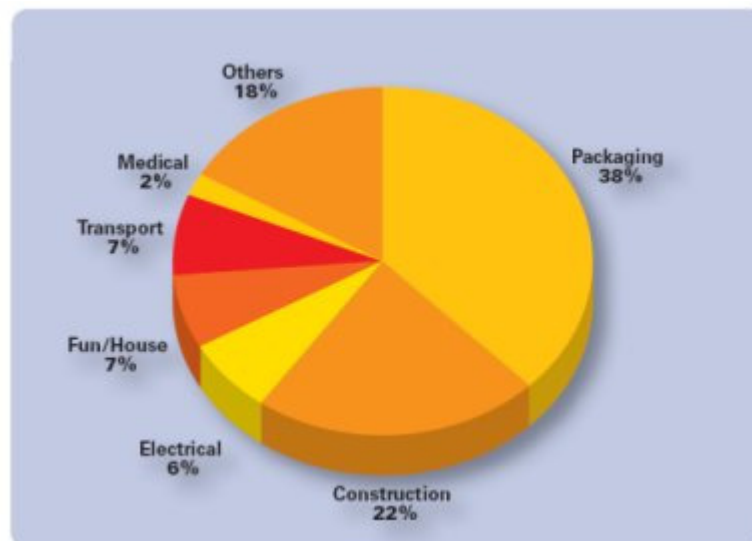


Figure 1.1 Plastic consumption in the UK by application (Web 1, accessed on 02.12.2010)

In everyday life, utilization of plastic materials in packaging has increased massively over the last thirty years since most of the consumer goods purchased come with a packaging. An extensive range of materials is being used for packaging applications, yet plastics are in the front line because of some significant features such as their light weight, anti-corrosive

properties and durability. The use of these plastics in packaging, which has continuously increased over the last twenty years to fulfill a consumer demand, has resulted in increased environmental issues such as increased emission of green house gases and an increased carbon foot prints. It has also resulted in the deposition of a large volume of plastic waste in rivers, sea and either in landfill or municipal waste recovery sites, where sorting and recovery are consuming energy and money. As a result, the plastic waste has also started to threaten living creatures. Harmful effects of fossil fuel based packaging waste have stretched to increase the death toll of sea animals and birds (Garlotta, 2001). While the trend is for polymer based packaging materials to replace most conventional materials, the consequence is that 60 m tonnes of waste is produced annually in Europe from “plastic packaging” engendering significant challenges for legislative controls and minimisation of environmental impact. The EU commission has published serious of environmental and economic concerns regarding waste disposal of PVC and Greenpeace (web 2, accessed on 20.10.2010) has categorised PVC, PU, PS, PC, ABS polymers in the high toxicity side of the poisonous plastics triangle whereas PET, PP and PE are in the low toxicity side, all of the polymers being categorised as oil-based polymers.

Over the time, our understanding has grown on the extent to which these fossil fuel based plastics has impact on human life. This has prompted industrialists, scientists and consumers to be concerned about ultimate consequences of discarding plastic products. Plastics can be recycled rather than being buried but limitations exist with different types of plastic products. Combining plastic products with natural systems has been identified as a potential solution to reduce their environmental impact. Many of the environmental challenges associated with packaging can only be resolved by a combination of industry, research institutes, and the government working together with a shared vision, along with consumer support for the excellence. Green campaigners, government, and most food retailers are all now demanding biodegradable packaging, which can be disposed of with minimum environmental impact. Therefore, continuous efforts in research and development are vital and the industry, government and the community need to welcome and embrace new developments.

There is less use of alternative materials derived from renewable resources, which are called bioplastics for many applications as they do not have comparable performance of commodity polymers. Processability and cost are the other major challenges for bioplastics to be able to compete with oil based polymers. Incorporation of fillers into biodegradable polymers like poly (lactic acid) (PLA), poly-caprolactone (PCL) and poly-hydroxybutyrate (PHB) give composites which have been identified as promising alternatives to petroleum based polymers. The basic building blocks of aliphatic polyester PLA are two stereoisomers L-lactic acid or D-lactic acid. These stereoisomers of lactic acid can be made commercially through carbohydrate fermentation technology. In other words, lactic acids are derived from bacterial fermentation of starch, mainly corn starch. Subsequently the desired isomer of lactic acid is polymerised into polylactic acid by different polymerization techniques such as condensation polymerization and ring opening polymerization. The product commonly called polylactide is derived from ring opening polymerization, and starts with lactide monomer, which is a cyclic dimer of lactic acid. PLA made from the direct condensation polymerization of lactic acid is called poly (lactic acid). Both these pathways of polymerization produce PLAs with similar mechanical properties (Wang, Sun & Seib, 2001).

Pure PLA can degrade slowly to carbon dioxide, methane, and water in the environment over a period of several months to 2 years, which compares with more than 500–1000 years for petroleum based plastics. PLA has many properties that are comparable to those of polyethylene, polypropylene, polystyrene, and polyethylene terephthalate, such as stiffness, tensile strength, and gas permeability (Auras, Harte & Selke, 2004). In the past few decades, the applications of PLA as a biodegradable polymer have mainly been limited to the biomedical field. However, ample production and supply of PLA to satisfy market demands have widened its applications. Therefore it has also been fabricated into a wide variety of consumer products, including compostable bags for waste, disposable table utensil, films and paper coatings, and has been spun into fiber and cloth. New applications of PLA as a short shelf-life food packaging polymer include some applications such as sundae and salad cups, drinking cups, lamination films and blister packages. Additives are also being developed today to improve some of the properties of PLA.

In general, natural polymers are hydrophilic as they contain a large number of hydroxyl groups and/or other polar groups and most synthetic polymers are hydrophobic or moisture resistant. Natural starch exists in a tiny, rigid, granular form and is mainly semicrystalline and has an abundance of hydroxyl groups. It has two major components amylose and amylopectine which are the main controlling parameters of starch properties. Amylose which is a straight chain polymer is present at the 20-30% level in starch where as the major fraction is branched amylopectin. Both PLA and starch derived from crops are completely biodegradable, therefore the composites of these polymers can be considered as biodegradable. Moreover, the introduction of low-cost starch as filler to PLA would result in a fully renewable biodegradable material. However, composites of hydrophobic PLA and hydrophilic starch do not have the processing and physical properties that are exhibited by fossil fuel derived polymers. In particular, some blends have poor mechanical properties, at high starch concentrations, because of weak interfacial attractions between starch particles and the PLA matrix.

The mechanical properties of a blend can be improved by the strong interfacial bonding between the filler and matrix. Reducing the interfacial tension and strengthening the interaction between polymer phases can transfer the internal stresses from the filler to the matrix and, consequently, enhance the strength of the blend. Strong interfacial adhesion can be achieved with the addition of a coupling agent to the blend system. A good coupling agent should have functional groups that react with both the matrix and filler. A few coupling agents with different reactive functional groups have been employed to couple starch and PLA. Methylenediphenyl diisocyanate (MDI), which is highly reactive with both hydroxyl and carboxyl groups able to form urethane linkages, could precisely be a good coupling agent between starch and PLA. Residues of untreated MDI are not expected in a blend because of the high reactivity of its isocyanate groups. In addition, the small amount of urethane linkages in the blend could be attacked by some fungi and absorbed by soil (Wang, Sun & Seib, 2001). Stearic acid, which also reacts with hydroxyl groups to form ester linkages, could also be a very good coupling agent for PLA and starch blends. On the other hand exposing the functional groups which are distributed in clusters in the filler

matrix could increase the natural bonding between polymer matrix and the filler. Some plasticizers could diffuse into the filler particles to expose reactive functional groups, thereby improving the bonding between polymer and the filler.

The purpose of this study is to determine some of the innovative and useful features of composites of biodegradable polymer and additives, and in particular, their mechanical properties, thermal behaviour, crystallization, microstructure, rheology, coupling behaviour, water absorption, and degradation behaviour. Furthermore, optimize the properties of these composites and to determine whether they have the potential to influence the future packaging industry.

1.2 Aims and Objectives

- To perform experimental extrusion and injection moulding trials within current processes and principally study how the incorporation of starch into the PLA matrix affects its processing, thermal behaviour, and mechanical properties.
- To understand and investigate how the addition of different additives to PLA and starch blends influences the current extrusion and injection moulding processes, as well as their thermal and mechanical properties.
- To study how starch and additive levels influence the blend properties.
- To identify minimum or optimum levels of additives within investigated limits that could confer substantially good properties to the blend systems.
- To improve material utilization within the current injection moulding process by experimentally investigating how the residence time of the material in the injection moulding barrel have an effect on its mechanical properties.

- To investigate mechanical properties of the blends upon physical ageing and extent of biodegradation that may occur when various blended materials are disposed of under domestic (home) composting conditions.
- To develop an alternative material to fuel based polymers that can be made from PLA and low cost renewable resource such as starch, with the following properties: high impact strength, elongation, biodegradable and compostable and suitable for injection moulding and packaging for dry foodstuff or cosmetic packaging.

2 CHAPTER TWO

LITERATURE REVIEW

2.1 Introduction

The theme of this research work was mainly based on biodegradable composites for packaging which are formed by addition of starch to a polymer matrix followed by coupling agents and plasticizers. A well known biodegradable polymer with versatile properties, obtained from renewable resources has been employed as the polymer matrix. The aforementioned polymer, known as Poly (lactic acid) (PLA) was widely studied but its commercial uses were restricted to biomedical applications due to biocompatible properties with the human body (Mohanty, Misra & Hinrichsen, 2000; Ikada & Tsuji, 2000; Mcmanus et al., 2000; Bleach et al., 2001; Tsuji & Sumida, 2001). Beside biocompatibility, its higher cost has immensely limited the initial focus on packaging. However, some opportunities are emerging in the field of packaging due to its versatile nature and comparable properties to most common synthetic petrochemical based polymers (Auras, Harte & Selke, 2004). Moreover, modern and emerging production technologies will lower the cost of PLA broadening the range of products in packaging applications (Lunt, 1998; Tsuji et al., 2000; Gruber & O'Brien.M., 2002). Incorporation of starch into biodegradable polymers like PLA (Wang, Sun & Seib, 2001; Jacobsen & Fritz, 1996; Jun, 2000; Ke & Sun, 2001b; Ke & Sun, 2003b; Zhang & Sun, 2004b; Zhang & Sun, 2004a; Zhang & Sun, 2004c; Huneault & Li, 2007), poly-caprolactone (PCL)(Koenig & Huang, 1995; Pranamuda, 1996; Shin et al., 2004; Dean et al., 2007) and poly-hydroxybutyrate (PHB) (Imam et al., 1998; Imam et al., 1999; Lai, Don & Huang, 2006; Zhang & Thomas, 2010) gives composites which have been studied as promising alternatives to petroleum based polymers. However, PLA/starch composites are not yet developed to a standard that could easily be adopted by industry. As the processing and mechanical properties of these composites reaches that of commercial polymers like PP or PE, more applications will be found where the reduction in cost and more environmentally friendly polymers are sought.

This literature survey contains a brief review of some of the environmental issues associated with plastics and some reviews of PLA, starch, and also starch with biodegradable polyester materials, in particular PLA-starch based bioplastics which were considered for this research. Although explicit information is available to understand other

materials such as PCL, PHB, Poly(vinyl alcohol)(PVA) which have also been used to develop compatible biodegradable composite, they were not considered to use in this study. Some of the additives that have been used with PLA/starch blends such as coupling agents or plasticizers are also reviewed. The polymer processing techniques that have used to process PLA/starch materials and research works in this area are then explored leading to the evolution of the concept of this research work. Literature related to the key conventional processing techniques for plastics, including extrusion and injection moulding processes which were also employed for the current study are then described.

2.2 A material of the modern era

A material is a substance that can be tailored into useful products and undoubtedly plastics comply with this elucidation. Moreover, plastics exhibit important additional features, which allow them to be able to compete with the other materials and therefore exist as a leader in the material market. A good mechanical strength of the plastics beside light weight is often a reason for plastics to progress gradually. Consequently, many other materials used to tailor products are being replaced by plastics. The ever increasing volume of plastic usage worldwide exceeds the volume of steel used to fabricate substances in the steel age and therefore it is reasonable to propose present era to be nominated as plastic age. Plastic encompasses broad spectrum of goals including some examples where plastic can be engineered to strong artificial human body parts, automobile and aircraft applications. Their specific barrier properties further extend its applications and purpose oriented plastics are now available which are designed to degrade with time. Another advantage of plastics over many other materials, the low cost in processing, have competed various markets other than packaging.

Large volumes of plastics are produced every year around the world and much is consumed for packaging, in fact, because of their performances such as low breakability and light weight. As a result, many individual items or small quantities, which were sold unpackaged in the past, are now packaged to provide benefit to the consumer, in many ways such as clean and longer freshness, information, protection and so on. Both the seller and the end-

user benefit from the other ways such as size and quantity, marketing and security benefits. While benefitting all the useful features of plastics, the time has come to consider disadvantages of plastics and their impact on human well-being.

2.3 Environmental impact of Plastics

Although plastic is flourishing as a material for a wide range of applications owing to its worth advantages over other materials, it is crucial to become concerned over the impact of plastics on the environment vis-à-vis massive consumption all over the world. The impact from the feedstock of the plastic materials comes in the first place. Until recently, almost all plastics were manufactured from petrochemicals which are non renewable natural resources. These material have taken millions of years to be developed on earth and how much of these materials exist are not known, though continued depletion of these materials will eventually limit its ability to meet demands. Furthermore, these fossil fuels are not distributed evenly throughout the planet and the estimated world's known oil reserves are in Middle East (Sawyer, 2003). Consequently, price of the raw materials of plastic products are highly vulnerable and dominate only in several parts of the world. Although materials like crude oil and coal provide resources for common synthetic packaging while cotton offer fiber based products, reserves are insufficient to keep pace with the challenging demand.

Plastic is purpose oriented and enormously useful when it is in use, but when it is discarded, could create awful impact on some of the living creatures. Estimates of the mortality rate have shown a high level of victims per year, particularly 1-2 million marine birds as well as 100,000 aquatic animals (Garlotta, 2001). In many paths, discarded plastics are in contact with human lives as well as put deleterious effects on natural biological cycle. The understandings of the people have recently grown of the impact of plastic materials on the environment and consequently on human life. However, plastics are not the entire cause of the environmental issues; they only contribute for part of it.

One of the major environmental concerns over the last decade is plastic waste and litter. Municipal solid waste (MSW) which accounts for part of the waste stream includes household waste, waste produced from other means such as institutions, business and industries. Most people are well aware of MSW since everyone generates it from a small scale. The public directly pay for its collection and handling is managed by councils. Plastics entering the waste stream from households are rapidly growing because almost all consumer goods now come with complete plastic packaging or part of the packaging being plastic. This accounts for half of the discarded plastics worldwide to come from packaging (Stevens, 2002) and the majority being discarded after single use. Plastic waste accumulates not only on land but also in rivers, lakes, and the sea and plastic litter has become another facet of the issue. Plastic waste management has always been expensive. In the midst of all these issues, stepping back to replace plastic with the materials used in the past such as glass, metals or paper are economically unfeasible and especially environmentally less attractive due to high carbon footprint.

The general perception of environmental conservation, together with 3R's concept, Reduce, Reuse and Recycle collectively contribute to the plastic waste management. However, there are limitations in all three categories with regards to plastic waste. Reduction counts for the decline of material entering waste stream through redesigning products by reducing size, shape and thickness etc. The contribution for source reduction is generally from producers and presumably consumer restraint cannot be considered for major source reduction. Reuse strategy has less effect towards waste management as many plastic applications do not facilitate reuse concept owing to health and safety because of the contaminants introduced in the original use. Recycling has long been in practice by plastic manufacturers and processors by recycling internal scrap and has become the most vital process for plastic. This is mainly because of a few reasons. Firstly, failures to control reduce and reuse concepts in the entire manufacturing process put pressure on recycling as it is the ultimate path to reduce the plastic waste stream. Out of three R concepts, recycling is the only path to reduce substantial plastic waste entering waste stream and finally it is the only way to prevent landfill and get the end use product from the consumer back to the re-processor. Incineration also known as energy recycling, and technologies based on pyrolysis where

waste material is heated in the absence of oxygen are already in practice. However, in conjunction with the collection and sorting, mixed plastics, composites and laminates complicate the recycling process. Recycled plastics have less demanding applications than its virgin material because deterioration of the material to some extent occurs during the recycling process (Sawyer, 2003). Some economic factors such as transport, energy cost and lack of suitable markets also set adverse efforts on recycling work. On the other hand manufacturing and recycling by incineration generate CO₂ which in turn increase global warming. Final destination of plastic waste ends up in landfill, which accounts for pollution, poses health risks, perhaps affecting re-use of land due to contamination and other unidentified effects.

2.4 Introduction to biopolymers

The development of bioplastics is of paramount importance today due to the aforementioned and some unidentified environmental issues posed by synthetic fuel based polymer packaging. Synthetic polymers are being used in plastic packaging, and in the last three decades they have become commonplace in our daily lives. Biodegradable plastics can be based on natural or synthetic biopolymers. Polymer backbone of biopolymers mostly have O or N atom in their backbone which is a mainly accountable feature for biodegradation (Stevens, 2002). Natural biopolymers are produced primarily from plants, invertebrate animals and microorganisms. Starch and cellulose exists in great abundance and are derived from renewable resources, and they intrinsically undergo biodegradation. Although polymers themselves are not produced naturally, synthetic biopolymers encompass properties of biopolymers, notably biodegradability and monomers derived from nature. Lactic acid is such a polymerisable biomolecule beside some amino acids and triacylglycerols.

In fact, biodegradability is a familiar concept and a characteristic of natural materials that are digested by micro-organisms and thus introduced into biological cycles. Natural organic materials undergo progressive decomposition and eventually disappear. This is a vital phenomenon for the environment, to get rid of waste and hence create a place for new

lives. Photosynthetic organisms such as trees, plants and algae, absorb CO₂ from the atmosphere and energy from the Sun, synthesize sugars, and other substances present in nature. In natural equilibrium, the opposite process also exists with the release of carbon dioxide to the environment from organic material. Hence, biodegradation is an important process where the primary role is played by microorganisms, in which the organic material is transformed back into carbon dioxide to complete the natural cycle. Table 2.1 shows some definitions associated with biodegradable plastics. Although these definitions are apparently non-uniform, the different standards and evaluation schemes are surprisingly congruent.

Table 2.1 Definitions used in correlation with biodegradable plastics adapted from Muller (Muller, 2004)

German Institute for Standardization (DIN)	A plastic material is called biodegradable if all its organic compounds undergo a complete biodegradation process. Environmental conditions and rates of biodegradation are to be determined by standardized test methods.
ASTM sub-committee D20-96	A degradable plastic in which the degradation results from the action of naturally occurring microorganisms such as bacteria, fungi and algae.
Japanese biodegradable plastic Society	Polymeric materials which are changed into lower molecular weight compounds where at least one step in the degradation process is through metabolism in the presence of naturally occurring organisms.
International standardization organization (ISO 472)	A plastic designed to undergo a significant change in its chemical structure under specific environmental conditions resulting in a loss of some properties that may vary as measured by standard test methods appropriate to the plastic and the application in a period of time that determines its classification. The change in the chemical structure results from the action of naturally occurring microorganisms.
European committee for standardization (CEN)	A degradable material in which the degradation results from the action of microorganisms and ultimately the material is converted to water, carbon dioxide and/or methane and a new cell biomass.

Unlike synthetic fossil fuel based polymers which remain for several hundred years, biopolymers conform to the natural biological cycle by smoothly undergoing the phenomenon, and disappear from the environment with time due to assimilation by microorganisms, eliminating water and CO₂ to the atmosphere. This phenomenon was successfully adapted by scientists, to answer the question ‘can the plastic be made from natural sources other than fossil fuels’ by producing alternative environmentally friendly bioplastics with properties which are comparable to traditional plastics such as PS, PET, LDPE (Auras, Harte & Selke, 2004) and hence available in the market today. One-way or the other, some of the properties of these plastics still have to be improved for them to be adopted for certain applications and it is now responsibility of researchers to evaluate these material properties and suitability.

2.5 Plastics from renewable resources

One of the most vital aspects of sustainable materials is the renewable resource base. Renewable materials originate from the natural system that complies with the phenomenon of biodegradation. These materials are mainly derived from agricultural feedstock, which are produced on a large scale, twice or more or throughout the year. Advantages of these renewable materials are that they are derived from natural system in massive quantities and their ability to reproduce. Starch is such a renewable agricultural resource and it is the major constituent in many agricultural feedstocks such as corn, wheat, maize, potato, rye and rice etc. Bioconversions within these plants give rise to a whole range of substances including sugar molecules. These molecules can be used as monomers that are polymerized into long chain molecules to produce completely biodegradable manmade polymers. Poly(lactic acid) from starch and Polyhydroxy butyrate (PHB) from bacteria are such derived polymers from renewable materials. Starch and PLA derived from lactic acid monomer produced from starch are both completely biodegradable thermoplastic polymers and their composites could be considered as completely biodegradable.

2.5.1 Starch

Starch is the major constituent in plant tubers and endosperm and a complex carbohydrate which is used by most plants to store excess glucose. The covalent nature of this molecule is firmly established with the general formula of $(C_6H_{10}O_5)_x$. It is a most important and abundant polysaccharide and is known as a food application material. However, ready availability and low cost of starch has drawn interest on non food applications. It has been identified as a potential alternative to synthetic polymers because of its renewability and biodegradability (Chiou et al., 2005; Golachowski, Kislenko & Drozdz, 2005). Starch has also been used as a filler for most of the synthetic polymers to increase biodegradability (Pranamuda, 1996; Rodriguez-Gonzalez, Ramsay & Favis, 2003; Wang et al., 2007). Native starch exists in granular form and mainly consists of two polysaccharide fractions, amylose, a straight chain (linear) molecule and amylopectin highly branched molecule. Both consist of polymers of D-glucose units in 4C_1 conformation.

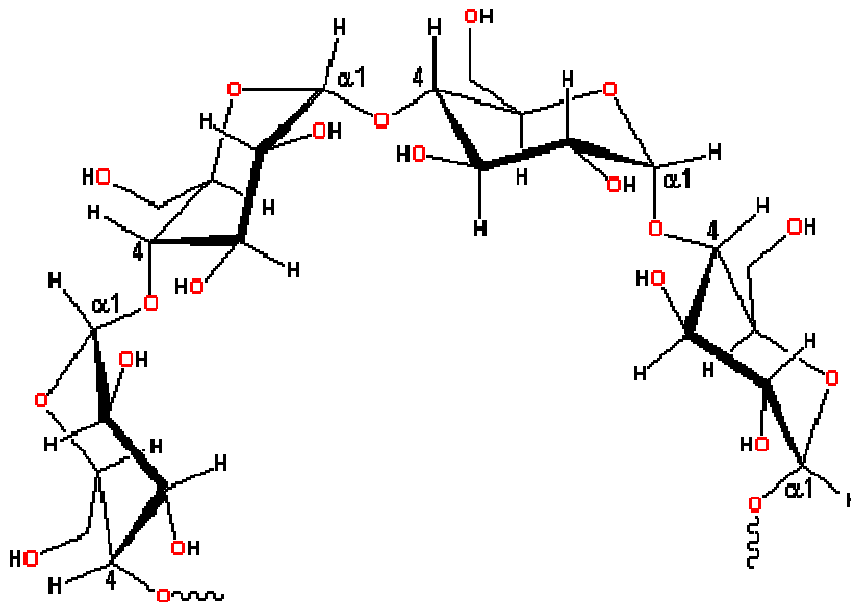


Figure 2.1 Part of the chemical structure of amylose in starch adopted from (web 3, accessed on 03.08.2010)

However, amylose contains 1-4 glucose units where as amylopectin consist of 1-4 linked chains and 1-6 linked branches. Amylopectin is a much larger molecule and the larger of the two fractions, has a Molecular weight in the range of 10^7 - 10^9 Da and amylose the smaller fraction has a Molecular weight in the range of 10^5 - 10^6 Da (Oates, 1997). Depending on the botanical source, the proportion at which they exist in a particular starch varies. Some genetic varieties only have amylopectin but no amylose.

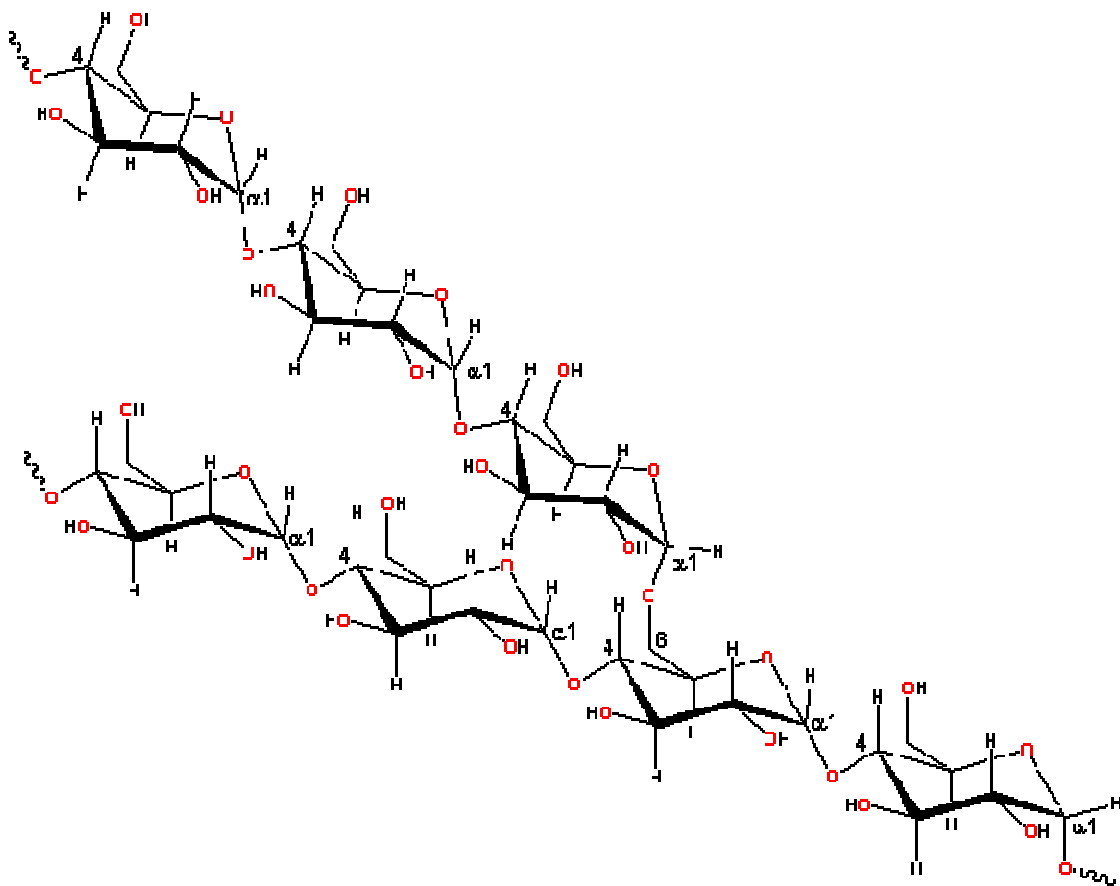


Figure 2.2 Part of amylopectin structure in starch adopted from (web 3, accessed on 03.08.2010)

2.5.2 Starch granule structure

Amylopectin and amylose both biosynthetically assembled as semi crystalline starch granules and structures consist of different types and populations of chains. The individual chains are specifically classified according to the chain length and position of the chain within the starch granule. Type A and B are most common types and present in almost equal proportions. They exist externally within the native granule and contribute to the double helices formation (Tester, Karkalas & Qi, 2004). Type A starch chains attach to the molecule by single link and are linear and shorter than average chain length of B type starch chains found in potato starch, whilst in B type starch, chains are connected to two or more other chains and usually branched (Oates, 1997). Type A chain structure is present in most cereal starches and packing of double helices within the structure is relatively compact where as B type crystalline structure is highly hydrated and has a more open structure (Parker & Ring, 2001) which can be found in high amylose starches and tubers. Type C starch is recognized as a combination of A and B types (Van Soest et al., 1996). All these proportions of crystalline nature vary with botanical source and the physical properties of starch, are biased by the ratio between amylose and amylopectin.

Starch experiences a phenomenon called gelatinization, where the starch granule is swelled and hydrated in the presence of water to form gel particles by disrupting the native crystalline structure. Calorimetric studies showing endothermic peaks for gelatinization is evidence to describe the process as the melting of starch crystallites (Whistler, BeMiller & Paschall, 1984). In general, the swollen granules are found to be enriched in amylopectin, whereas the amylose diffuses out of the swollen granules and creates the continuous outer phase to the granules (Fredriksson et al., 1998). Crystalline structure and water content have a major contribution towards the melting temperature. Due to thermal degradation, the melting temperature is experimentally unreachable for starch with the low water content, and it can only be estimated for dry A-type starch to be in the range from about 220 to 270°C. (Parker & Ring, 1995)

Retrogradation is another facet of starch, in particular, a characteristic feature of gelatinized starch which is described as the time dependant process of changes that occur upon cooling and storage of gelatinized starch. During the process, re-association in an ordered structure of poorly soluble chains takes place to form insoluble aggregate (Whistler, BeMiller & Paschall, 1984). The molecules in the starches re-associate at a different rate thus amylose has greater propensity to re-associate than amylopectin and forms polymer precipitate relatively rapidly. Short-term development of crystallinity in starch gels is thus attributed to the gelation and crystallization of the amylose fraction. The development of crystallinity in starch gel by amylopectin spans over a period of time and may be acquired at a relatively short life of the starch based products and can be identified as the physical ageing of the starch.

2.6 Starch based biopolymers

There are two main categories of biodegradable starch based polymers which are distinguished as thermoplastic starch and starch blends with other polymers. Thermoplastic starch consists of a considerably high level of gelatinized starch usually amylose. Plantic (web 4, accessed on 10.08.2010), Potatopak (web 5, accessed on 10.08.2010), Plastarch (web 6, accessed on 10.08.2010) are such commercially available thermoplastic starch materials. In starch based polymers, biodegradation takes place as a result of an enzymatic degradation at the glucosidic linkages of polysaccharides resulting in a reduction in the chain length to monosaccharides, disaccharides and oligosaccharides.

The polymer blend is the other category of biodegradable starch based polymers where starch is often blended with other biodegradable polymers. Some of the commercially available starch-polymer blends are given in table 2.2.

Table 2.2 Commercially available starch-polymer blends

Polymer type	Trade name	Supplier/Origin
Starch-polycaprolactone (PCL) blends	Mater-Bi™	Novamont/Italy
Starch-polycaprolactone (PCL) blends	Bioflex™	Biotech/Germany
Starch-Polyvinyl Alcohol (PVOH) blends	Novon™	Chisso Corp/Japan
Starch-Polyvinyl Alcohol (PVOH) blends	Novon™	Warner Lambert/USA
Starch-Polyvinyl Alcohol (PVOH) blends	Mater-bi™	Novamont/Italy
Starch-polycaprolactone (PCL) blends	Bioplast	Biotech/Germany

2.7 Starch derived biopolymers

Despite the fact that starch itself is a biopolymer, it is also a prime material for commercial production of the basic constitutional unit of some other biopolymers. PLA polymer is one such biopolymer which is commercially available in large scale, from NatureWorks LLC in the USA being the dominant manufacturer of PLA in the present market. There are a few other PLA manufacturers worldwide. These include:

1. PURAC, Netherlands (web 7, accessed on 15.08.2010)
2. Hisun Biomaterials Co.,Ltd, China (web 8, accessed on 15.08.2010)
3. Galactic in Belgium (Futero) (web 9, accessed on 15.08.2010)
4. Hycails in Finland (web 10, accessed on 15.08.2010)
5. Toyota in Japan (web 11, accessed on 15.08.2010)

There are several ways in which PLA can be manufactured; however Cargill Dow LLC has developed a process which combines substantial economic and environmental benefits of synthesizing both PLA and its monomer unit lactic acid (Drumright, Gruber & Henton, 2000). This process provides a commercially feasible biodegradable polymer from renewable resources. A French company NaturePlast, also market different grades of PLA under their trade name natureplast PLA and the material is recognized as a genetically modified organisms (GMO) free certified PLA manufactured elsewhere (Web 12, accessed on 03.10.2010).

2.7.1 Polylactic acid biopolymer

Polylactic acid is not a novel thermoplastic polymer material, it has been known to researchers for many years because of its unique properties. Its applications have been widely studied, but, limited to the biomedical industry (Mohanty, Misra & Hinrichsen, 2000; Mcmanus et al., 2000) until recently due to its biocompatible properties in the human body and cost (Lunt, 1998; Sinclair, 1996). Latest developments of economically feasible monomer from the bioconversion of starch and its unique properties have placed PLA material in the forefront of the biodegradable polymer industry. In the plastic industry, PLA is now known as the first commercial product manufactured in such a large scale from renewable resources. A versatile polymer, PLA is made by the well known food ingredient lactic acid (2 hydroxy propionic acid) and converted into polylactic acid polymer.

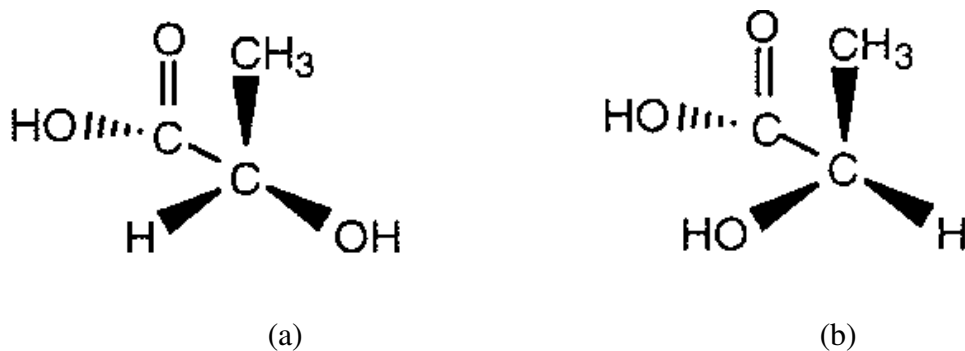


Figure 2.3 Chemical structure of (a) L lactic acid (b) D lactic acid adopted from (Dorgan et al., 2001)

Lactic acid is a chiral molecule and the simplest hydroxyl acid (asymmetric carbon atom) and exists as two optically active stereo isomers, D(-) and L(+) forms. An equimolar amount of these two isomers give a racemic mixture and they differ by the effect on the polarized light. D-lactic acid rotates the plane of polarized light in dextro direction (clockwise), whereas the L form in the leavo (anticlockwise) direction. The optically inactive meso compound (DL lactic acid) contains an improper rotation. Based on the D and L proportions, they give a range of properties to the polymer. Lactic acid, the basic constitutional unit of PLA can be manufactured by different methods including an economically unviable chemical synthesis. The majority of lactic acid is made through the popular bacterial fermentation process of carbohydrate. Although lactic acid is globally produced from sugar beet, rice, wheat or cassava, any other starch sources could also be used as the feedstock for lactic acid production. In the first commercial stage, agricultural product, corn starch was the most economically feasible option; however, technology is being developed to allow by-products such as corn-stover as the feed source for lactic acid production. (Sawyer, 2003) Lactic acid is then converted in to PLA by commercially available methods.

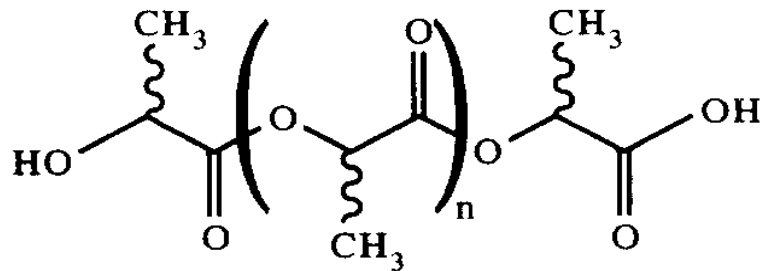
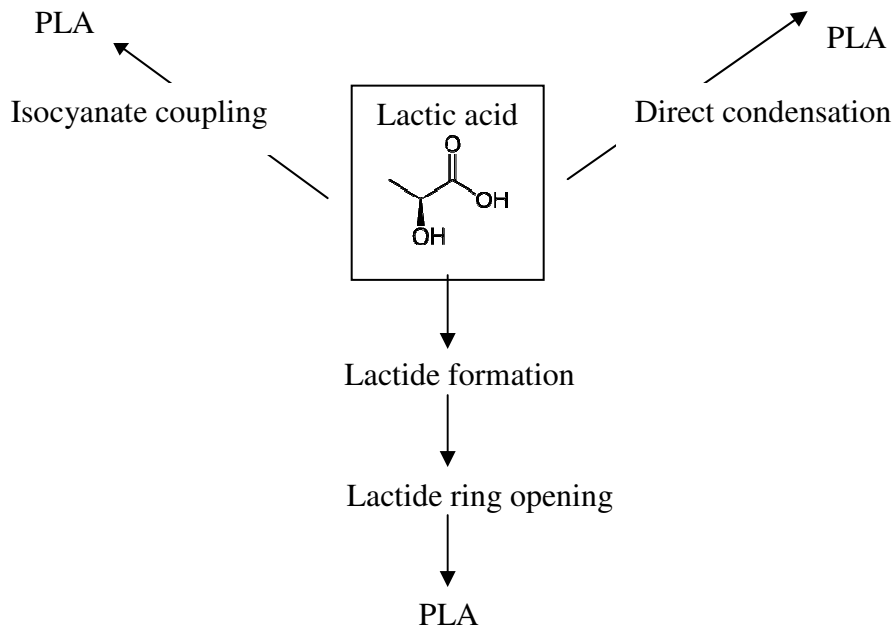


Figure 2. 4 Chemical structure of poly lactic acid adopted from (Conn et al., 1995)

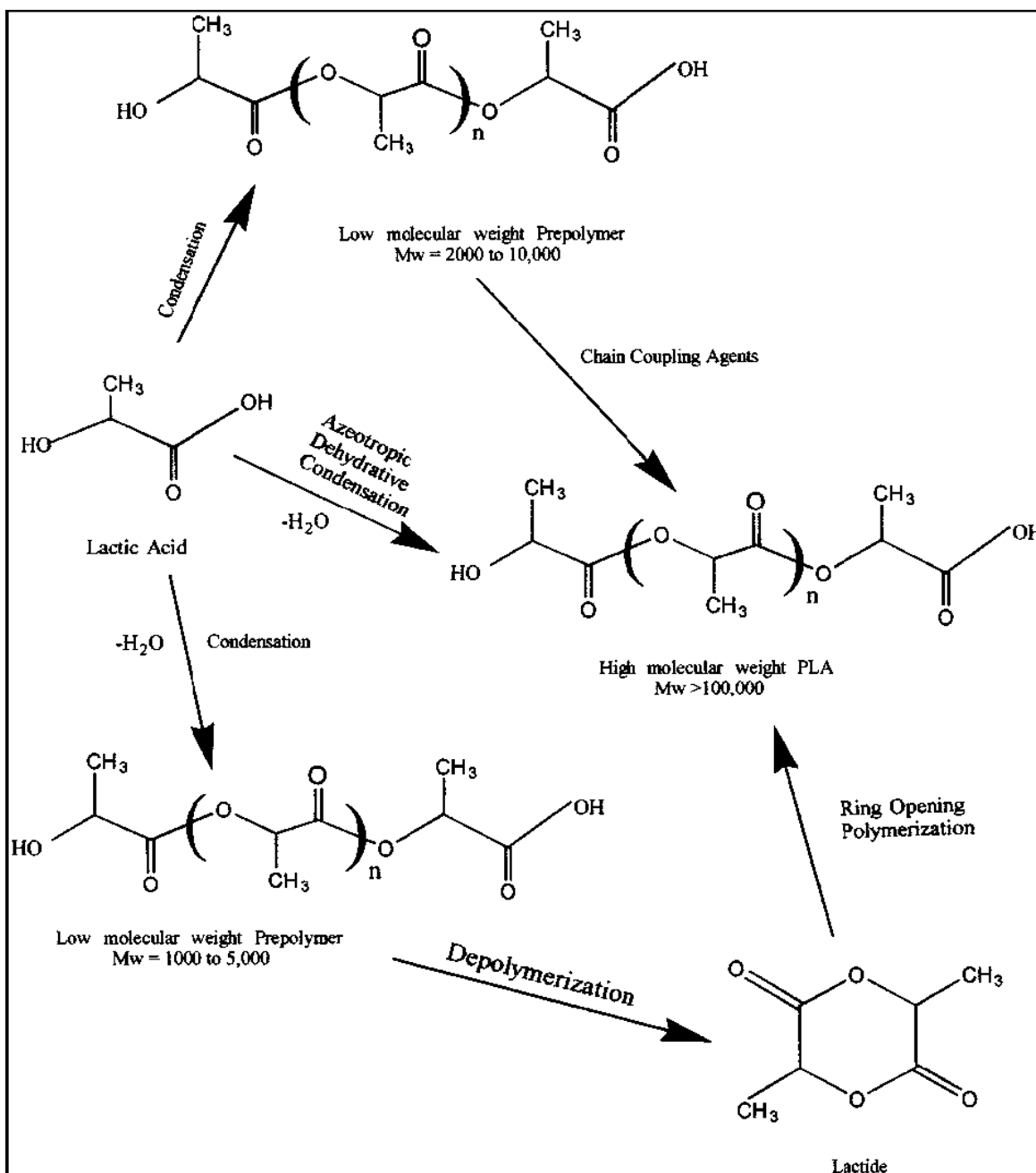
2.7.2 Synthesis of PLA

Process options for PLA production are given in scheme 2.1. Direct coupling of lactic acid with isocyanate also produces PLA, but not suitable to put onto practice because of the hazardous nature of the isocyanate which is not accepted as safe to use (Sawyer, 2003). There are two commonly used paths for synthesis of lactic acid into PLA. One path follows polymerization of the lactic acid monomer by direct condensation polymerization to yield a low molecular weight brittle glassy polymer where external coupling agents are used to increase the molecular weight to employ in any useable application. The molecular weight of this condensation polymerization is usually low because of the presence of water, impurities, viscous polymer melt, and lack of reactive end groups and also the backbiting reaction which forms a six-member lactide ring. The other route, ring opening polymerization of lactide monomer which is a cyclic dimer of lactic acid gives high molecular weight polymer. The product from direct condensation polymerization of lactic acid is called polylactic acid and the latter is called Polylactide. PLA derived from both these chemical pathways has similar mechanical properties (Wang, Sun & Seib, 2001).



Scheme 2.1 Process options for PLA production

Scheme 2.2 shows the known routes of conversion of lactic acid into high molecular weight PLA. The ring opening polymerization of lactide method was the sole method of producing pure high molecular weight PLA until Mitsui Toatsu chemicals commercialized a process where a catalyst and lactic acid is azeotropically dehydrated under reduced pressure (Garlotta, 2001). Although condensation route is least expensive, it is difficult to obtain high molecular weight polymers in a solvent free system and therefore enhances the cost with additional expenses for coupling agents and chain extenders. Azeotropic condensation produces high molecular weight polymers with a high level of residual catalytic impurities that result in problems during further processing such as unwanted degradation, catalyst toxicity or uncontrolled hydrolysis rates. Cargills Dow LLC has developed a process for production of PLA which combines both environmental and economics benefits of synthesizing both lactide and PLA in the melt and provides a polymer made from renewable resources (Drumright, Gruber & Henton, 2000). Process follows condensation polymerisation to produce a pre-polymer which is then converted to a mixture of lactide stereo-isomers eventually produce high molecular weigh PLA by tin catalyzed ring opening polymerization.



Scheme 2.2 Synthesis methods for high molecular weight PLA adapted by Garlotta (Garlotta, 2001)

2.7.3 Properties of PLA

Like many other polymers, the properties of PLA are determined by the molecular weight and the stereochemical structure of the polymer backbone. Precise control of the polymer architecture facilitates control of the degree of crystallinity and as a consequence the processing temperatures, the mechanical properties and degradation behaviour. PLA crystallization is principally determined by the initial distribution of the proportions of basic building blocks of the PLA, lactic acid isomers. Thus PLA resin tailored from 50 to 93% L-lactic acid produce amorphous polymer whereas L-lactic acid greater than 93% produces semicrystalline polymer. PLA polymers are transparent, and therefore attract the packaging market as a material. Beside transparency, properties such as easy printability, barrier properties, and resistance to fatty foods are noteworthy to include.

2.7.3.1 Glass transition temperature

PLA polymers are available from amorphous polymers with a glass transition temperature of 60⁰C to semicrystalline and highly crystalline polymers. Their crystalline melting points vary from 140⁰ to 180⁰C and products are transparent. The glass transition temperature (T_g) is one of the vital parameter for amorphous PLA for the reason that significant changes in mobility of polymer chain take place at this critical point and above. Both the T_g and melting temperature (T_m) are important for semicrystalline PLA. For a semicrystalline PLA polymer, T_g designates to the brittle and ductile transition. The T_g of poly-L-lactic acid (PLLA) is reported to be greater than poly-D-lactic acid (PDLA) due to the crystallinity differences within the two polymers (Auras, Harte & Selke, 2004). The crystallinity of the polymer tends to decrease with increasing M_w but increasing M_w increases melting temperature and attains an optimum practical value. Presence of different proportions of lactic acid also affects the glass transition temperature and may range from 50⁰C - 80⁰C (Ikada & Tsuji, 2000).

The relationship between the glass transition temperature of PLA, and number average molecular weight can be represented by the Flory-Fox equation as follows;

$T_g = T_g^\infty - K/M_n$ where T_g^∞ is the glass transition temperature at infinite molecular weight (M_w) and K is a constant which represent the free volume of the end group of the polymer chains and M_n is the number average molecular weight.

The PLA is not thermally stable and immediately loses its stability when heated above its melting temperature. Upon heating of PLA few degrees above its melting temperature and holding the temperature for a considerable period, substantial molecular weight degradation occurs in the material (Garlotta, 2001). Nevertheless, PLA has very similar thermal stability to PVC but PS, PP, PE and PET are noticeably more thermally stable than PLA (Auras, Harte & Selke, 2004).

2.7.3.2 *Rheology*

Most of the thermal processes of PLA such as thermoforming, extrusion, injection moulding, film blowing, and sheet forming are greatly affected by the rheological properties, in particular, by shear viscosity of the PLA polymer. Shear thinning is a characteristic behaviour of PLA melt similar to PS. High molecular weight PLA has melt viscosities in the range of 500-1000 Pa-s at the frequencies 10-50 s⁻¹(Garlotta, 2001). In general, structured semicrystalline PLA has higher viscosity than unstructured amorphous PLA. However, both PLA melt viscosities show temperature dependence by decreasing shear viscosity upon increasing temperature. The amount of plasticizer as well as the molecular weight has considerable control over the melt viscosity. The processing temperature of PLA basically depends on the amount of plasticizer, shear rate, weight average molecular weight dependent melt viscosity, type of melt processing and the amount of work put into the polymer (Sinclair, 1996). Degradation is increased with increasing plasticizer, and shelf life is favored by decreasing plasticizer content and orientation. The Power law equation sufficiently describes the behaviour of PLA polymer melt as a pseudoplastic non-Newtonian fluid (Fang & Hanna, 1999).

2.7.3.3 Mechanical properties

Similar to the crystallization behaviour, mechanical properties of PLA are highly reliant on the polymer architecture and the molecular weight. The PLA is a clear, colorless thermoplastic when quenched from the melt and is similar in many aspects to polystyrene. According to Sinclair (Sinclair, 1996) when plasticized with its own monomers, PLA becomes increasingly flexible so that a continuous series of products can be prepared that can mimic PVC, LDPE, LLDPE, PP, and PS. Mechanical properties of the oriented and unoriented PLA have been reported (Garlotta, 2001) and wide variation in oriented properties is due to the stereochemical composition and the degree of orientation. Some mechanical properties shown by different stereochemical structures of PLA (specimens obtained by injection molding at a temperature of 195.8 °C) are presented in table 2.3.

Table 2.3 Mechanical properties of poly(L-lactide), adapted from Auras et al (Auras, Harte & Selke, 2004)

Property	Amorphous L-PLA (M _w =66000)	Annealed L-PLA (M _w =66000)	D,L-PLA (M _w =114000)
Tensile strength MPa	59	66	44
Elongation at Break %	7.0	4.0	5.4
Modulus of Elasticity MPa	3 750	4 150	3 900
Yield strength MPa	70	70	53
Flexural strength MPa	106	119	88
Unnotched izod impact J.m ⁻¹	195	350	150
Notched izod impact J.m ⁻¹	26	66	18
Rockwell hardness	88	88	76
Heat deflection Temperature °C	55	61	50
Vicat Penetration °C	59	165	52

M_w is the molecular weight.

PLA polymers show very high flexural properties and tensile modulus but low elongation at break compared to many commodity polymers such as HDPE and PP. Mechanical properties of PLA have shown to be most comparable to PS (Dorgan et al., 2001). In general, PLA polymers with viscosity average molecular weight above 55,000g/mol show highest tensile strength and modulus.(Auras, Harte & Selke, 2004) Molecular weight and crystallinity play a role in the impact strength and Vicat softening temperature which are, in turn, increase with increasing levels (Garlotta, 2001).

2.7.3.4 UV light transmission

One of the important parameter of the food packaging polymers is their ability to transmit Ultra violet (UV) and visible light and hence minimize food product damage to maintain the food quality. Light has been found to affect dairy products, such as cheese (Mortensen et al., 2004) by changing its flavour. Therefore when designing the food packaging, light transmission ability of the packaging material is an important parameter to consider, in order to protect the food product until it safely reaches the end-user. Most energetic component of the UV light that reaches the earth, which causes damages to most plastics by photochemical degradation, is in the range of 315-280 nm. Light transmission ability of PLA in the visible range has been shown to be more than 90% (Holm, Mortensen & Risbo, 2006). Light barrier properties of PLA have been studied and found that no UV transmittance is shown by PLA within the range of UV radiation generated by artificial light source (280-100nm) (Auras, Harte & Selke, 2004). Therefore, additives such as UV absorbers may be mixed with PLA for its applications in food packaging where UV transmission is essential.

2.7.3.5 Barrier properties

Carbon dioxide and oxygen barrier properties of PLA have been measured by different investigators. Auras et al (Auras, Harte & Selke, 2004) reported that the CO₂ permeability coefficient for PLA resins are lower than that of PS but higher than that of the value

reported for PET at 25⁰C temperature. Authors have also reported that PLA show a significant increase in the oxygen permeability coefficient when the temperature increased while processing conditions and crystallinity also play a role. The higher crystallinity in the polymer prevents the permeation of oxygen molecules through the material than the amorphous polymers. Both PLA and PET polymers form hydrophobic films and low water absorption is exhibited (Auras, Harte & Selke, 2004). Furthermore, water permeation of PLA has been studied, although the diffusion mechanism in a PLA polymer membrane is not yet well understood. Although the PLA is a polar polymer, the water permeability of 98% L-lactide polymers has shown to be practically constant over the range of 40-90 percent relative humidity.

2.7.4 PLA and the packaging industry

Increasing awareness of ecological concerns pressurize packaging materials of consumable goods to be highly eco-friendly. Essentially, PLA being a typical environmentally friendly biodegradable polymer, it has gained enormous attention as a replacement for synthetic commodity plastic packaging materials. In addition to the intrinsic properties, evolution of new technologies for production of PLA from renewable resources has targeted single use disposable market and found wide variety of applications including diversity of consumer products, including thermoformed articles, table utensil, household waste bags which are compostable, paper coatings, and has been spun into fiber and cloth. Moreover, PLA is being used as a food packaging polymer in many common applications such as drinking cups, sundae and salad cups, overwrap and lamination films and blister packages (Auras, Harte & Selke, 2004).

As a polymer, PLA show many advantages such as

1. it can be obtained from renewable agricultural sources
2. consume significant amounts of CO₂ for production(Dorgan et al., 2001)
3. it saves considerable energy(Dorgan et al., 2001)

4. reduce current issues related with landfill problem
5. recyclable and compostable(Drumright, Gruber & Henton, 2000)
6. its physical and mechanical properties can be modified and controlled (Auras, Harte & Selke, 2004; Dorgan et al., 2001; Ljungberg & Wesslén, 2002; Dorgan et al., 2006)

PLA has been identified as an economically feasible material for packaging (Sawyer, 2003; Bogaert & Coszach, 2000), in particular, packaging which comes into contact with food. Findings of toxicological studies have shown that PLA is safe and generally recognized as safe for use in manufacturing food contacting packaging because of the level of lactic acid that migrates to food from packaging containers is much lower than the amount of lactic acid used in common food ingredient(Conn et al., 1995). Accordingly, PLA polymer which is derived from a lactic acid monomer unit has been identified as a good candidate for packaging applications (Ikada & Tsuji, 2000; Gruber & O'Brien. M, 2002; Dorgan et al., 2006). However, cost of the polymer and processing constrain limits the use of PLA as a packaging material. Nevertheless, PLA has been blended with starch to make a more cost effective composite and alternatively to accelerate biodegradation.

2.8 PLA and starch composites

Material science research has expanded its boundaries including rapid growth in the area of multi component systems which are usually known as composites. Materials may be combined to make composite in search of novel properties or desirable intermediate properties, particularly when the material on its own is unable to fulfill requirements or more expensive material is of no use for an application. The composite is produced by incorporating two or more discrete phases containing a matrix material and a fibrous or a particulate material. The addition of one component to the other can compensate largely the weaknesses of the other, for example stiffness of some polymers can improve by addition of fibers. The matrix material mainly serves as a binder but is also modified to make final composite in order to gain specific strength, impact resistance and other properties. A

composite is broadly defined not only as a heterogeneous material but also homogeneous blends (Stevens, 2002).

The development of a new blend from existing material is relatively easy and cheaper than synthesizing entirely new polymer (Miles & Rostami, 1992). The rationale of tailoring a composite is to unite versatile properties of individual elements thereby producing intermediate properties to the final product. Compatibility of individual materials contributes immensely on the ultimate outcome. Interfaces are usually created between polymer-polymer and polymer-additive when the additives are insoluble in the matrix. A weak physical and chemical interaction between components implies high interfacial energy and tension. This feature eventually has significant power in controlling performance of the composite. Low interfacial energy is coupled with high thermodynamic work of adhesion, and the adhesive strength enhances with increasing compatibility between the phases (Miles & Rostami, 1992). Close binding of surfaces together could be identified as adhesion resulting in stress being transmitted between the phases.

The relationship between filler content in the composite to the tensile strength and elongation at break of the composite is represented using the Nielsen and Nicolais-Narkis equations (Miles & Rostami, 1992). Nielsen equation is represent as,

$$\epsilon_{comp} = \epsilon_0 (1 - (\varphi_f)^{1/3})$$

Where

- ϵ_{comp} = Elongation at break of the composite
- ϵ_0 = Elongation at break of the matrix
- φ_f = Volume fraction of the filler

There are few assumptions that Nielsen equation made,

- shape of the filler particles is spherical
- The matrix or the binder is homogeneous
- A perfect adhesion between matrix and the filler exist

The Nicolais-Narkis equation is as follows:

$$\sigma_{comp} = \sigma_0 (1 - 1.21(\varphi_f)^{1/3})$$

where σ_{comp} = Ultimate tensile strength of the composite

σ_0 = Ultimate tensile strength of the matrix

φ_f = Volume fraction of the filler

There are few assumptions that Nicolais-Narkis equation also made,

- shape of the filler particles are spherical
- The matrix or the binder is homogeneous
- There is no adhesion between matrix and the filler

Plastics have been blended together to bring intermediate properties to the resultant composite because of their unique properties and advantages over other traditional materials. Apart from the general advantages of plastics, both PLA and starch apparently exhibit an important property of the materials that has recently taken high significance than in the past, the correlation with the ecosystem. As a consequence, extensive efforts have been carried out to fabricate a composite from PLA and starch with adequate mechanical properties that can be employed for applications. In general, the availability of either hydroxyl or polar groups facilitates most natural polymers to be hydrophilic in contrast most manmade polymers are hydrophobic. Different approaches that have been studied to tailor composites of hydrophilic starch and hydrophobic PLA includes blending with a range of additives, varying composition of the starch, employing a variety of starches, using different additive levels, altering substituent groups, grafting of additive to PLA (Wang, Sun & Seib, 2001; Jun, 2000; Ke & Sun, 2001b; Zhang & Sun, 2004b; Zhang & Sun, 2004a; Zhang & Sun, 2004c; Huneault & Li, 2007; Wang et al., 2007; Wang, Sun & Seib, 2002b; Ke, Sun & Seib, 2003; Lin, Sundararaj & Guegan, 2006; Jang et al., 2007; Wang & Zheng, 2009).

The thermal behaviour of PLA filled with native corn starch in a Haerke Rheomix kneader system has been studied in the presence of a plasticizer, polyethylene-glycol. (Jacobsen & Fritz, 1996) Blends were prepared with 20% and 50% corn starch levels, in each situation, T_g of the blend remains at 54⁰C temperature which is the T_g of the virgin PLA and no crystallization has occurred. The results have suggested that the addition of starch has precisely not affected the thermal behaviour of PLA. Studies carried out on biodegradable polymer blends of L-PLA/cornstarch and star PLA/cornstarch starch composites by Park et al (Park et al., 1999) and reported by Garlotta (Garlotta, 2001) have demonstrated that when starch was added the glass transition temperature of both composites remained unaffected. Moreover, results reported that rising starch content had increased enthalpies of crystallization ΔH_c and melting ΔH_f by starch behaving as a nucleating agent resulting in an increase in crystallinity. However, star shape PLA/starch composite has exhibited maximum enthalpies only at 5% starch content and increasing starch had decreased both enthalpies of crystallization and melting.

Melting behaviour and crystallization kinetics of PLA/starch blends have shown that the composition and the crystallization temperature can highly influence crystallization behaviour of PLA/cornstarch blends (Ke & Sun, 2003). Furthermore, even the starch concentration as small as 1% in the blend can effectively enhance the rate of crystallization of PLA and this result is consistent with the outcomes reported by Park et al (Park et al., 1999). Results of the thermal degradation study of PLLA/cornstarch composite carried out by Kim et al (Kim et al., 1998) and reported by Garlotta (Garlotta, 2001) revealed that the onset of thermal degradation was 220-230⁰C and the majority of the decomposition has taken place at 280-340⁰C and the higher cornstarch in the composite showed lower onset temperature. A somewhat different study on the biodegradable polymer blends of Poly(L-lactic acid) and gelatinized starch in the presence of water/glycerol mixtures have been investigated (Park et al., 2000) and the results have been reported that 10% gelatinized starch in the composite depressed the T_g and T_m when the plasticizer content increased but ΔH increased owing to the plasticizing effect. Gelatinization of starch lead to a decrease in the starch crystallinity by diminution of H bonding but nucleating behaviour of starch was still observed (Park et al., 2000).

Efforts have been taken to address the major drawback of starch/PLA blend, the brittleness, by studying the group of plasticizers at various levels ranging from 5% to 25%, (1) acetyl triethyl citrate (ATC) and triethyl citrate (TC), (2) poly (ethylene glycol) (PEG) and poly (propylene glycol) (PPG), (3) glycerol and sorbitol (Ke & Sun, 2001b). The PLA/cornstarch blend of 60:40 weight ratio have been studied in a fixed extruder condition. The glass transition temperatures and first cold crystallisation temperature of the blends were not affected by the glycerol, sorbitol and PPG polyols which are immiscible with PLA and hence inefficient to influence PLA mobility, however, the pronounced decrease has been observed as ATC, TC, and PEG contents increased. Nevertheless, the second crystallisation peak has been observed for most situations and showed a slightly different behaviour. The ATC and PEG have enhanced the crystallization of PLA.

Zhang and Sun (Zhang & Sun, 2004b) have studied poly (lactic acid)/ starch blends in the presence of Dioctyl Maleate (DOM). PLA and starch at a fixed ratio of 55/45 with various DOM contents have been extruded in a twin screw extruder and dog-bone shaped tensile bars have been compression moulded. The thermal behaviour has shown a very slight decrease in T_g with increasing DOM levels and it has shown to be lower than the T_g values of a similar study carried out with acetyl triethyl citrate (ATC) (Zhang & Sun, 2004c) at same ATC levels. Moreover, an upper limit exist in the cold crystallization of PLA/starch blends at 2% DOM level while the depression in the melting temperature is less prominent than the ATC.

The reduction in the T_g of a polymer component can be employed to assess the miscibility and therefore can be used as a measure of the brittle-ductile transition of the PLA/starch binary polymer systems. The similar study of PLA and cornstarch with ratios of 55:45, 60:40 and 65:35 together with 1% MA and 1% Luperox initiator have been premixed with a stand mixer by adding different ATC levels. Blends have been extruded at a fixed screw profile and injection moulded (Zhang & Sun, 2004c). Results have shown that T_g values of PLA /starch blends decrease with increasing ATC levels and was in agreement with results reported by Ke et al (Ke & Sun, 2001b). Furthermore, T_c and T_m showed a similar trend

with ATC, however, the decrease in T_g was more profound. Ke and Sun (Ke & Sun, 2001b; Ke & Sun, 2000) have reported that PLA plays a major role in controlling the thermal behaviour of the blends. A comparable study of the blends of PLA and various starch levels with fixed methyldiphenyl diisocyanate (MDI) content have demonstrated that the starch levels in the blend had no influence on the T_g of the blend and remained at the T_g of pure PLA. (Wang, Sun & Seib, 2002b). However, thermal studies of PLA/starch/MDI with TC plasticizer conducted by Ke and Sun (Ke & Sun, 2003b) illustrated that all transition temperatures of the blends including T_g , crystallisation temperatures T_c , and melting temperatures T_m decreased as the plasticizer content increased. In addition, TC reduced the viscosity and facilitated crystallisation, and also the processing method and annealing temperatures have an influence on crystallinity (Ke & Sun, 2001a). Under the processing conditions used in the study, the samples prepared by injection moulding or extrusion processes have the low crystallinity compared to those prepared by compression moulding (Ke & Sun, 2001a).

The incorporation of starch into PLA would indeed produce a characteristically brittle material owing to poor adhesion between granular starch and the PLA matrix. Mechanical properties of high molecular weight PLA and starch composites made by twin-screw Brabender extruder and compression moulded tensile test bars were investigated by Kim et al (Kim et al., 1998) and reported by Garlotta (Garlotta, 2001) showed that the tensile strength and elongation of the blends decreased, but the modulus increased with the rising starch content. Moreover, water absorption studies of PLA/starch blends have shown higher levels of water absorption with higher starch fillings. The blend compatibilization can be improved by two approaches that include the introduction of a third component to the polymer system, reducing the interfacial energy, improving dispersion and as a result increasing adhesion between the polymer phases. The other approach, reactive blending facilitates the chemical reaction between polymers in a molten state either by introducing a catalyst or a third component with reactive functional groups (Zhang & Sun, 2004a).

The effect of a plasticizer as well as a compatibilizer is closely associated with its molecular arrangement. In general, a primary requirement of a compatibilizer is the

presence of reactive functional groups that react with the polymer matrix thereby reducing the interfacial tension between two polymers. The PLA/wheat starch blends compatibilized by DOM (Zhang & Sun, 2004a) have illustrated that upon increasing the DOM concentration, the elongation has markedly enhanced but the tensile strength of PLA/starch blends achieved maximum limit at 2% DOM level and is in agreement with the reported results of a similar study of Zhang and Sun (Zhang & Sun, 2004b). Compatibilization effects of DOM have been suppressed at higher concentration due to its enhanced molecular mobility resulting in a decrease in tensile strength (Zhang & Sun, 2004a). Moreover, water absorption of PLA/ starch blends increased with DOM concentration, however, the superior rate of water absorption was shown by ATC (Zhang & Sun, 2004a). The mechanical properties of melt blends of PLA and starch gelatinized with water/glycerol levels showed a reduction in the tensile strength and modulus although a slight increment in the elongation at break has been observed. Some poor interfacial adhesion between the PLA and starch has been reported, in particular with star PLA/cornstarch (Park et al., 2000). However, PLA/starch/MA blends plasticized by ATC (Zhang & Sun, 2004c) have demonstrated a noticeable increment in elongation above the 8% ATC level, and PLA/starch ratio which influences tensile strength and elongation (Ke & Sun, 2000) have also been reflected in the study.

Plasticizers distinctively improve the elongation at break but, tend to reduce tensile strength and modulus. Generally, a plasticizer improves the processability and flexibility of a polymer. PLA cornstarch blends at 60:40 weight ratio with a range of plasticizers have shown that as the concentrations of all the plasticizers increased, the tensile strength and Young's Modulus of the extruded and moulded blends significantly decreased due to the reduction in the intermolecular forces and enhanced intermolecular mobility as a consequence of the plasticizer (Ke & Sun, 2001b). In contrast, with the sorbitol plasticizer, the properties increased. The small molecular weight of ATC and TC have shown increments in elongation upon increasing levels of plasticiser and the results coincide with the reported results of a previous study of citrate esters (Ke & Sun, 2003b; Labrecque et al., 1997), but sorbitol had no effect.

The effects of moisture content and heat treatment on the mechanical properties of PLA/starch blends have been studied (Ke & Sun, 2001a). In his study, although the degree of gelatinisation of starch has increased, the moisture content did not show significant influence on the mechanical properties. Furthermore, the samples prepared by injection moulding process showed higher tensile strength and elongation at break and lower moduli compared to those prepared by compression moulding process under the processing conditions employed in the investigation. Ke et al (Ke, Sun & Seib, 2003) who also studied blends of PLA and corn starch with varying amylose content and different moisture content demonstrated a decrease in strength, elongation and moduli with an increasing starch content irrespective of starch type and composition because of the reduction of the cross sectional area of the PLA continuous phase. The results further accounted for no significant difference in mechanical properties between dried starch and starch with 30% moisture content. Starch and PLA blends with equal weight proportions have been blended with different weight ratios of poly(vinyl alcohol) (PVOH) and 30% PVOH with different molecular weights to improve the compatibility between the two components (Ke & Sun, 2003a). The authors have reported that the tensile strength of the starch/PLA (w/w 50:50) blends increased as PVOH concentration increased up to 40% and decreased as PVOH molecular weight increased. PVOH has not shown any effect on elongation at break because the PVOH itself is brittle as reported by the authors, but modulus has increased and is in a higher range than the blend without PVOH. The blend containing gelatinized starch and PVOH has shown the highest tensile strength. However, gelatinized starch has also resulted in the superior water absorption. Blends with 40 and 50% PVOH also showed the greater water absorption. Nevertheless, the molecular weight of PVOH had only a slight effect on water absorption at a concentration of 30%.

Further attempts have been made to improve blend compatibilization in terms of reactive blending by Jun (Jun, 2000) where the approach promotes the chemical reaction between the two polymers in a molten state with a third reactive component. Poly (lactic acid) (PLA) and starch (25 and 50 %) was extruded with a coupling agent using a single screw extruder. Each of the agent's, toluene diisocyanate (TDI), 4, 4'-methylenebis (phenyl diisocyanate) (MDI) and diethylene triamine, 1,6-diisocyanatohexane (DIH) was employed

during the extrusion process. Significant improvements of the reactive blending have been confirmed by the increased tensile strength due to cross linking reaction thus increasing compatibility. More flexible aliphatic DIH was found to be a very effective agent for the reactive blending of PLA/starch with its long chains. The polyethylene-polypropylene glycol copolymer with hydrophobic-hydrophilic structure has also been investigated as a plasticizer. As the plasticizer was added, the strength of the blends decreased but 10% plasticizer with 25% starch showed considerable improvement in the blend elongation.

The effect and interactions of extrusion parameters on the tensile strength of starch and PLA blends at various water contents have been studied with 50:50 blends of PLA/cornstarch blended by twin screw extruder and injection moulded into tensile bars (Pan & Sun, 2003). Irrespective of the zone temperatures and moisture content, the tensile strength reached a maximum point upon increasing screw speed and then decreased as the screw speed continued to increase. At higher screw speeds, the increased shear force caused mechanical degradation of both the PLA and starch to make short polymer chains resulting in a lower tensile strength. The high screw speed also reduced residence time and as a result granular starch remained in the blend resulting in poor association in the interpenetration network between PLA and starch to produce lower tensile strength. Results have also shown that increasing moisture content decreased the optimum first zone heating temperature of the PLA/starch blends but increased the optimum screw speed to attain the maximum tensile strength.

Water loving starch and water resistant PLA are thermodynamically immiscible and this leads to weak adhesion resulting in very poor performances due to weak interfacial interaction between the two components. Compatibilizers together with an array of additives have been used to study the interface between the two materials, with the view of reducing the interfacial tension thereby increasing compatibility. Methylenediphenyl diisocyanate (MDI) has been used by Wang et al. (Wang, Sun & Seib, 2001) to strengthen the interaction between the polymer phases of the blend of 55/45 (w/w) mixture of polylactic acid and dried wheat starch in an intensive mixture. The improved tensile strength by 7% in the blends compared to pure PLA has been reported that could be

explained by the in situ formation of a block copolymer acting as a compatibilizer and reducing the interfacial tension between the two phases but the elongation at break dropped off by 1/4th. The authors also reported that starch and MDI both had a constructive effect on Young's modulus but the effect from starch was more prominent.

The properties of polylactic acid and wheat starch blends have also been investigated with the fixed methylenedipheny diisocyanate content (Wang, Sun & Seib, 2002b) with various levels of wheat starch and PLA, on specimens hot mixed at 180°C and hot-pressure molded at 175°C. The blend with 45% wheat starch and 0.5 wt % MDI have shown utmost tensile strength of about 68 MPa with about 5.1% elongation compared to a tensile strength of 62.7 MPa and elongation of 6.5% of pure PLA. For a material to behave as a highly tough material, the surface energy at the interface of cracking necessarily needs to be smaller than or equal to the fracture energy. Authors (Wang, Sun & Seib, 2002b) have also noted that the blends with MDI had the higher fracture energy than the blends without MDI and the blend with 20% starch and 0.5 wt % MDI had the lowest tensile strength of about 58 MPa with about 5.6% elongation. The Young's Modulus and storage modulus increased but $\tan \delta$ decreased as the starch level increased in the blend, but almost leveled off when starch level reached 45% or higher. Water absorption of the blends increased significantly with the starch content. The effect of starch moisture content on the interfacial interaction of an equal-weight blend of wheat starch and PLA containing 0.5% MDI was also studied by Wang et al. (Wang, Sun & Seib, 2002a), however, the starch moisture (10% to 20%) posed a negative effect on the interfacial binding between starch and PLA. As reported by the authors, the tensile strength and elongation of the blend both decreased as starch moisture content increased due to the competition of water between PLA and starch in reactions of MDI. At the highest moisture level of is 20%, the starch granules embedded in the PLA matrix were observed to be swollen, resulting in poor strength properties and the high water absorption by the blend.

The properties as affected by physical ageing on blends of similar weight ratios of PLA and different starches in the presence of a fixed MDI level have been evaluated (Wang, Sun & Seib, 2003). As the ageing proceeds, tensile strength, elongation and Young's modulus of

thermally blended and compression moulded samples decreased irrespective of the starch type or presence or absence of the MDI in the blend. Although all the samples exhibited the phenomena of physical ageing, the samples with MDI aged more slowly, showing a slower reduction rate of the excess enthalpy relaxation, than those without MDI. A reduced interaction between starch and PLA around the interface has been reported in the microstructure with ageing (Wang, Sun & Seib, 2003).

A different approach to mixing MA grafted PLA and starch gelatinized by a glycerol/water mixture has been employed by Huneault (Huneault & Li, 2007). The starch was plasticized and the water was removed before the PLA was added as a side feeder to the mid extruder and extruded through a strand die. The grafting of the PLA with the MA and the consequent mixing with thermoplastic starch exhibited the greatly improved elongation at break in the range of 100-200% compared to non modified control. Rheological properties of starch PLA blends investigated on the HAAKE rheocord have shown that the viscosity decreased with increasing shear rate but melt viscosity of the blend increased with the rising starch level in the blend and this was more prominent at starch levels of 30% and above (Xie et al., 2007). The authors also reported that the MDI in the blend of starch and PLA had no effect on the melt viscosity when it was distributed in the starch phase, however, influenced the viscosity when it was dispersed in PLA phase. This effect was attributed to the ability of moisture contained in the starch phase to destroy the function of MDI.

2.9 Introduction to Extrusion and Injection moulding

2.9.1 Extrusion Process

Extrusion is a process in which plastic materials in the form of pellets are continuously converted into products like tubing, rods, films, sheets or a product of a specified shape or cross section. This process is also used as a technique for mixing additives, fillers to polymers for property modifications. To bring the high viscosity systems like polymer melts, polymer pastes to a uniform state, it is required to reorient the parallel layers generated during mixing by making them intersect each other. Simple blades are not

suitable for mixing in such conditions as they make parallel layers. The extruder acts as a mixer when the mixing process requires high shear stress for the dispersion and large shear strain and continuous reorientation for good distribution. There are extruder machines that are designed only for mixing purposes. Depending on applications, different types of extruders can be used.

The extruder consists of a single screw or two screws within the barrel which can be heated or cooled to obtain the required temperature profile. It also consists of the feeding part for material or other additive input and a die fitted at the exit for shaping the extrudate. The extruder can also be classified as continuous or discontinuous according to its operating cycle. The continuous extruder has a rotating screw and process the material in a continuous flow into products such as rods, pipes etc. The discontinuous extruder has a reciprocating screw, operate in a cyclic fashion and suitable for batch type processes like injection moulding, blow moulding. There are five operations take place within the extruder.

- Feeding
- Polymer melt or plasticise
- Convey forward
- Melt mix
- Form a shape

During the processing of polymers in an extruder, raw material is conveyed from the feed zone to the die, on the way, material is heated by internal shearing and the external heating devices in the barrel to attain to required plasticising temperature. It is further mixed and homogenises and extruded through the die by the pressure generated due to the variation in the channel depths of the screw.

2.9.2 Extruder screw

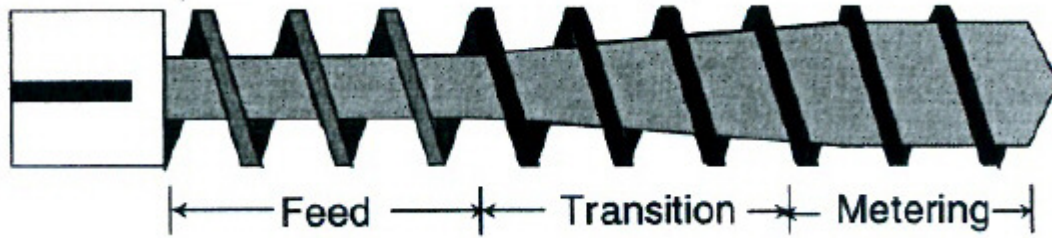


Figure 2.5 Extruder zones

The screw of an extruder is principally divided into three sections and are shown in figure 2.5

- Feed Zone (Deep flight)-channel depth (a) is greater than the other two zones therefore the material is easily conveyed and forced to the compression zone. Because of heat, the thin film of molten plastic is developed.
- Compression Zone or Transition Zone- channel depth decreases gradually and hence pressure is developed on the material and increase heat generation. The pellets are plasticised into the smooth melt and the melt pool is developed.
- Metering Zone (shallowest flight) – The channel depth is smaller than the other two zones. Homogenisation of plastic occurs and the polymer melt is pumped at a uniform rate to the die.

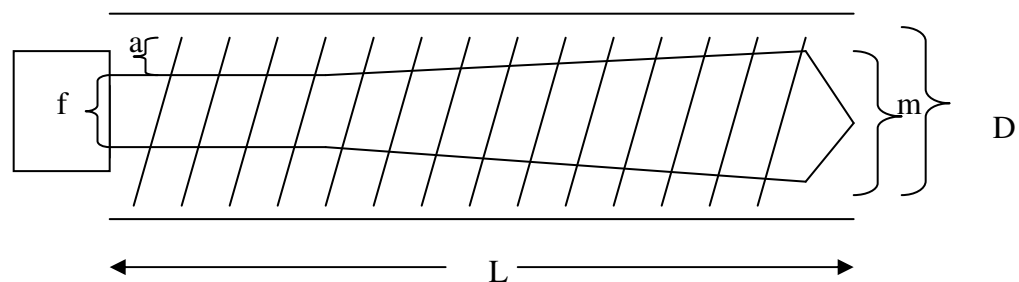


Figure 2.6 Schematic diagram of an extruder screw with screw elements

A typical schematic diagram of a twin screw extruder is shown in figure 2.6. The screw elements are shown in figure 2.7 and the screw nomenclature is defined below.

- Channel depth - Distance from top of the flight to the root (a)
- Channel - Space between flights
- Screw diameter - distance between furthest points of the flight across the shafts (D)
- Pitch - Distance between consecutive flights
- Length - Hopper to screw tip (L)
- L/D ratio - Screw length/screw diameter
- Compression ratio - Ratio between feed and meter channel depths

Compression ratio = Feed zone channel depth/ metering zone channel depth

Feed depth = (distance between outside of gauge blocks-(2 x thickness of the gauge block))- root diameter in the feed zone(f)

Meter depth= (distance between outside of gauge blocks-(2 x gauge block thickness))- root diameter in the metering zone (m)

The screw compression ratio is very important for polymeric materials during processing because different materials process efficiently at different compression ratios due to their varied viscoelastic behaviours. Extruder screws are classified by their length (L) to Diameter (D) ratio. For plastics, L/D ratio is generally 12-30. The higher the L/D ratio designates that surface available for mixing, shearing and plasticising the granules is high.

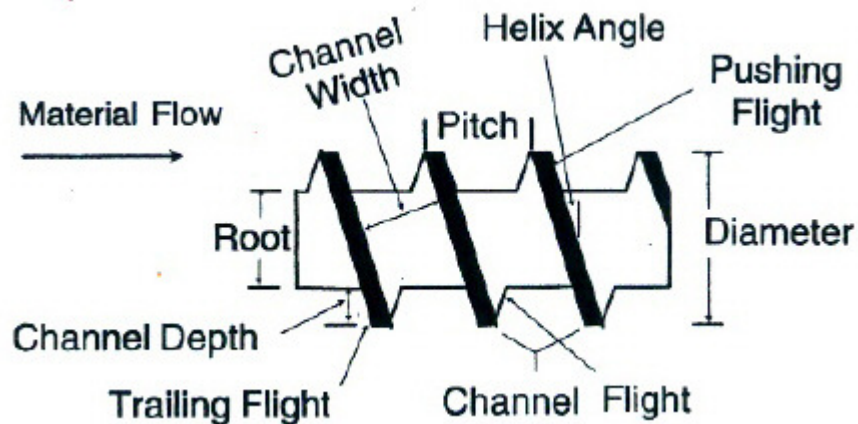
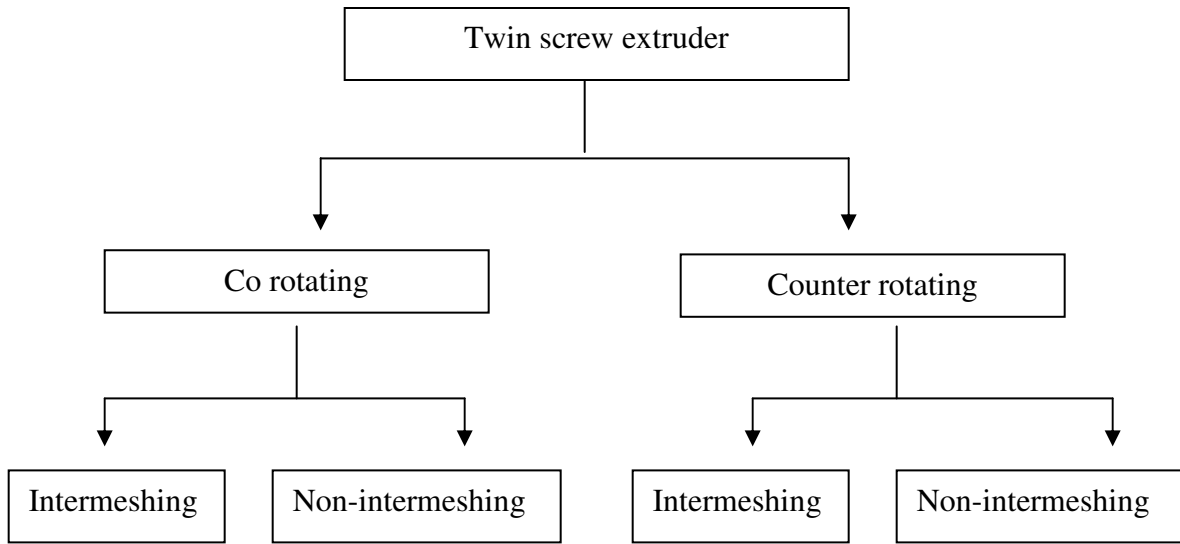


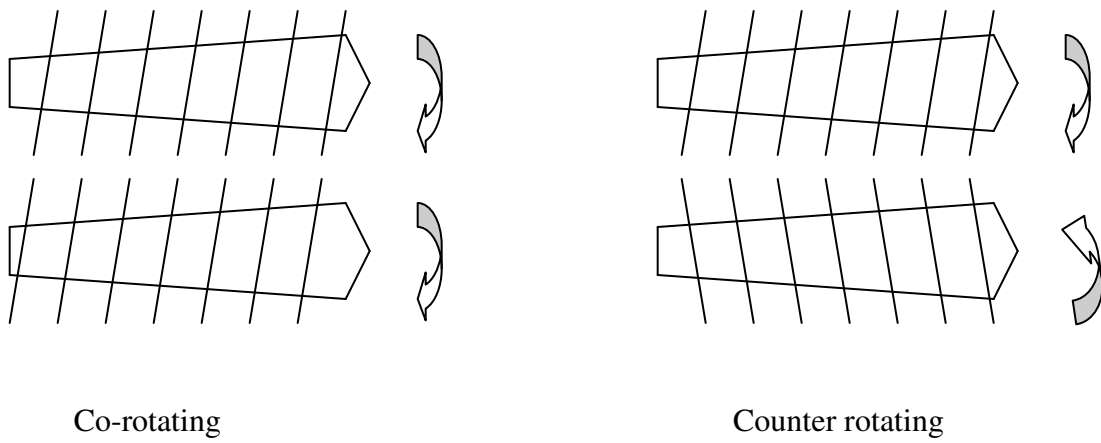
Figure 2.7 Screw elements adapted from (Giles, Wagner & Mount, 2005)

2.9.2.1 Types of twin screw extruders



Scheme 2.3 Available models of twin screw extruders

Twin screw extruder models can be either co-rotating in which both screw shafts rotate in one direction or counter rotating where the two screws rotate in the opposite direction and provide very intensive mixing. With the varying distances between screw shafts in the co-rotating or counter-rotating models, it can further divide to intermeshing or non-intermeshing in which there is a small space between screws and no engagement between two screws.



In a corotating screw extruder, high and low pressure regions are generated for the material near the extruder apex whereas polymer flow in the counterrotating extruder is forced between the two screws generating high pressure region at the nip and low pressure region at the nip exit as can be seen by figure 2.8 (a) and (b).

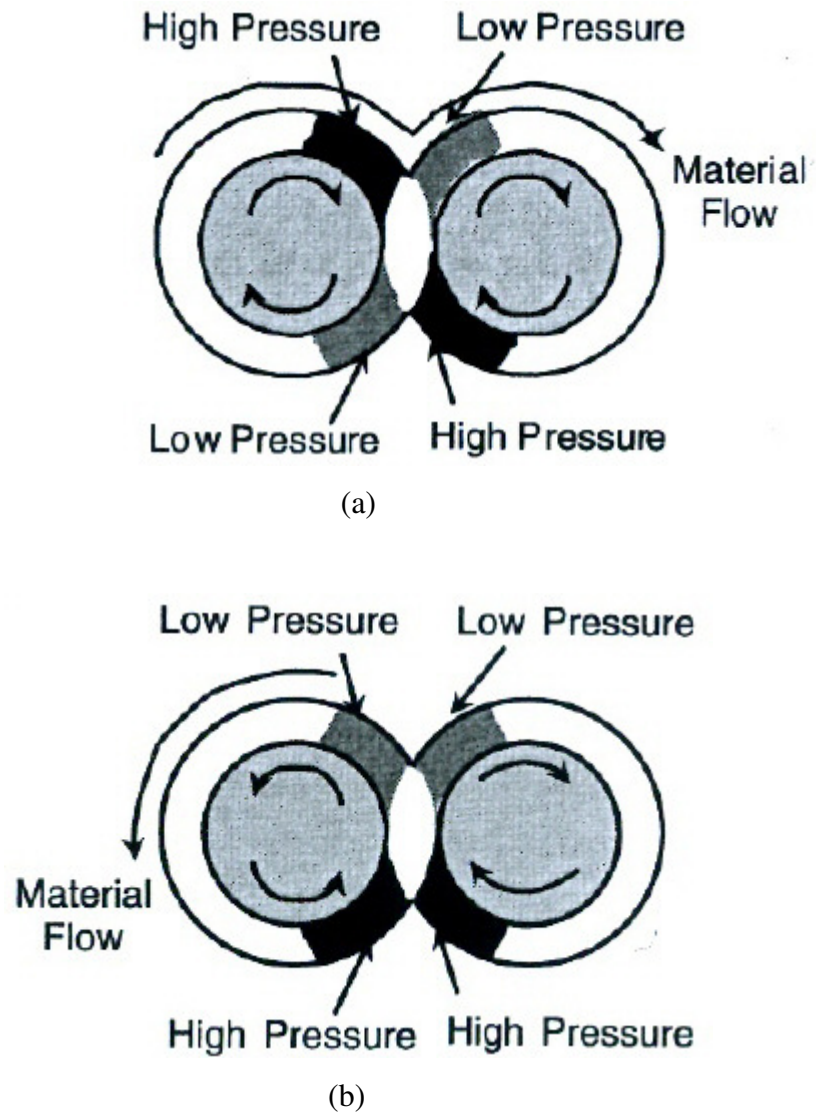


Figure 2.8 Material flow (a) in a corotating screws (b) in a counterrotating screws adapted from (Giles, Wagner & Mount, 2005)

2.9.2.2 Feed zone

In a simplest feed system, conveying is generally induced by gravity in which pellets, powder, additives etc are pushed from the hopper into the screw channel. The driving force is mainly gravity. The low density systems do not feed well on conventional equipments (Giles, Wagner & Mount, 2005). The material compressibility, in other words, the ability of loose materials to occupy less volume is another feature affecting feed. The feed problems such as bridging, rat holing with some entrapments are usually caused by the materials with more than 20% compressibility. Bridging at the bottom of the hopper can happen either slowly or sometime rapidly, preventing the polymer from flowing into the extruder. If bridging is caused by heat, material builds up slowly, owing to softening or due to tackiness, until the feed throat is completely blocked. As a result, the gradual decrease in the product dimensions is also observed, accompanied by a drop off in the extruder motor load.

2.9.2.3 Polymer plasticisation

The melting starts in the feed zone within few screw diameters from the feed opening. The polymer melts due to conduction from the barrel as well as due to viscous shear heating. The majority of the heat necessary for polymer melting is generated through the shear by the screw rotation, while the other heating comes from the barrel heaters. Shear heat is generally produced by two ways. Primarily in single screw extruders, it is created due to the shearing of the material coming into contact with the barrel wall and secondly for both single and twin screws by the individual layers of polymeric materials sliding with each other during laminar flow, generating viscous heat. As a consequence of the polymer flow, the resistance of one layer over the molecules in another layer results the heat produced and thereby melt the polymer. Due to a high shear rate in an extruder and reasonably high viscosity of the polymer, viscous heat generation is the most important factor contributing to polymer melting.

2.9.2.4 Mixing

Regardless of the type of extruders, two types of mixing occur in a twin screw extruder namely distributive mixing and dispersive mixing. In distributive mixing, particles are uniformly distributed throughout the melt and it is a low shear process where breaking and recombining of the melt stream occurs. In the dispersive mixing, large particles are broken down and dispersed as small particles throughout the melt. Dispersive mixing is a high shear process and the effectiveness of the mixing is dependent on the screw speed, temperature, percent fill in the screw channel and screw geometry.

2.9.2.5 Melt conveying

The next operation in the extruder is melt pumping, where melt is conveyed from the metering zone to the die. As the screw rotates, the melt is forced down stream, move across and turns upwards towards the barrel surface by pushing and trailing flights. This is a figure of eight motion where the polymers are subjected to shearing, mixing and conveying forward towards the exit. Polymer flow in the metering zone near the die is accomplished by drag flow and the flow created by the screen pack of the die head.

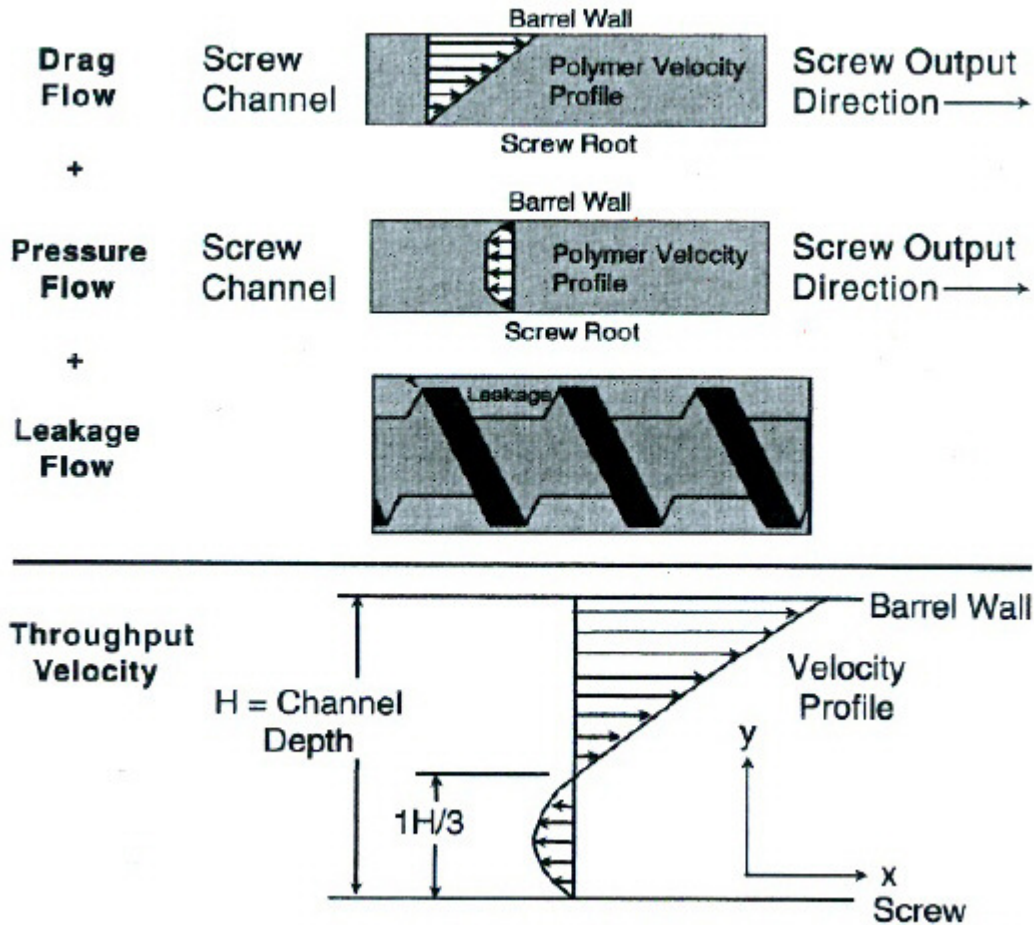


Figure 2.9 Plastic melt flow profile adapted from (Giles, Wagner & Mount, 2005)

The rotation of the screw in the barrel creates drag flow, which has higher velocity at the barrel wall and zero velocity at the screw root. When the melt pushes forward, the extruder melt pressure is generated near the die, which is called head pressure or back pressure. The velocity profile of the pressure flow is opposite to the drag flow velocity, where zero velocity is near the barrel wall and screw surface while high velocity is in the centre. Therefore, actual flow of the polymer melt is evidently due to the difference between these two flows and leakage flow, which is the flow over the top of the extruder flights that becomes significant for a worn screw. Plastic flow profile is given in equation 2.1 and shown in the figure 2.9.

$$\begin{aligned}
 \text{Plastic melt flow (Q)} &= \text{Drag Flow} - \text{Pressure Flow} - \text{Leakage Flow} \dots\dots\dots 2.1 \\
 &= (Q_d) - (Q_p) - (Q_l)
 \end{aligned}$$

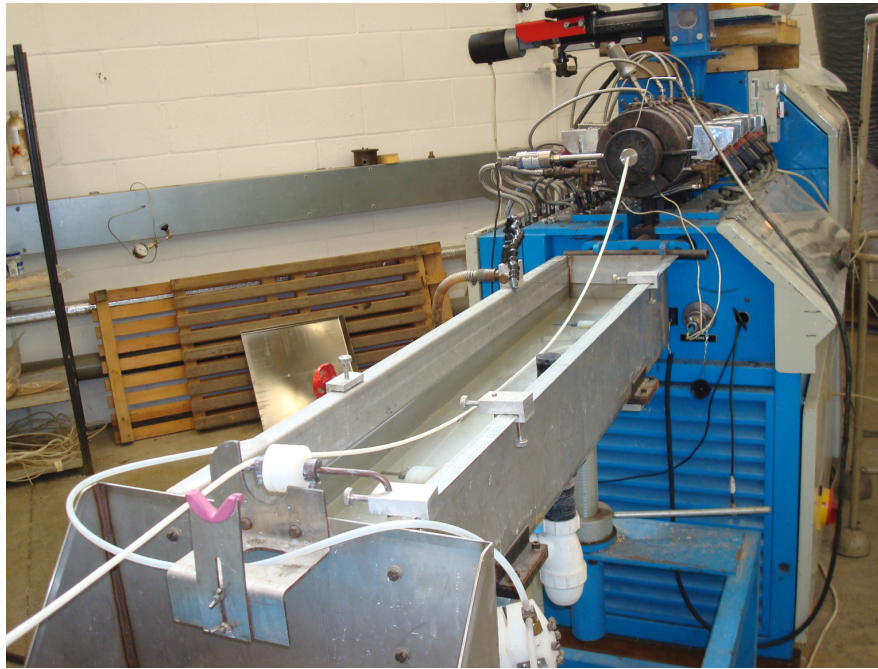


Figure 2.10 Lab-scale co-rotating twin screw extruder in process and extruding a PLA/starch composites string

When the material leaves the die outlet, molecular relaxation due to the change in flow velocities occurs, so there is a possibility for a dimensional change in the extrudate. This phenomenon is called die swelling. Die swell depends on the speed at which material is transported in the die and the die temperature. As a result of die swell, melt blasting will take place. This problem can be fixed by reducing the screw speed, increasing the melt temperature and increasing die length. After the melt leaves the die, the shape and dimension is fixed and cooled sufficiently. Extrudate cooling is usually achieved with air, water or contacting with a solid surface. For example, sheets and films cool by rolling while profiles, strands, tubes and cables are passed through a water bath. The take off device draws the extrudate from the die through the cooling unit at a constant rate. Cut off and stacking is the final stage for rigid tubes and sheets while winding is done for films cables etc. Figure 2.10 represent the lab scale co-rotating twin screw extruder extruding PLA/starch composite string.



Figure 2.11 Pelletiser in the process of pelletizing extruded string

The pellet preparation of a composite is principally based on the pelletisation of the mixed polymers and additives that have been plasticised and homogenised in an extruder and shaped through a strand die with a specific diameter. A pre-blended mixture is fed through the hopper system to the extruder or materials are fed to the separate feeders at the same time at the same feeding rate or different predefined feeding rates. The extruded strand is passed through a water bath through to a pelletiser where continuous plastic string is trimmed into small pieces of approximately 2mm size. Figure 2.11 shows trimming process of a PLA/starch composite string. Pellets are stored after long strings being pelletised to make different dimensions of finished articles by separate processing such as injection moulding.

2.10 Injection moulding Process

Injection moulding is an automated process that can be used to manufacture plastic parts in one production step. The process is suitable for mass production of articles as the raw material can be converted into products by a single procedure, though there may be several automated steps embedded within the moulding cycle. The most significant advantage of injection moulding is that the process can be used to make complex geometric articles which can be found every where in daily life, in one fabrication step. The conversion is done by plasticising the moulding material and injecting it under pressure into the mould, where it solidifies in the shape of the mould cavity.



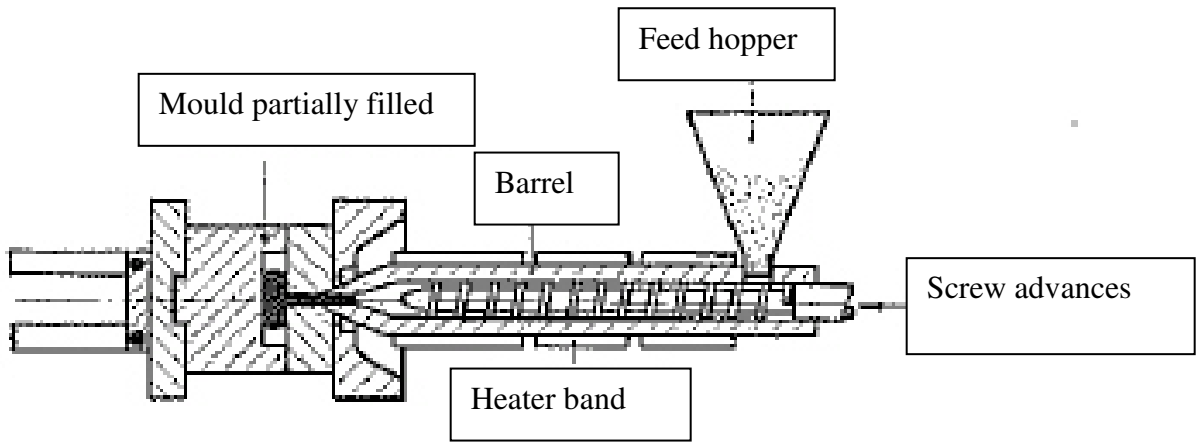
Figure 2.12 Demag injection moulding machine in process

Figure 2.12 represents injection moulding machine processing a tensile test bar of a PLA/starch composite. The complete moulding equipment necessary for injection moulding mainly consists of three parts, the injection moulding machine which is universal, the injection mould which vary and is mounted onto the machine depending on

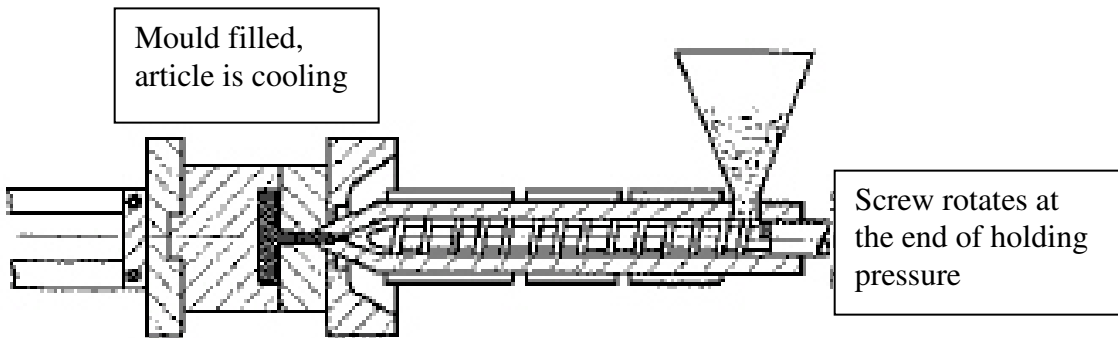
required different shaped articles and mould temperature control unit. Each mould contains a cavity into which plasticated material is injected and the final part is formed. The injection moulding machine also consists of two essential parts, the injection unit and the clamping unit. Though the process is spontaneous, the complete injection moulding cycle occurs in several steps.

- a. Start of plastication- The reciprocating screw rotates and simultaneously takes up materials from the hopper and melts the material by means of internal shearing, friction and external heater bands, conveyed towards screw chamber in front of the screw tip. The conveying action of the screw builds up pressure in front of the screw tip and therefore the screw is allowed to return sliding back until the chamber is filled with sufficient melt volume.
- b. End of plastication- When the screw chamber is filled with just sufficient melt to fill the cavity, the screw rotation is switched off.
- c. Closing the mould- The clamping unit with cavity plate move forward to close the mould
- d. Start of injection- At this time the sudden pressure surge in the hydraulic cylinder moves the screw forward without rotation, pushing the melt from the chamber through the nozzle to the mould cavity
- e. End of injection and cooling- When the mould cavity is completely filled with hot melt and as the injected melt solidifies in the cold mould, screw presses additional melt into the mould to compensate volume contraction of the material. Afterwards, the injection unit re-starts step (a) and prepare material for the next shot while further cooling take place.
- f. Ejection of the article- When the mould part has cooled and hard enough, the mould opens and article is ejected by the ejector pins and complete the injection cycle. By this time step (b) which is the plasticating step is completed and next moulding can start. step (c)

The injection stage of the process is shown in figure 2.13 (a) where (b) and (c) illustrate the holding pressure, plastication and ejection stages respectively.



(a)



(b)

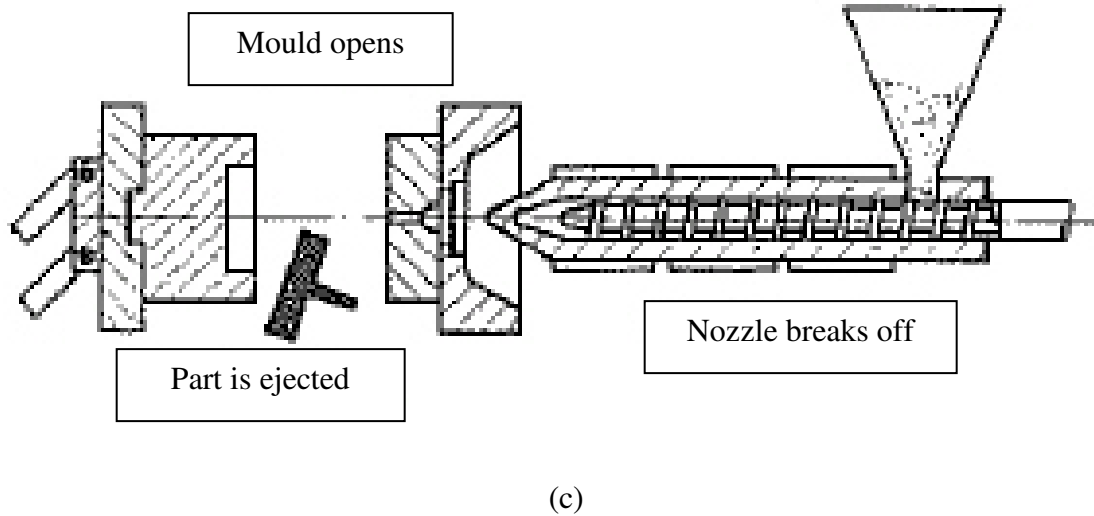


Figure 2.13 Three stages of injection moulding (a) injection (b) plastication (c) ejection adapted from (Johannaber, 1983)

An injection moulding machine consists of four functional entities; injection unit, clamping unit, drive systems and the control systems. The machines are normally classified by the maximum clamping force, maximum injection pressure or screw diameter. Conventional machines are generally within the range of 18-120mm screw diameter, 1500-2500 bar injection pressure and 20-10,000 bar clamping force. Classification of machine sizes uses the clamping force and a term P where

$$P = (V_{\max} \times P_{\max}) / 1000$$

Where V_{\max} = maximum shot volume (cm^3)

P_{\max} = Maximum injection pressure (bar)

2.10.1 Injection unit

The injection unit has to fulfil a few main tasks and some obvious additional tasks to accomplish the process. The main functions include accepting a free flowing polymer

pellets entering from the hopper conveying them, heating and melting them, injecting the melt into the cavity and holding the moulding with additional pressure during the cooling process. More implicit additional tasks usually performed by screw injection unit nowadays include moving forward and backward to get in contact with mould bushing and sealing the connection with nozzle and sprue bushing. The hopper, screw, check valve at the screw tip, nozzle and the heater bands are the most important elements in the injection unit. Although difficulties using pellets are low, the risk of bridging processing powders in the hopper stagnate material flow. Therefore, funnel type hoppers with a closing slide at the lower end satisfy some requirements that are easy to operate, easy to mount, capable of being fully emptied, dust tight and easy to clean. Figure 2.14 represent reciprocating screw injection unit with its important elements.

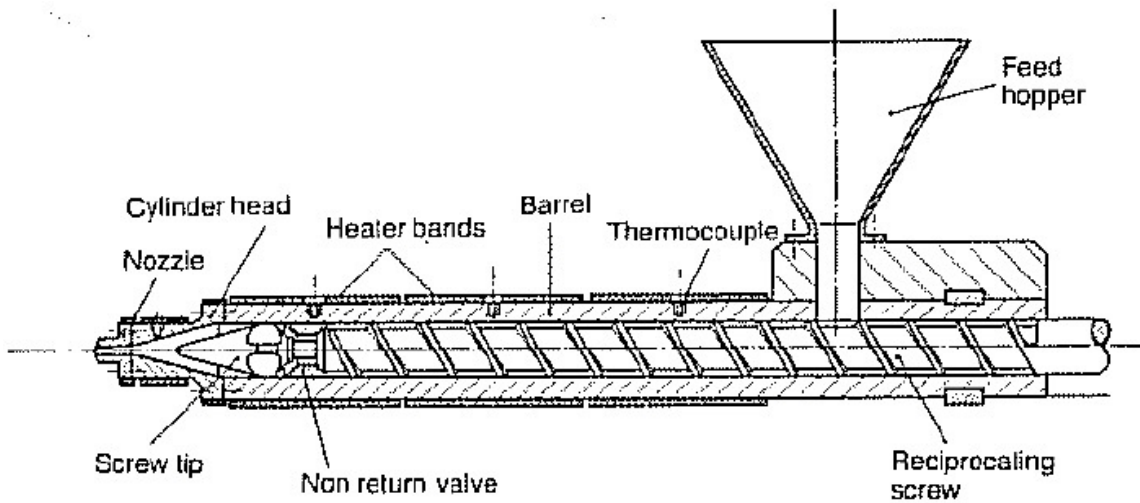


Figure 2.14 Reciprocating screw injection unit (Johannaber, 1983)

The screw essentially plasticises and injects the polymer into the mould cavity. Efficient conveying, sufficient plasticisation, effective melting and homogeneous mixing are necessary demands. The most commonly, a screw rotating and moving axially in a barrel fulfils most of the above demands. The screw is similar to extruder screw and consists of three zones, which are different in their functions.

- Feeding zone- large flight depth allows adequately flow, material is transported
- Compression zone-material is compressed and completely molten at the end of the zone
- Metering zone-thermoplastic melt is homogenised and heated to required final processing temperature

The screws are described by the L/D ratio and different types of screws are available such as screws for elastomers, thermosets, thermoplastics etc. The stroke s which controls the maximum injection volume has to be less than a particular value ($s < 3D$) (Potsch & Michaeli, 1995). The check valve in the injection screw allows the screw to behave as a piston during the injection and holding pressure phases, by simply sealing off the screw duct thereby preventing backflow of the melt down the screw channels. The plasticising barrel ends at the mould in a nozzle which is forced against the sprue bushing of the mould and produces locking the force to the connection prior to injection. Figure 2.15 shows open and shutoff nozzles with internal needle.

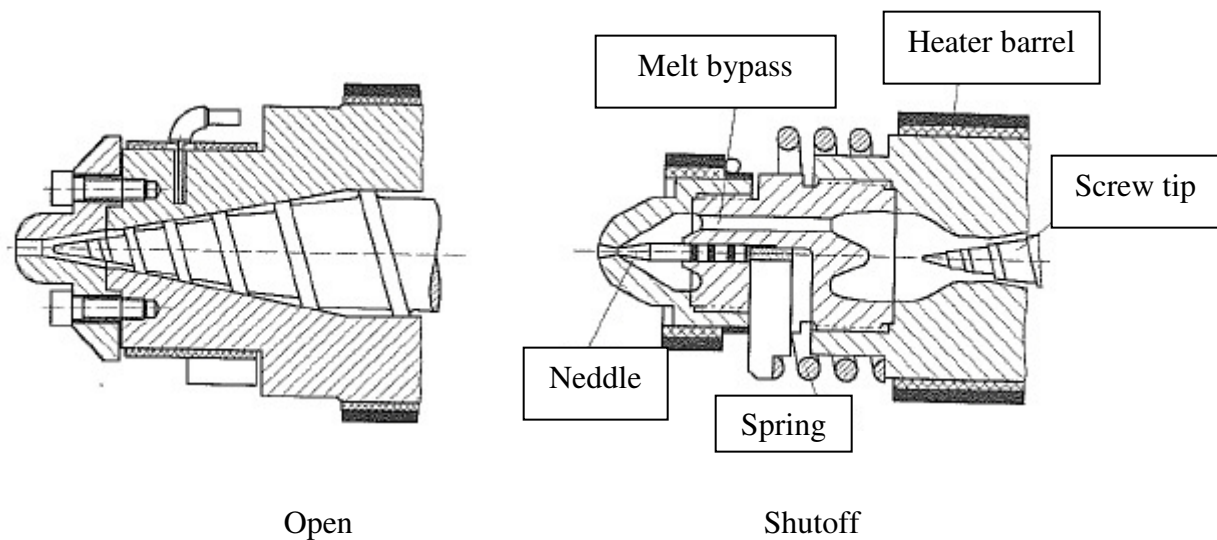


Figure 2.15 Open nozzle and shutoff nozzle with internal needle (Potsch & Michaeli, 1995)

The injection pressure is an important parameter, which is the pressure exerted on the melt near the screw tip during the injection stage with the screw acting as a plunger.. It affects the screw moving forwards as well as process of filling the mould cavity.

2.10.2 Clamping unit

The injection moulding process is a continuous process, so the machine opens the mould for ejecting the part and closes it immediately for the next shot. The clamping unit, which accommodates the mould, provides motion needed for closing, clamping and opening and produces the force necessary to accomplish the continuous moulding process. The unit consist of movable and stationary platens, tie bars and a mechanism for opening, closing and clamping. Three clamping unit designs are available namely mechanical, hydraulic and combined system of mechanical-hydraulic clamping systems. The mechanism that holds the mould efficiently closed throughout the injection and holding pressure phases is the clamping system.

Mechanical clamping is provided by toggle clamp system, which functions hydraulically for closing and opening of the mould where as in the hydraulic clamping system, the ram of the hydraulic clamp cylinder which is usually positioned in the centre, provides the entire closing and opening strokes for the movable platen. The ram is tightly attached to the moving platen. Combined clamping systems provide separate operations for closing and opening and producing clamping force. In the toggle clamping system several different forces take place in the system during mould closing, filling, breaking and opening. Figures 2.16 and 2.17 represent clamping unit with single toggle lever and hydraulic clamping unit respectively. Figure 2.18 shows hydraulic-mechanical clamping unit.

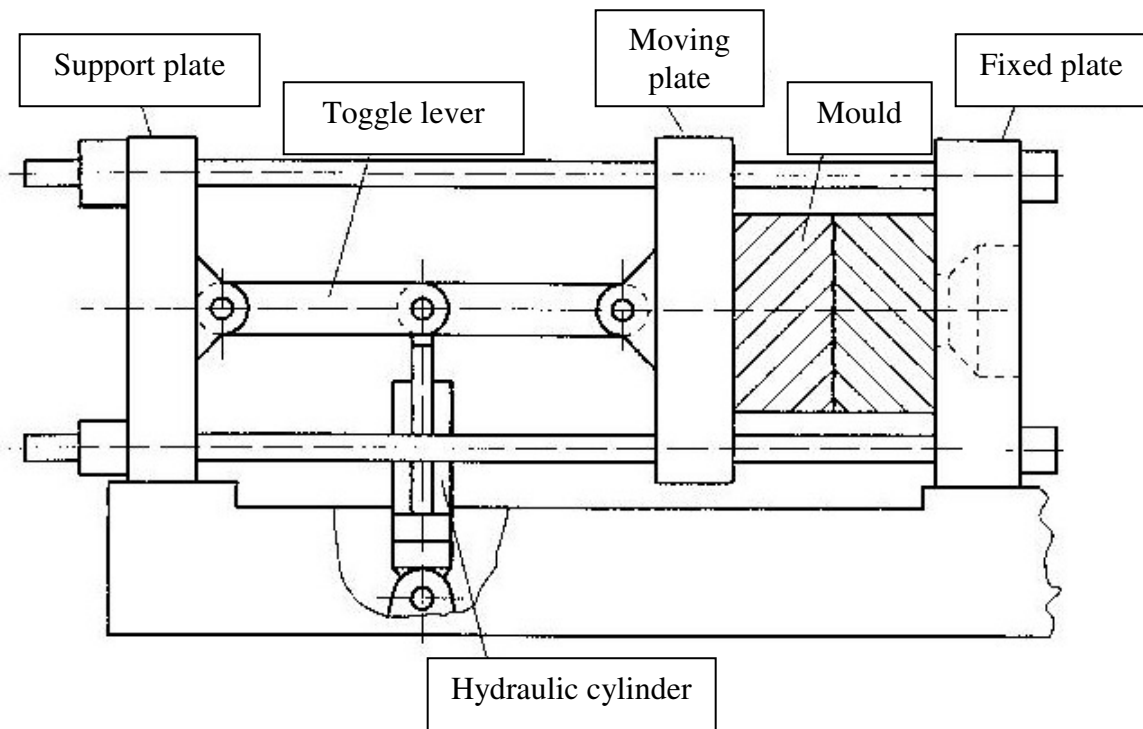


Figure 2.16 Clamping unit with single toggle lever (Potsch & Michaeli, 1995)

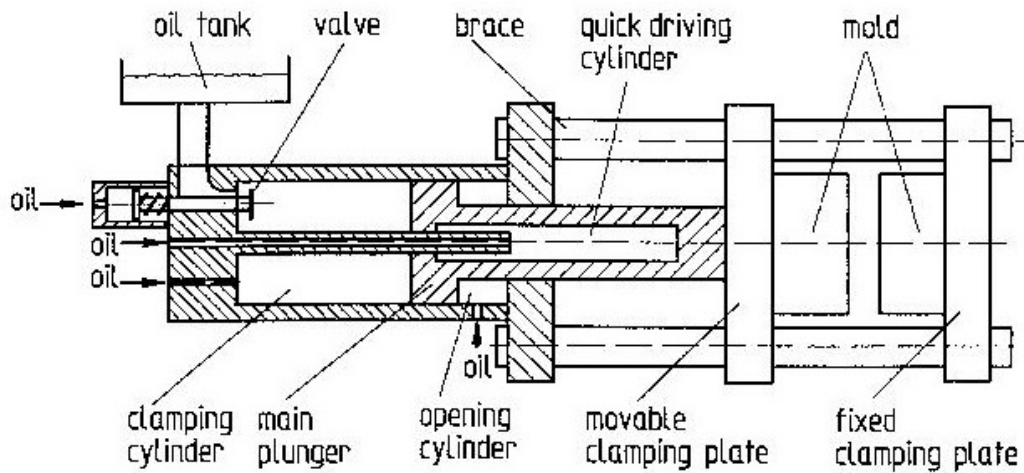


Figure 2.17 Hydraulic clamping unit (Johannaber, 1983)

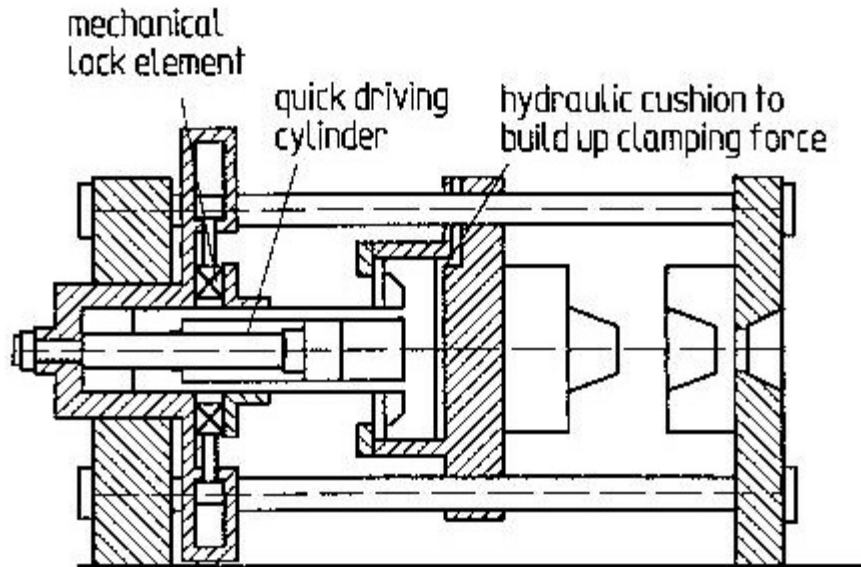


Figure 2.18 Hydraulic-mechanical clamping unit (Potsch & Michaeli, 1995)

2.10.3 Control system

The control system mainly consists of a control unit and coordinates the machine sequences. The system controls all motion sequences of the machine, initiation and the correct order, signalling of the position etc. The control unit in particular controls the following separate parameters.

- barrel temperature
- screw rotation
- melt temperature
- mould temperature
- temperature of the hot runner system
- injection speed
- holding pressure
- injection pressure
- Times
- Strokes-injection unit, clamp unit, ejectors
- Plastic press

2.10.4 Injection mould

The mould accommodates in the clamping unit. Thermally softened material in the injection machine barrel is transferred to the injection mould by the movement of the screw forward without rotation, pushing the melt from the barrel through the nozzle to the mould cavity. In the mould cavity, setting of the shaped article take place. Followed by sufficient hardening and cooling of the component, it is then ejected from the cavity. The mould functions as a heat exchanger and an ejection device. It behaves more than a shaping device because it is capable of separating feed system from the mouldings. There are many different injection mould types available of which two plate moulds are relatively simple and low cost.

In a two plate mould system, the mould separate into two main pieces from the mould split line. The two plate injection mould with two mouldings is shown in figure 2.19. The cavities are filled by a feed system, which consists of the sprue, the runner system and gates. The sprue is a tapered circular channel within the sprue bush in the cavity block, through which the material flows after leaving the nozzle of the machine. The mould cavity is connected to the sprue by channels which are known as runners and the main function of which is the efficient filling of the cavities. In between the mould cavity and the runner, there is a narrow restriction, which is much smaller in size than runner and this is called a gate, which allows easy separation from the feed system at this point. The gate also functions to heat the melt to improve flow. The half of the mould that moves with the clamp is known as moving-half and is associated with the ejection system. Therefore, the moulding is usually retained in this half. A two plate injection mould is shown in figure 2.19 and figure 2.20 represent moving part of the moulding plate used in the experimental work to produce test articles.

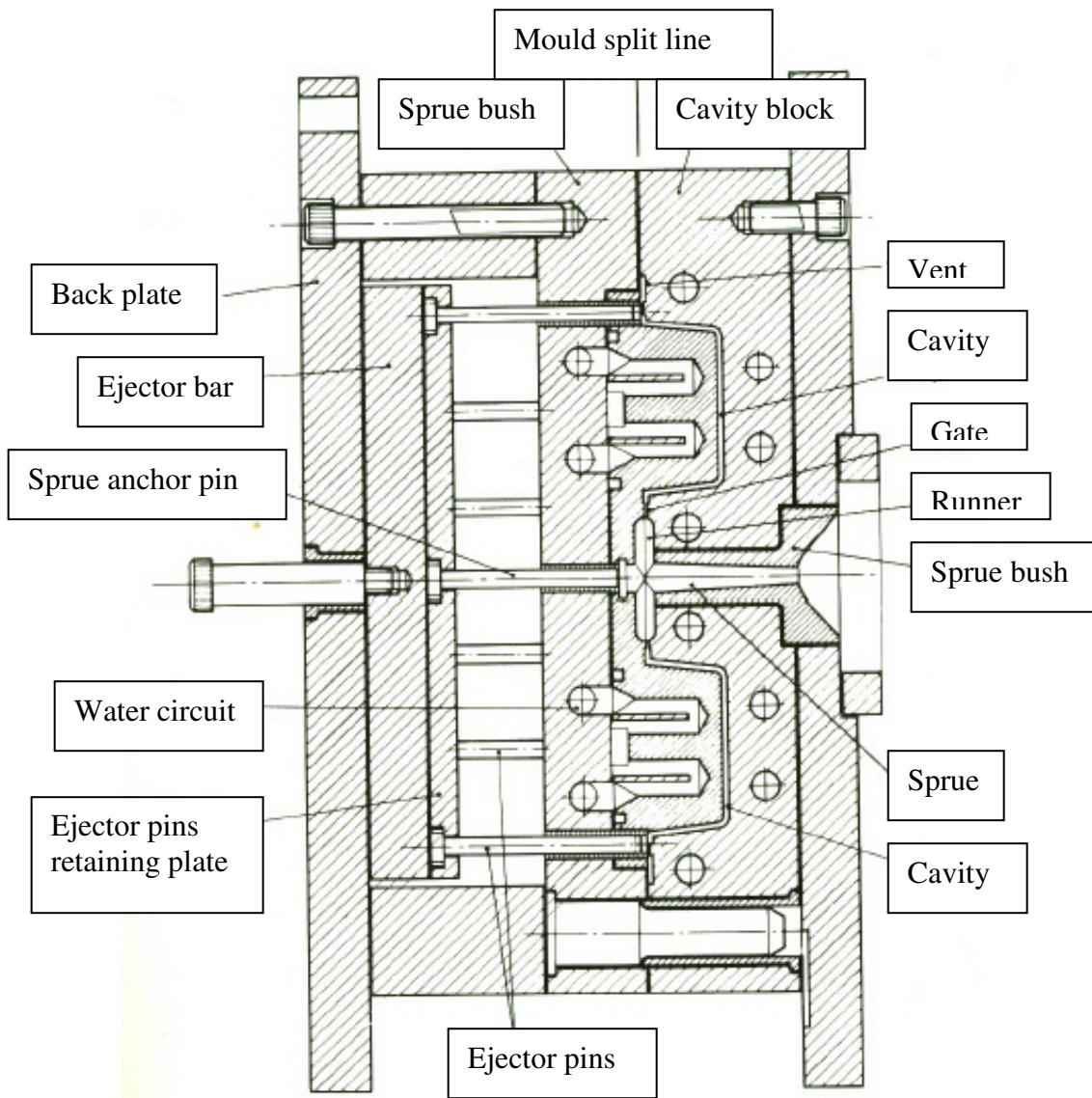


Figure 2.19 Two plate injection mould (Whelan, 1984)

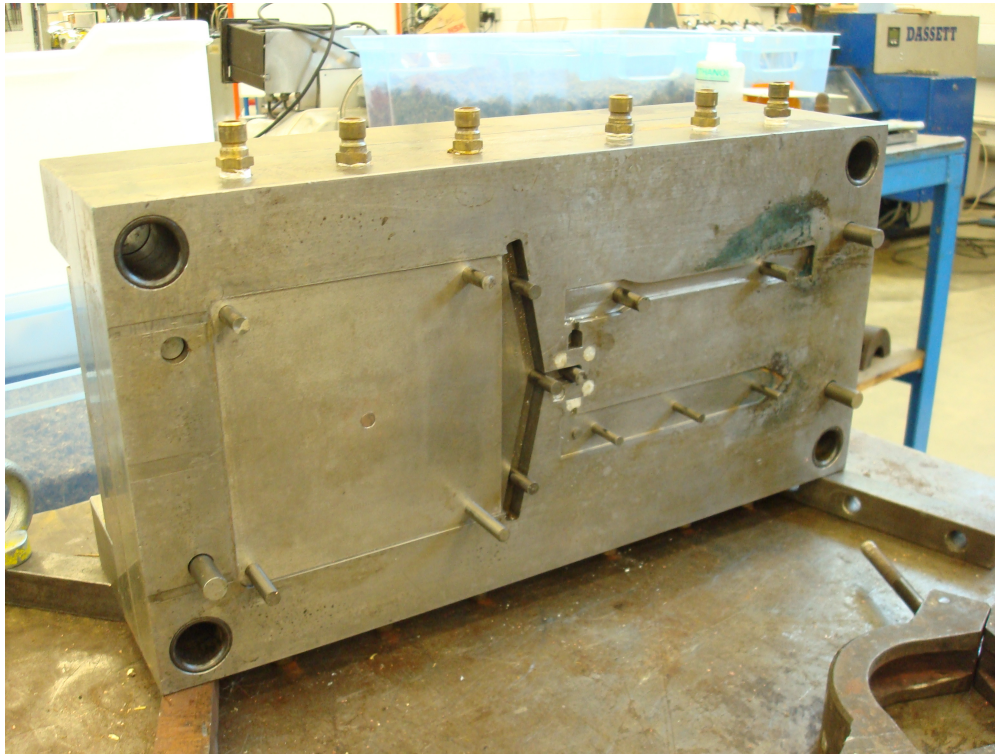


Figure 2.20 Moving part of the moulding plate used to make test articles

3 *CHAPTER THREE*

EXPERIMENTAL WORK

3.1 Experimental Summary

The essential experimental procedures carried out to characterize and understand the behaviour of the composite materials prepared in this study are described in this chapter, aligned together with extrusion and injection moulding processes and other experimental techniques. The materials used the methods of preparation and conditioning prior to testing and the description of testing of the sample materials are explained. The characterization of the injection moulded samples are described and the effect of residence time of the materials in the injection moulding machine and the variation of property associated with additives are also presented in this chapter. The blends of PLA and wheat starch prepared for the experimental work of this study are arranged under the following sections.

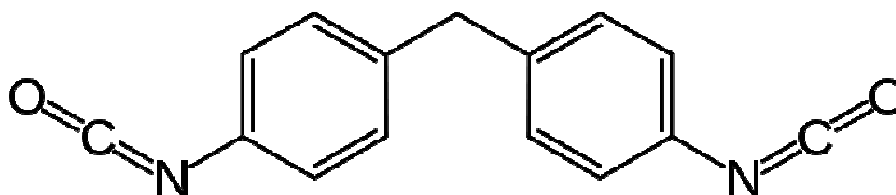
1. Function of MDI and different additives on the properties
2. Role of biostrength materials on the property variation
3. Examination of the effect of glycerol on the properties
4. Study of the behaviour of natural rubber latex on the properties
5. Investigation of the impact of adipic acid on the properties
6. Investigation of the outcome of impact modifier material and pistachio nut shell powder on the properties

The studies carried out on the listed subheadings above have entailed experimental work on the following areas.

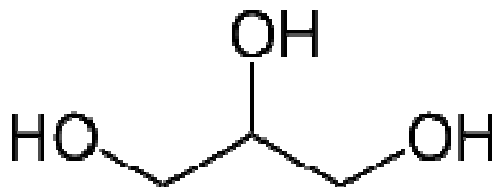
- Extrusion
- Parallel plate rheometry
- Injection moulding
- Differential scanning calorimetry (DSC)
- Thermal gravimetric analysis (TGA)
- Tensile testing
- Impact testing
- Scanning electron microscopy (SEM)
- FTIR analysis
- Degradation
- Physical aging
- Water absorption
- Biodegradation

3.2 Materials used

The polymeric materials used in the experiments of this study were polylactic acid and wheat starch derived from agricultural feedstock. The wheat starch (Maritena 200 BA) was purchased from Food Ingredient Technology Ltd., UK. The PLA known as LACTY 1012 polymerized mainly from L-lactic acid was obtained from Shimadzu, Inc., Japan. Extrusion grade genetically modified organisms free (GMO Free) PLA, PLE 005 (PLAn) was purchased from NaturePlast, France. The other forms of additives that were used in small quantities in the study were as follows. Methyldiphenyldiisocyanate (MDI), a yellowish brown liquid having 4, 4'-diphenylmethane–diisocyanate isomers, was obtained from the manufacture Bayer AG, Leverkusen, Germany. It has the following chemical structure with two reactive isocyanate groups at the end of the chain.



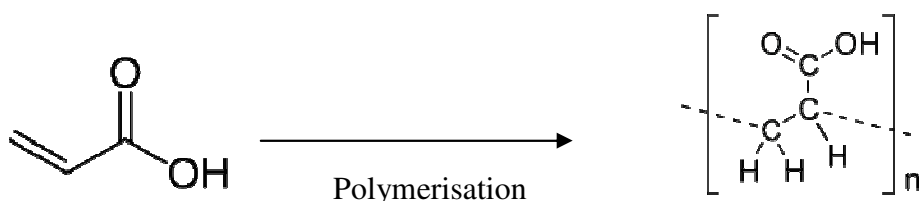
Glycerol with 98% purity was obtained from Fisher Scientific, UK. This compound is a simple polyol, exists as a colourless, odourless viscous liquid with three hydrophilic hydroxyl groups attached to the ends of the chain and the middle carbon atom, the chemical structure is given below. Glycerol is mostly used in the food industry as a sweetener or a thickening agent with some applications in medical, pharmaceutical and personal care industries.



General purpose reagent grade stearic acid (SA) with 97% purity, with a relative molecular mass of 284 and a melting point of 67-69⁰C was obtained as a white powder from BDH Laboratory supplies, England. Stearic acid compound consisting of an 18 carbon chain whose terminal carbon is connected to a carboxylic group with the chemical formula, CH₃(CH₂)₁₆COOH. Stearic acid is a saturated fat belonging to a class of materials known as fatty acids, produced primarily from natural fats and oils. It is more commonly available in animal fat rather than vegetable fat and the elemental structure is shown beneath.

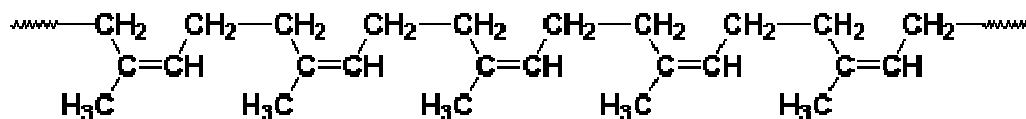


Other materials used in the study were additives with trade names Biostrength 700 and Biostrength 130 are copolymers, which were generously provided by Arkema Europe, Colombes, France. The physical form of biostrength 130 is a white powder with specific gravity 1.09 (at 23°C), bulk density 0.50 g/cm³ (31 lb/ft³) and maximum percent volatiles 1.0%. Biostrength 700 also exist as a white powder with specific gravity 1.17, bulk density 0.30 - 0.60 g/cm³ and percent volatiles of 1.2% maximum. The biostrength 700 (IM) is known to be an acrylic copolymer, which originates from an unsaturated carboxylic acid known as acrylic acid, which has a vinyl group connected to the acid terminus with the structures given below.

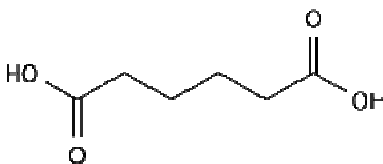


The natural rubber latex was kindly provided by Specialised Latex Services Limited, Oxford, UK. The natural latex is a cloudy white fluid, resembles cows milk but much denser. Many trees produce this white milky liquid in small quantities, nevertheless latex is mainly produced from *Hevea brasiliensis* rubber tree and it is the protective fluid contained beneath the bark. The latex is collected by cutting a thin slanted strip of the bark from the tree and allowing the latex to exude into a collecting vessel over a considerable

period of hours. Latex is a colloidal dispersion used to make rubber and the major chemical constituent in latex is 1,4 polyisoprene with the given chemical structure below.



Analytical reagent grade adipic acid (AA) which is also called 1,6 hexanedioic acid with 99.5% assay, the molecular mass of 146.14 and the melting point in the range of 151^o-154^o C was obtained from Fisher Scientific, UK as a white powder. It has the molecular formula, HOOC(CH₂)₄COOH with two reactive carboxylic acid groups at the two ends of the carbon chain. From the industrial perspective, it is the most important dicarboxylic acid produced annually, mainly for the production of nylon and its chemical structure is shown beneath.



3.2.1 NaturePlast PLA (PLE005)

Natureplast PLA polymer, PLE 005 (PLAn) is a thermoplastic resin derived from annually renewable resources and is specifically designed for extrusion applications. Its primary feedstock is corn starch and it is the GMO-free certified transparent resin. The PLE 005 resin has the following key features.

- The primary raw material source is renewable and sustainable
- The raw materials used for production of PLAn are non genetically modified
- It is suitable for food contact applications
- It is certified biodegradable and compostable according to EN 13432:2002
- It is inherently oil resistant
- Is it sealable, printable and laser etchable

Selected mechanical and physical properties of the material are presented in table 3.1

Table 3.1 Mechanical and physical properties of PLE005 Resin

Property	PLE 005	Test Method
Density (g/cm ³)	1,25 (±0,05)	ASTM D792 and ISO 1183
Melt Index, g/10min (190/2.16kg)	2-10	ASTM D1238 and ISO 1133
Optical properties	transparent	
Melting Point (°C)	145-155	GB/T19466.3-2004
Glass Transition Temperature (°C)	48-50	GB/T19466.2-2004
Degradation Temperature (°C)	240-250	
Tensile yield Strength (MPa)	57	ISO 527
Tensile strength at break MPa	48	ISO 527
Young's Modulus MPa	2690	ISO 527
Tensile yield elongation (%)	2	ISO 527
Tensile elongation at break (%)	4.6	ISO 527
Charpy Impact (non notched) 4J, kJ/m ²	23	ISO 179
Impact Strength (kJ/m ² , Izod)	2-2.9	GB/T1043-1992

3.3 Preparation of PLA and wheat starch blends

3.3.1 Investigation of the function of MDI and different additives on the properties

The polymeric materials obtained from the suppliers were first dried before use. The wheat starch was dried in an air circulating oven at 130°C for about 2 hours. Wheat starch and PLA pellets dried overnight at 60°C, were premixed in an airtight polyethylene

(PE) bags at PLA/starch weight ratios (w/w) of 90:10. The MDI, glycerol and stearic acid were added to the blends in three different bags as 2 parts based on 100 parts of the PLA/starch blend. All these blends, with coupling agents, were then mixed and stored for 2-3 hours in the same PE bag before extrusion. The MDI was also added to the remaining 3 bags of PLA/starch as 2 parts based on 100 parts of dried PLA/starch total weight. A combination of PLA/starch/MDI/glycerol blends was then prepared by adding 2, 5 and 10 parts of glycerol based on 100 parts of PLA/starch blend to the aforementioned bags.

The wheat starch and PLA were also premixed at PLA/starch weight ratios (w/w) of 90:10 and 70/30 at ambient conditions. 2wt % MDI was added and the mixtures were well mixed and stored for few hours in sealed PE plastic bags before extrusion. The blends without MDI were also prepared in the same method. Another set of blends of PLA/starch/MDI were prepared with weight ratios 90:10:2 and 70:30:2 and stored overnight in PE bags before extrusion. The material compositions of the blends and their unique identification codes are listed in table 3.2

Table 3.2 Material codes and their compositions

Sample no	Material code	Composition parts		
		PLA	Starch	Additive
1	PLA	100	0	0
2	10S90P	90	10	0
3	30S70P	70	30	0
4	10S90P2M	90	10	2 MDI
5	30S70P2M	70	30	2 MDI
6	10S90P2G	90	10	2Glycerol
7	10S90P2SA	90	10	2 Stearic acid
8	10S90P2M2G	90	10	2 MDI 2 Glycerol
9	10S90P2M5G	90	10	2 MDI 5 Glycerol
10	10S90P2M10G	90	10	2 MDI 10 Glycerol

3.3.2 Investigation of the role of biostrength materials on property variation

PLA pellets obtained from the supplier were dried overnight at 60°C and wheat starch was dried in an air circulating oven at 130°C for about 2 hours. The biostrength 130 was first added to the PLA pellets as 6wt% based on 100 parts of the PLA and premixed in a self sealing PE bag. Similarly, the biostrength 130 was also added to the PLA pellets as 6wt% based on 100 parts of the PLA/starch blend and premixed in another tightly sealed PE bag. Dried wheat starch was then added to a second bag to make PLA/starch weight ratios (w/w) of 70:30 and mixed thoroughly.

PLE 005 pellets dried for 4 hours at 70°C were put in a PE bag and biostrength 700 was added to PLA pellets and blended as 4 parts based on 100 parts of the PLE. In a similar approach, biostrength 700 was also added and blended as 4 parts based on 100 parts of the PLA/starch blend. Dried wheat starch was added afterwards to the latter mixture to make PLA/starch weight ratios (w/w) of 70:30 and blended thoroughly. All blends were stored at ambient conditions for 2-3 hours in the same airtight PE bags before extrusion. Material compositions of the blends and their distinctive codes are listed in table 3.3.

Table 3.3 Material codes and their compositions with biostrength materials

Sample no	Material code	Composition parts		
		PLA	Starch	Additive
1	PLA	100	0	0
2	PLA6IM	100	0	6 Biostrength 130
3	30S70P6IM	70	30	6 Biostrength 130
4	PLE 005	100	0	0
5	PLE4MS	100	0	4 Biostrength 700
6	30S70P4MS	70	30	4 Biostrength 700

3.3.3 Examination of the effects of glycerol on properties

Genetically modified organism free PLE 005 pellets from the manufacturer were ground to a small particle size in a cutting mill by passing through a 4mm sieve and then through a 1.5 mm sieve. Wheat starch was dried in an air circulating oven at 130°C for about 2 hours. PLA particles were dried for 3 hours at 50°C. The glycerol was added to the

dried wheat starch at 2, 5, 8, 10, and 15 parts based on 100 parts of the PLA/starch blend and were premixed in tightly sealed PE bags for 2 hours at 30 minutes interval hand mixing. Dried PLA particles were then added to the mixture and mixed thoroughly until no lumps were observed. The PLA/starch blend without glycerol was also prepared in the same way. PLA/starch blend with 5% glycerol was prepared in a similar manner with PLAn in the form of pellets as received from the manufacturer for a comparison of the particle size on the properties and labelled as15S85P(P)5G. Material compositions of all the blends prepared with and without glycerol and their identification codes are listed in table 3.4.

Table 3.4 Material codes of the blends with glycerol and their compositions

Sample no	Material code	Composition parts		
		PLA	Starch	Glycerol
1	PLA	100	0	0
2	15S85P	85	15	0
3	15S85P2G	85	15	2
4	15S85P5G	85	15	5
5	15S85P(P)5G	85	15	5
6	15S85P8G	85	15	8
7	15S85P10G	85	15	10
8	15S85P15G	85	15	15

3.3.4 Study of the behaviour of natural rubber latex on properties

PLE 005 pellets were ground into small particle size as explained in section 3.3.3 and ground PLA particles were dried 3 hours at 50⁰C. Wheat starch was dried in an air circulating oven at 130°C for about 2 hours. Latex with 60% total solid content was added to dried wheat starch at 1, 3, and 5 parts based on 100 parts of PLA/starch blend, the materials were then premixed in airtight PE bag for 2 hours. Pre-mixing was mainly carried out by hand mixing for 30 minutes followed by 30 minute intervals. Dried PLA particles were then added to the mixture and mixed thoroughly until no lumps were observed in the blend. PLA/starch blend without latex was also prepared in a same method. Material compositions of the blends and their identification codes are listed in table 3.5.

Table 3.5 Material codes of the blends with latex and their compositions

Sample no	Material code	Composition parts		
		PLA	Starch	Latex
1	PLA	100	0	0
2	15S85P	85	15	0
3	15S85P1L	85	15	1
4	15S85P3L	85	15	3
5	15S85P5L	85	15	5

3.3.5 Investigation of the impact of adipic acid on blend properties

PLE 005 pellets were ground into a small particle size as explained in section 3.3.3 and particles were dried 3 hours at 50°C. Wheat starch was dried in an air circulating oven at 130°C for about 2 hours. The adipic acid was first added to dried wheat starch at 0.5, 1.5, 2.5, 3.8 parts based on 100 parts of PLA/starch blend. Then the mixtures were premixed in an air impermeable PE bags for 2 hours by hand mixing at 30 minutes intervals. Dried PLA particles were then separately added to the each mixture and mixed thoroughly until no lumps were observed. The PLA/starch blend without adipic acid was also prepared by the same procedure. The material compositions of the blends and their distinctive material codes are listed in table 3.6.

Table 3.6 Material codes of the blends with adipic acid and their compositions

Sample no	Material code	Composition parts		
		PLA	Starch	Aidpic acid
1	PLA	100	0	0
2	15S85P	85	15	0
3	15S85P0.5AA	85	15	0.5
4	15S85P1.5AA	85	15	1.5
5	15S85P2.5AA	85	15	2.5
6	15S85P3.8AA	85	15	3.8

3.3.6 Investigation of the effect of biostrength 130 material and pistachio nut shell powder on properties

Ground PLE 005 pellets as explained in 3.3.3 and dried wheat starch in an air circulating oven at 130°C for about 2 hours were used to prepare the blends. Ground PLA particles were dried 3 hours at 50°C. Impact modifier material was first added to dry PLA at 10 parts based on 100 parts of PLA/starch blend. Then the mixtures were premixed in tightly sealed PE bags for 2 hours at 30 minutes interval hand mixing. Dried wheat starch was then added to the each mixture and mixed thoroughly until no lumps were observed. Another blend with same composition and same materials was prepared similar to aforementioned blend and powdered pistachio nut shell (PNS) was added to the mixture at 2 parts based on 100 parts of PLA/starch blend. The PLA/starch blend without impact modifier was also prepared by mixing PLA and starch together providing the same conditions. Material compositions of the blends and their identification codes are listed in table 3.7.

Table 3.7 Material codes of the blends with impact modifier and PNS with their compositions

Sample no	Material code	Composition parts		
		PLA	Starch	IM
1	PLA	100	0	0
2	15S85P	85	15	0
3	15S85P10IM	85	15	10
4	15S85P10IM2PNS	85	15	10

3.4 Twin screw extrusion processing

Extrusion processing is a well established processing technique, where raw plastic materials are continuously converted into products of a specified shape or cross section. The technique is also employed as a mixing technique for polymer modifications with additives where the mixing process requires the high shear stress for dispersion and large shear strain and continuous reorientation for good distribution. In this study, the twin screw

extruder was used together with the features explained in chapter 2, section 2.9.1 to facilitate mixing as well as a shaping device with the attachment of a die for making strands which were then pelletised for further processing.

Prior to the extrusion, pre-mixed blends were metered through the feeder at various speeds to determine the settings required to achieve the approximate feed rate of 2.5 kg/h. Prepared blends and pure PLA were then extruded in a lab-scale co-rotating twin screw extruder (BTS 30, BETOL Machinery Ltd. England), with a screw diameter of 30 mm, a length to diameter ratio of 25:1 through a 6 mm diameter strand die with a temperature profile of 150⁰C (feed inlet), 185⁰C for the other zones including the zone near to the die to produce approximately 3 kg of each of samples 1 to 5 and 1 kg each of samples 6-10 listed in table 3.2. The screw speed was fixed at 80 rpm. Approximately 0.3 kg of material was passed through the extruder when the blend type was changed in order to prevent cross contamination of samples. Figure 3.1 shows the smooth extrusion of the pre-blended materials under the given conditions. All the samples were extruded through 6mm diameter die before being drawn off through a water bath. The extruded strands were concurrently pelletized into small pellets using a Betol pelletiser (1306, Betol Machinery Ltd., England). The samples were then dried at 60 ⁰C for 2 hours and stored in airtight PE bags at ambient temperature until they were analysed.

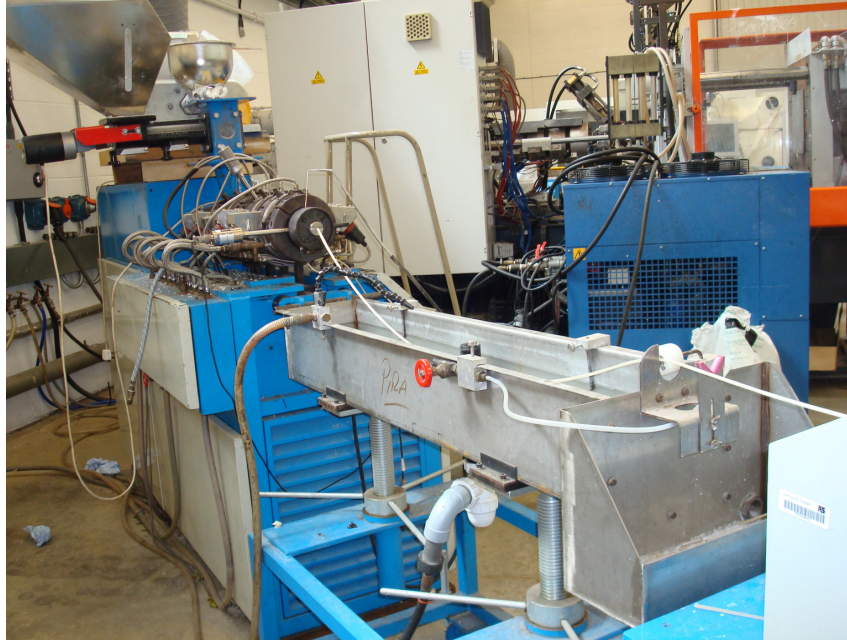


Figure 3.1 Pre-blended materials extruding smoothly under the given conditions

Similarly, prepared blends and pure PLA listed in table 3.3 were extruded in the aforementioned lab-scale co-rotating twin screw extruder with similar screw parameters to produce approximately 3 kg of each of samples 1 to 3. A temperature profile of 130⁰C (feed inlet), 150⁰C for other zones including the zone nearer to the die was employed to produce approximately 3 kg of each of samples 4 to 6. As with previous extrusion, attempts were made to prevent cross contamination of samples by passing 0.3 kg material through the extruder when the blend type was changed. All the samples were extruded through the same die, drawn off through a water bath and strands were pelletized into small pellets using the pelletiser. Samples were dried and stored ready for further investigation.

The materials given in the table 3.4 were also extruded similar to the previous batch at a temperature profile of 130⁰C (feed inlet) and 150⁰C for the other zones including the zone nearer to the die and approximately 3 kg of each of blends 1 to 8 were produced. As explained before the cross contamination of samples was minimized. The screw speed was fixed at 120 rpm. All the samples were extruded, cooled, pelletized, dried and stored in airtight PE bags.

The samples listed in table 3.5 with different identification codes were extruded at the same feed rate with a temperature profile of 120⁰C (feed inlet) 150⁰C for the other zones including the zone nearer to the die to produce around 3 kg of each of samples 1 to 5. Similar efforts were taken to minimize the cross contamination of the samples as aforementioned when the extrusion blend type was changed. The screw speed was fixed at 100 rpm. All the samples were extruded, granulated and stored as mentioned before.

Similar extrusion process was carried out for the samples listed in table 3.6. All the conditions were identical to the extrusion conditions used for the previous batch prepared and listed in table 3.5. All the samples were extruded, cooled, simultaneously granulated into small pellets and were then dried at 60 ⁰C until the moisture content was less than 0.05% and stored in airtight PE bags at ambient temperature until they were subjected to different analyses.

Comparable work was carried out to extrude the blends listed with the distinct material codes in table 3.7 with a temperature profile of 100⁰C (feed inlet), 145⁰C in the second zone and 150⁰C for other zones including the zone nearer to the die and approximately 3 kg of each of samples 1 to 4 were produced. Different temperature profiles and different screw speeds were employed for different blends to run a smooth extrusion and to optimize the surface finish of the extrudate. The screw speed was fixed at 90 rpm. All the samples were extruded, cooled, granulated into small pellets and then dried at 60 ⁰C until the moisture content was less than 0.05% and stored in self sealed PE bags at ambient temperature for further physical and mechanical investigations.

3.5 Injection moulding

A significant technique used in the polymer industry to convert raw materials into complex shapes. The technique transforms materials, blends of different types or composites in the form of pellets into intricate geometric shapes by following specified sequence of processes within a precise time known as cycle time. The raw material is fed to the hopper section of the machine and it is then melted by means of internal shearing, friction and external heater bands and conveyed towards screw chamber in front of the

screw tip through the barrel which has a reciprocating screw. The screw moves forward and injects the melt from the chamber through the nozzle to the mould cavity with the desired shape.

Different injection moulding machines with varying barrel capacities and models (eg. D60NCIII, D150 NC III-K) were employed with the materials throughout the course of the study. The DEMAG (D60NCIII, DEMAG Germany) injection moulding machine was used to mould tensile test bars for the first batch of PLA and blends prepared by extrusion with concentrations and material classifications given in table 3.2. The blends and PLA materials were injection moulded with a temperature profile of 160⁰ (first heating zone), 170⁰ (second heating zone) and 185⁰ C for other zones including the nozzle, together with the other conditions given in the table under profile 1 given in Appendix G. Figure 3.2 illustrates the D60NCIII injection moulding machine in operation under the given conditions to convert extruded pellets into tensile test bars. The DEMAG machine with a higher barrel capacity (D150 NC III-K, DEMAG, Germany) was used to mould plaques according to the conditions set in the profile 1 given in table Appendix H.

Six blends prepared by extrusion including pure PLA and GMO free PLA with material identification codes given in table 3.3 were also conventionally injection moulded using injection moulding machine (D150 NC III-K, DEMAG, Germany) for both tensile test bars and plaques with the conditions given in the table under profile 2 listed in Appendix G and Appendix H respectively. Pellets of the eight blends prepared by extrusion including pure PLA with concentrations given in table 3.4 were also conventionally injection moulded using the same injection moulding machine as above with the conditions given in the table under profile 3 of Appendix G for tensile bars and Appendix H for plaques correspondingly.



Figure 3.2 Injection moulding machine D60NCIII in operation under the given conditions to make tensile test bars

For the batch prepared with latex, two types of injection moulding machines used, the DEMAG injection moulding machine D60NCIII, for the dumbbell specimen moulding and a smaller machine with a lower barrel capacity an ERGOTECH PRO 25-80 (DEMAG, Germany) for the plaque moulding.. Five samples of PLA and blends prepared by extrusion with concentration and material codes given in table 3.5 were injection moulded using the conditions given in profile 4 of the table listed in Appendix G for dumbbell specimens and Appendix H for plaques moulding respectively. Six samples of blends including virgin PLA prepared by extrusion with the concentrations given in table 3.6 were also injection moulded in the same machine to dumbbell specimens and plaques using the conditions given in table under profile 5 of Appendix G and Appendix H respectively. The blends prepared by extrusion with the concentrations given in table 3.7 and PLA were then conventionally injection moulded using the conditions given in table under profile 6 listed in Appendix G for dumbbell specimens and Appendix H for plaques moulding respectively.

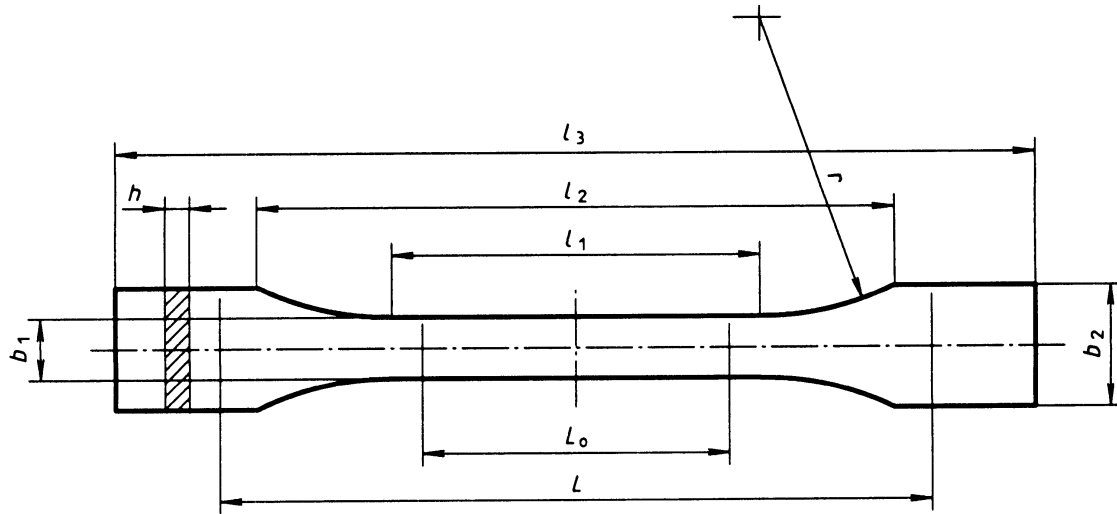
As with the extrusion, attempts were made to prevent the cross contamination of samples at each situation by purging the barrels between samples approximately by 0.25 kg of each material, then the equivalent of several shots were run out through the nozzle and several samples were moulded before collection of the test samples. The injection moulding of the tensile test bars was carried out according to BS EN ISO 527 and rectangular plaques were injection moulded according to BS EN ISO 6603 testing geometry. The sprue parts of the mouldings were carefully removed and they were stored in sealed PE bags until they were analysed.

3.5.1 Tensile test bar moulding and determination of tensile properties

The capability of a material to resist breaking under tensile stress is one of the most pivotal and broadly measured properties of materials used in productive applications. This important characteristic test serves to investigate the variety of information about the material being tested, including tensile strength, ultimate strength, elongation, yield point and modulus of the material. These so called tensile tests are commonly performed on substances during material selection and designing processes to acquire prior knowledge on the limitations of materials before actual failure occurs. A test piece with a standard shape is gripped and fixed to a machine throughout the test and a controlled uniformly increasing tension force is applied from both sides or from one side until the specimen changes its shape and ruptures. The stress-strain diagram is produced and expresses a relationship between a load applied to a material and the deformation of the material, caused by the load.

To apply this test method on the prepared composites, all the blends from different batches listed in table 3.2 to table 3.7 were injection moulded into tensile test bars according to BS EN ISO 527 testing geometry using the conditions given in different tables in Appendix G with the DEMAG injection moulding machine as described above in section 3.5. The 4mm thick injection moulded dumbbell test bars were produced from each sample and five of these were randomly selected to allow errors and variations to be eliminated. The remaining samples from moulded tensile test bars were stored in an airtight PE bag at

room temperature in a plastic barrel until they were analysed. Figure 3.3 below shows the shape and dimensions of the dumbbell test specimen.



Specimen type	Dimension in mm
l_3 Overall length	$\geq 150^a$
l_1 Length of narrow parallel-sided portion	80 ± 2
r Radius	20 to 25
l_2 Distance between broad parallel-sided portions	104 to 113 ^c
b_2 Width at ends	20.0 ± 0.2
b_1 Width of narrow portion	10.0 ± 0.2
h Preferred thickness	4.0 ± 0.2
L_0 Gauge length	50.0 ± 0.5
L Initial distance between grips	115 ± 1

a For some materials, the length of the tabs may need to be extended (e.g. $l_3 = 200$ mm) to prevent breakage or slippage in the testing jaws.

$$b \ r = [(l_2 - l_1)^2 + (b_2 - b_1)^2] / 4 (b_2 - b_1)$$

Figure 3.3 Dumbbell test specimen type 1A adapted from BS EN ISO 527-2:1996 BS 2782-3:Method 322:1994 standard



Figure 3.4 Some of the injection moulded dumbbell specimens before testing

Some of the injection moulded dumbbell specimens are shown in figure 3.4. These tensile test specimens and all other specimens were labelled and preconditioned at 50% relative humidity and 23°C temperature for at least for 24 hrs before testing. The tensile strength, elongation at break and elastic modulus were determined with a Zwick tensometer (SMART. PRO, Zwick Roell, UK) according to BS EN ISO 527 with a crosshead speed of 5 mm/min and a 50mm gauge length. Five replicates were tested for each treatment. Figure 3.5 revealed below illustrate a dumbbell specimen set up in the tensometer just before the investigation.



Figure 3.5 A dumbbell specimen set up in the tensometer before the test

The injection moulding process under actual processing conditions occasionally may not continue smoothly to produce these articles and there may be some delays in the process. During these unfavorable situations, materials will be retained in the barrel for longer periods of time than expected. These extended exposures of material to the elevated temperatures could dramatically influence the mechanical properties of the final product. To investigate the aforementioned concern, tensile test bars were also prepared to scrutinize the consequences of the residence time of the material in the injection moulding barrel.

Tensile test bars were moulded using the materials listed in table 3.5, table 3.6 and table 3.7 for this purpose and effect of the residence time of the blends on the tensile properties of the material was investigated as follows. The number of shots in the barrel was estimated by filling the barrel completely with material and then injection moulding under the same conditions used for the dumbbell specimen moulding until the material in the barrel was exhausted. The number of shots in the barrel upto this point was approximately five. The residence time of the material in the barrel was then calculated as follows.

Residence time of the material = number of shots in the barrel x cycle time3.1

The residence time of the material in the barrel was then increased to 1.5 times the normal residence time leaving the other conditions the same as the previous conditions used for the particular batch and the moulding was carried out. The first five bars of each blend were rejected before collection of actual dumbbell test bars to obtain similar residence time for all specimens. Ten dumbbell test bars were produced from each batch and five samples were randomly selected and tested. For the materials listed in table 3.7, the residence time of the material in the barrel was double the normal residence time leaving the other conditions as same as the previous conditions applied for the particular batch and injection moulding was carried out. The first five bars of each blend were rejected before collection of actual dumbbell test bars in this situation also to obtain equal residence time for all dumbbell specimens. Eight dumbbell test bars were produced from each batch and five samples were randomly selected and tested to contemplate the effect of the increased residence time on the tensile properties.

3.5.2 Rectangular plaques moulding and determination of impact properties

One of the paramount mechanical tests on materials is the impact test and it provides an understanding of the performance of a finished product or component and eventually the most desirable utilizing conditions. In particular, among the vital mechanical characterizations of plastic products, the response of the component to impact conditions is one of the several considerations to determine the material behaviour and engineering

application. There are several instruments engaged in impact test, nonetheless, to perform impact tests with an energy rate higher than that obtainable using the pendulum, to break different specimen shapes or finished products, a drop weight instrument with the variety of strikers can be employed. In this method, a known weight is allowed to free fall from a particular height to reach the sample at a specific velocity. The failure can be defined by deformation, crack initiation, or complete fracture, with no preferential direction. Failures usually originate at the weakest point in the sample and propagate from there.

To investigate the aforementioned performance, all blends of the prepared composites from the six batches listed in table 3.2 to table 3.7 were injection moulded into plaques according to BS EN ISO 6603 using the conditions given in table listed in Appendix H with a DEMAG injection moulding machine as described under the injection moulding in section 3.5. Rectangular 150x150x4 mm plaques were injection moulded from materials listed in table 3.2, table 3.3 and table 3.4. The moulded specimens were then cut into 60x60 mm squares using a bench saw and labelled for impact testing. As with the tensile test, attempts were taken to eliminate errors and variations by randomly selecting six test pieces out of these cut pieces which were then tested. Figure 3.6 shows some of the labelled injection moulded plaques which were selected for testing.



Figure 3.6 Some of the injection moulded plaques before testing

Pure PLA and the blends of prepared composites listed in table 3.5, table 3.6 and table 3.7 were also injection moulded into smaller size plaques according to BS EN ISO 6603 using a DEMAG injection moulding machine (ERGOTECH PRO 25-80, DEMAG, Germany) using the conditions given in profile 4, profile 5, and profile six of table Appendix H respectively. Thirty rectangular 60x60 mm plaques with 2mm thickness and thirty plaques with 4mm thickness were injection moulded. Six test plaques were randomly selected and tested as aforesaid as a requirement to eliminate errors and variations.

The 60x60mm squares were preconditioned at 50% relative humidity and 23°C at least for 24 hrs before testing. The impact energy and force were determined according to BS EN ISO 6603 by the drop weight technique with a Fractovis Plus impact tester (Model 7520, CEAST, Italy) shown in figure 3.7 below.



Figure 3.7 Plaques have been placed in the chamber and ready for investigation

3.6 Physical Ageing

3.6.1 Investigation of physical ageing by tensile properties

The remaining samples of injection moulded tensile test bars that were stored in airtight PE bags at room temperature in a plastic barrel until being analysed were used to investigate the tensile properties of the materials after physical ageing. Out of these samples, five dumbbell specimens made from materials listed in table 3.2 and table 3.3 were tested after one year to investigate the divergence in the tensile properties upon physical ageing.

The remaining stored tensile test bars of the materials listed in table 3.5, table 3.6 and table 3.7 were also considered for physical ageing. Five samples of these at a time were tested at 3 months intervals to investigate tensile properties upon physical ageing.

3.6.2 Investigation of physical ageing by impact properties

Remaining samples of moulded plaques, which were stored in sealed PE bags at room temperature in a plastic barrel until analysed were used to examine material's impact properties upon ageing. The impact properties were determined by the falling weight technique with a Fractovis Plus impact tester (Model 7520, CEAST, Italy) according to BS EN ISO 6603. The 60x60mm six plaques obtained from blends listed in table 3.2, table 3.3, were analysed after one year while blends listed in table 3.5, table 3.6 and table 3.7 were analysed after 3 months intervals to examine the variation in impact properties after physical ageing.

3.7 Differential scanning calorimetry

Differential Scanning Calorimetry is employed to determine the thermal behaviour of a polymer, in particular, the transition temperature such as the glass transition temperature T_g , or the degree of crystallinity. The samples are encapsulated in aluminium pans and thermocouples are in contact with the outside of the pans. The sample to be tested is placed

in one pan while a reference sample which has no transition is placed on the other pan. The temperature difference between two pans over a constant temperature change is measured. The heat flow to and from the sample is plotted against temperature and an endothermic transition is indicated at the T_g where the glass-like areas become free above the T_g and the molecules freely move. With further heating the melting of the crystalline areas produces another endothermic peak. Upon cooling crystallization takes place and releases energy resulting in an exothermic peak.



Figure 3.8 Sample holder of the DSC where sample is placed before transferring to the cell

The thermal behaviour of the samples of PLA and its blends prepared and listed in table 3.2, table 3.3, table 3.4, table 3.5, table 3.6 and table 3.7 were investigated by heating in a Differential Scanning Calorimetre (DSC). The test was carried out using a DSC Q2000 series instrument (TA Universal analysis, TA instruments Inc., USA) according to the ASTM Method D 3417-83.

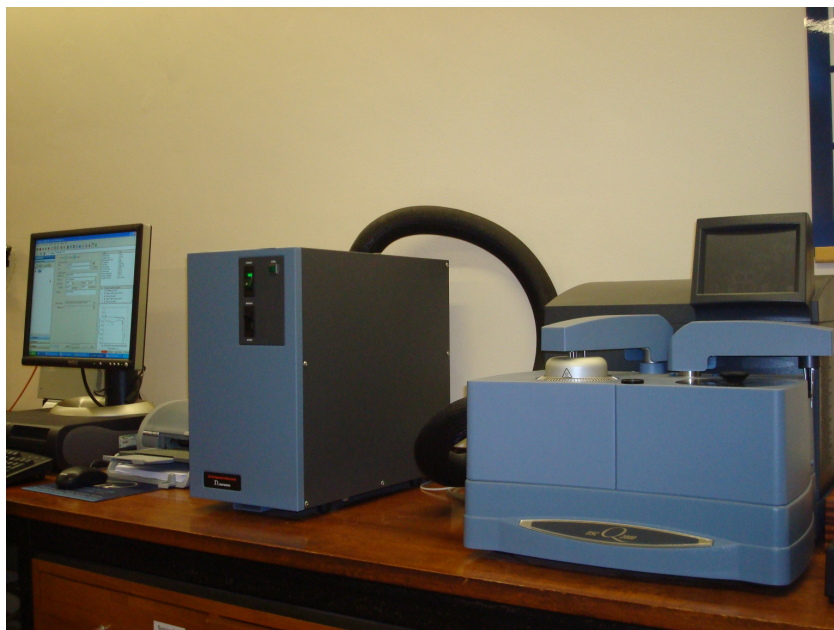


Figure 3.9 Samples sealed in an aluminium pan have transferred into the cell part in the left side of the sample holder for investigation

About 4–10 mg of each sample was sealed in a Tzero aluminum pan, with an empty sample pan being used as a reference in all cases. The aluminium pans were placed on the sample holder shown in figure 3.8 and were transferred to the cell by an automated sample holding arm. The thermal history of a sample was erased by heating it from 20 to 190°C at a rate of 10°C/min, holding it at 190°C for 10 min, and then cooling it to 20°C at the same rate. The thermal behavior was then recorded by reheating the sample from 20 to 190°C at the same rate. The heat of fusion (ΔH_m) and heat of crystallization (ΔH_c) were determined for the samples listed in table 3.1. The heat of fusion of 100% PLA was taken as 93.6 J/g (Wang, Sun & Seib, 2001) and the crystallinity of the PLA in the blend was calculated.

3.8 Thermogravimetric analysis

Qualitative analyses of volatile constituents in substances are usually conducted by thermogravimetric analysis (TGA) and it is also used to determine the degradation temperatures of polymers, fillers and other incorporated additives. The degradation temperatures obtained from the TGA lead to decisive information on the successful

processing conditions of the materials as a result of the determination of the temperature limits. The measuring system comprises of a beam balance with a measuring chamber, the temperature of which can be controlled by an oven. The oven is controlled from the base unit. The integrated control thermocouple is used to maintain a constant heating rate and to determine the temperature.

The degradation temperatures of the samples were determined by thermo-gravimetric analysis (TGA Q500 series, TA Universal analysis, TA Instruments Inc., USA). A small amount of each sample (approximately 5-10mg) listed in table 3.2, table 3.3, table 3.4, table 3.5, table 3.6 and table 3.7 was individually placed in a clean platinum pan and they were placed in the sample holder. Samples were then carried on to the beam balance and the oven was closed and heated from room temperature to 600⁰C at a heating rate of 10⁰C/min under the nitrogen pressure of 90 ml/min. Samples listed in table 3.5, table 3.6 and table 3.7 were also investigated similarly under air at a pressure of 90ml/min.



Figure 3.10 Platinum pan with the sample holds by the beam balance before placed in the oven

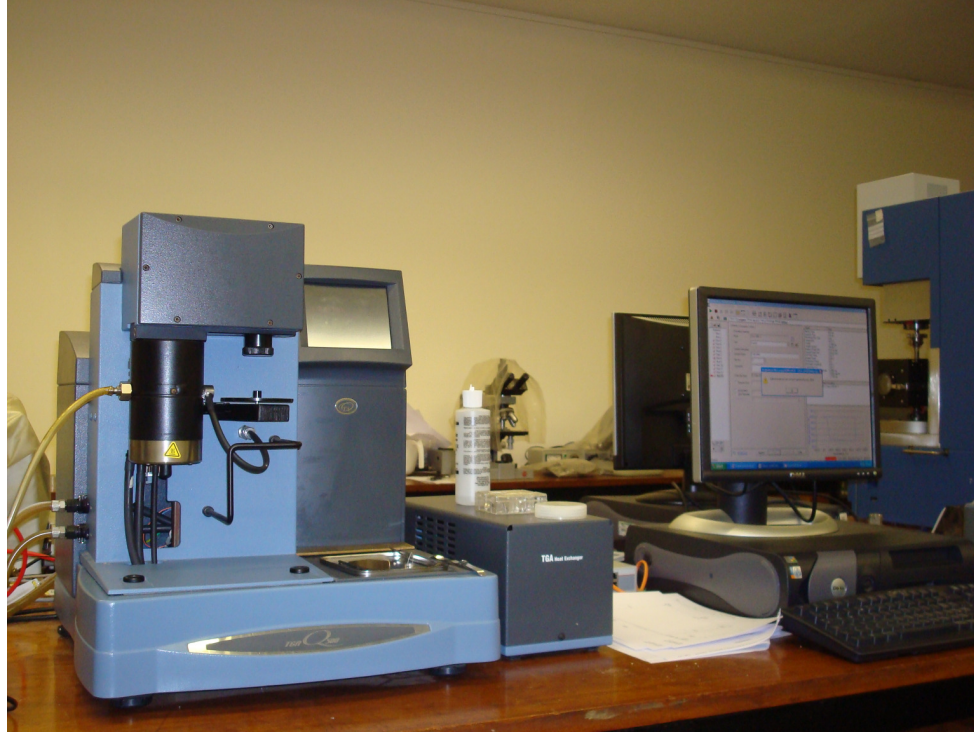


Figure 3.11 Sample placed in a platinum pan have located in the oven before the test begin

3.9 Determination of morphology

Scanning Electron Microscope (SEM) was developed to exploit the analytical capabilities which results from a many different interactions between electrons and materials. The interaction between solid surfaces and electrons from the beam of the SEM result in electron scattering as well as electron excitation of radiation. These effects provide crystallographic information via diffraction data, chemical identification, morphological information, photoelectron characterization of surfaces and many more. The main components of the SEM consist of an evacuated column which contains an electronic gun, electromagnetic lenses, apertures, specimen stage and possibly other detectors (x-ray spectrometers). Figure 3.12 shows the sample stage and the column part of the SEM. The control unit is isolated from the electron column and situated around. The electron gun produces a consistent beam of virtually monochromatic electrons which are focused by an electromagnetic lens onto the sample.

The samples for investigation by SEM are mounted onto the specimen stage located within the vacuum system. The samples usually have to be dry and able to withstand a vacuum. The sample stage has five axes of movement, X, Y, and Z, translation together with tilt and rotate facility to enable the accurate examination. The stage is electrically grounded to the microscope to supply a conducting pathway for the electrons. Non conductive materials such as polymers, ceramics or biological materials may be examined without charging effects by reducing acceleration potentials and suppressing the emission of secondary electrons. However, better results are obtained by making electrically conductive specimen by coating with a thin layer of the electron dense conducting material such as gold or platinum.

SEM was conducted to examine the morphology of the prepared composites. The fractured surface of a dumbbell specimen after the tensile test was used to study the morphology of the blends. Each specimen from a fractured tensile test bar was mounted on an aluminum stub using carbon tape, and the fractured surface was coated with gold particles with a sputter coater (Polaron desk sputter coater, Quorum Technologies, UK) for 2 minutes (30 seconds x 4) before observation. The stub with the coated specimen was then placed on the stage within the microscope by venting the machine. Vacuum is then pumped after closing the door. The microstructures of the blends were then observed in the instrument (SEM; Zeiss Supra 35, Carl Zeiss AG, Oberkochen, Germany) with a 30 μ m aperture, 10Kv accelerating voltage and 0.0123 nm wavelength that results in 0.0075 nm resolution ($d=0.61\lambda/\alpha \sin \alpha$ (where $\alpha \sin \alpha=1$ for SEM)). Specimens of the fractured tensile test bars from the samples listed in table 3.2, table 3.3, table 3.4, table 3.5, table 3.6 and table 3.7 were investigated.

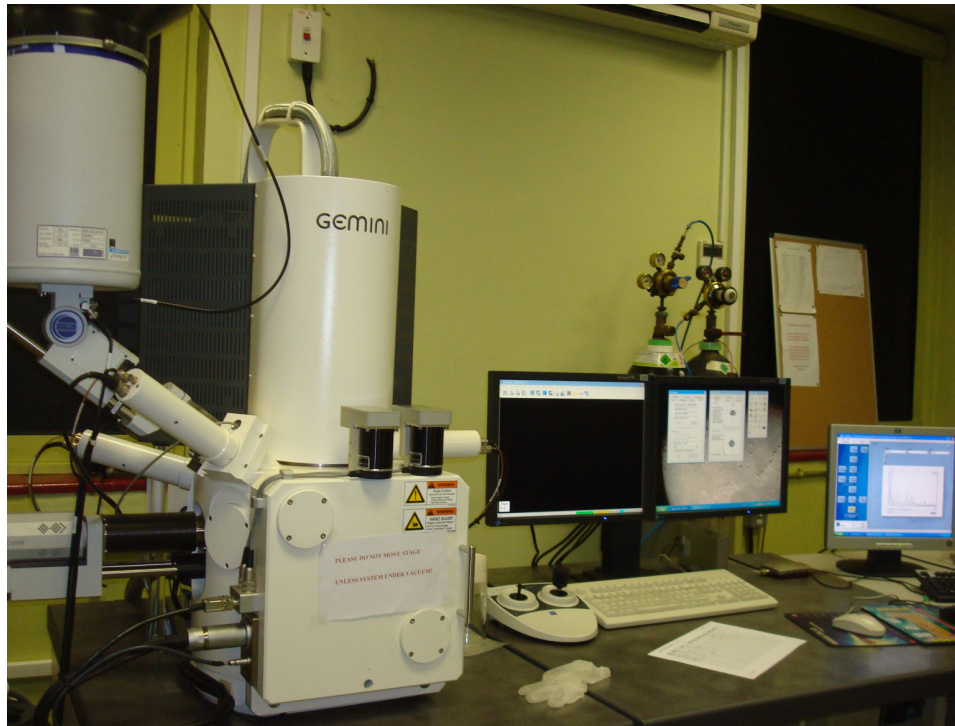


Figure 3.12 Sample stage and column part of the SEM

3.10 Determination of water absorption

Moisture sensitivity of the material is a pivotal requirement for rapid degradation although it is a negative effect for certain packaging applications. Therefore a compromise between these two factors needs to be maintained for certain packaging materials. This feature is more crucial with nature derived polymers such as starch as they usually show water absorption. The distribution of water within the starch is very important with regards to the physical properties as well as an understanding of the processing of starch containing materials. Therefore it is very essential to investigate how rapidly the material absorbs water when immersed in excess water for the benefit of material degradation. Injection moulded standard tensile test bars were used for the water absorption test. The dumbbell specimens made from the blends listed in table 3.2, table 3.3 and table 3.7 were dried at 50°C for 24 h and cooled to room temperature before they were weighed. The dried specimens were then soaked in distilled water at ambient temperature for specific intervals,

removed from the water, blotted with tissue paper to remove excess surface water, and then weighed. Three replicates from each blend were tested. The water absorption was calculated on a dry basis as follows.

$$\text{Water absorption} = \frac{(\text{Wet weight} - \text{dry weight})}{\text{Dry weight}} \times 100 \% \quad \dots\dots\dots 3.2$$

3.11 Fourier Transform Infra-red Spectroscopy

The Fourier Transform Infrared Spectroscopy (FTIR) technique connects with various changes in energy and position with the infrared region of the electromagnetic spectrum and is universally recognized as an important tool for polymer characterization. This well established technique serves to identify functional groups in a molecule based on its vibration modes at diverse frequencies. The most common vibration modes are the stretching mode which involves the change in the inter-atomic distance along the axis and the bending mode which involves change in the angle between two bonds. The infrared spectrum with near, mid and far radiation covers the electromagnetic spectrum with the most used region in the wave number range 4000 to 670 cm⁻¹ (Frequency range 1.2x10¹⁴ to 2.0x10¹³ Hz). In the FTIR process, the infrared light (IR) beam from a polychromatic light source is passed through a beam splitter and is divided and reflected through the mirrors and recombined and guided towards the sample. This light is absorbed by the sample and then passes to the detector. Because of the interference between the light reflecting from mirrors, the energy observed by the detector which is directly recorded shows an unusual pattern over time. The signal represents the light output as a function of the mirror position but the data-processing technique called Fourier transform turns this raw data into the desired sample's absorbance or transmittance spectrum showing at which IR wavelengths the sample absorbs as a function of infrared wavelength. Usually absorption occurs when the frequency of the IR is the same as the vibrational frequency of a bond in the sample. The examination of the transmitted light reveals how much energy was absorbed at each wavelength. Analysis of these absorption characteristics reveals details about the molecular structure of the sample. An investigation of the material is

always compared with the reference sample. Some of the characteristic vibration types of PLA and starch, which are the main materials used in the current study are listed in the table 3.8 with their respective peak wave numbers.

Table 3.8 Characteristic vibration types of PLA and starch

Material	Vibration type	Peak wave number cm-1
Starch	-C-O- stretching of -C-O-H group	1156 and 1081
	-C-O- stretching of -C-O-C-	1020
	C-H stretching	2850,2920
	C-H ₂ bending	1462
	C-H bending and wagging	1445-1325
	C-O stretching	960-1190
	O-H bending	1243, 1205
PLA	C=O stretching	1749
	-C-O- in -CH-O-	1180
	-C-O- in -O-C=O	1127, 1080, 1040

This universally recognised technique has been employed in the investigation of the prepared composites. The virgin PLA material was first scanned with 1, 5, 10, 50 and 100 scans on a Perkin Elmer Spectrum One Fourier Transform Infrared (FTIR) spectrometer, using a Specac Golden Gate Single Reflection ATR accessory, consisting on a Diamond crystal at a fixed angle of 45°. The spectra were collected over the 4000 cm-1 to 650 cm-1 wavenumber range, at a resolution of 4 cm-1. As there were no significant differences in the spectrums of 10, 50 and 100 scans, the number of accumulations for the FTIR experiment was set at 10 for rest of the sample analysis.



Figure 3.13 FTIR instrument

The samples listed in table 3.4, table 3.5, table 3.6 and table 3.7 were also scanned on the Perkin Elmer Spectrum One Fourier Transform Infrared (FTIR) spectrometer and the spectra were collected over the same wavenumber range and at the same resolution. “10” accumulations were collected for each sample. Any contaminations of the previous blends were minimized by cleaning the surface with ethanol.

3.12 Parallel plate rheometry

The Advanced Rheometric Expansion System (ARES) has been developed to examine the science of the flow and deformation of matter, more scientifically known as the rheological properties of materials. The ARES is suitable for characterizing a broad spectrum of materials including polymer melts, solids and reactive materials, as well as a wide range of medium to high viscosity fluids. This mechanical instrument is an extremely capable and versatile strain control rheometer that incorporates the standard resolution (HR) motor that provides very precise and accurate motion in both the dynamic and steady modes and the

force rebalance transducer which is an active type transducer that provides excellent resolution and temperature stability. The measurements can be made over a wide range of temperatures using a forced air convection oven with dual-resistive heaters and counter-rotating airflow for optimum temperature stability. This mechanical device is capable of subjecting a sample to either a dynamic (sinusoidal) or steady shear strain deformation measuring the resultant torque expended by the sample in response to this shear strain. The shear strain applied by the motor, the torque is measured by the transducer. The strain amplitude and frequency are set by the operator, with the actual sample deformation determined by the measured motor, and transducer, displacement.



Figure 3.14 Two parallel plates of ARES inside the furnace where sample was placed to make a small disc

Extruded pellets of the samples listed in table 3.5 and table 3.6 were subjected to this parallel plate rheometer to measure the viscosity, storage modulus, loss modulus and tan delta. Approximately 1.5 g of each sample was investigated by making a small disc inside the furnace part of the ARES parallel plate rheometer (ARES, TA Instruments Inc., USA).

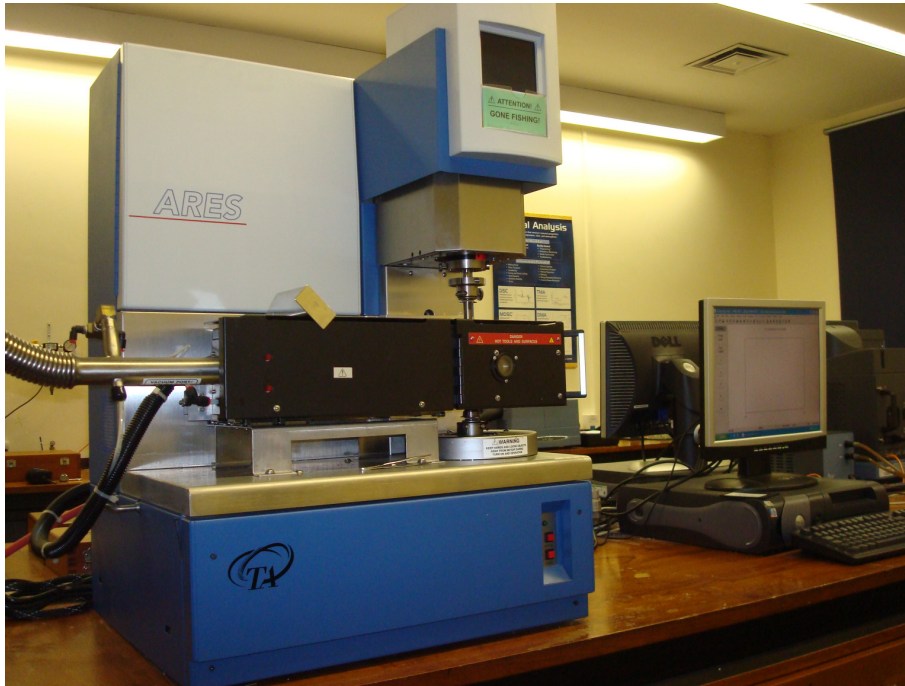


Figure 3.15 Samples placed and a small disc have made in the furnace for testing

The instrument was first heated to 150⁰C and then the material was placed between the two cylindrical parallel plates shown in figure 3.14 with the support of a small metallic cylinder. The 2mm thick and 25 mm diameter discs were made by controlling the two parallel plates. The furnace was then closed as shown in figure 3.15 leaving the material disc inside. The variation in viscosity was investigated with increasing frequency from 1.0 rad/s to 450.0 rad/s and energy absorption as storage modulus, energy dissipation as loss modulus and dissipation factor as tan delta were derived from the plot. The experiment was carried out at 160⁰ C, 170⁰C and 180⁰C to study the effect of temperature on the variation of properties. The extruded pellets listed in table 3.7 were also subjected to the parallel

plate rheometer in a similar procedure. At this occasion the instrument was first heated to 170⁰C before the discs were made and the experiment was carried out at 180⁰C temperature and the frequency range between 1.0 rad/s to 490.0 rad/s.

3.13 Degradation of the material

3.13.1 Discolouration by heat test

The appearance and smell of a material will instigate the initial approximation to identify whether the material has undergone any degradation. Therefore, a small amount of each blend material was subjected to a heat treatment in a conventional oven to investigate the appearance of the samples after heat treatment for a specified time. A known weight (5g) of each sample listed in table 3.5 table 3.6 and table 3.7 was placed in a petri dish, spread over the dish area and photographed. The oven was preheated to 180⁰C and the samples in the dish were placed in the oven and then heated at 180⁰C for 30 minutes. The samples were then removed from the oven and brought to room temperature before the visual inspection to see whether they have discoloured. Photographs were also taken of the heat treated samples. Samples were then compared to see the appearance before and after heat treatment.

3.13.2 Weight loss by TGA

Each sample listed in table 3.5, table 3.6 and table 3.7 was subjected to thermogravimetric analysis as in section 3.8 in air and the inert atmosphere but with an isothermal condition to contemplate any weight loss at the processing temperature due to degradation. Approximately 5-10mg was placed in a clean platinum pan and the furnace was then heated from room temperature to 180⁰C at a heating rate of 10⁰C/min under air and nitrogen pressure both of 90 ml/min. The samples were then hold for 30 minutes at this temperature and heated to 600⁰C at a heating rate of 10⁰C/min. The degradation patterns were then compared to see any weight loss at the isothermal temperature.

3.14 Home composting trials

The technique of composting has been identified as a significant way of reducing the biodegradable waste stream, in particular to minimise the quantity of waste collected. Composting contributes to the compliance with the reductions in biodegradable waste disposal to landfill and therefore achieves great attraction worldwide. Biodegradation is the natural process of biological decomposition of organic material such as kitchen scraps, yard trimmings, wood shavings, cardboard and paper. A controlled biological decomposition of organic waste under regulated conditions that are predominantly aerobic is primarily known as “industrial composting”. The “home composting” which is also known as “backyard composting” practices, refers to the similar definition including cooler aerobic breakdown of massive wastes in small scale composters by a treatment method known as ‘slow-stack’, where the temperatures are in the range of (0-20 °C) to (20-45 °C). In the slow stack technique, the consumer regularly adds organic matter to the composting container and this will spontaneously decay over time to form the compost. One of the important parameter in industrial composting as well as in the home composting is the carbon to nitrogen ratio. This ratio is typically maintained in the range of 25-30 to 1. Carbon rich materials such as cardboard, paper, straw, leaves, shrub trimmings can be mixed together with nitrogen rich materials such as grass cuttings, raw fruit and vegetables and nettles to achieve the required condition. Although industrial composting and home composting have been given a similar designation the ecological conditions of the two technologies are quite different.



Figure 3.16 The composting bin used for home composting trials (picture taken by Alex Tarverdi)

Formerly, the materials to be composted were piled up in order to form a compost heap in the home composting process. Composting bins made with air openings on the side walls and provided with a lid on top or well structured boxes are commonly used by many home composters for current practice in order to save space and accelerate decomposition. Usually, a higher temperature can be reached inside as a result of the material decomposition and hence these vessels are referred to as “thermocomposters”. Figure 3.16 illustrates frequently used composting bin by modern home composters. Composting behaviour of the prepared blends of biodegradable PLA and wheat starch were investigated. A working home composting bin prepared mainly by the carbon and nitrogen rich materials listed above was used as the composting site for the study. The temperature

in the compost bin was measured and recorded. The impact test bars made by materials listed in table 3.4 and table 3.7 were used for composting study. The home composting bin prepared and maintained according to the aforementioned conditions by Dr Karnik Tarverdi at his residence at London borough of Harrow was exploited for the investigation purpose. The 60x60mm plaques were first visually inspected and photographed. The samples were then placed inside the compost for three months. There has been a temperature fluctuation inside the bin. Nonetheless, the average temperature was recorded as 45⁰ C. The samples were removed from the vessel after 3 months period and cleaned with a tissue paper and subjected to visual inspection. Photographs were also taken on composted samples. A visual comparison between initial samples and the composted samples were then carried out.

CHAPTER FOUR

***RESULTS AND DISCUSSION
OF WORK WITH
DIFFERENT ADDITIVES***

4 The function of different additives on the properties of PLA and wheat starch blends

Chapter four presents the principal outcomes of the experimental work carried out and described in chapter 3, about the blends prepared and listed in table 3.2, for the investigation of the function of MDI and other additives on the properties of the PLA and wheat starch blends detailed in section 3.3.1.

4.1 Thermal behaviour

The PLA and wheat starch materials received from the suppliers were analysed by TGA in the first instance to investigate their degradation patterns and the data is presented in figure 4.1. The complete degradation pattern of PLA and the initial weight loss of the wheat starch, approximately about 12-14% due to moisture content in starch, are presented. The pellets of the prepared blend materials with the respective material codes listed in table 3.2 were then analysed for the thermal behaviour.

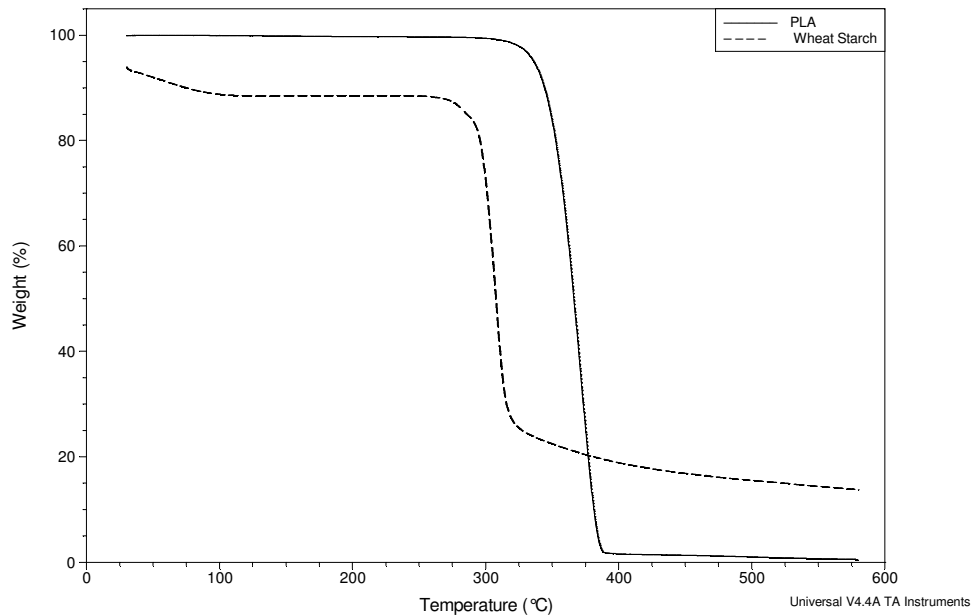


Figure 4.1 Degradation patterns of PLA and wheat starch

The degree of crystallinity is one of the most technically important parameters, and several methods have been developed to measure it. Differential scanning calorimetry is one technique often used, which involves determining the change in enthalpy (ΔH_m) during the melting of a semi-crystalline polymer. The enthalpy of a 100% crystalline sample is then compared to calculate the degree of crystallinity. Figure 4.2 illustrates DSC thermograms of the study exhibiting the thermal behaviour of raw PLA and the blends of wheat starch and PLA with the various coupling agents, and the DSC data are summarized in table 4.1.

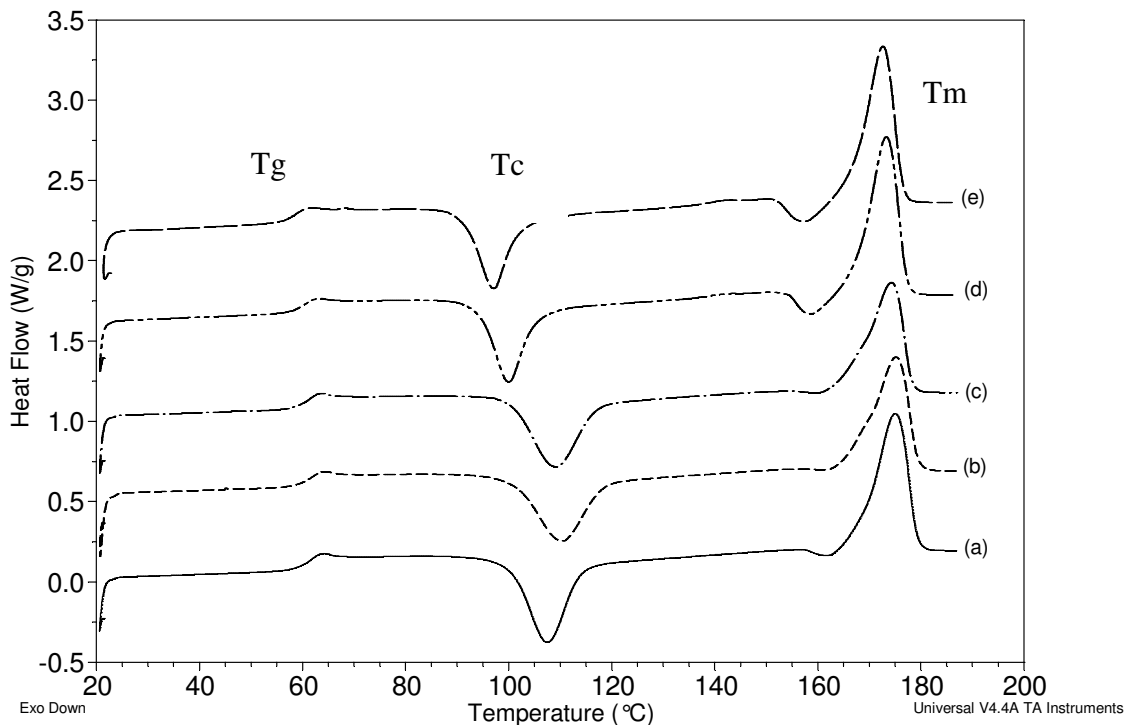


Figure 4.2 DSC thermograms of PLA and wheat starch/ PLA blends with and without different coupling agents (a) PLA (b) 10S90P (c) 10S90P2M (d) 10S90P2G (e) 10S90P2SA

The molecular motions of amorphous polymers are greatly restricted at low temperatures (Birley, Haworth & Batchelor, 1991). These polymers exhibit a characteristic transition when they are heated above a certain temperature and become softer. This glassy to amorphous transition of a material is called the glass transition and the temperature at which this transition is taken place is called the glass transition temperature (T_g). The

polymer shows remarkable rubber like physical properties immediately above the T_g . This critical temperature has, therefore, been investigated on the PLA and the prepared blends. The DSC thermograms evidently showed that the glass transition of PLA and all other blends is about 60°C and an exothermic peak on the high temperature side of the glass transition is assigned to cold crystallization (Yasuniwa et al., 2004; Mezghani & Spruiell, 1998). According to figure 4.2 the glass transition temperature and the melting temperature (T_m) of PLA and the blends have not been significantly affected by the type of coupling agents used but the crystallization temperature (T_c) differed by approximately 10°C for glycerol and stearic acid (SA) blends although it remained almost the same for the MDI blends. Furthermore, the extent of crystallization of PLA was affected greatly by starch as well as by the coupling agents. Upon the addition of the wheat starch to the PLA, the ability of crystallization of the PLA was reduced. The granular starch existing as concentric growth rings (Whistler, BeMiller & Paschall, 1984; Yasuniwa et al., 2004) might have disturbed the persistent PLA phase and its molecular motion (Wang, Sun & Seib, 2001) thus reducing crystallinity. The addition of MDI slightly increased the degree of crystallinity as a result of the interfacial interaction between the PLA and the starch in the 10S90P2M blend.

Table 4.1 Crystallization and melting properties of raw PLA and PLA/wheat starch blends with different coupling agents

Sample	$T_c(^{\circ}\text{C})$	$\Delta H_c (\text{J/g})$	$T_m(^{\circ}\text{C})$	$\Delta H_m(\text{J/g})$
PLA	107.37	26.55	175.02	38.04
10S90P	110.34	24.84	175.11	33.60
10S90P2M	109.00	25.21	174.13	32.82
10S90P2G	99.83	21.19	173.24	38.23
10S90P2SA	97.01	20.49	172.59	37.47

Wheat starch and PLA blends with glycerol and stearic acid coupling agents lowered the crystallization temperatures (100°C and 97°C respectively) compared to the raw PLA (107°C), as can be seen from Table 4.2. These decreases in T_c suggest that small, disordered crystals are formed (Yasuniwa et al., 2004). As a consequence of the effect of glycerol and SA in the blend, chain slipping would have been confined during

the extrusion, thus favouring crystallization. Furthermore, the extent of the discontinuous phase between the PLA and starch might have been reduced in the blend by increasing the chain flexibility which would allow molecular motions and thus shift the crystallization temperature to lower levels. According to Wang and coworkers (Wang, Sun & Seib, 2001; Wang, Sun & Seib, 2002b), bonding interactions between starch and PLA restrict the molecular slippage during mechanical shearing and thereby make shorter chains to accelerate the crystallization. Therefore, it is possible that glycerol and SA promoted bonding between the PLA and the starch. Such interactions, in the form of hydrogen bonds or ester linkages, would have controlled the release from the restraint of the chains at the interface during mechanical shearing and favoured fragmentation of PLA to enhance the number of short chains in the blend. An increased percentage of these short chains consequently supported crystallization, lowered the crystallization temperature of the blends and gave rise to large melting peaks. The results demonstrate that wheat starch decreased the ΔH_m and ΔH_c of the raw PLA. In the presence of MDI, the heat of fusion and ΔH_c exceeded those of the PLA/starch blend. However, glycerol and SA have restored the heat of fusion of the blends but further reduced the ΔH_c .

Cold crystallization depends on the internal structure present at the time of crystallization and not on external constraints (Gowd et al., 2004) and it is apparent that coupling agents as well as the starch have altered the internal structure of the blend. Incorporation of starch containing bulky polysaccharides formed a discontinuous PLA phase in the blend and resulted in a lower ΔH_c , ΔH_m and crystallinity. However, the blends with MDI having active difunctional isocyanate groups promoted interfacial interaction between starch and PLA and thus have decreased the discontinuity and maintained the crystallinity. Therefore, the crystallinity of the blend with MDI was higher than that of the blend without MDI. Stearic acid and glycerol (Ke & Sun, 2001b; Oates, 1997) might have plasticised the starch molecules by leaching out smaller amylose molecules with hindered O-H groups in the wheat starch to the starch granule surface resulting in an increased molecular mobility of chains. As a result of this liberation and exposure of the O-H groups of sugar molecules at the surface, increased interactions with other molecules might have favoured an increase in entanglements. The free ends of such molecules

might have better molecular motions. On the other hand, plasticised starch could have been entrapped in the PLA matrix in an ordered pattern or the formation of bonds between starch and PLA in the presence of glycerol and SA might have supported molecular fragmentation thus increasing crystallinity as discussed above. It is also noted that re-crystallization has taken place in the presence of glycerol and SA. The re-crystallisation suggests that the small and disordered crystals have eventually changed into more ordered crystals.

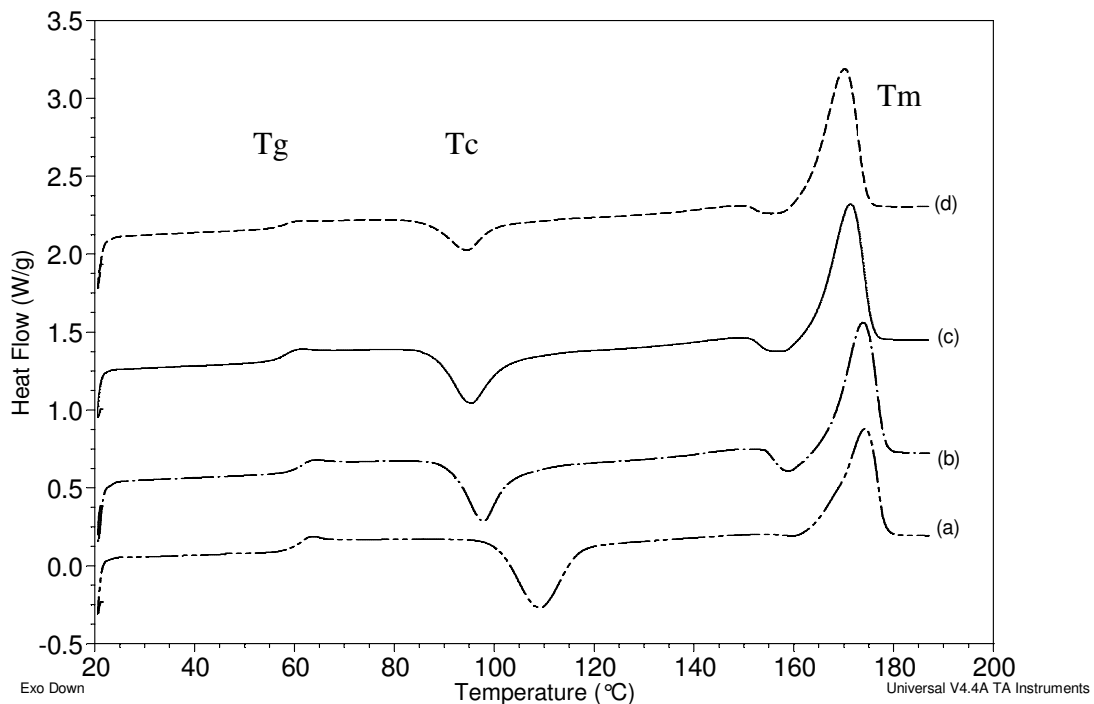


Figure 4.3 DSC thermograms of Wheat starch/PLA/MDI blends with various glycerol levels (a) 10S90P2M (b) 10S90P2M2G(c) 10S90P2M5G (d) 10S90P2M10G

Differential scanning calorimetry thermograms of PLA/wheat starch blends with MDI and different glycerol levels are presented in figure 4.3 and the DSC data are summarized in table 4.2. According to the data, all three temperatures T_g , T_m and T_c have shifted to lower levels with an increasing percentage of glycerol compared to the blends without glycerol. It is apparent that the ΔH_c has decreased but the heat of fusion has increased with increasing glycerol level in the blend. With 10% glycerol, ΔH_c has been reduced by

more than 60% with respect to the blend without glycerol. The cold crystallization and heat of crystallization are very sensitive to chain orientation. In the absence of molecular orientation, crystallization is a slow process (Mezghani & Spruiell, 1998) and therefore there is a possibility that the polymer remains in its amorphous state. According to these results, the decrease in the ΔH_c with increasing glycerol level is due to the better plasticization of starch and hence an increase in the chain flexibility in the blends.

Table 4.2 Crystallization and melting properties of wheat starch/ PLA/MDI blends with various glycerol levels

Sample	T_g ($^{\circ}\text{C}$)	T_c ($^{\circ}\text{C}$)	ΔH_c (J/g)	T_m ($^{\circ}\text{C}$)	ΔH_m (J/g)
10S90P2M	60.42	109.00	25.21	174.13	32.82
10S90P2M2G	60.42	97.59	17.78	173.64	36.53
10S90P2M5G	58.24	95.32	17.21	171.40	36.92
10S90P2M10G	57.85	94.26	9.60	170.20	37.37

Furthermore, an exothermic peak near to the melting peak is observed with glycerol in the blend due to re-crystallization taking place in the blend. Increased chain mobility in the starch incurred by the glycerol and the smaller amylose chains, which have been liberated from the granules, could have made more stable crystals. Most probably, the glycerol has penetrated throughout the granule and randomly packed amorphous amylopectin chains, which were entrapped between the crystalline amylopectin chains (Oates, 1997), and has increased the free volume increasing the mobility of the amorphous lamella. This arrangement could have favoured crystallization. Also, the amylopectin double helices within the crystalline lamellae could have taken up a favourable crystalline arrangement. However, these peaks get smaller with increasing glycerol content. It is assumed that the decrease in the enthalpy of crystallization occurred due to the better plasticization of the amylopectin as well as the amylose molecules in starch with higher glycerol (Qi et al., 2007) content in the presence of MDI causing molecular entanglement rather than crystallization. Therefore, there was no increment in the crystallization observed towards the increasing glycerol level from 2% to 10 % in the blends.

Table 4.3 Crystallization and melting properties of PLA/wheat starch blends with and without MDI

Sample	$T_c(^{\circ}\text{C})$	$\Delta H_c (\text{J/g})$	$T_m(^{\circ}\text{C})$	$\Delta H_m (\text{J/g})$
PLA	107.37	26.55	175.02	38.04
10S90P	110.34	24.84	175.11	33.60
30S70P	101.83	14.50	174.04	33.13
10S90P2M	109.00	25.21	174.13	32.82
30S70P2M	108.65	17.08	174.97	25.87

The summarized DSC data of PLA/wheat starch blends with and without MDI are presented in table 4.3 and the relevant thermographs are shown in figure 4.4. There is no significant difference in the melting temperatures of the blends and PLA but the crystallization temperatures are different. The blend 30S70P without MDI shows unusual results having a very low T_c and a low ΔH_c . It is believed that the blend has absorbed moisture and as a result the starch has been plasticized. The resulting molecular orientation might have favoured crystallization thus reducing T_c . The presence of an exothermic peak (see figure. 4.4) near the melting peak is a result of re-crystallization. Compared to the 10S90P blend, the MDI in the 10S90P2M blend has increased the ΔH_c as a result of the formation of urethane linkages (Zhang & Sun, 2004a; Chanda & Roy, 1997) between the isocyanate and OH groups. Consequently, chain flexibility is restricted due to the steric hindrance of the benzene rings in the MDI (Jun, 2000). A better coupling between PLA/ poly(butylene succinate) and corn starch with respect to aliphatic isocyanates was also reported (Ohkita & Lee, 2004). The crystallinity of PLA was reduced with increasing starch due to the scattered dispersion of starch in the base matrix and also owing to the growth of a continuous starch phase.

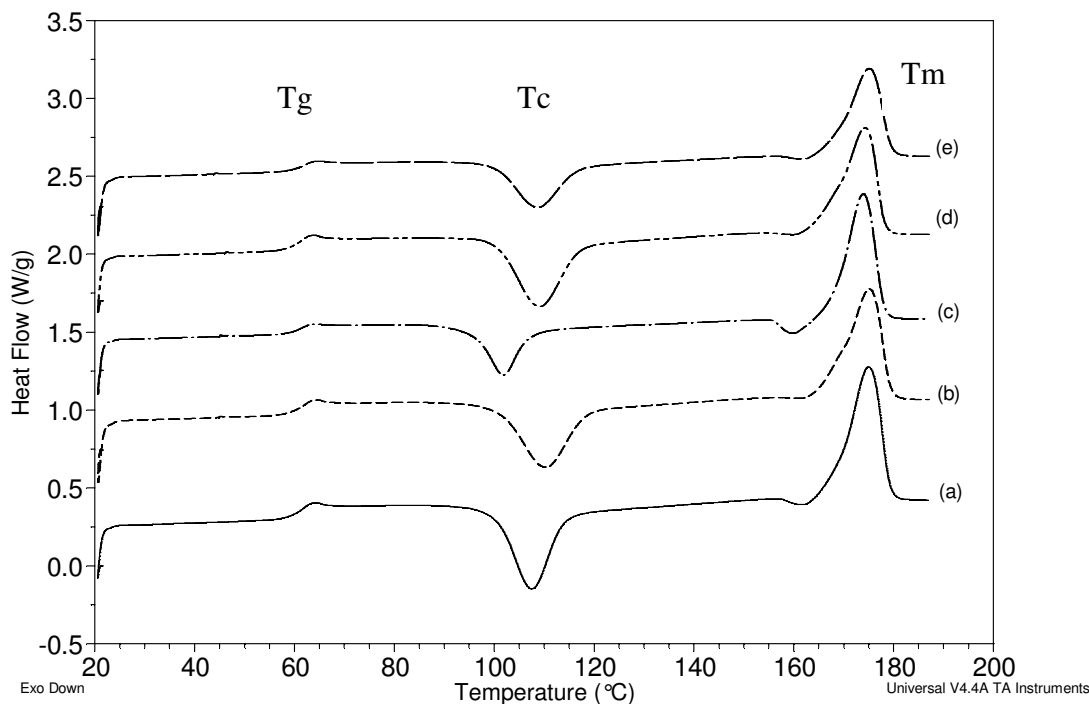


Figure 4.4 DSC thermograms of wheat starch/PLA blends with and without MDI (a) PLA (b) 10S90P (c) 30S70P (d) 10S90P2M, and (e) 30S70P2M.

4.2 Appearance of the dumbbell specimen

The appearances of the tensile test bars of virgin PLA and PLA/ wheat starch blends with and without MDI prepared by injection moulding were different from each other. The clarity of tensile test specimens of only PLA was very high but with the inclusion of starch, the clearness of the specimen changed. The blend containing 10% starch was slightly opaque but the blend containing 30% starch had much higher opacity. Furthermore, a yellowish brown MDI coloured the dumbbell specimens turning them light yellow in the 10S90P2M blend. The appearance of the tensile bars of the blend 30S70P2M was almost dark brown and also seemed to be degraded due to the processing difficulties encountered during extrusion. It was apparent that the clarity of the PLA was greatly reduced with the incorporation of the starch and MDI.

4.3 Mechanical Properties

The mixing of two polymers could result in a coarse structure due to incompatibility between the polymers that could compromise their mechanical properties. Therefore, the tensile properties of the PLA/wheat starch blends with and without the MDI coupling agent were investigated and these are presented in table 4.4

Table 4.4 Mechanical properties of pure PLA and wheat starch/PLA blends with and without MDI

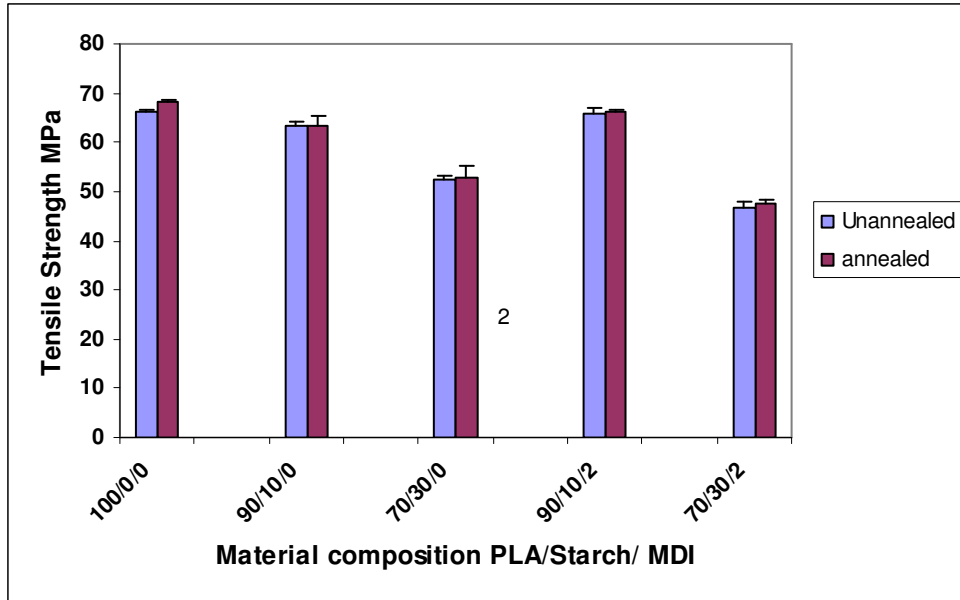
Sample	Tensile Strength (MPa)	Elongation (%)	Young's Modulus (GPa)
PLA	66.32 ±0.05	3.14±0.38	4.25±0.50
10S90P	63.53 ±0.11	1.94±0.51	4.29±0.08
30S70P	52.20 ±0.18	1.50±0.89	3.90±0.18
10S90P2M	65.94 ±0.03	2.12±0.91	3.79±0.14
30S70P2M	46.83 ±0.07	1.36±0.92	3.92±0.23

The tensile strength and elongation at break of the samples 10S90P and 30S70P in table 4.4 under ambient conditions decreased with increasing starch levels compared with those of only PLA. However MDI, in the blend of 10% starch was capable of restoring the strength of raw PLA. Furthermore the elongation which decreased by almost 38% in the blend 10S90P reduced to 30% in the blend 10S90P2M. The Young's modulus of the 10S90P2M blend was lower than the raw PLA and PLA/ starch blends indicating lower stiffness in the blend. The 30S70P blends with and without MDI show poorer properties than raw PLA. From its appearance, 30S70P2M blend seems to be non uniform as a consequence of denatured starch during extrusion and degradation due to the difficulties encountered in uniform feeding. The blend 10S90P2M showed properties similar to those of PLA, except for the Young's modulus.

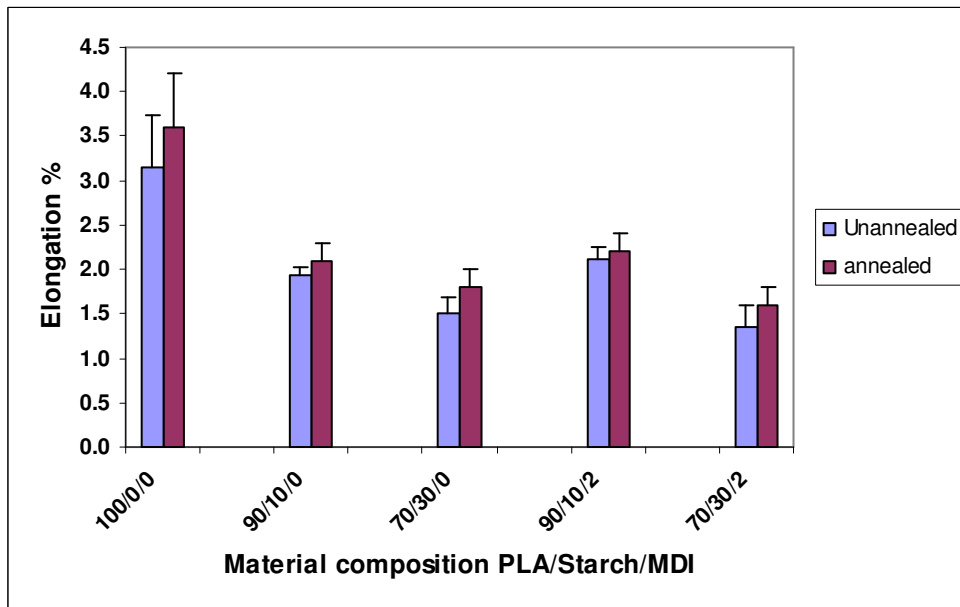
A low strength and elongation at break when starch is incorporated into the PLA matrix is due to the continuous phase of PLA being destroyed by starch granules. Consequently, the loss of crystallization as shown by DSC immensely contributed to the

low strength. The starch granules might have acted as stress consolidating points, thereby initiating cracks in the material. When MDI is incorporated into the 10S90P blend the strength increased by 4% with respect to the starch PLA blend. It is apparent that the interfacial adhesion between PLA and wheat starch enhanced the superior properties in the blend. These results are also compatible with the results of compression moulded blends of 0.5% MDI with PLA/starch blends carried out by Wang et al (Wang, Sun & Seib, 2001). This current study shows an increased elongation in the 10S90P2M blend but it is less than that of the raw PLA. It is well known that the size of the groups in the polymer relate to the chain flexibility of the polymer. Therefore two phenyl groups in the MDI as well as starch might have restricted the chain flexibility of the blend resulting in a lower elongation than the raw PLA.

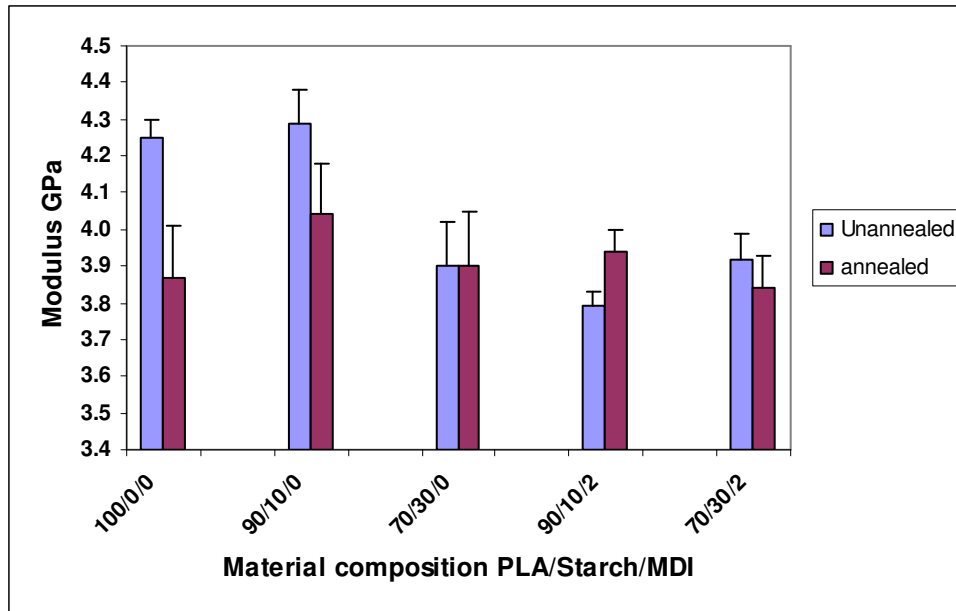
Figure 4.5 shows the comparison of tensile properties with respect to annealed and un-annealed conditions of samples of raw PLA and PLA/ starch blends with and without MDI. There is only a little effect on the tensile strength of the materials upon heat treatment. It is apparent that the enhanced molecular mobility due to the heat treatment of the employed temperature in the study was not efficient in favouring crystallization in the blend. However, the elongation at break of the blends has slightly increased in almost all the blend samples and the raw PLA. Upon heat treatment, due to the energy induced molecular mobility, amorphous orientation might have increased causing the material to deform. The moduli of the blends decreased except from that of 10S90P2M. This is consistent with the elongation results upon heat treatment. As a result of annealing, changes in the chain orientations with MDI in the blend might have increased the modulus of the 10S90P2M blend.



(A)



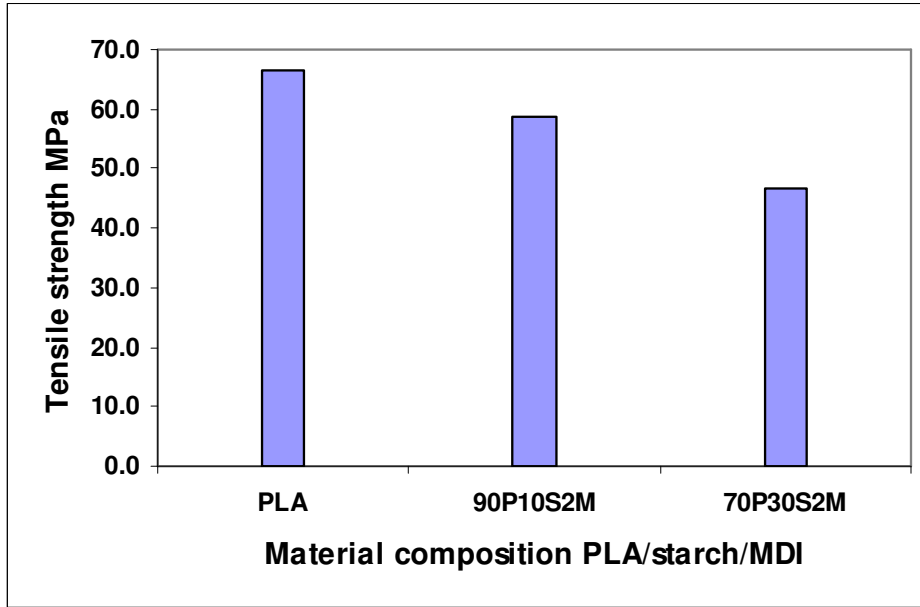
(B)



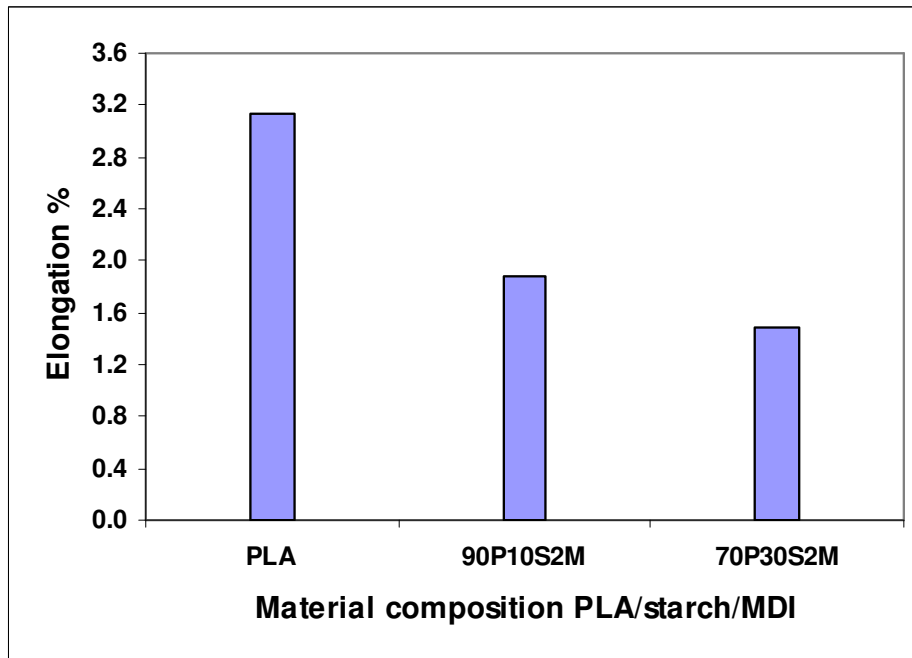
(C)

Figure 4.5 The tensile properties of PLA, PLA/wheat starch blends with and without MDI and with and without heat treatment. (A) Tensile Strength, (B) Elongation, and (C) Young's Modulus.

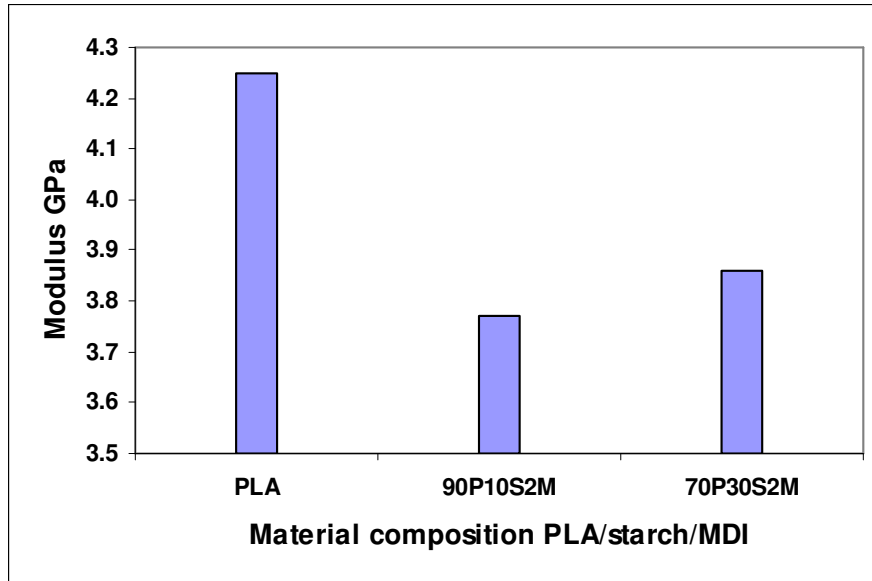
The blends of PLA/wheat starch with MDI, which were stored overnight before measurements were taken, are shown in figure 4.6. According to figure 4.6, the results revealed that leaving the blends overnight before extrusion has reduced the tensile properties compared to the blends processed immediately after preparation. Upon overnight storage, the possible weak urethane links formed between PLA and starch might have broken due to the stress relaxation of the molecules or that the PLA chains might have fragmented to shorter chains, resulting in poor mechanical properties. Although the short chains favour crystallisation, they decrease the strength of the material. On the other hand, if the moisture is absorbed by the blend upon prolonged exposure to the environment, this could result in hydrolysis of urethane linkages giving rise to the corresponding amine and carboxylic groups and resulting in a poor mechanical properties of the blend.



(a)



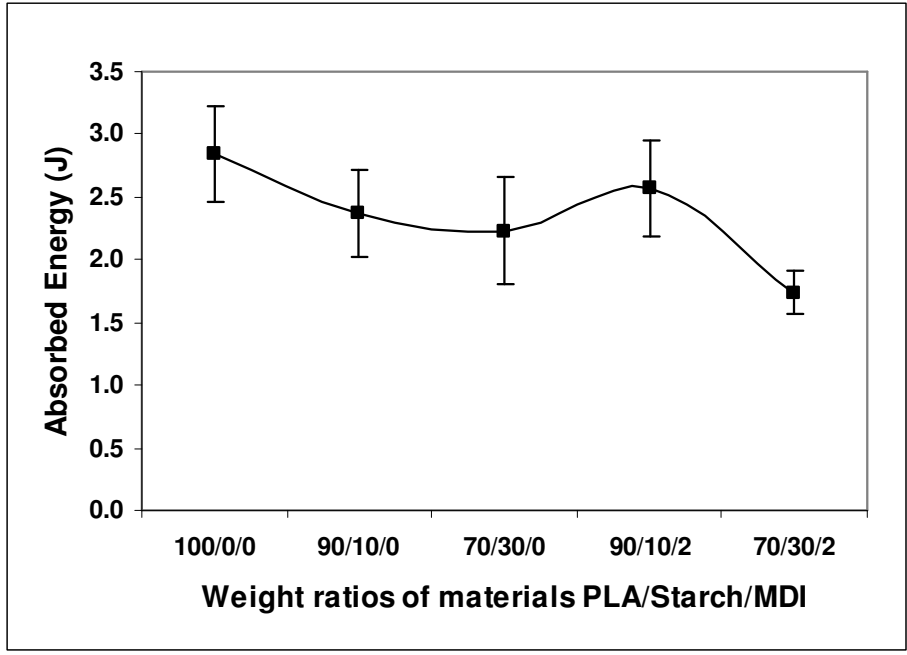
(b)



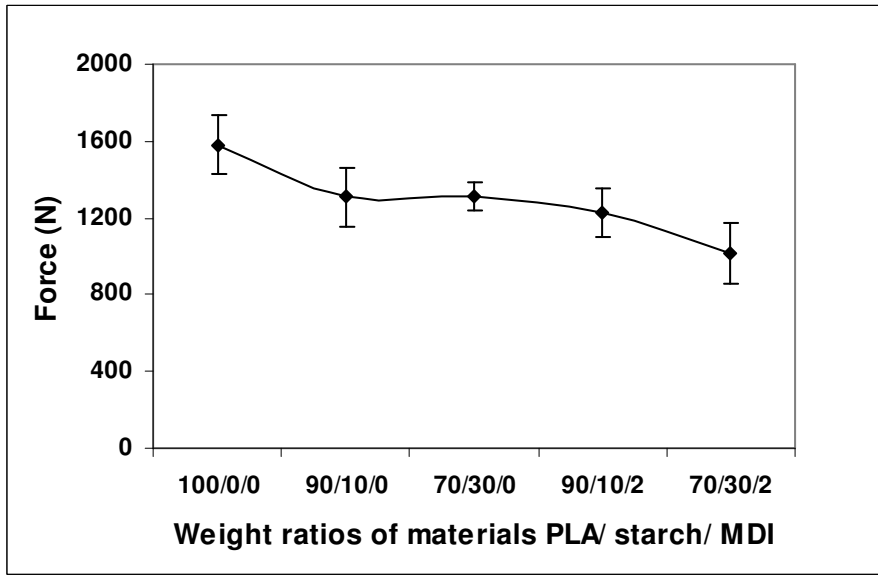
(c)

Figure 4.6 The tensile properties of PLA, PLA/wheat starch blends with MDI blended and left overnight before extrusion. (a) Tensile Strength, (b) Elongation and (c) Young's Modulus.

The impact behaviour of the PLA and PLA/ wheat starch blends with and without MDI is shown in figure 4.7. With increasing starch level there is a progressive decrease in the energy absorption in the blends. Because of the nature of the granular starch, it behaves as a stress concentrator rather than dissipator. However, the blend 10S70P2M shows an energy absorption very similar to that of raw PLA although the peak force is little less than that of the raw PLA. The starch and PLA are coupled by an interfacial adhesion of MDI. Perhaps the urethane linkages which formed between starch and PLA resulted in longer chains. These long chains might have crystalline regions as well as amorphous regions. Amorphous regions in the chains show better toughness, behaving as shock absorbers.



(A)

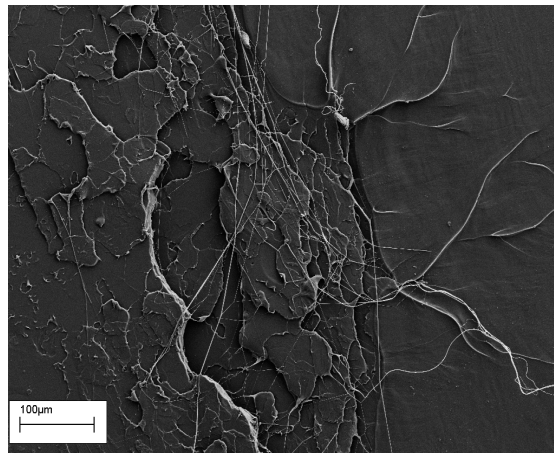


(B)

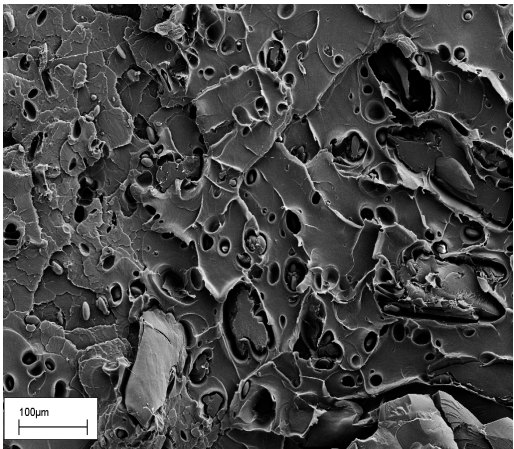
Figure 4.7 The impact behaviour of the PLA and PLA/wheat starch blends with and without MDI (A) Absorbed Energy, and (B) Force.

4.4 Morphology

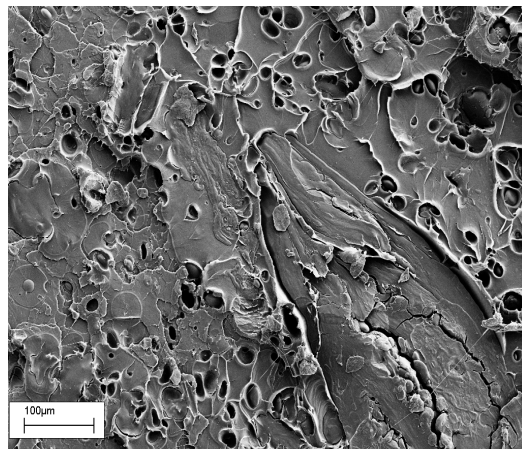
Scanning electron micrographs have been obtained of the tensile fracture surfaces of PLA (Figure 4.8A), PLA/wheat starch blends (Figure 4.8B and C) and PLA/wheat starch /MDI blends (Figure 4.8D and E). Two phases can be clearly seen, the starch granules were pulled out and voids have been created as can be seen in the figure 4.8 (B) and (C).



A



B



C

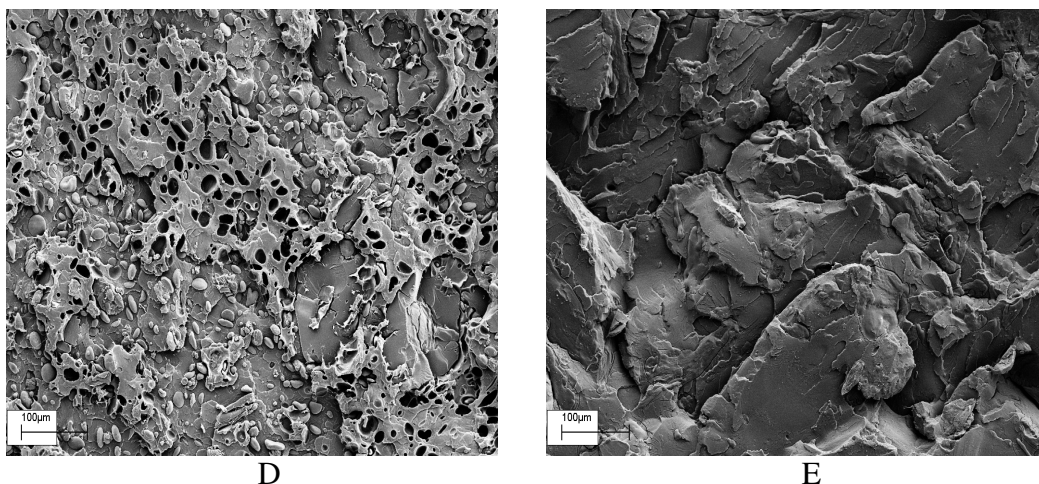
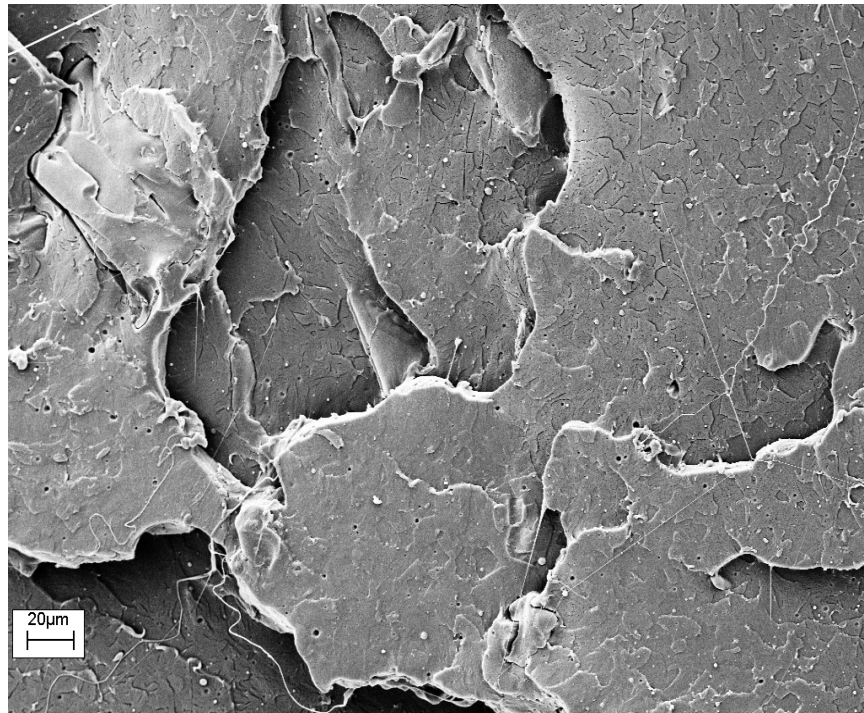


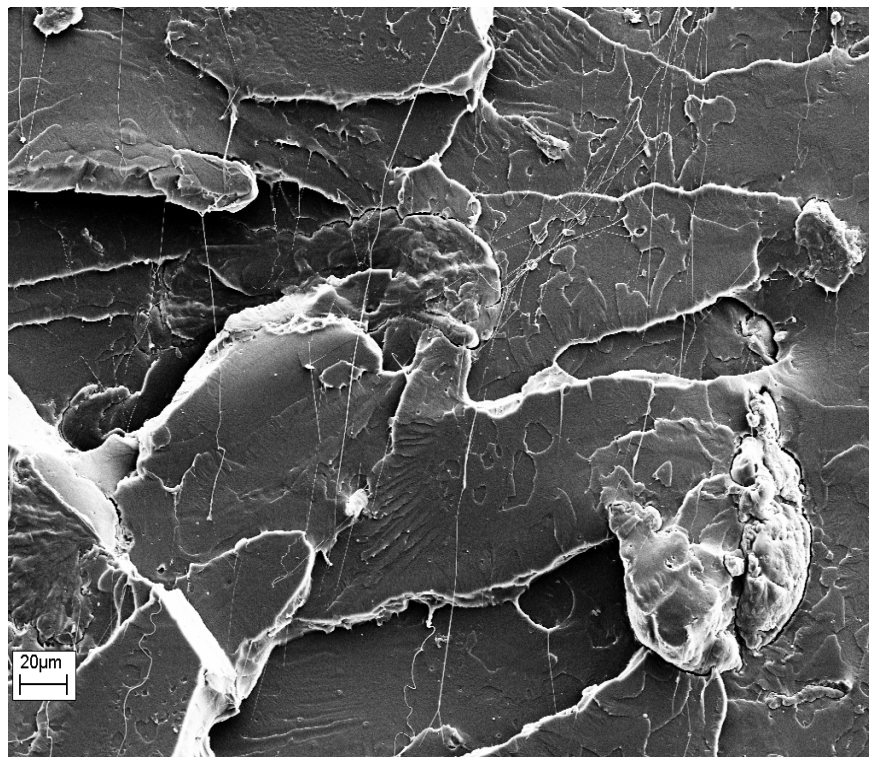
Figure 4. 8 SEM micrographs of PLA and wheat starch/ PLA blends with and without MDI. (A)Pure PLA (B) 10S90P (C) 30S70P (D) 10S90P2M, and (E) 30S70P2M

The better interfacial adhesion of starch and PLA with MDI is observed in figure 4.8 (D). However a continuous starch phase is difficult to discern with the MDI but a starch granular form is still visible in the SEM micrograph. According to the SEM micrographs in figure 4.8 and figure 4.9, blends with coupling agents show a better continuous phase between the starch and the PLA than the blend without coupling agents. It is noticeable that the continuous phase is more prominent with SA and glycerol. The blend with MDI has a continuous phase but the starch granular form is still observed and indicates that MDI does not have the plasticization ability of starch. It is apparent from the molecular structure that glycerol and SA can plasticize starch better than MDI. However, their coupling effect upon the tensile properties has still to be investigated.

Figure 4.9 (A) and (B) show micrographs of blends compounded with 2% glycerol and 2% SA respectively. The stearic acid shows almost the same phase appearance as the raw PLA. With glycerol, small starch granules are seen to be entrapped in PLA matrix. Both the SA and glycerol coupling agents showed a better interfacial adhesion between the PLA and starch in the SEM images.



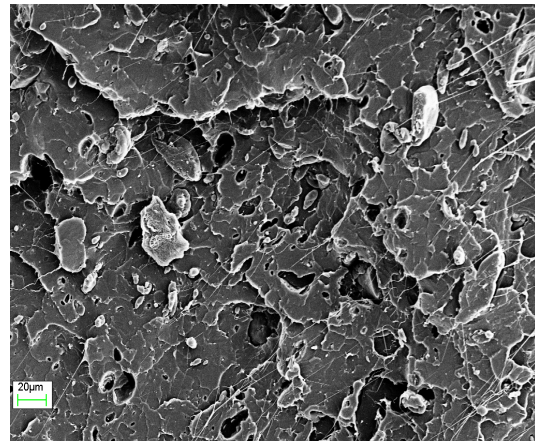
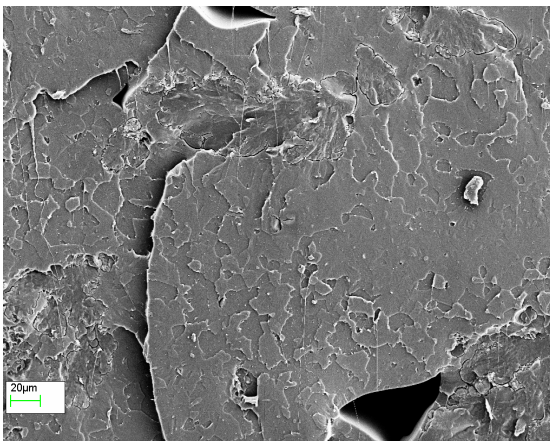
(A)



(B)

Figure 4.9 SEM micrographs of the PLA/wheat starch blends with different coupling agents (A) 10S90P2G, and (B) 10S90P2SA.

Scanning electron micrographs of blends with MDI and different glycerol levels are shown in figure 4.10. The fracture surface of the blend 10S90P2M10G was more ductile than blends with 2% and 5% glycerol. Appearance of the extrudate of the blend with 10% glycerol is smooth and according to the SEM micrograph, most of the starch granules have been plasticized and disappeared with 10% glycerol. It has been suggested that starch granules exist in a form of a concentric growth ring. The reducing ends more randomly organized and located in the centre of the granule with the non reducing ends of the amylose and amylopectin pointing outwards allowing the glucose residues to add on and extend the amylopectin chains (Oates, 1997). In the presence of glycerol, the amylose chains can leach out to the granular surface from concentric growth ring of the the granular starch (Oates, 1997). The small size and nature of the glycerol with its high hydrogen bonding density has the ability to penetrate and reach the amorphous region of the granule. It is well understood that glycerol can infiltrate the amorphous amylose molecular chain arrangements more than the orderly packed amylopectin crystals. A porous structure is observed in the blends in the SEM images with the glycerol and the porosity increased with an increasing glycerol level. In the presence of glycerol, amorphous regions penetrate throughout the granule and on hydration they form a continuous gel phase resulting in porosity. This result is consistent with the results discussed and reported by Oates (Oates, 1997). The higher glycerol content in the blend shows the better plasticization of the starch in the figure 4.10(C). The fracture surface of the materials showed ductile fracture and the material was flexible at room temperature and upon storage. However, as MDI is a toxic material, further studies have not been carried out in this area with MDI.



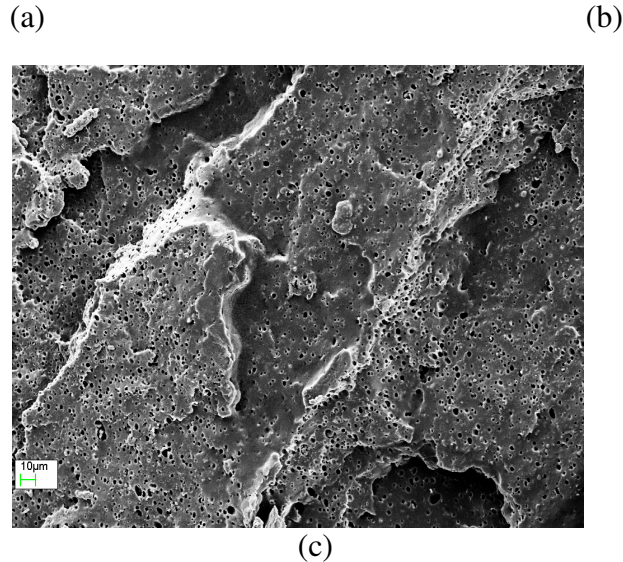


Figure 4.10 SEM micrographs of the PLA/wheat starch blends with different glycerol levels (a) 10S90P2M2G (b) 10S90P2M5G, and (c) 10S90P2M10G.

4.5 Water absorption

Starch consists of a glucose monomer joined by $\alpha(1-4)$ linkages, labelled as amylose and a glucose monomer connected by $\alpha(1-4)$ linkages with branched $\alpha(1-6)$ linkages, known as amylopectin, both having an abundance of hydroxyl groups and showing a highly hydrophilic character. However, PLA has been classified as a hydrophobic polymer (Shogren, 1997). Depending on the water permeability of the polymer, it can accelerate or decelerate the polymer degradation. Figure 4.11 shows the water absorption of PLA, PLA/wheat starch blends with and without MDI. All the blends except 30S70P2M show less than 2% water absorption. The blend without MDI having 30% starch shows 3% water absorption, and the blend of 70P30S2M with loosely packed extruded pellets shows more than 11% water absorption. No significant difference in water absorption occurred between the blends with and without MDI. The water absorption of raw PLA also had a similar tendency as that of the blend with starch but levelled off at about 0.5%. The blend 10S90P2M shows identical properties to PLA.

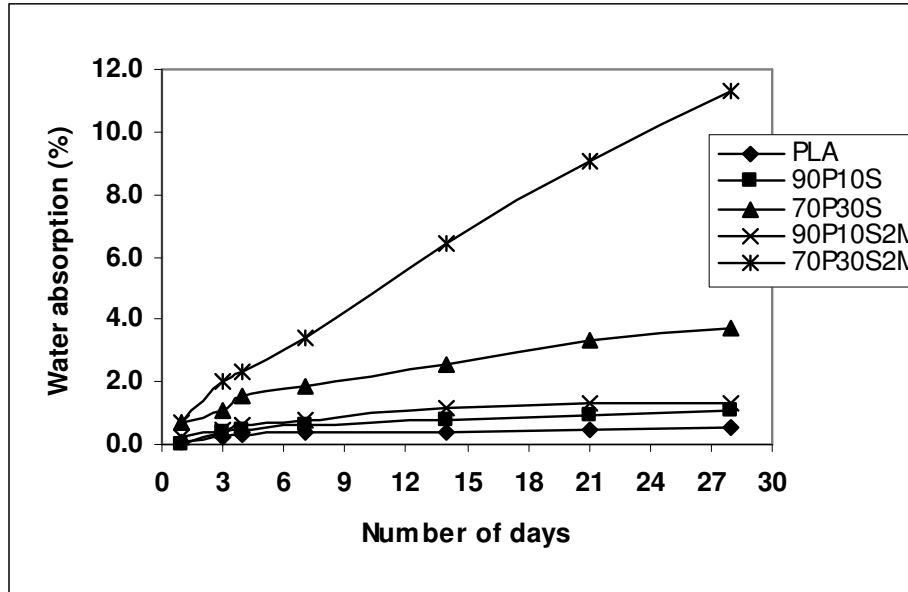


Figure 4.11 Water absorption of PLA, wheat starch/ PLA blends with and without MDI at different time intervals.

The water absorption carried out on tensile test bars of both blends with or without MDI increased during the first two weeks and then levelled off at about 3%. Similar patterns with slightly increased water absorption figures were exhibited on the measurements taken on broken tensile bars (Zhang & Sun, 2004c). Wang (Wang, Sun & Seib, 2002b; Wang, Sun & Seib, 2002a)(Oates, 1997; Wang, Sun & Seib, 2002b; Wang, Sun & Seib, 2002a) and Ke (Ke, Sun & Seib, 2003; Ke, Sun & Seib, 2003) also reported that water absorption gradually increased during the first 15 days before levelling off. However, in Wang's study, water absorption of PLA/starch blend with and without MDI was fairly high compared to the current study. The reason behind this variation is that two different moulding techniques, compression moulding for Wang's study and injection moulding for current study were used in preparing tensile bars for the investigation of water absorption. A previous study (Ke & Sun, 2001a) also found that the water sorption rates of injection mouldings were comparatively slower than those of the samples prepared by compression moulding. Therefore, injection moulded bars that have been employed for investigation in the current study, have led to the slow rate of water absorption. However, the results apparently indicate that the starch content in the blend is the dominating factor for the water absorption of the PLA/starch blends.

4.6 Chapter synopsis

PLA and wheat starch were blended with a range of additives, DSC, tensile and impact properties, morphology and water absorption were investigated. Starch can be incorporated in a PLA matrix at 10% level without difficulty in processing in the presence of 2% MDI. Pellets can be made by extrusion and pelletising technology and the pellets can be injection moulded to make shaped mouldings, with slightly opaque appearance induced by starch. With 10% wheat starch and 2% MDI, blends of wheat starch/PLA can regain the tensile strength, elongation, and impact strength properties of raw PLA. Furthermore, in the presence of 10% wheat starch, the blend has a lower modulus than raw PLA and the water absorption properties are similar to those of raw PLA. Glycerol and stearic acid have the ability to improve the crystallinity of PLA and heat of crystallization better than MDI and hence there could be better physical properties when these two materials are added. A higher glycerol level in the presence of MDI can better plasticize starch, making a ductile material. MDI behaves as a coupling agent and glycerol and SA behave more like plasticizers. Nonetheless, MDI is known to be a toxic material and therefore further studies with this additive were not carried out in the current research, but more work was concentrated on environmentally benign materials. Two such materials having trade name biostrength modifier materials produced by Arkema Inc. were employed in the study with PLA/wheat starch, in search of desirable properties and the outcomes are disclosed in chapter 5.

CHAPTER FIVE

***RESULTS AND DISCUSSION
OF THE INVESTIGATION WITH
BIOSTRENGTH MODIFIERS***

5 The role of biostrength modifier materials on property variation of the blends

In this chapter, the author principally intends to convey the experimental results of the work carried out and described in chapter 3, on the blends prepared and listed in table 3.3 for the investigation of the role of biostrength modifier materials on the property variation of the PLA and starch blends described in section 3.3.2.

5.1 Thermal behaviour

Two materials having the trade name biostrength modifier materials, melt-strength modifier (MS) and impact modifier (IM) were incorporated into PLA and wheat starch blends and the material codes of the prepared blends are listed in table 3.3. Thermogravimetric analyses of the pellets of these listed materials were carried out and the relevant TGA data are presented in figure 5.1, which shows the degradation behaviour of the PLA and its blends with biostrength modifiers. The corresponding 5% degradation temperatures ($T_{5\%}$) and the maximum rate of weight loss temperatures (T_{\max}) are presented in table 5.1.

Table 5.1 Temperatures of 5% degradation and maximum rate of weight loss.

Material	$T_{5\%}$ ($^{\circ}\text{C}$)	T_{\max} ($^{\circ}\text{C}$)
PLA	333	366
PLA6IM	331	365
30S70P6IM	289	366
PLAn	336	368
PLAn4MS	329	366

According to the TGA analysis, the PLA and the blends without starch were thermally stable up to 350°C in an inert atmosphere. The blend with starch degraded at about 290°C . The degradation of the blend with starch has occurred prior to PLA degradation due to the presence of starch. These results of the starch degradation are in agreement with the

degradation results of starch/PLA blends reported by Jacobson (Jacobsen & Fritz, 1996). After starch degradation, the PLA phase is degrading at the same temperature following the same pattern as it is degraded in its raw form. The addition of biostrength modifiers to pure PLA does not influence at all the melt stability of the PLA or the blend itself. Looking at the results in figure 5.1, it can be concluded that the degradation behavior of PLA is not affected in any way by the addition of starch or modifiers, though the melt stability of the total blend is now dependent on the stability of the starch. However, degradation temperatures demonstrate that the blends are thermally stable at and even well beyond their processing temperatures. Furthermore, the results revealed that the maximum weight loss temperature T_{max} of the PLA and PLAn remained in the temperature range of 366-367⁰C, but integration of biostrength modifiers and starch into PLA and PLAn matrices has resulted in a decrease in both $T_{5\%}$ and T_{max} temperatures.

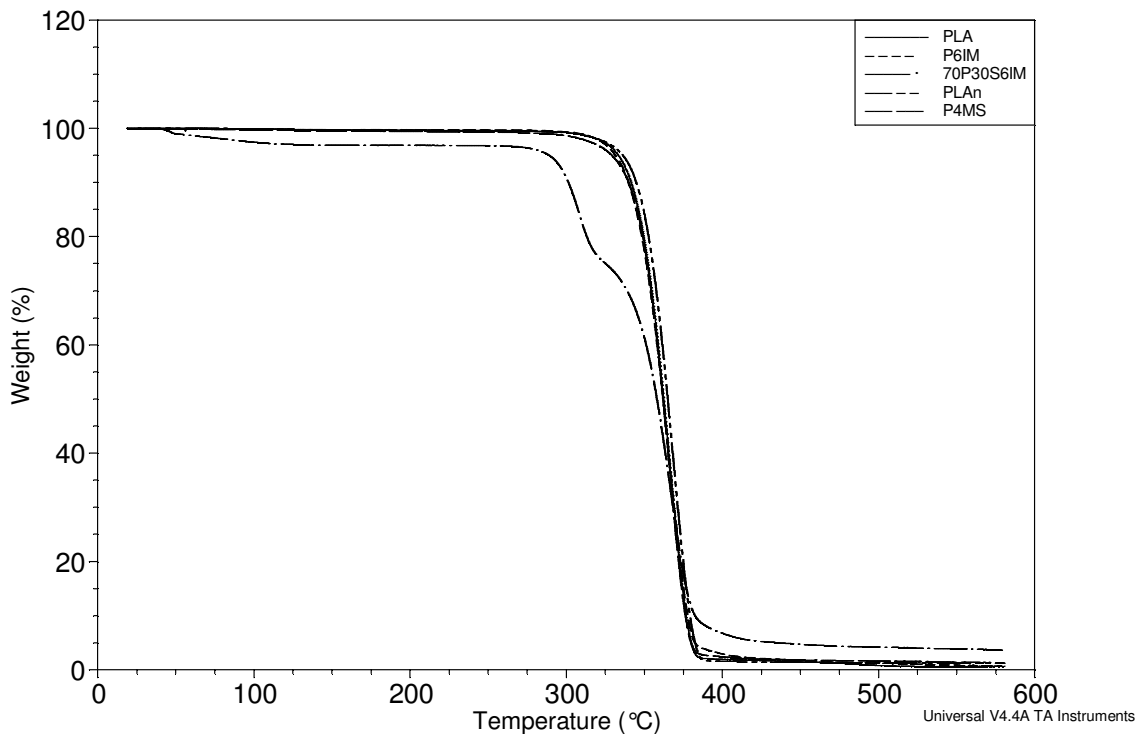


Figure 5.1 Degradation behaviour of PLA and the blends in N₂ atmosphere

5.2 Investigation of phase transitions

As it can be seen from figures 5.2 and 5.3, one can determine the influence of the starch and biostrength modifier addition on the thermal behaviour of the corresponding blends from the first and second heating runs respectively. The glassy to amorphous transition temperature (T_g) is observed around 60°C for both PLA and PLAn, where as the melting temperature differs only slightly in the base materials and accordingly in the blends. The PLA shows melting temperature (T_m) around 175°C and crystallisation temperature (T_c) around 105°C . When the impact modifier is blended with the PLA, the thermal behaviour shows a shift of the T_g to a higher temperature and no crystallisation occurs, resulting mostly in amorphous material at the current heating rate. In the tri-blend system with starch, a considerably broader melting peak is observed. In each case the melting temperature slightly decreases with a reduction in the melting peak. In contrast, no sharp crystallisation peak is discerned with PLAn and a small melting peak is conspicuous around a temperature of 140°C . Incorporation of a melt strength modifier reduces T_g , and a similar broad melting peak occurs with starch in the tri- blend with MS, but there is no crystallisation in each case. These materials are therefore assumed to be mostly amorphous.

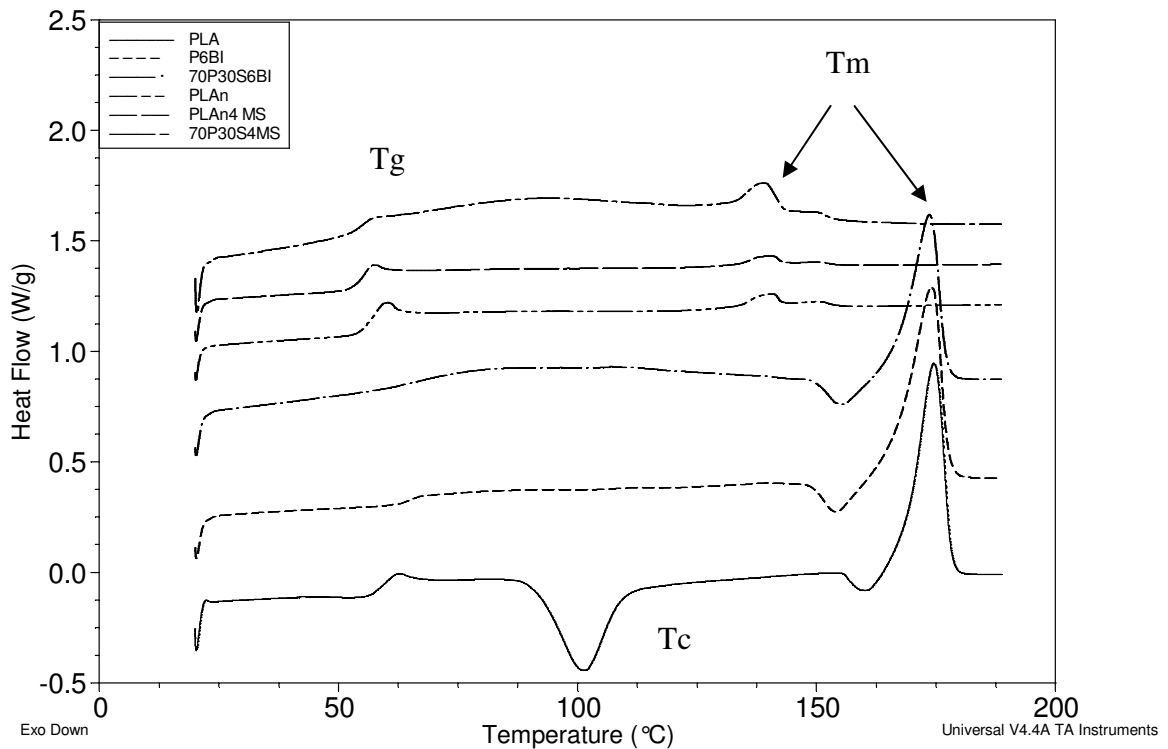


Figure 5.2 DSC thermograms for the first heating run with a heating rate of 100C/min

The second heating cycle in figure 5.3 shows a different pattern to that of the first heating run. This pattern shows an evidence of the presence of a thermal history in the materials. The observed glass transition temperatures of the pure materials are not affected by the starch or the additive, but there are considerable differences in the crystallisation and melting temperatures. In the presence of impact modifier the PLA which showed a T_c around 105⁰C has changed to 115⁰C. The T_m around 175⁰C with a single melting peak splitted and two peaks at 167⁰C and 175⁰C were discerned. The starch in the tri-blend system exhibits a similar behaviour in the both cases the crystallisation enthalpy and melting enthalpy reduced illustrating a cutback in the crystallisation. With PLAn, no sharp crystallisation is discerned, but a small melting peak is conspicuous around 140⁰C. The incorporation of a melt strength modifier does not influence the T_g , nor does it influence

the melting peak or crystallisation in each case. These materials are, therefore, assumed to be mostly amorphous.

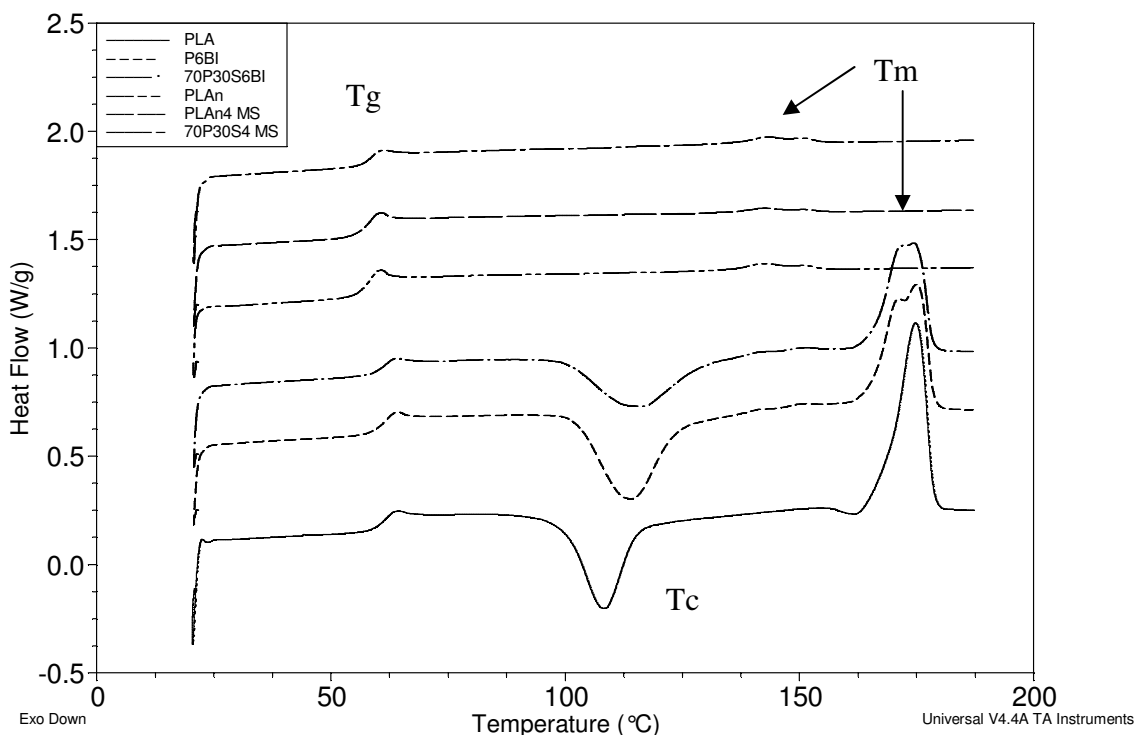


Figure 5.3 DSC thermograms for the second heating run with a heating rate of $10^{\circ}\text{C}/\text{min}$.

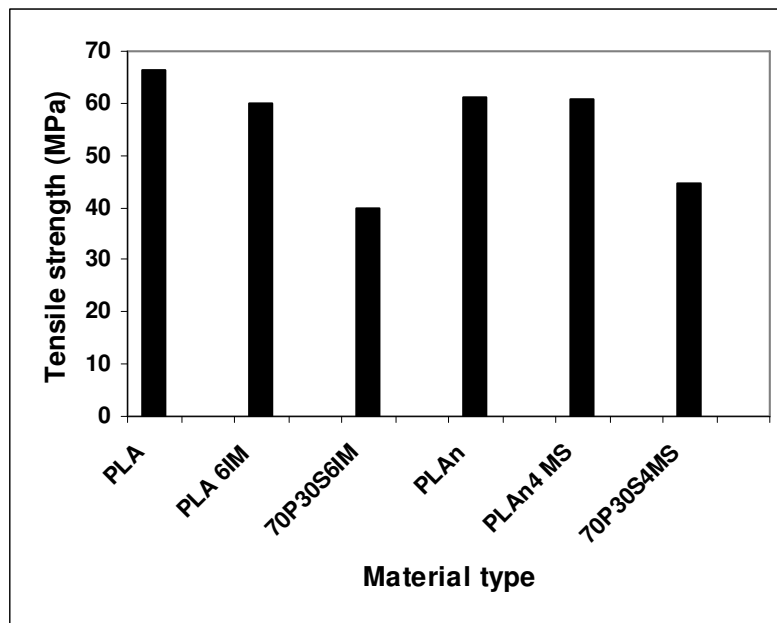
Some evidence (Wang, Sun & Seib, 2001) confirms that the extent of the crystallisation can be affected by the starch by restricting molecular motion of the PLA. This fundamental principal is clearly observable in the current study with a similar result for the starch addition, which could also perturb the continuous PLA phase. However, in both di-blend with PLA/IM and tri-blend with PLA/starch/IM, it appears that IM has large effect, where the starch has influenced to cause a further reduction in crystallinity. The IM shifts cold crystallisation temperature of PLA to higher temperature. There are several structural requirements that are essential before the polymer molecule can crystallise. Necessarily, the polymer chain plays a vital role to limit the extent of crystallisation though it is not

completely stopped. The literature suggests that crystallinity can vary based on factors such as polymer chain length, tacticity, and substituent groups in the polymer structure (Fried, 2005). It is also found that atactic vinyl polymers will not crystallise when the substituent group is large (Young & Lovell, 1991). The IM is known to be an acrylic copolymer, which originates from an unsaturated carboxylic acid known as acrylic acid, which has a vinyl group connected to the acid terminus with the structures given below. Depending on the functional groups attached to the vinyl carbon, there is a range of acrylic acids, which can be polymerised to give polyacrylic acid. As discussed above, the features such as tacticity and substituent groups in the acrylic copolymer could have influenced the blend, resulting in a limited crystallinity in the current study.

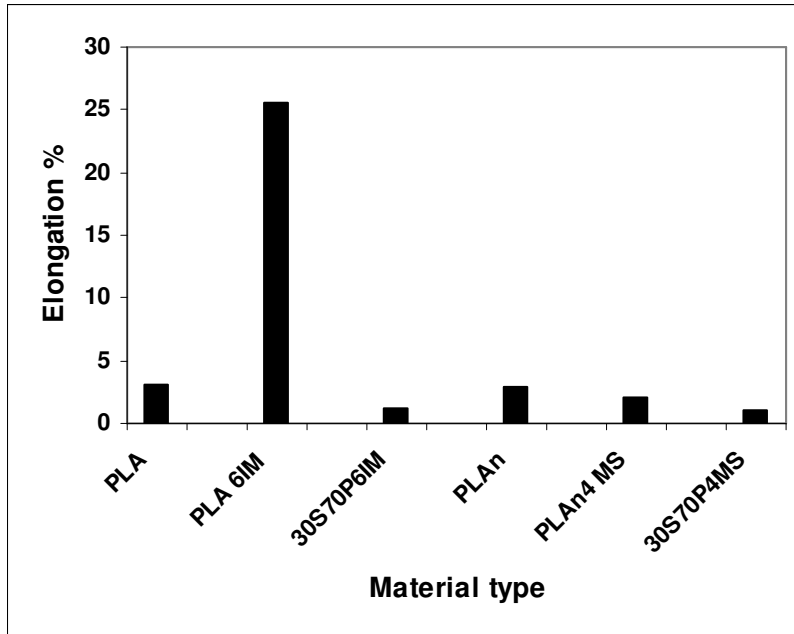
5.3 Mechanical Properties

The determination of the stress-strain behaviour of a material is extremely useful as it provides vital mechanical properties such as strength, Young's modulus and brittle-ductile failures. Figure 5.4 illustrates the tensile properties of the samples of raw PLA and PLA/wheat starch blends with IM and MS modifiers. Both the starch and impact modifier demonstrate negative effects towards the tensile strength as shown in Figure 5.4(a), but the effect from the IM is less pronounced compared to the more significant effect from starch. The melt strength enhancer is more neutral on tensile strength, though a prominent reduction, similar to the blend with IM, is exhibited in the tri-blend of PLA/starch/MS. The results suggest that the association of starch in the blend is the most controlling element of the composite's mechanical properties. This explanation is empirically supported by the similar tensile strength values shown by PLAn and PLAn/MS enhancer blends. The PLA and PLAn both as virgin materials have approximately 3% elongation. The integration of the impact modifier is beneficial towards the elongation of PLA, which shows more than 20 % increase as shown in figure 5.4(b), but the melt strength enhancer slightly reduces the elongation of the blend. However, the effect on elongation from starch is less beneficial when compared with the MS.

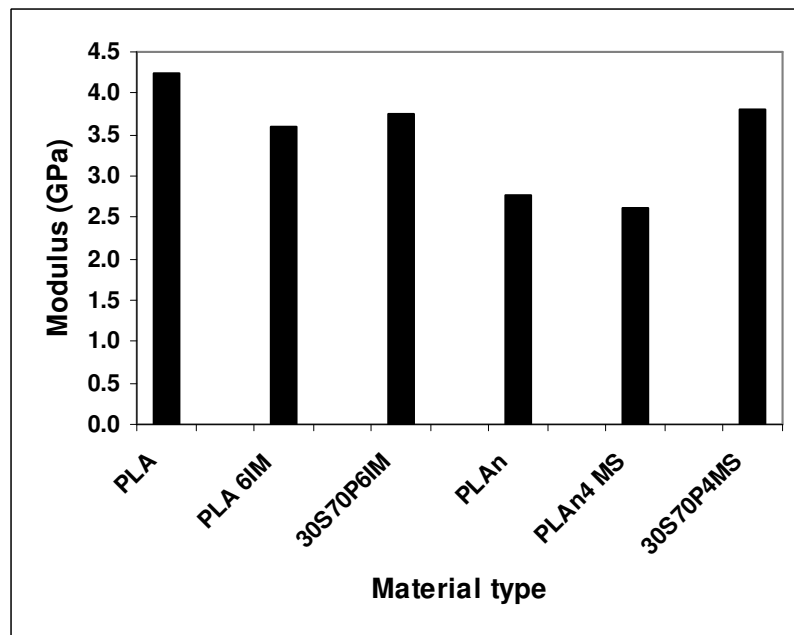
The integration of two polymers could generally produce immiscible blends, with a coarse structure, meta-stable morphology, with the most affected properties being tensile strength, elongation at break and toughness owing to poor adhesion between the phases. As reported by Wang (Wang, Sun & Seib, 2001), Ke (Ke & Sun, 2000; Ke & Sun, 2001a) and Kozlowski (Kozlowski et al., 2007), in a binary system of PLA and starch, the tensile strength and elongation decreased with increasing starch content. The poor interfacial adhesion between the two polymers has led to poor properties. It is well understood that the neat PLA phase is disrupted by starch and disorders are created in the PLA phase. The granular form of starch and the gaps in the binary blend initiated crack formation upon tensile testing, thereby reducing properties. The poor tensile strength was also confirmed by the increased crystallization temperature and the reduced crystallinity in the presence of starch, demonstrated in the DSC results.



(a)



(b)



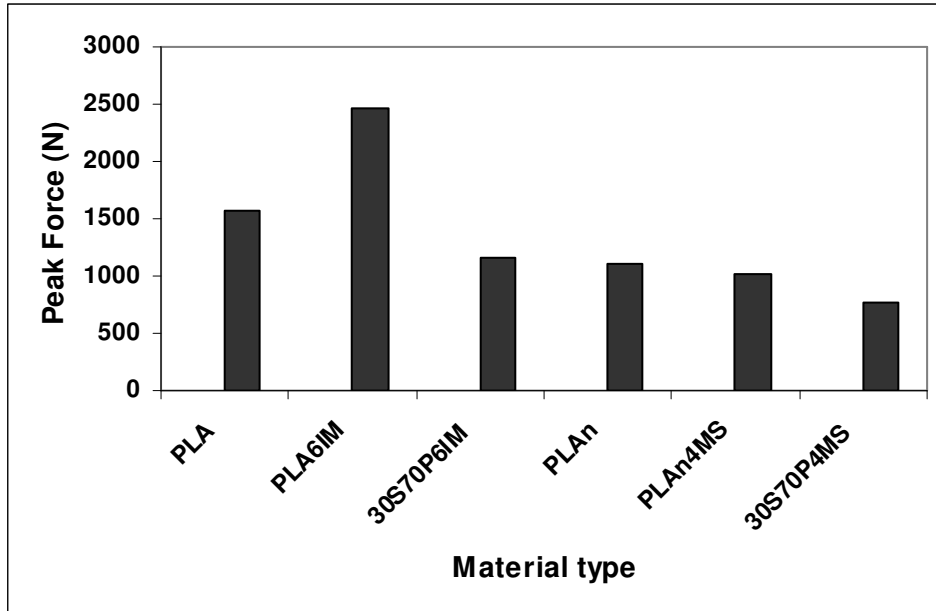
(c)

Figure 5.4 Tensile properties of PLA, wheat starch/ PLA blends with biostrength modifiers (a) Tensile Strength, (b) Elongation and (c) Young's Modulus.

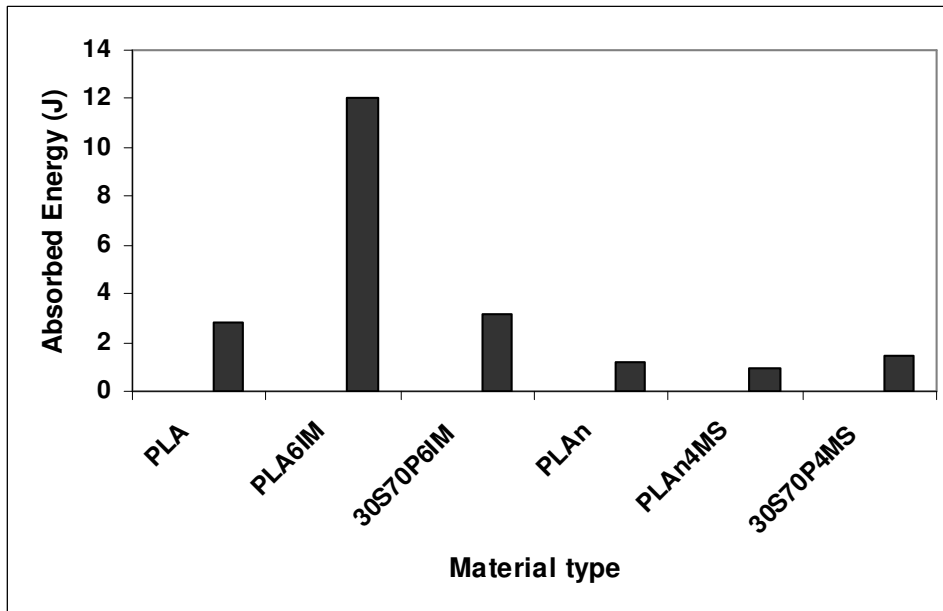
The calculation of the area under the stress-strain curve provides the fracture energy of the corresponding blends, which mainly govern the fracture toughness. A highly tough material has a high fracture energy and vice versa. The reaction between the hydroxyl group and carboxyl group in PLA with the hydroxyl groups on the starch, or reactions of these two polymers with modifiers could lead to a high interfacial adhesion, thus acquiring the high fracture toughness. Ajji (Ajji & Utracki, 1996) has reported that the chemical structure of the copolymer plays an important role, and showed that grafts and tri-blocks easily form micelles but di-blocks have higher interfacial activity than tri-blocks or graft copolymers, possibly owing to the steric hindrance at the interface. The di-block more readily interacts with the two polymer phases, forming appropriate entanglements that result in reduction of the interfacial tension, and enhanced interfacial adhesion. According to the results shown for the blends with the copolymer, it appears that there has been a strong chemical bonding between the polymer surfaces during mixing at high temperature. The effective compatibilization of binary blends by the addition of a copolymer depends on the molecular weight of the principal ingredients and mixing time (Anastasiadis, Gancarz & Koberstein, 1988) equipment, size of the dispersion, and the relative affinity of the compatibilizer to the two polymers (Ajji & Utracki, 1996). However, it is assumed that the size of the PLA pellets employed in this study, which was approximately 5-6mm in size, and the molecular weight of starch as well as the nature of the copolymer, have not positively affected the entire compatibilization of the PLA/starch/modifier blend system.

The Young's modulus of both PLA and PLAn shown in figure 5.4(c) tends to decrease with the inclusion of biostrength additives conversely starch tends to facilitate the resistance of the blend to deformation under the applied force, making the blend more stiff and brittle. The general principle of homogeneous stress distribution within the material facilitates to decrease The Young's modulus. Some factors affecting Young's modulus in general are intermolecular forces such as hydrogen bonding and dipole forces which increase modulus, whereas disorder in the crystal lattices and flexible linear side chains decrease the modulus. Although PLA itself has a high modulus value, the impact modifier brought it down by about 20%. The impact modifier is a copolymer consisting of the acrylic copolymer, which is believed to have interacted with the PLA to disorder its

original crystal packing or the polymer network, thereby reducing Young's modulus. The MS has resulted in a similar behaviour in modulus. The fact that the PLA molecules are now more restricted to stretch, resulted in the apparently high modulus shown in figure 5.4(c) with starch in the blends, even in the presence of the IM and MS.



(a)



(b)

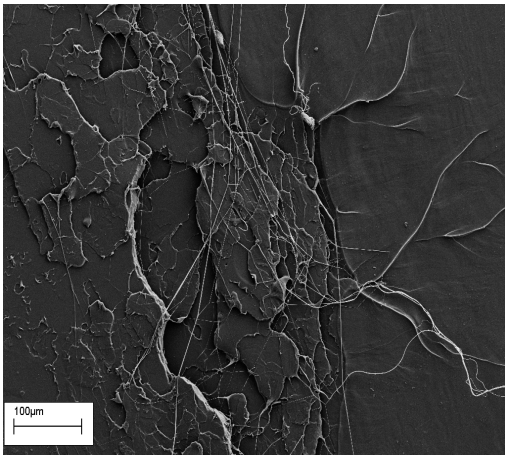
Figure 5.5 Variation of impact properties of PLA, wheat starch/ PLA blends with biostrength modifiers. (a) peak force, and (b) absorbed energy.

Upon mixing of the two polymers, toughness is one of the most vulnerable properties that suffers from the consequences of the rough dispersion, instability of morphology, and poor interfacial adhesion between the phases. The toughness of a polymer can be improved by a modification, for example by incorporating reinforcement to the polymer matrix. As such, the impact toughness and the capacity of resisting shock, in the form of peak force and the energy absorption, were investigated for the blends with biostrength impact modifiers and melt strength enhancer. The results are shown in figure 5.5(a) and (b) respectively. The starch, in the PLA and starch blend shows negative effect owing to the disruption caused by starch to the continuous PLA phase. The granular form of starch concentrates the stress at the grain boundaries and thus produces a poor capacity of resisting shock. However, the empirical results showed a prominent increase in the peak force as well as in the absorbed energy before failure, in the blend with the impact modifier. The slightly increased energy absorption in the blend 30S70P6IM also persists due to the presence of IM in the blend, although the presence of the starch has almost hindered the effect of the IM when making the blend. The observations clearly suggest the presence of some additional bonding or cross linking within the network and in the ordered crystal structure in the presence of IM. The failure occurs as a consequence of the propagation of the crack initiation or small crazes that result by breaking the stressed chemical bonds originating from the applied stress. One of the failure modes, brittle fracture, is typically a result of highly localized crazing confined to a very small volume of the material. In ductile fracture, multiple crazing initiated in a relatively large volume of the polymer (multiple deformation mechanism) or shear yielding (plastic flow without crazing) occurs (Perkins, 1999). Polymer toughness can therefore exist depending on one of the multiple crazing or shear yielding modes of energy dissipation.

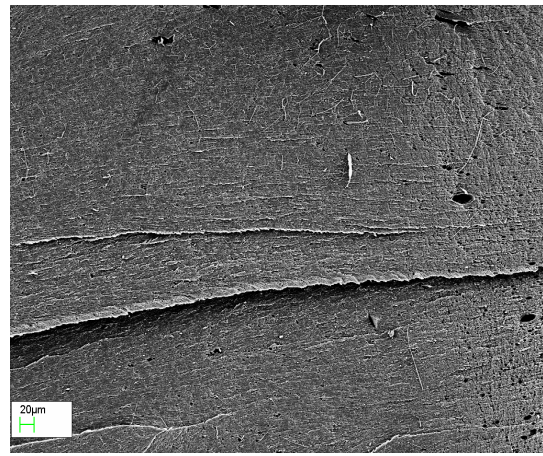
5.4 The Microstructure

Analysis of morphology has paramount importance as it apparently helps understanding the failure of the respective blend materials. Consequently, scanning electron microscopic studies of the PLA and PLA/wheat starch blends with biostrength modifiers were conducted and micrographs are shown in figure 5.6. On the SEM micrographs, PLA

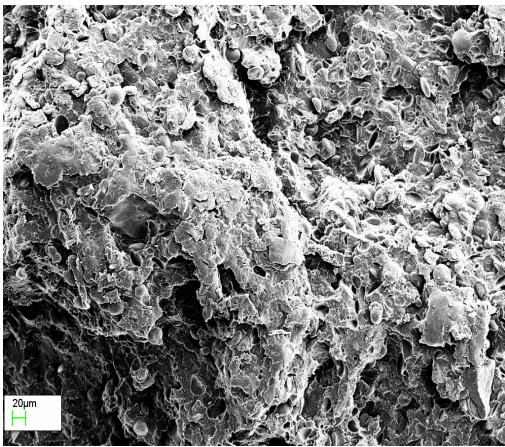
exhibited fiber like micro structure as shown in figure 5.6(a). A very neatly aligned structure was observed when IM was incorporated into PLA, as illustrated in figure 5.6(b). Nevertheless, when the starch was added, the effect of IM disappeared and suffers difficulty in maintaining the neat structure, as can be seen in figure 5.6(c). There were no distinguishable differences in the micro structures of PLAn and MS incorporated into PLAn, as illustrated in figure 5.6(d) and (e). However, the starch induced a noticeable difference in the continuous phase of the PLAn and showed an irregularly associated starch with clear voids. This is due to the detached starch granules from the surface, as can be seen in figure 5.6(f).



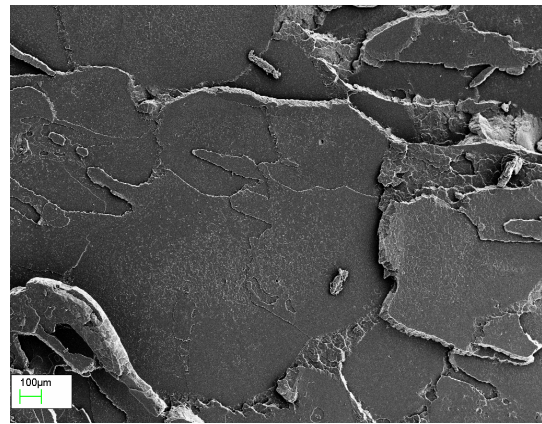
(a)



(b)



(c)



(d)

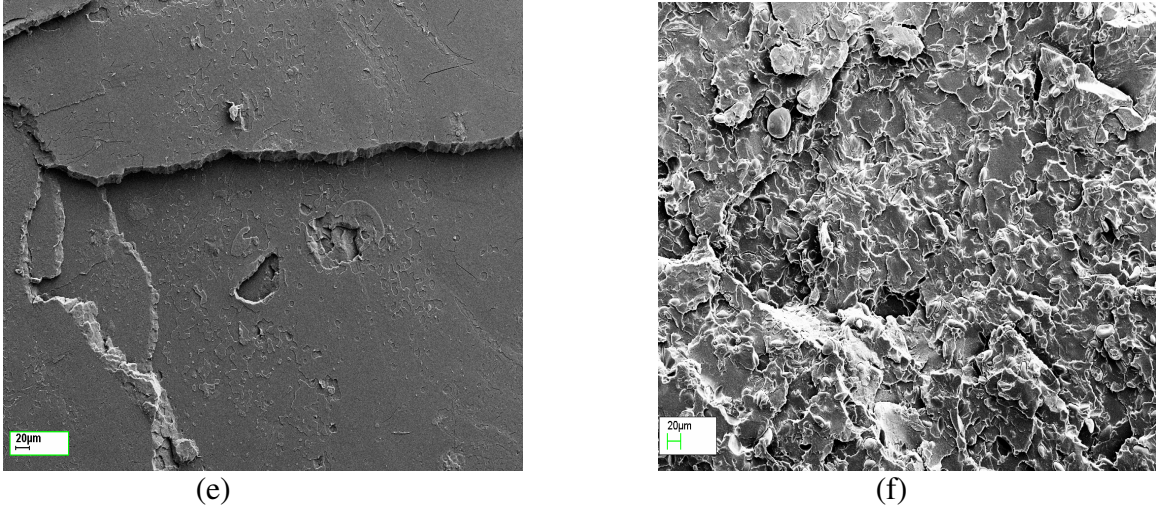
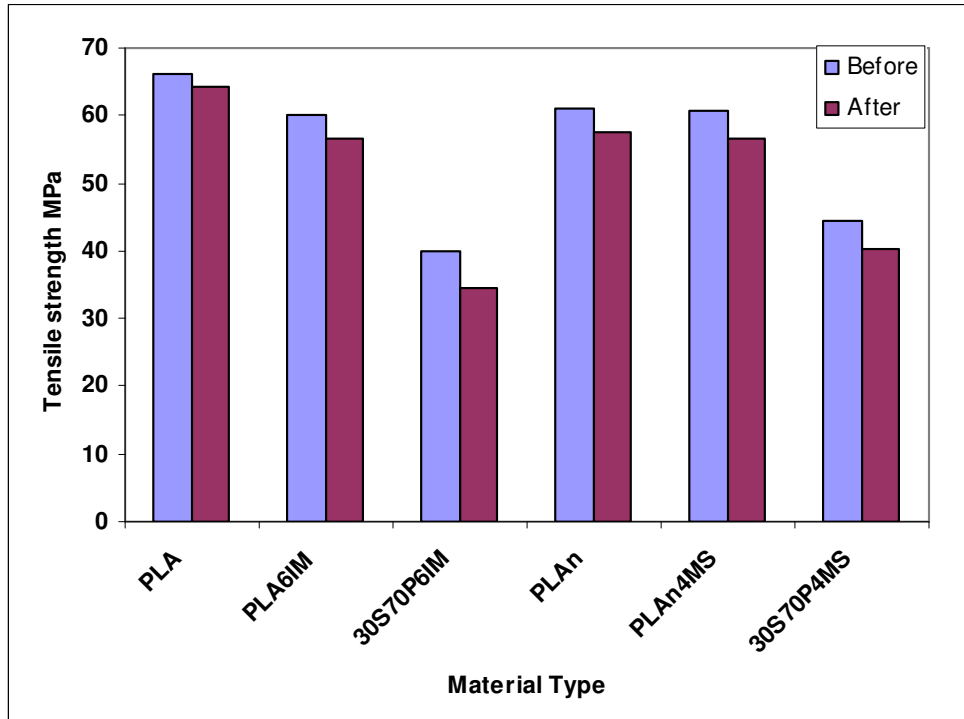


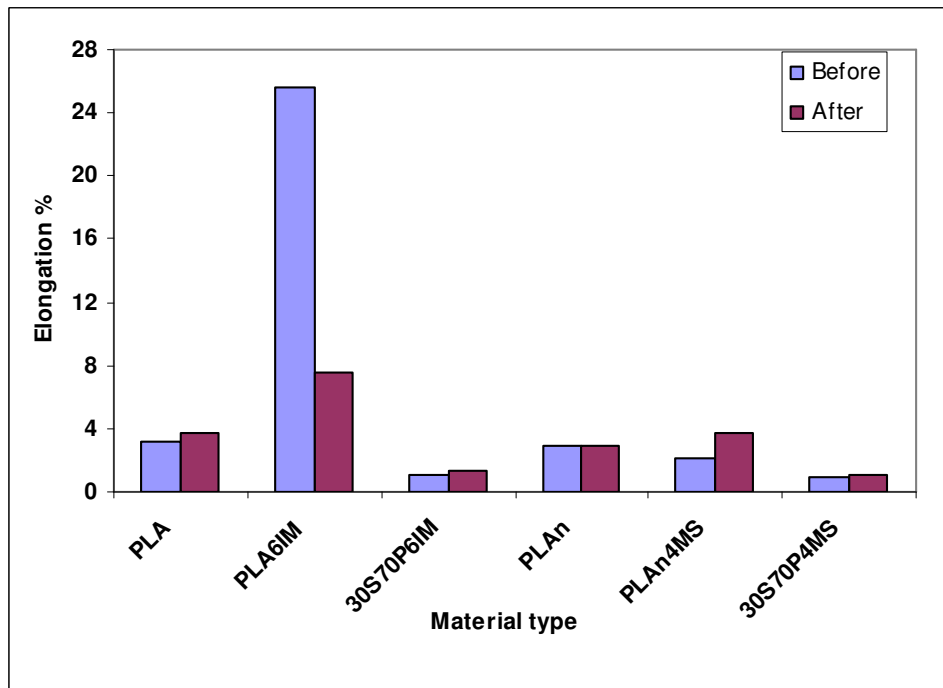
Figure 5.6 SEM micrographs of the PLA, PLA/wheat starch blends with biostrength modifiers (a) PLA (b) PLA6IM (c) 70P30S6IM (d) PLAn (e) PLAn4MS, and (f) 70P30S4MS.

5.5 Effect of physical ageing on mechanical properties

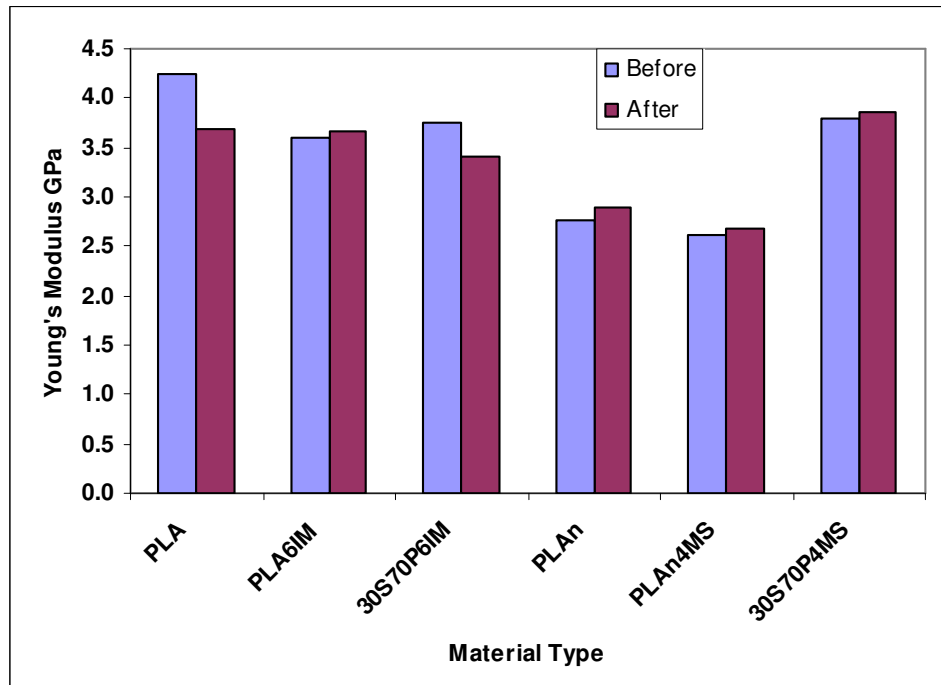
Figure 5.7 illustrates a comparison of the mechanical properties of the blends investigated after ageing for one year. The results revealed that all the blends together with the virgin materials undergo a natural phenomenon called physical ageing. The tensile strength of all the blends and raw materials decreased with the ageing time, yet there is no significant contribution from either the starch or biostrength modifiers towards the reduction in the tensile strength as shown in figure 5.7(a). However, the elongation and modulus show slightly dissimilar behaviour to the tensile strength as can be seen in figures 5.7(b) and (c) respectively. The elongation of the PLA tends to increase by about 1%, whereas GMO free PLA remains the same. Surprisingly, the elongation of the PLA6IM blend considerably decreased by about 18%, when it was stored for one year, though it maintained more than twice the value of virgin PLA. This is believed to be due to the effect of ageing of IM loosing its initial effect. The elongation of PLAn4MS blends show 2% increase of the elongation with reference to the initial material investigated a year ago. The starch incorporated blends show insignificant changes due to the effects of the modifiers.



(a)



(b)



(c)

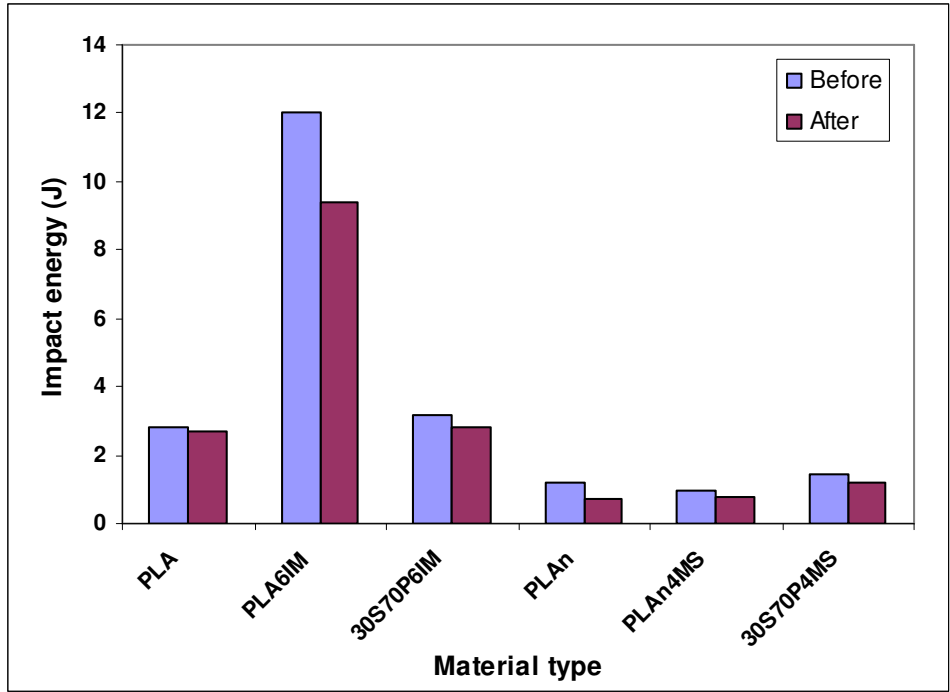
Figure 5.7 Comparison of tensile properties of PLA, PLA/wheat starch blends with biostrength modifiers upon physical ageing after one year (a) Tensile strength (b) Elongation (c) Young's modulus

The presence of crystals in a polymer has a profound effect upon its mechanical behaviour, in particular the strength and stiffness which is also known as the modulus. The Young's modulus of a material is expressed as the quotient of the stress and strain and is measured within the elastic region. The time dependence of this property has been investigated and the modulus of PLA shown in figure 5.7(c) decreased compared to the Young's modulus value of the PLA sample from the same batch investigated a year earlier. These results coincide with the increased elongation results reported in figure 5.7(b). Under the same experimental conditions, the decrease in modulus implies that the elongation has increased or vice versa. The effective modulus of a material depends not only upon the degree of crystallinity also known as the proportion of the crystalline material, but also upon the size, shape and the distribution of the crystals within the sample (Young & Lovell, 1991). Therefore, the decrease in modulus is apparently due to a loss of crystallinity or size and shape of crystals in the PLA material upon storage. This could have been a consequence of

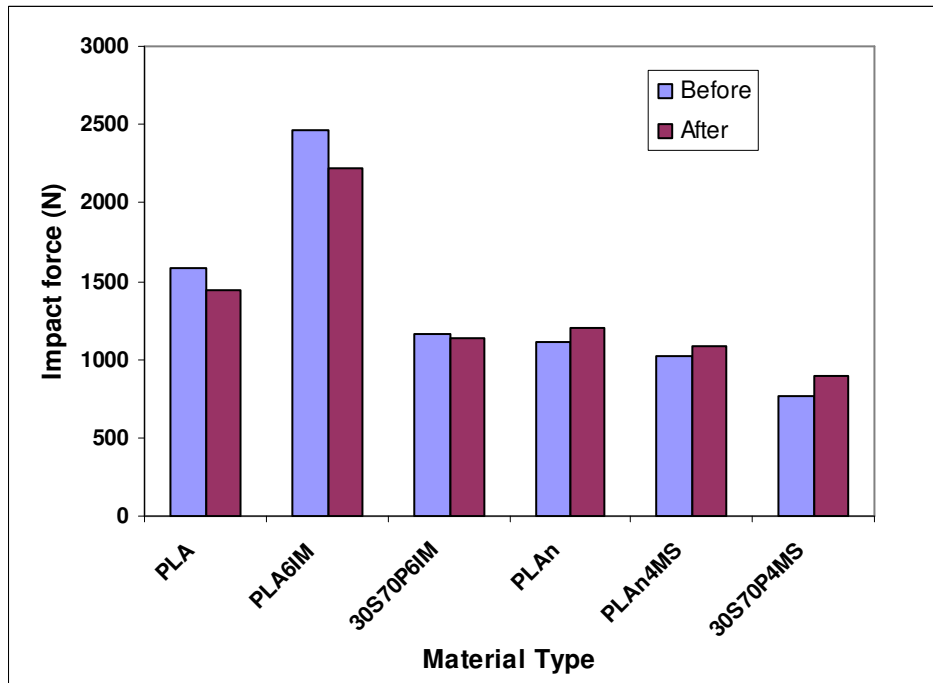
the natural degradation of the PLA material. However, the IM material in the blend has been able to sustain its initial modulus value upon prolonged storage.

The GMO free PLA and its blends showed a small change in modulus that occurred due to crystallisation which can occur during storage similar to the effect of storage hardening found in most semicrystalline materials. In a composite, the observed modulus is a reflection of the combined modulus of all the materials. Similarly, in a semicrystalline polymer, the modulus is an indication of the modulus of crystalline and amorphous regions. It is believed that the crystals in amorphous rubber behave like cross-links and produce stiffening through an increase in the crosslink density (Young & Lovell, 1991). Therefore, it is suggested that the amorphous regions in GMO free PLA behave like cross-links and stiffen through an increase in the crosslink density rather than through their inherent stiffness similar to the crystals in amorphous rubber.

The impact resistance of a material or a fabricated artefact is a quantification of its ability to withstand the application of a sudden load without failure. This parameter is a multifaceted function due to the mode of loading, loading rate and material properties such as chain length, packing, tacticity, alignment and bonding forces, and, of course, the definition of what constitutes failure (Perkins, 1999). Therefore, the measured impact strength of a polymer must be computed by considering the contributions of all processes that dissipate any of the energy of the impact blow. This property could possibly be the most critical mechanical property of plastics, because it relates to the service life of the article, and involves the increasingly essential affairs of product safety and liability. This important property has been studied upon physical ageing after one year and results are shown in figure 5.8.



(a)



(b)

Figure 5.8 Comparison of impact energy and impact force of PLA and PLA/wheat starch blends with biostrength modifiers upon physical ageing after one year (a) Impact energy, and (b) Impact force.

5.6 Water absorption

Amylose and amylopectin are the major constituents in starch having an abundance of hydroxyl groups as described in chapter 4. PLA itself consist of three reactive functional groups including carboxylic acid groups, hydroxyl groups and the ester functional groups in the middle. Figure 5.9 shows the water absorption of PLA and wheat starch/ PLA blends with the impact modifier and melt strength enhancer. The PLA and PLA/biostrength modifier blends show less than 1% water absorption, in contrast to blends of 30S70P6IM and 30S70P4MS which show the higher water absorption.

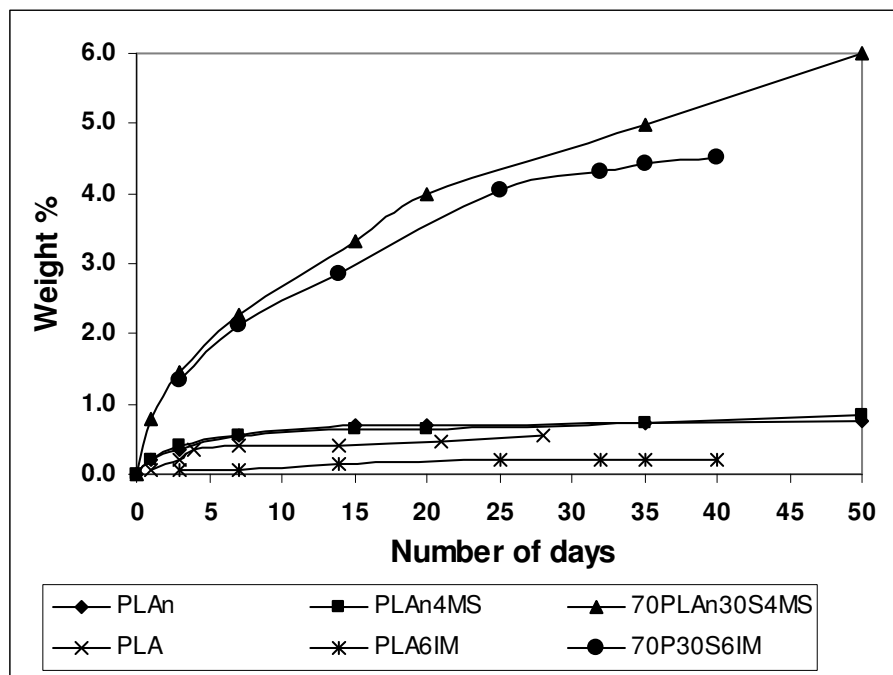


Figure 5.9 Water absorption of PLA, PLA/wheat starch blends with biostrength modifiers

Both PLA samples show a comparable water absorption but the IM shows a capability of reducing the water absorptivity in the blends of PLA6IM and 30S70P6IM. The water absorption of PLA and modifier blends increased during the first week of storage and then levelled off. Previous studies by a few other authors (Wang, Sun & Seib, 2002b; Ke, Sun &

Seib, 2003; Wang, Sun & Seib, 2002a) have also found that water absorption steadily increased during the first two weeks and then levelled off. The PLA with impact modifier shows the lowest water absorption and irrespective to the modifier, blends with starch show the highest potential. Even at 40 days storage, the blends with starch have not levelled off, but show a growing tendency to absorb water. The results in fact point to the starch playing a major role in the blend, being responsible for the water absorption of the PLA/starch blends.

5.7 Chapter summary

The pellets were made using extrusion technology followed by pelletisation and shaped test samples were made by extrusion and injection moulding using the pellets of the PLA and MS modifier blend, PLA/IM as well as both blends in the presence of starch. However, a starch content of 30% was found to make processing a little difficult due to the starch powder being separated from the larger PLA pellets. Starch and both modifiers were in a powder form and the 5-6mm diameter PLA pellets separated during extrusion. The transparency of PLA was not destroyed with both IM and MS. Compared to the blends with starch in the previous study, a more whitish appearance was induced in the blends of PLA/starch/modifier. The addition of IM to PLA is very beneficial for the elongation at break and impact properties, which resulted in 20% growth for the elongation and more than 50 and 300 percent increases for the impact force and energy absorption, respectively. The effect of the melt strength modifier and impact modifier was found to be less prominent in the presence of starch. Furthermore, all mechanical properties were decreased after one year storage, except for the GMO free PLA, which showed a higher impact force. It is also noticeable that GMO free PLA with MS has shown a 2% growth in elongation whereas PLA with IM has shown a 19% reduction after one year of storage. Similar to the previous study, starch exhibited a prominent effect upon water absorption.

The higher starch content exhibited many negative effects towards the properties of the PLA/ starch blend, but 10% starch in the previous study discussed in chapter four

demonstrated a facile processability and therefore the starch content was fixed at 15% to further investigate the PLA/starch blend properties. Glycerol in the previous study showed considerable attractive properties, behaving more like a plasticizer, and the author's subsequent effort was to investigate the coupling effect of glycerol without MDI by employing different glycerol levels in the blend. Furthermore, the particle size of the PLA crucially affected the processing, therefore the PLA pellets were ground into small particles in a cutting mill by passing through a 1.5 mm sieve. The glycerol was mixed with ground PLA and wheat starch and the blend was extruded and injection moulded. Results of the investigated properties are presented in chapter 6.

CHAPTER SIX

***RESULTS AND DISCUSSION
OF THE EFFECT OF GLYCEROL***

6 The effects of glycerol on the properties of PLA and wheat starch blends

Chapter six describe the outcomes of the experimental work conducted and outlined in chapter 3 pertaining to the blends prepared and listed in table 3.4 for the investigation of the effects of glycerol on the properties of the PLA and wheat starch blends described in section 3.3.3.

6.1 Decomposition by thermogravimetric analysis

The blends prepared with glycerol with their respective compositions and material codes listed in table 3.4 were analysed by Thermogravimetric analysis (TGA). Tests were performed for the PLA, and fabricated blends of PLA/wheat starch and glycerol, and the weight loss due to the volatilization of the plasticizers and the degradation have been monitored as a function of temperature, as shown in figure 6.1, which also shows the thermal stability of pure PLA. The temperatures at the maximum rate of weight loss, T_{max} of the blends were determined by derivative thermogravimetric curves and the 5% weight loss $T_{5\%}$ was determined using figure 6.1 and summarized in Table 6.1. The results demonstrate that the PLA degradation upon heating starts well above 300⁰C and the decomposition temperature is around 375⁰C. The incorporation of starch and glycerol reduced the decomposition temperature and eventually has reached 366⁰C by decreasing at most the 8⁰C compared with that of pure PLA. The effect of starch on the T_{max} is higher than the effect caused by the glycerol. The T_{max} of PLA in the 85P15S blend decreased by about 5⁰C compared to virgin PLA, and the findings were consistent with the results reported elsewhere (Ning, Jiugao & Xiaofei, 2008)(Wang et al., 2008) for PLA/corn starch blends. It appears that starch degradation and the degradation products of starch possibly accelerated the thermal degradation of PLA. The presence of glycerol has further reduced the T_{max} of PLA in the PLA/starch/glycerol blends as listed in table 6.1

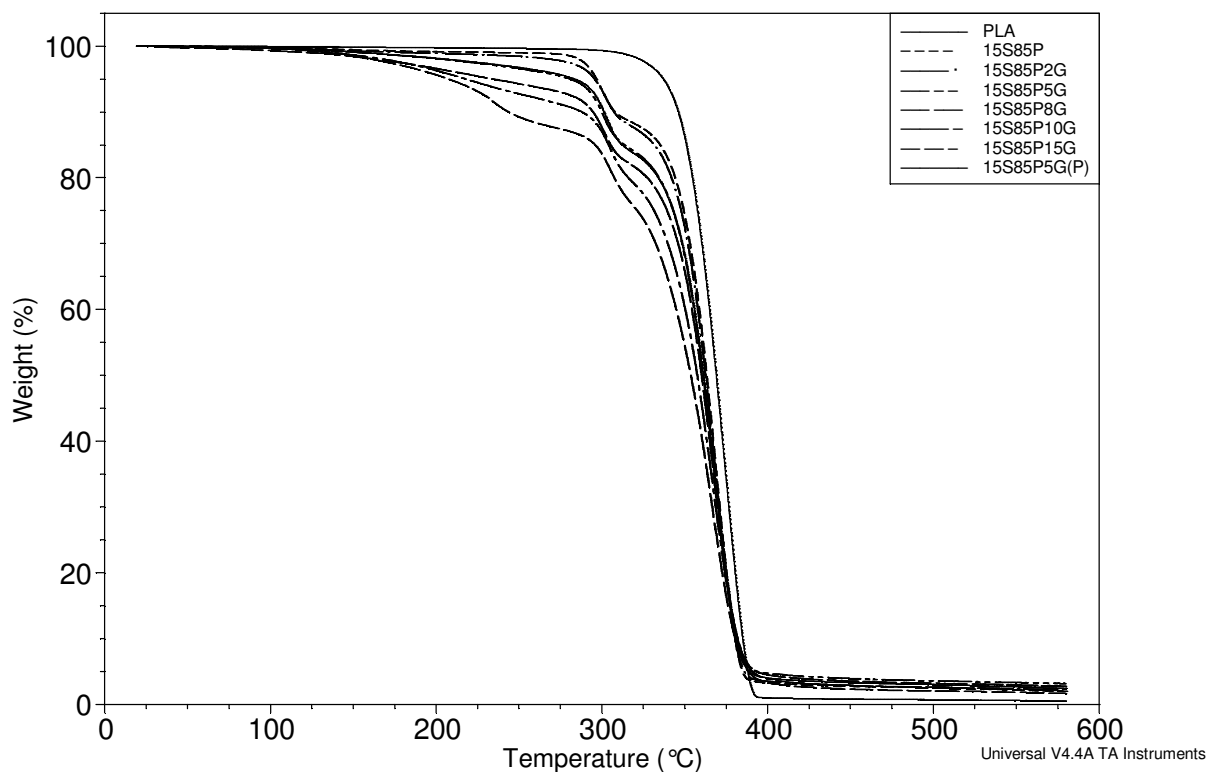


Figure 6.1 TGA curves of the pure PLA, PLA/Starch blend, PLA/starch blends with different glycerol levels.

Apparently, the T_{\max} of starch in the PLA/starch blend increased because of the high thermal stability of PLA. However, $T_{5\%}$ of pure PLA, which is 337°C reduced in the corresponding blends because of the starch as well as the glycerol. The effects from both the starch and glycerol are prominent, at the highest glycerol level, $T_{5\%}$ decreased almost by 130°C compared to that of pure PLA. The explanation for the significant decrease could be attributed to many reasons including depolymerisation of the starch, degradation of the starch and volatilization of the plasticizer. When PLA is in the pellet form, $T_{5\%}$ of PLA and T_{\max} of both the PLA and starch are higher than the $T_{5\%}$ and T_{\max} of the materials in the blend with ground PLA. These results clearly demonstrate that the small particle size of PLA in the blend facilitates decomposition compared to when it is in pellet form.

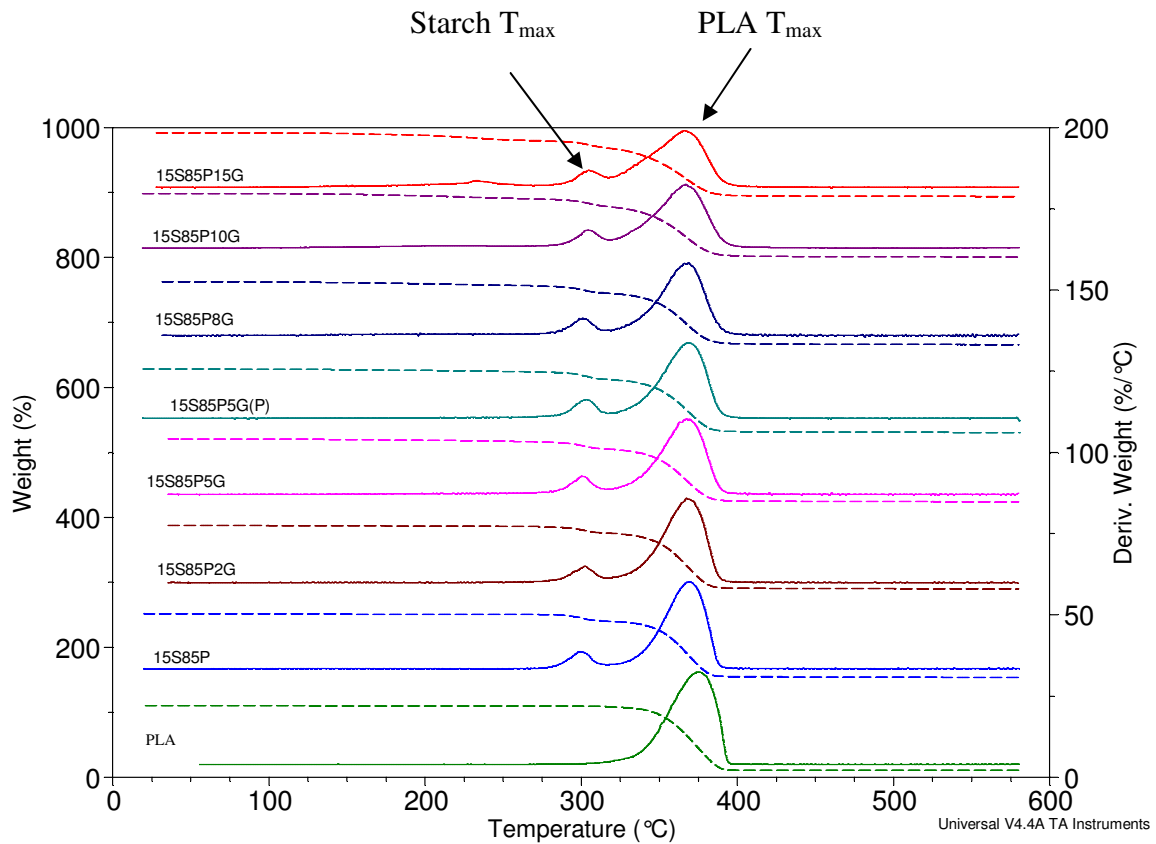


Figure 6. 2 Derivative TGA thermograms of PLA and its blends as affected by glycerol concentration

Table 6.1 Maximum degradation temperatures of pure PLA and wheat starch when associated in the blend and 5% degradation temperatures of the blends

Material	PLA T _{max} (°C)	Starch T _{max} (°C)	T _{5%} (°C)
PLA	374.4	-	337.1
15S85P	369.7	298.6	296.5
15S85P2G	367.3	302.4	295.3
15S85P5G	367.2	300.4	280.5
15S85P5G(P)	368.8	303.2	283.5
15S85P8G	368.7	300.8	234.3
15S85P10G	366.9	304.1	217.6
15S85P15G	366.2	304.4	207.1

6.2 Thermal behaviour

A polymer, upon heating exhibits a number of phase transitions, from glassy to rubbery to its melt. The phase changing temperatures, the glass transition, crystallisation and melting temperatures are vital to determine, as they affect the processing temperatures and the eventual properties of the end product. The dry starch degrades before it melts, therefore when processing starch, degradation is possible in the presence of heat. A plasticizer can ensure gelatinization rather than degradation, and the effect of glycerol on the thermal transition of PLA/starch was examined, because the plasticizers can reduce the intermolecular forces and increase the intermolecular mobility.

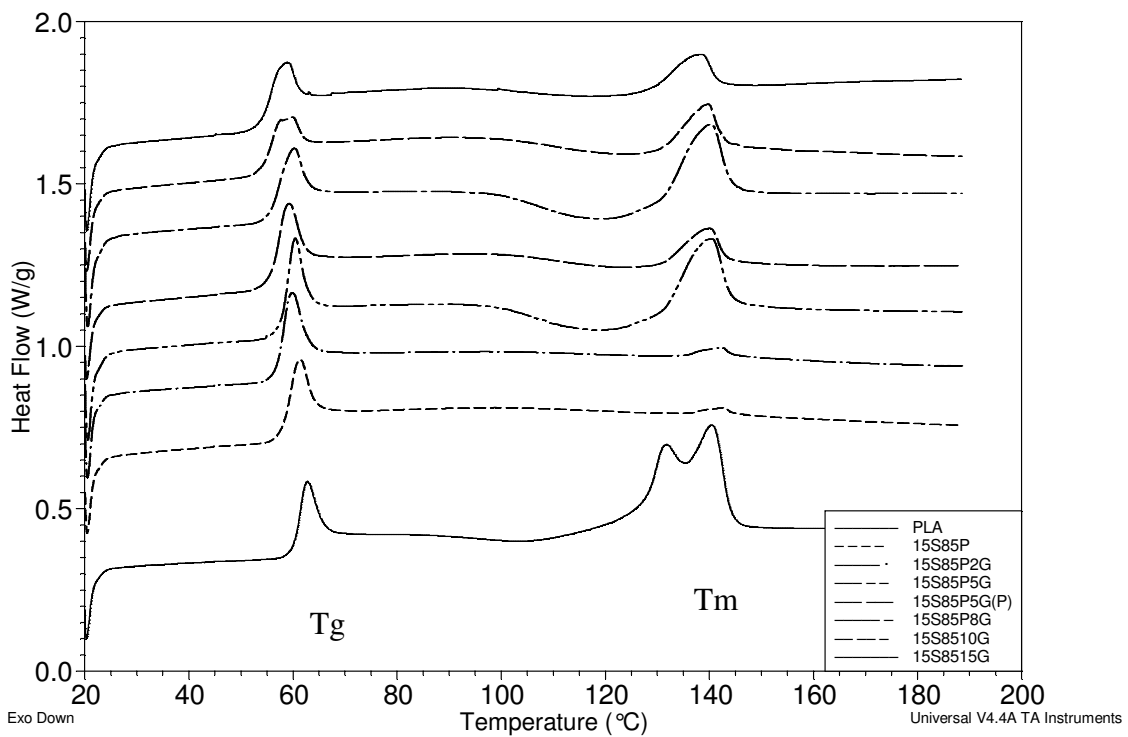


Figure 6.3 Thermal behaviour of pure PLA, PLA/starch blend, PLA/starch blend with different glycerol levels in the first cycle of heat/cool/heat method

Figures 6.3 and 6.4 respectively show the first and second heating runs of the DSC thermograms exhibiting the thermal behaviour of the batch of PLA and wheat starch blends with glycerol, investigated by the heat/cool/heat method. According to the thermograms,

raw PLA and all other blends show a thermal history. A high enthalpy relaxation is observed in the raw PLA as well as in the blends illustrated in figure 6.3. The enthalpy relaxation of the samples is known as the physical ageing of the materials. The second heating cycle was conducted to erase the thermal history in the sample and these are recorded in figure 6.4. According to figure 6.4 the glass transition temperature decreased with increasing glycerol level in the blend, with a noticeable change from 2% glycerol to 5% glycerol, but the effects of other glycerol levels are minimal. These results are in agreement with the 2001 study on PLA/corn starch blends by Ke (Ke & Sun, 2001b), who has also discussed the immiscibility of glycerol with PLA that didn't influence its mobility.

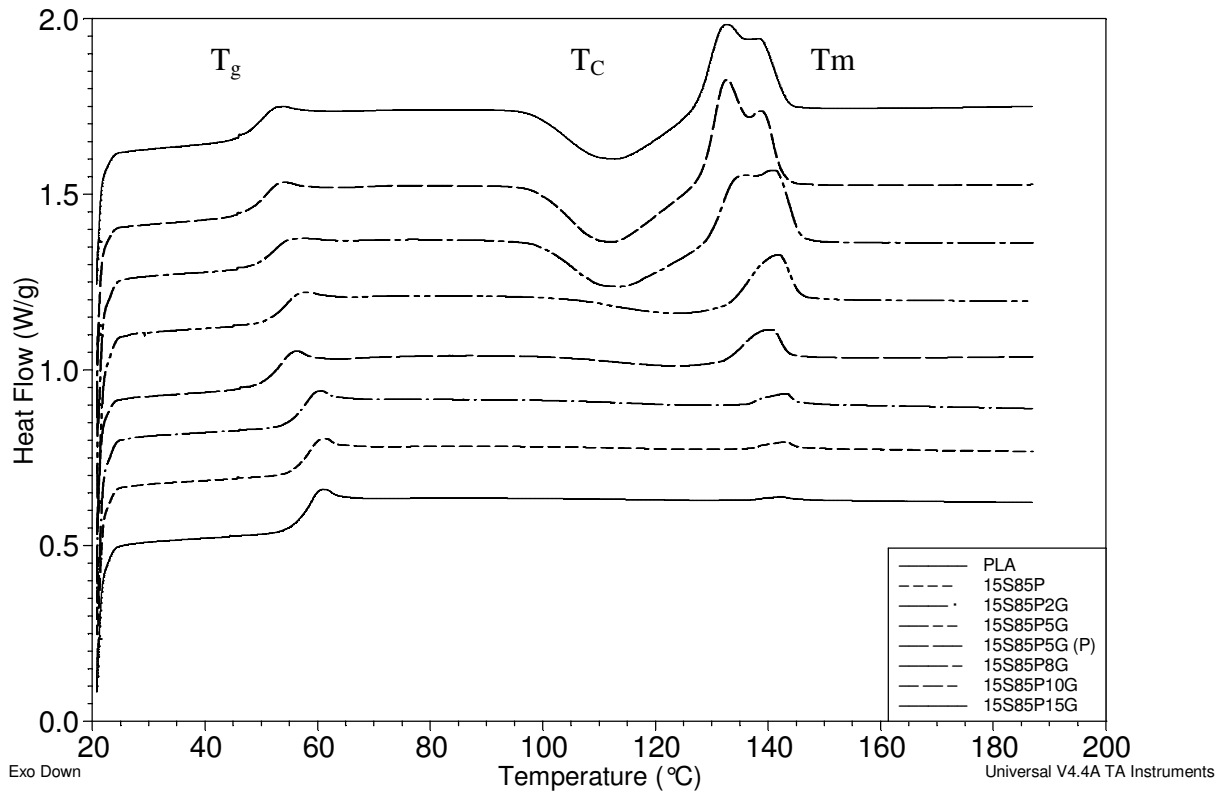


Figure 6.4 Thermal behaviour of pure PLA, PLA/Starch blend, PLA/starch blend with different glycerol levels in the second cycle of heat/cool/heat method

A study by Averose (Averous et al., 2000) has also reported that T_g is strongly dependent on the amount of glycerol; the higher it is, the lower the temperature attributed to a glass transition due to increasing amounts of the plasticizer. T_g is a characteristic of the non-crystalline portion of the material and at this temperature, the onset of segmental motion of the polymer backbone occurs. Many factors including polymer structure contribute to the magnitude of T_g . The low flexibility of macromolecules and intensive intermolecular forces, increased molecular weight, crosslinking and lack of free volume increase the T_g . A polymer having T_g around room temperature makes the polymer more brittle at room temperature and hence makes it difficult for processing at room temperatures using processing equipments such as extruder and injection moulding and also have poor heat resistance.

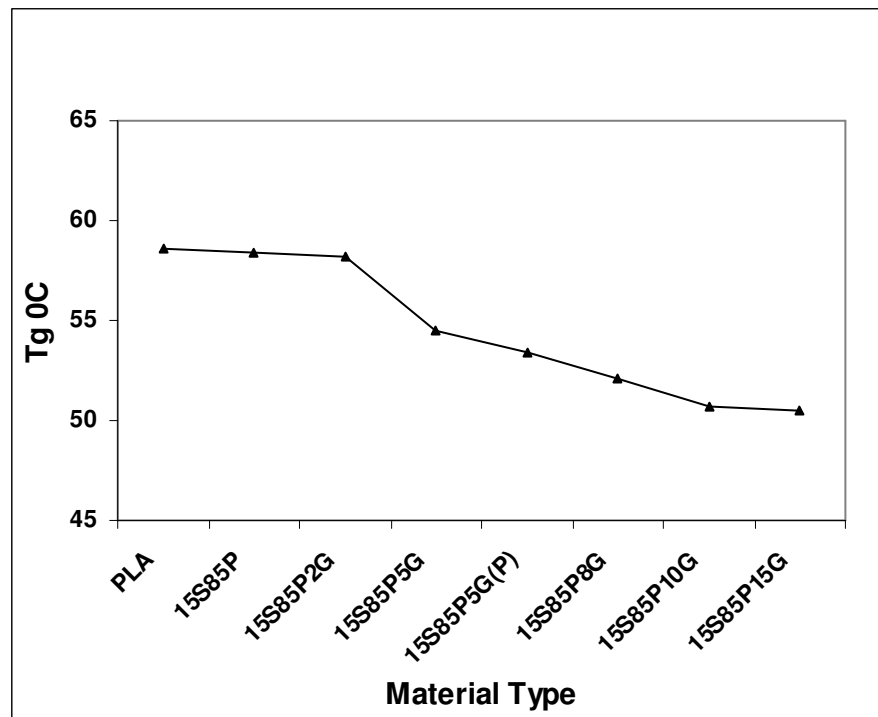


Figure 6.5 Glass transition temperatures of PLA and starch blends as affected by glycerol concentration

Even if some arguments suggest that glycerol is immiscible with PLA, it is a polyhydric alcohol, which is miscible with starch and a good plasticizer for starch. Therefore, it is

possible that the intensively held starch molecules either by intra or intermolecular hydrogen bonds are disintegrated by glycerol under heat and shear during extrusion.

In addition, glycerol can also increase the free volume of the polymer blend V_f .

$$V_f = V - V_s$$

where V = the total volume

V_s = the volume of solidly packed molecules

The free volume is the volume of the polymer mass not actually occupied by the molecules themselves and it creates more space for molecules to move. So, molecular motion can take place relatively easily as the unoccupied volume allows more room for the molecules to move, so they change their conformations resulting in a decrease in the T_g of the polymer blend. Further, Martin and Averose (Martin & Avérous, 2001) reported that T_g decreased and that a very small melting peak of PLA reappeared in the TPS and PLA blends, with a reduction in T_m . Similar melting behaviour with two distinct peaks appear in the current study with glycerol. Martin and Averose (Martin & Avérous, 2001) have also reported that the glycerol has the ability to plasticize PLA to some degree, thereby reducing T_g and T_m . Moreover, Park and IM (Park et al., 2000) have evidently shown that PLA can be plasticized by glycerol.

Figure 6.4 also demonstrates a small exothermic peak, which begins to appear and become a broader crystallization peak above the 5% glycerol level and is very prominent above the 8% glycerol level. Above the 5% levels, the additional crystallisation becomes apparent and as a result, a change in the melting peaks. It has been reported that glycerol contributes to an improvement in the crystallinity of the blend (Park et al., 2000; Martin & Avérous, 2001). The 8% and above glycerol levels have a visibly lower melting temperature peak followed by the major melting peak, which has gradually shifted to a lower melting temperature. Clearly, two reasons can be inferred to explain the observation. Firstly, a T_m is visibly depressed when a semicrystalline polymer is miscible with an amorphous polymer (PLA which is mostly amorphous in this case). A low level of miscibility between blend components can be inferred because of the low level of reduction in T_m . On the other hand glycerol can influence PLA plasticization. The broad crystallization peaks may possibly be

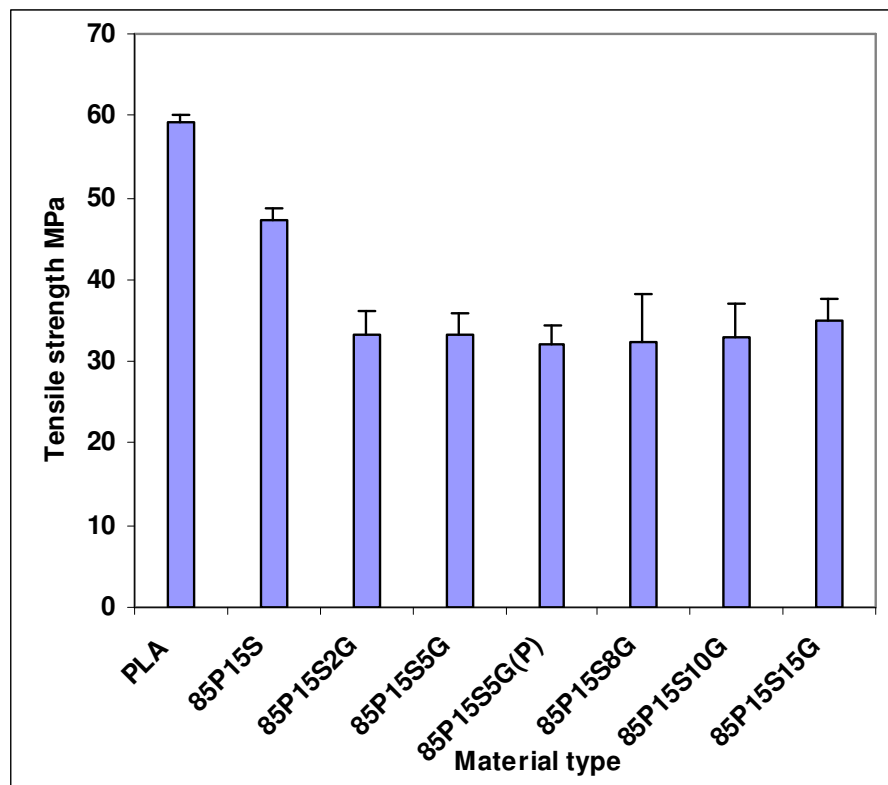
attributed to PLA crystallization in the presence of glycerol or crystallinity might be induced in PLA by a loss of structure or disintegration of starch and glycerol as discussed by Ke (Ke & Sun, 2001b). The two clearly distinguishable melting peaks at low and high temperatures can be ascribed to the lamellar rearrangement during crystallisation as reported by a few authors (Yasuniwa et al., 2004; Liao et al., 2007).

6.3 Mechanical properties

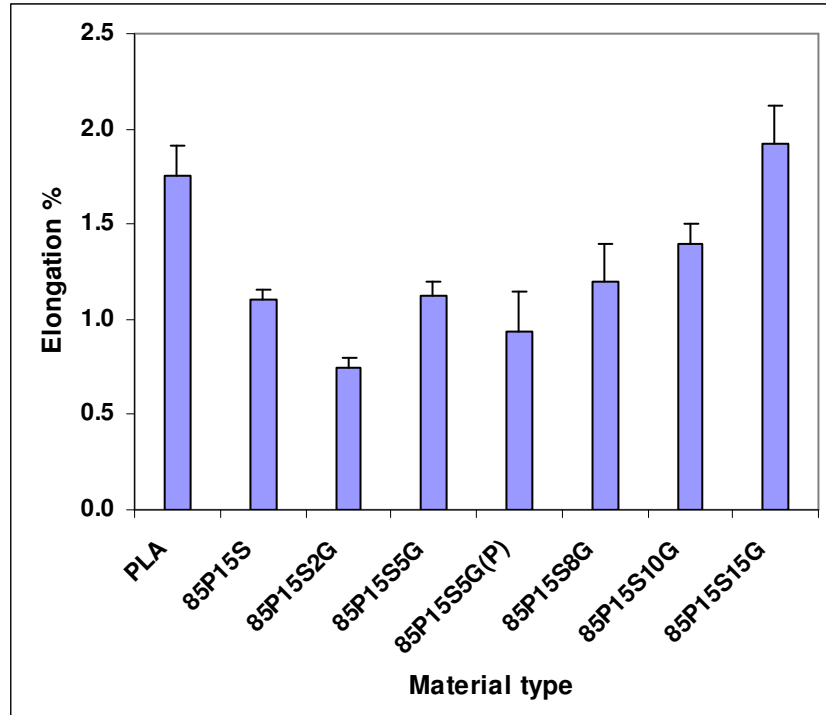
6.3.1 Tensile properties

The mechanical properties of materials have the large impact on the material application, as they provide useful information about the material, and therefore it is of paramount importance to investigate them. The mechanical properties of composite materials can broadly vary depending on the manufacturing process, additives, reinforcement architecture and also on the polymer-reinforcement combination (Reynolds & Paharaoh, 2010). The injection moulded dumbbell bars were used to investigate the tensile strength, elongation at break and the Young's modulus of the prepared blends with glycerol and the results of the tests were averaged from 5 data samples, and they are presented in figures 6.6 (a), (b) and (c), respectively. According to figure 6.6(a), the tensile strength of the blends decreased with starch as well as with the glycerol. It is noticeable that the starch itself has a critical influence on the blend and decreased the tensile strength and elongation of the PLA by 20% and 37 % respectively and increased the modulus by 33%. The starch and glycerol incorporation plunged down the tensile strength by about 44% compared to the tensile strength of the raw PLA. Remarkably low strength and elongation at break were apparent when starch was incorporated into the PLA matrix due to the disruption of the ordered arrangement of the continuous PLA phase by the large starch granules. Starch granules consisting of amylose and amylopectin chains, exist as concentric growth rings (Oates, 1997) and might have acted as stress accumulating points initiating cracks in the material resulting in the poor properties of the blend. The results agree with the diminishing broad crystallization peak in the DSC thermogram shown in figure 6.3 with the starch incorporation. The obvious diminution in crystallinity evidently supported the

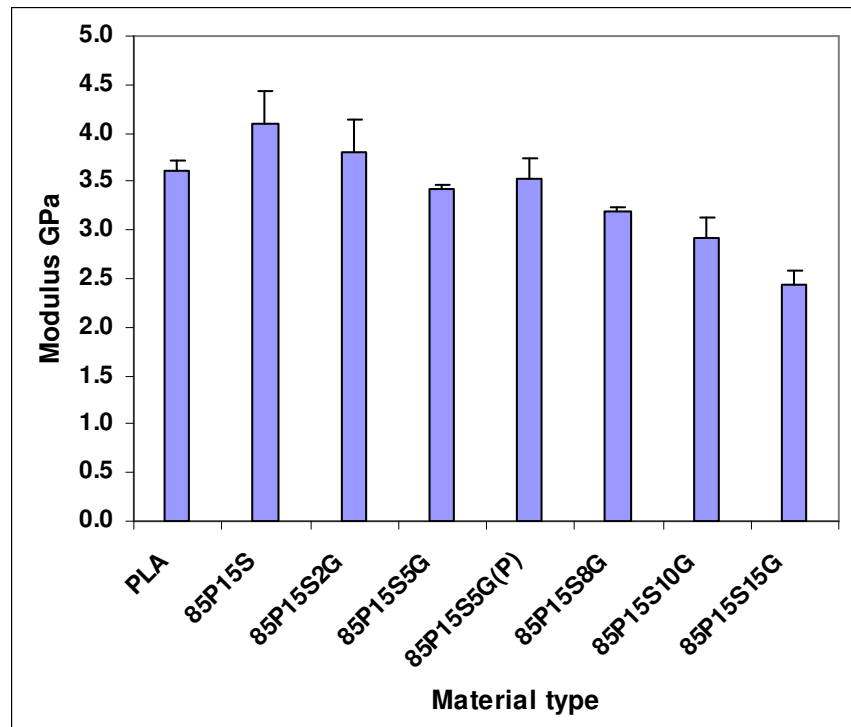
aforementioned decrease in tensile strength in the blend. The addition of glycerol increased the crystallinity but further reduced the strength due to the plasticization effect of glycerol. Due to the flowability of glycerol, voids were also created and weakened the blend. However, no significant difference was exhibited in the level of the decrease in the tensile strength with the glycerol concentration. Insufficient mixing in the starch/glycerol/PLA blend leaving some lumps in the blends could be attributed for this. A previous study by Ke (Ke & Sun, 2001b) reported that the reduced intermolecular forces and increased intermolecular mobility resulted in the low strength for glycerol plasticized blends.



(a)



(b)



(c)

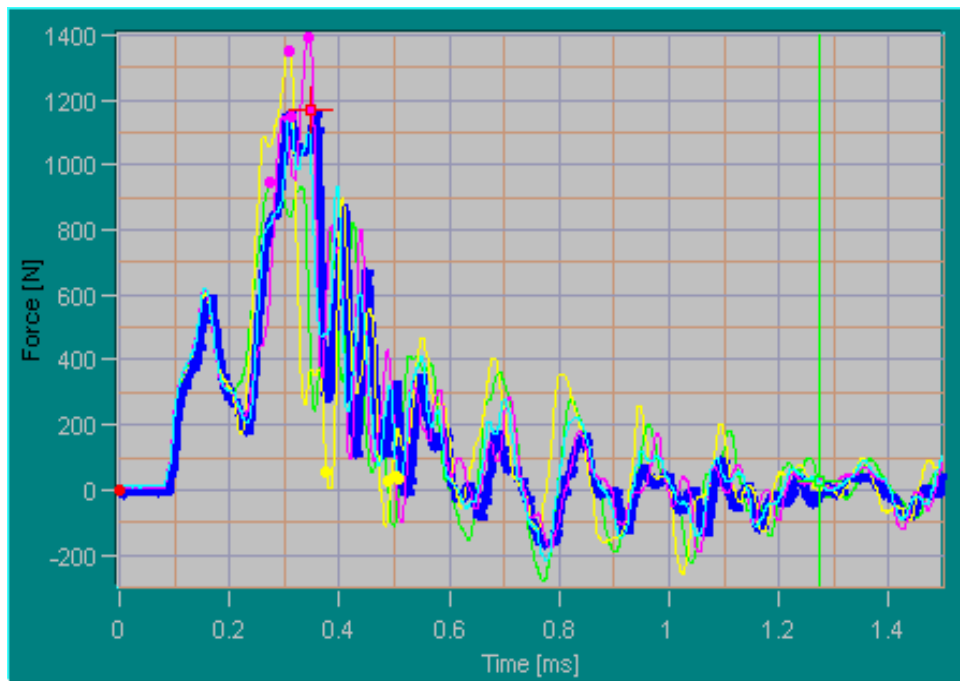
Figure 6.6 Tensile properties of pure PLA, PLA/starch blend, PLA/starch blend with different glycerol levels (a) Tensile strength (b) Elongation, and (c) Young's modulus.

Although the strength was compromised, as expected, glycerol extended the elongation at break of PLA, and at most, it increased the elongation of the blends by 10% compared to raw PLA, because of the increased free volume. Moreover, there is an increasing trend in the elongation and a decreasing trend in the modulus with increasing glycerol levels. According to one viewpoint, the higher glycerol level has better plasticized the starch by increasing the free volume of the polymer as discussed above. Alternatively, the small size and nature of the glycerol would have the ability to penetrate the ring and to reach the amorphous region of the granule. Consequently, the amylose chains can leach out from the concentric growth rings of the granular starch. The rigid structure of the starch could have thereby been disrupted and resulted in some flexibility to the blends. Furthermore, the results also revealed that the PLA in the form of large pellets has a decreased elongation at break but an increased modulus compared to the corresponding small particle size PLA. Undoubtedly, the small particle size of the PLA has a larger surface area for better mixing and thus has obtained higher elongation and higher modulus results. When looking at the characteristics of the blends, two kinds of behaviour are observed. PLA, 85P15S, 85P15S2G are high modulus and low elongation at break materials. Conversely, all other blends with glycerol are low modulus, highly deformable materials. In a previous study, Martin and Averose (Martin & Avérous, 2001) identified thermoplasticised starch blends as low modulus blends, which is in agreement with the findings of the current study.

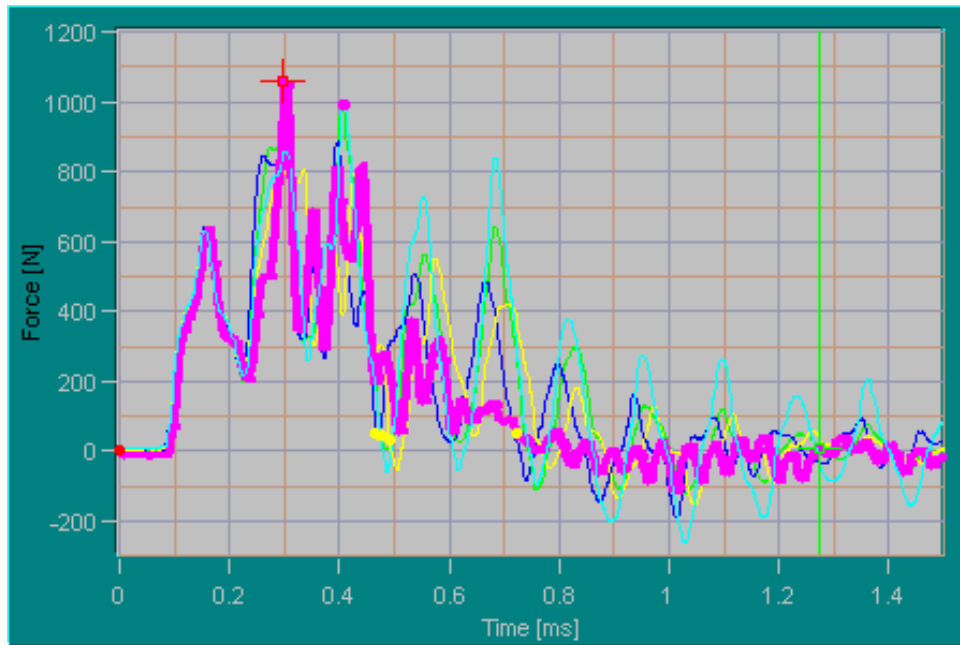
6.3.2 Impact behaviour

The impact forces of PLA, 85P15S and 85P15S15G attained during drop weight method, as a function of time, are illustrated in figure 6.5. The diagrammatic presentation of the variation patterns of the impact force and energy absorption of the blends pertaining to the material type are shown in figure 6.6(a) and (b) respectively. The results revealed that the effect from starch on the energy absorption of the blend was insignificant but the maximum force of the blow was decreased considerably. The incorporation of glycerol into starch and PLA blends facilitated energy absorption but it is inefficient at 5, 8 and 10% glycerol due to insufficient mixing, which can clearly be observed from inhomogeneities in the SEM

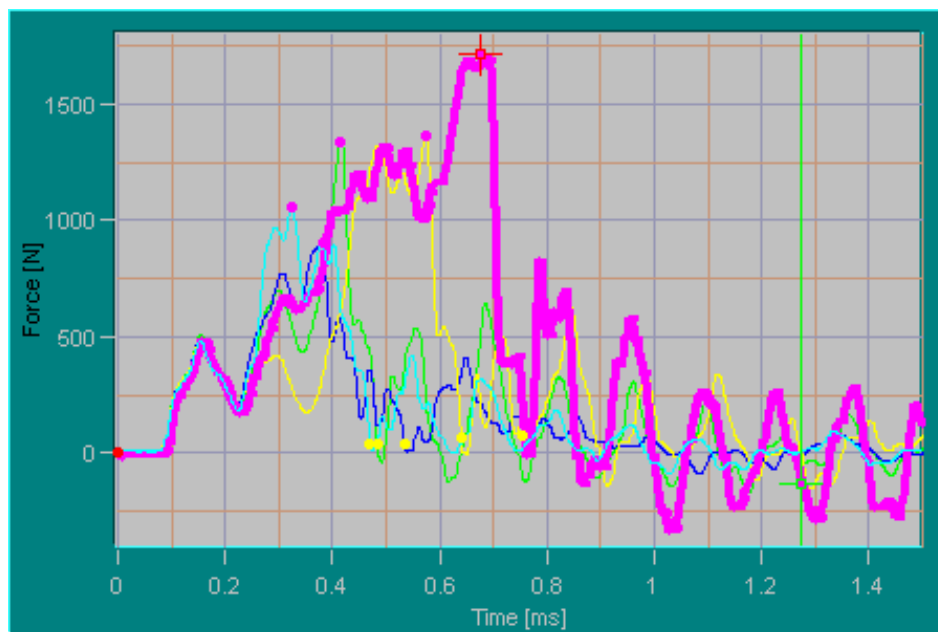
micrographs of the corresponding blends (Figure 6.9). At the 15% glycerol level, very high energy absorption is observed and it was almost 43% greater than that of raw PLA. At a lower level of glycerol, the toughness is low whereas a higher toughness than PLA is observed at the 15% glycerol level. The impact behavior of the material is related to the amorphous and crystalline proportions of the blends; highly amorphous blends have high energy absorption, whereas the highly crystalline materials have a high peak force since a large force is necessary to break the material. For the 15% glycerol level, a larger force was required to break the material than the force required for raw PLA and the total energy absorbed by the blend was superior to PLA. This observation could be attributed to the better plasticization caused by the glycerol by the disruption of the rigid starch structure. The penetration of the glycerol into the growth rings could have broken the H bonding to suppress the rigidity. The increased crystallinity in the blend, as can be seen from the DSC thermograms also contributed.



(a)

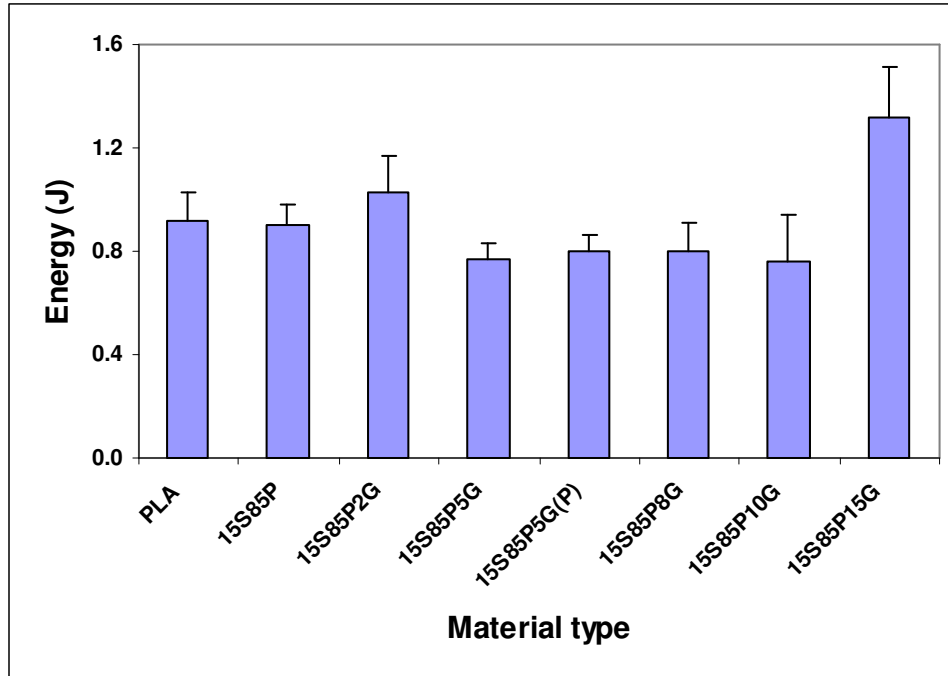


(b)

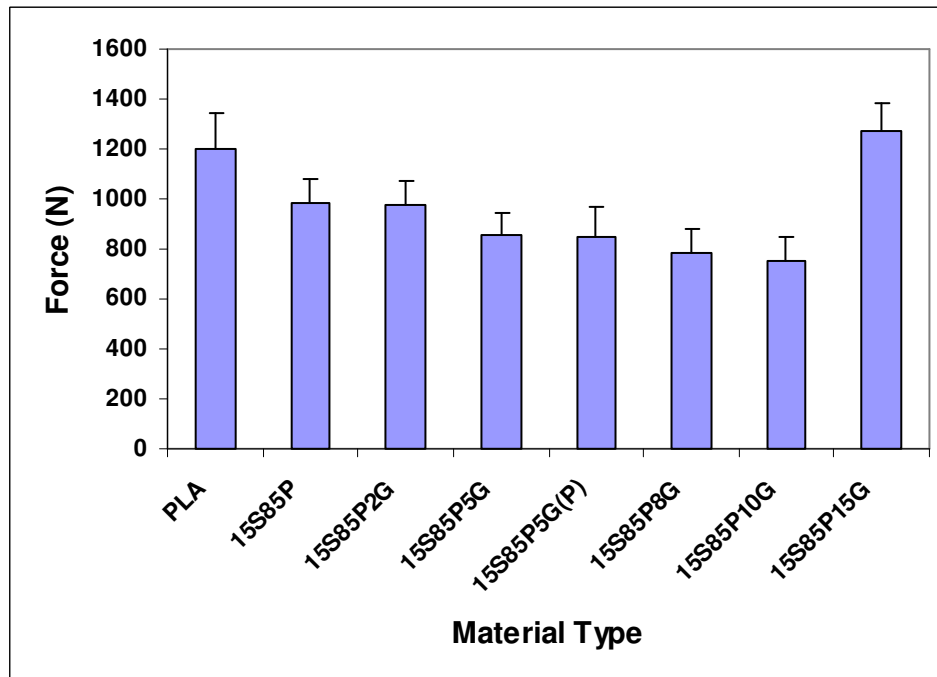


(c)

Figure 6.7 Change in impact force as a function of time for (a) PLA, (b) 85P15S, and (c) 85P15S15G.



(a)



(b)

Figure 6.8 The behaviour of pure PLA, PLA/starch blend, PLA/starch blend with different glycerol levels on the impact blow, in terms of (a) energy absorption, and (b) peak force.

6.4 Micro structure

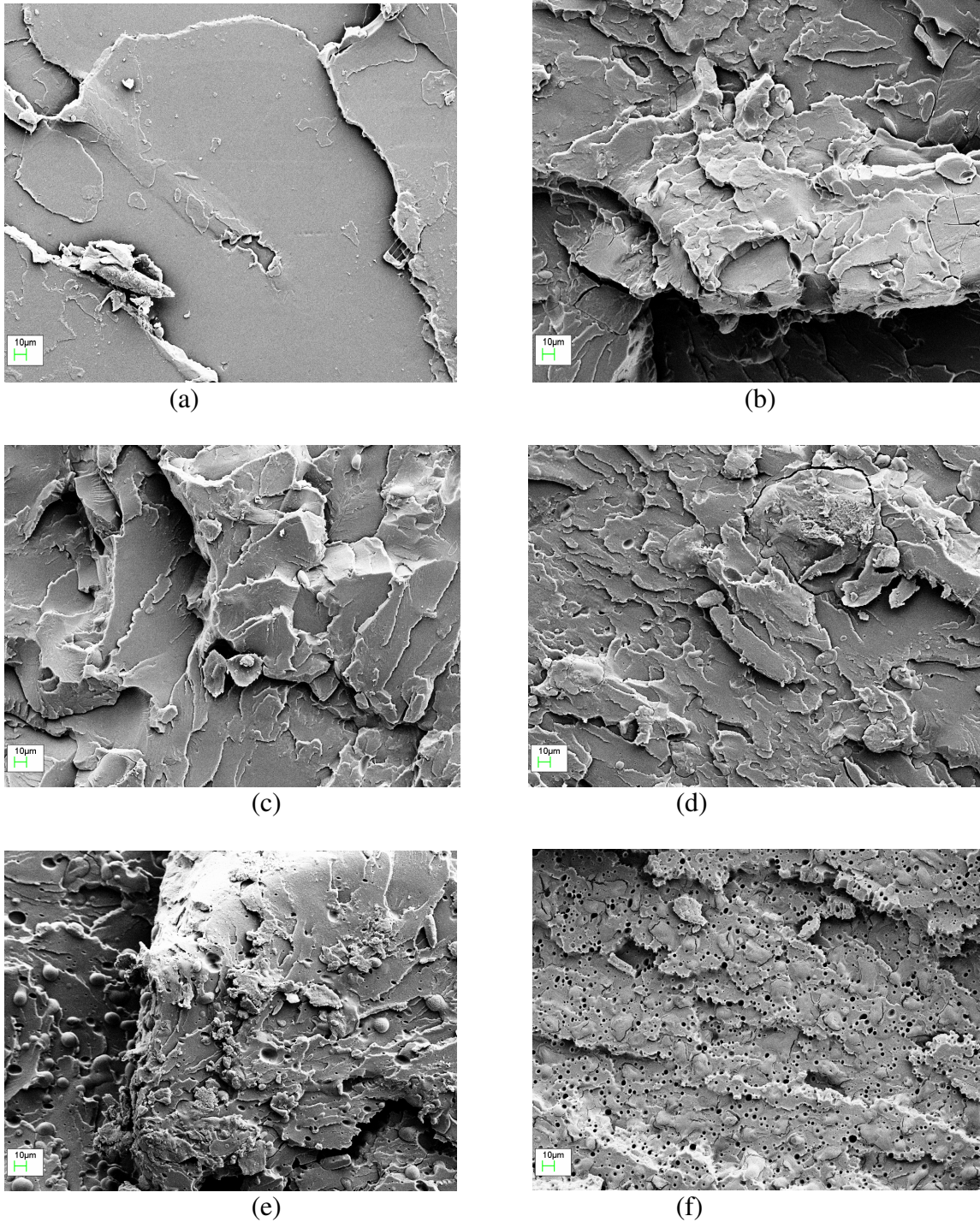


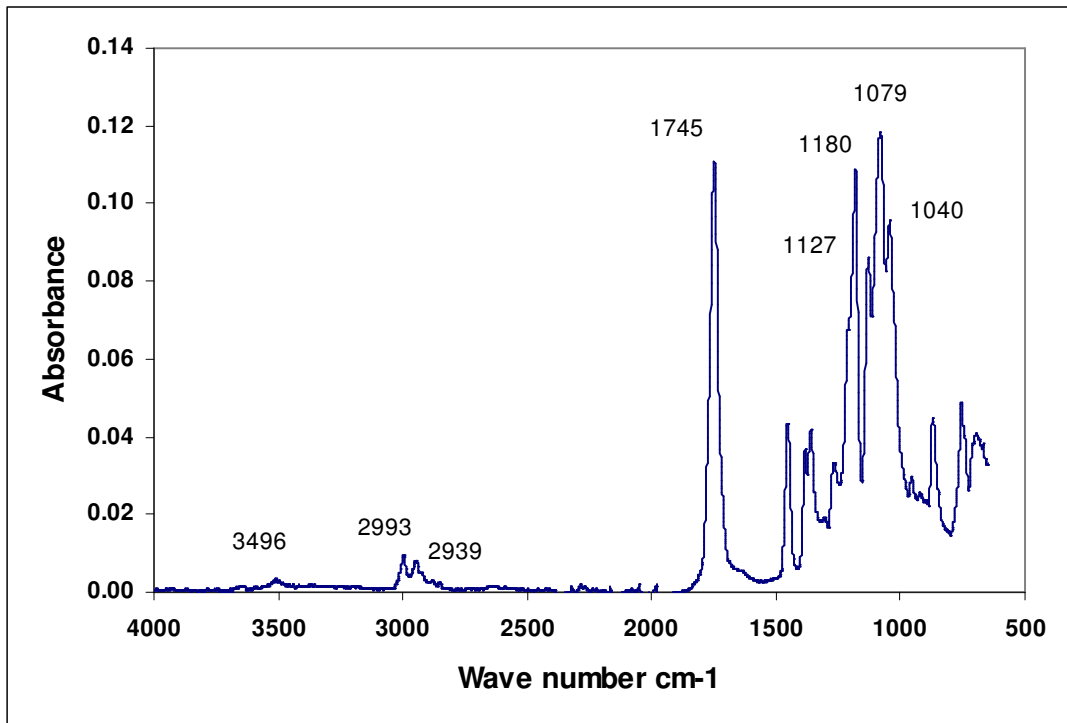
Figure 6.9 Scanning electron microscopy of fracture surfaces of broken tensile test bars of pure PLA and PLA/starch blends as affected by glycerol levels (a) PLA (b) 15S85P (c) 15S85P2G (d) 15S85P5G (e) 15S85P10G, and (f) 15S85P15G

The morphologies of the blends and pure PLA were observed by scanning electron microscopy on broken tensile test pieces, as shown in figure 6.9. The clear continuous phase of PLA can be seen in figure 6.9(a), has apparently been disrupted in the presence of starch, figure 6.9 (b). A few smaller particles in all the micrographs indicate that starch granules have been crushed to some degree during extrusion and thereby reducing the starch granule size. Some of the micrographs show non uniform mixing (Figure 6.9 d, e). However, the aggregation of starch in the presence of glycerol is also observed mainly in the PLA/starch blend with 10% glycerol, figure 6.9 (e), although it is not clearly visible for the blend with 15% glycerol, figure 6.9 (f). Ke and Sun (Ke & Sun, 2001b) have also reported the aggregation of the continuous starch phase as the glycerol content increased. Many voids were also observed with more uniform morphology with 15% glycerol. The voids were created due to the high flowability of the glycerol. The results show the better dispersion between PLA and starch in the presence of 15% glycerol. In the current investigation, the blends of PLA and starch filled with glycerol were principally prepared by hand mixing in the first instance followed by extrusion. This two way method of starch and glycerol mixing, initially by hand, and then, after the addition of PLA, by extrusion seems to have an effect on the blend morphology. Although efforts were taken to maintain uniform hand mixing, the results indicate that it was not satisfactory. The plasticization effect of glycerol, as well as its coupling effect, depends on the extent of the mixing and this is controlled by the mixing techniques and mixing times.

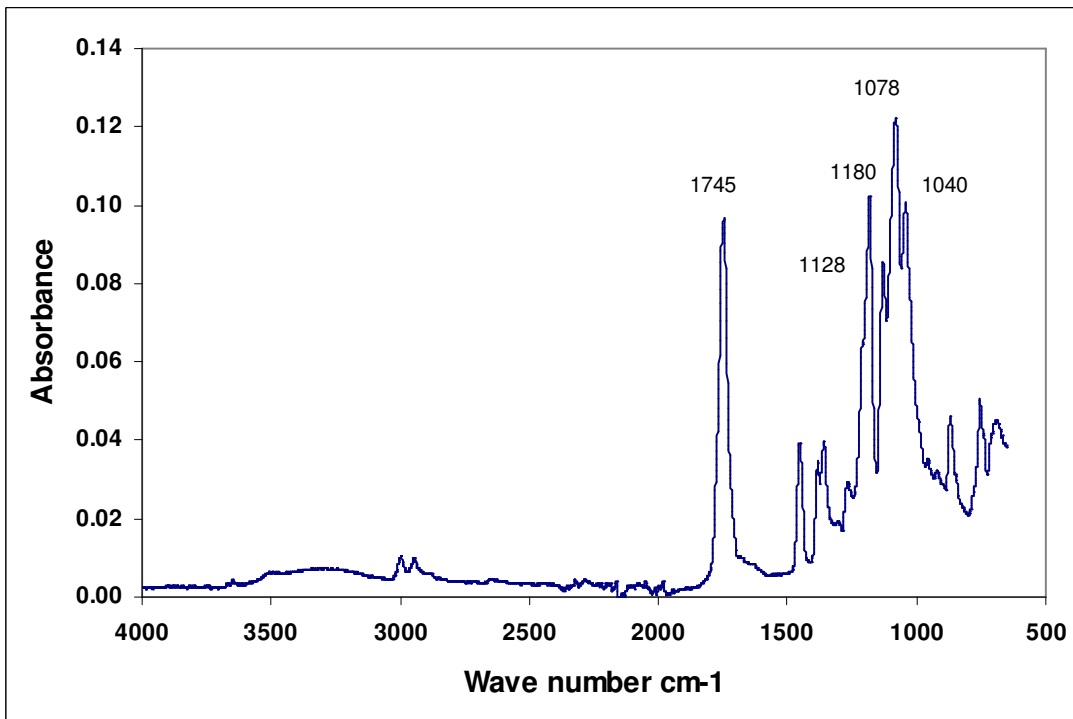
6.5 Fourier Transform Infrared Spectroscopic analysis

Information on different types of bond vibrations of polymers namely bending, stretching, wagging, torsional vibrations etc. give rise to characteristic bands in the IR spectra and therefore, the molecular interactions in the polymer blends can be identified. Appreciable changes in the FTIR spectra can demonstrate immiscibility or miscibility of blends with respect to the addition of each component. Moreover, distinct chemical interactions such as hydrogen bonding or dipolar interactions exist between the chains of the different polymers, as reflected by the IR spectra of the blends, if polymers are compatible (e.g., and shifts and broadening) (Peng, Wang & Dong, 2005). Therefore, FTIR spectroscopy can be

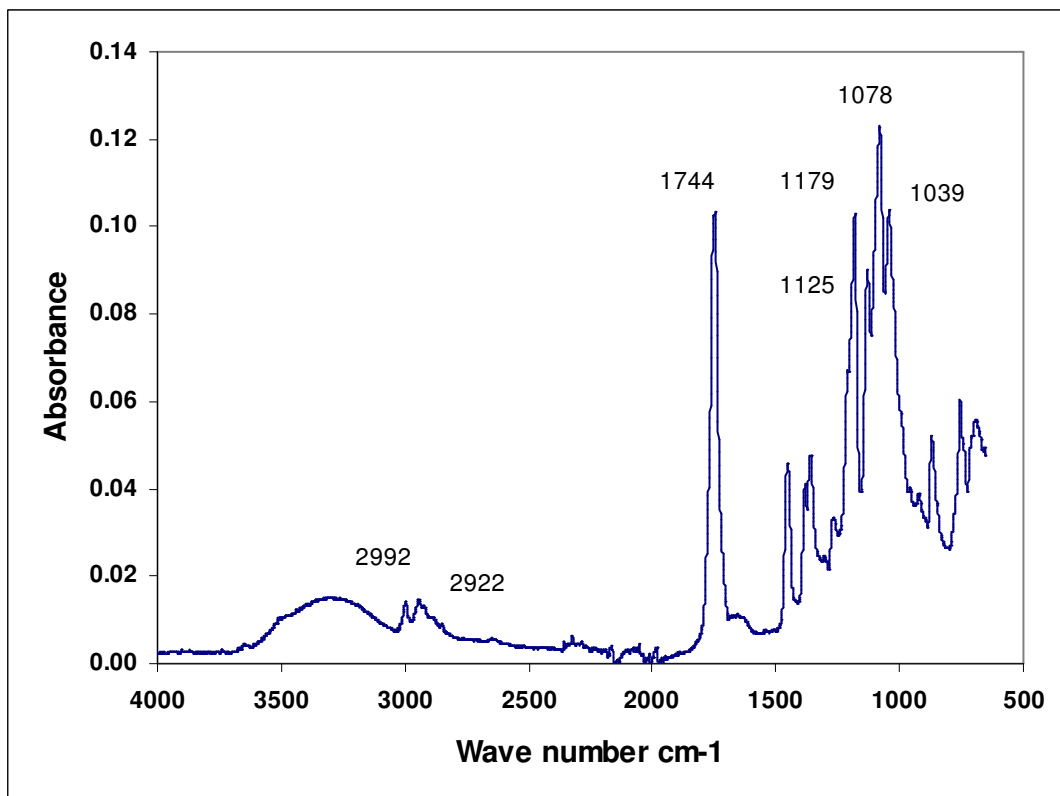
used to identify interactions within the polymer segments and provide information about the behavior of polymer blends.



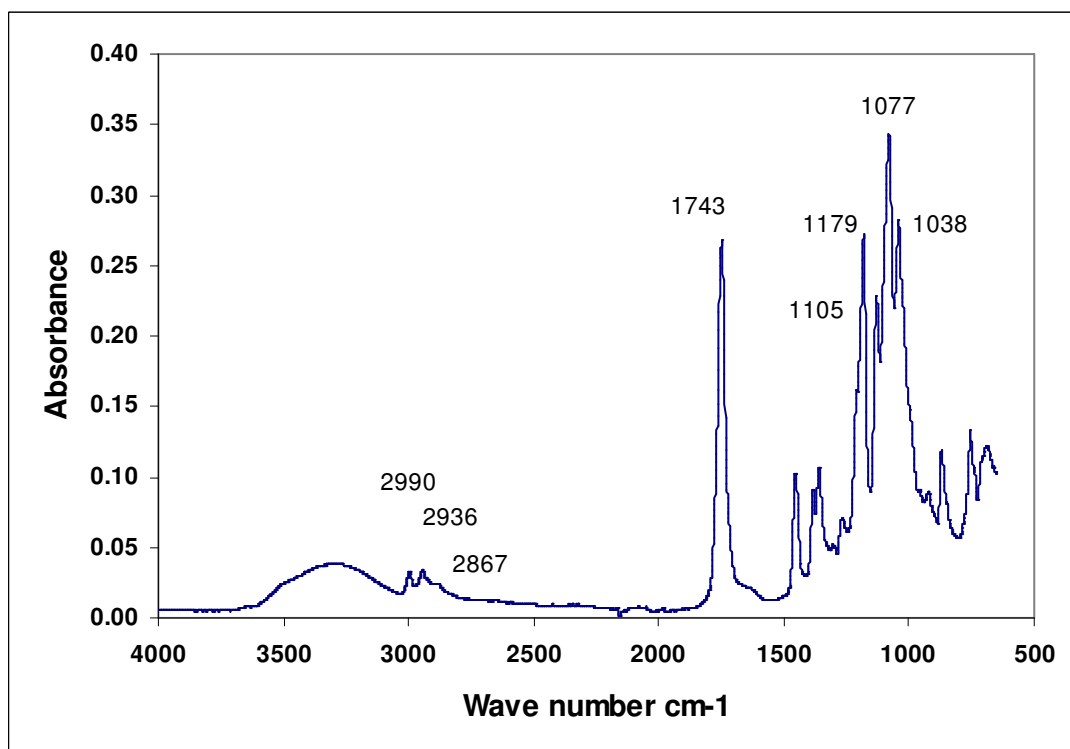
(a)



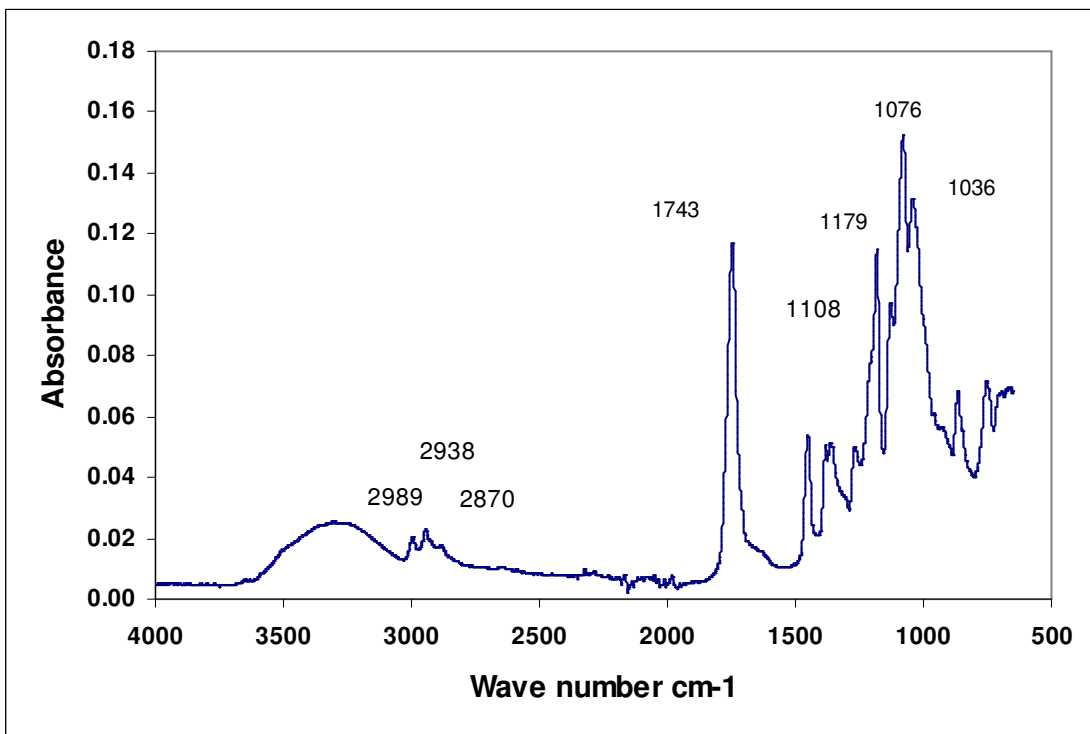
(b)



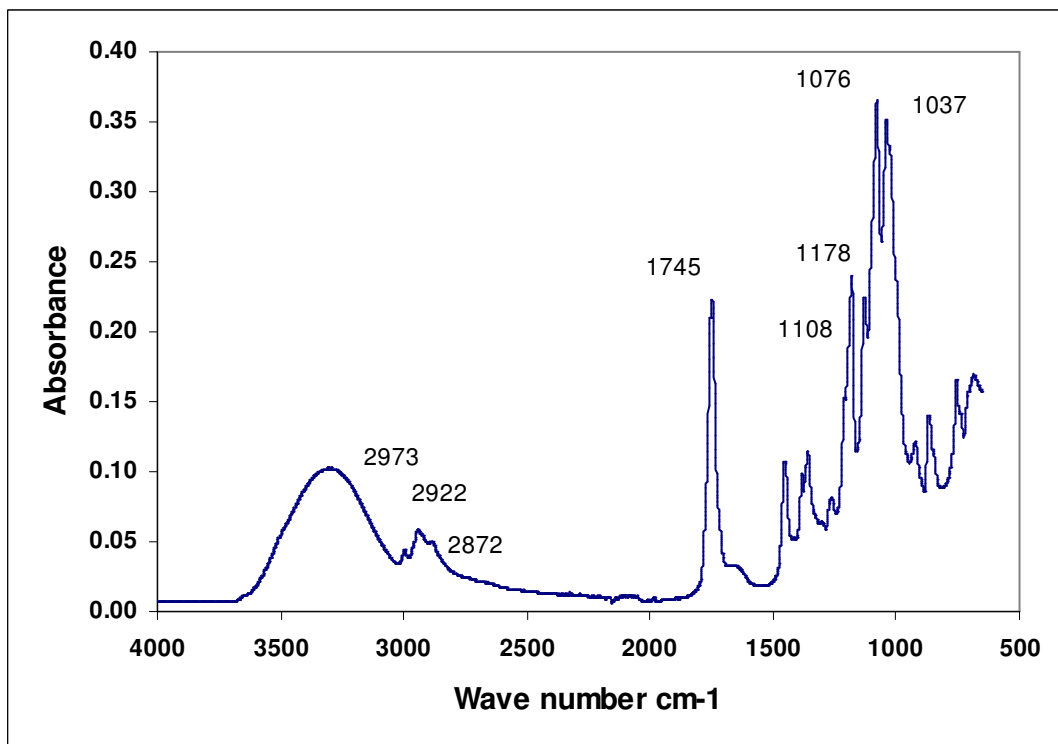
(c)



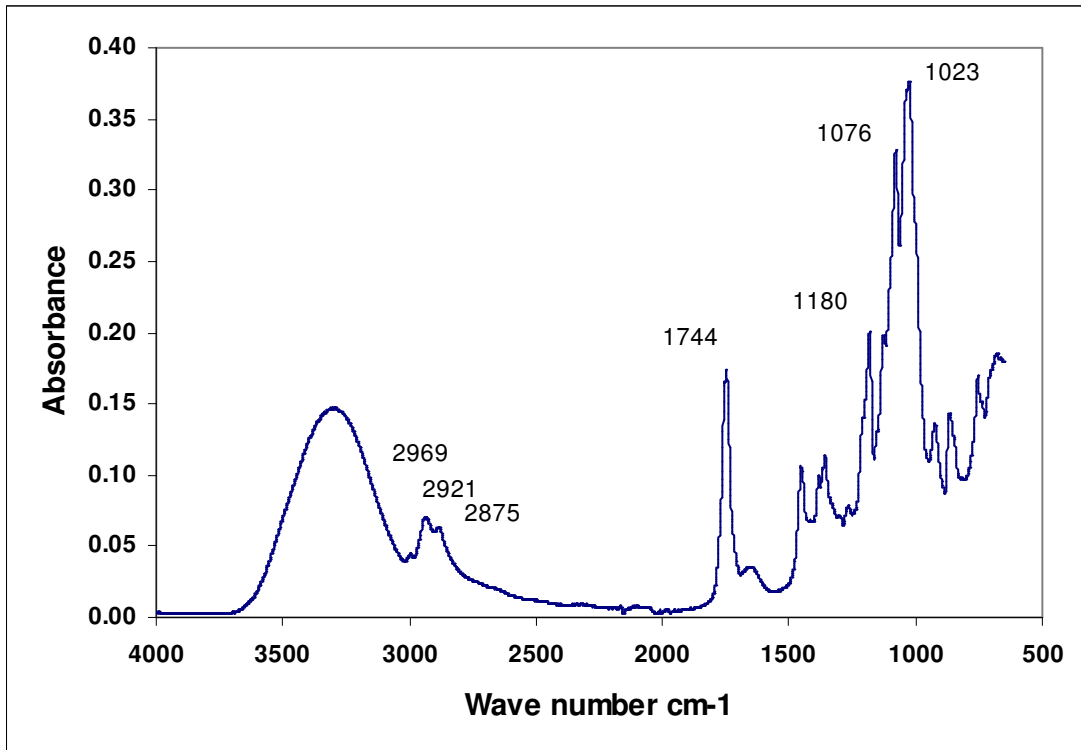
(d)



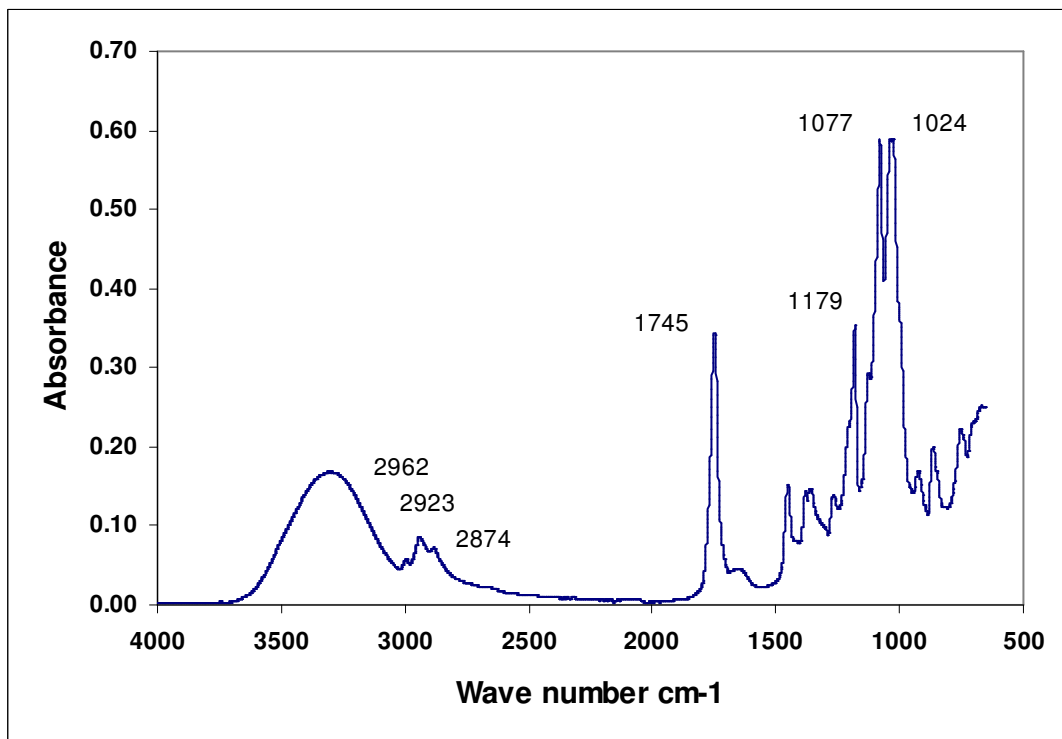
(e)



(f)



(g)



(h)

Figure 6.10 FTIR spectra of (a) PLA (b) 85P15S (c) 85P15S2G (d) 85P15S5G (e) 85P15S5G(P) (f) 85P15S8G (g) 85P15S10G, and (h) 85P15S15G

Figure 6.10 presents FTIR spectra obtained from pure PLA, and PLA starch blends with glycerol for different glycerol concentrations. PLA has a strong characteristic peak due to a carbonyl stretching absorption at about 1745 cm^{-1} as can be seen in the figure 6.10(a). After blending with starch, there are no significant changes in the peaks, except for the OH band shown around 3490 cm^{-1} . The OH stretching vibrational band of starch which typically occurs between 3000 and 3500 cm^{-1} (Park et al., 2000) is clearly observed in the PLA/wheat starch blend. However, in the presence of glycerol a narrower band was observed at lower wavenumber in the O-H stretching region. The strong carbonyl peak has been reported to shift to a lower wavenumber, due to the weak interaction between starch and PLA (Wang et al., 2007). However, in the current work this band does not appear to shift to lower wavenumber within experimental error when the content of glycerol is increased up to 15% (see figures 6.10 (a)-(h)) Therefore it can be suggested that carbonyl groups take part in the interaction between PLA and glycerol plasticized starch only to a limited extent, giving a small degree of miscibility between two phases. The same phenomenon can be found for -C-O- in -CH-O- (1180 cm^{-1}) and -C-O- in -O-C=O (1127 cm^{-1} , 1079 cm^{-1} , 1040 cm^{-1}) of PLA in PLA /starch blends with glycerol. Moreover, the triple peak of -C-O- in -O-C=O changes to a clear double peak after plasticizing by glycerol. This change is more pronounced in the presence of higher glycerol, possibly because glycerol can interpenetrate through stable intermolecular and intramolecular hydrogen bonds in starch, resulting in an improved interaction between starch molecules and glycerol. As a result of this penetration, amylose can leach out to the granule surface (Park et al., 2000), thereby increasing hydroxyl fraction for interactions with PLA. It is also noticeable that the double peak of PLA around 3000 cm^{-1} transforms to a triple peak in the presence of glycerol. These results further support the interactions and miscibility of the polymers in the blend up to a certain extent.

6.6 Home composting investigations

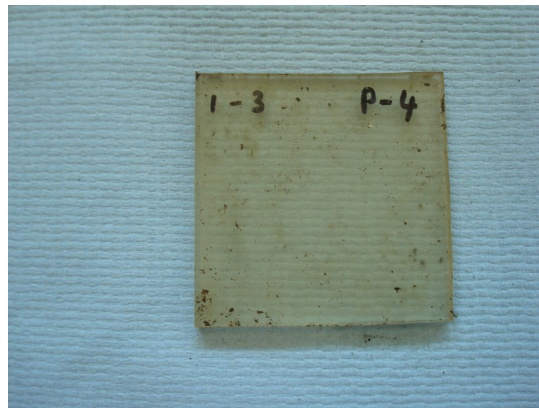
The usage of plastics in the UK is approximately 7 million tonnes per year, accounting for a very broad range of applications including plastic packaging, of which only about 1 million tonnes are recycled (Tarverdi, 2010). Most plastic products that get into the market

mainly as packaging are disposed, largely being consigned to landfill, as co-mingled plastic waste. One of the main concerns of developing biodegradable plastics at the current time is to reduce this significant quantity of plastic waste collected for disposal to landfills. A technique that follows the natural process of biodegradation and known as composting has been identified, specifically to minimize the biodegradable waste stream. Two methods of composting, industrial and home composting are currently practiced. Similar to the industrial composting technique, home composting is also a controlled biological decomposition of organic waste but under cooler aerobic breakdown and much more cost effective. The technique follows frequent addition of organic matter to the composting container and this will gradually decay over time to form compost. The carbon to nitrogen ratio is an important parameter in both industrial composting as well as in home composting. The consumer regularly adds carbon rich materials such as cardboard, paper, straw, leaves, shrub trimmings together with nitrogen rich materials such as grass cuttings, raw fruit and vegetables and nettles to achieve the required condition. The temperature of the compost pile is usually in the range of 0-20⁰ C for psychrophilic organisms or 20-45⁰C for mesophylic organisms.

Home composting trials of the blends developed in the present work by blending completely biodegradable materials were investigated using a compost bin. Given in figure 6.11 are pictures of the home composting trial samples carried out in a working home composting bin in Middlesex. The average temperature of the compost pile was observed to be 45⁰C.



(a- before composting)



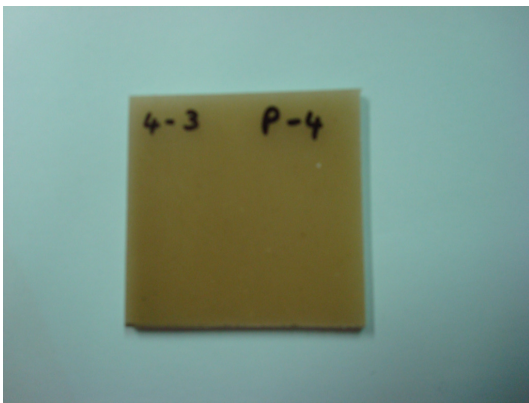
(a- after composting)



(b- before composting)



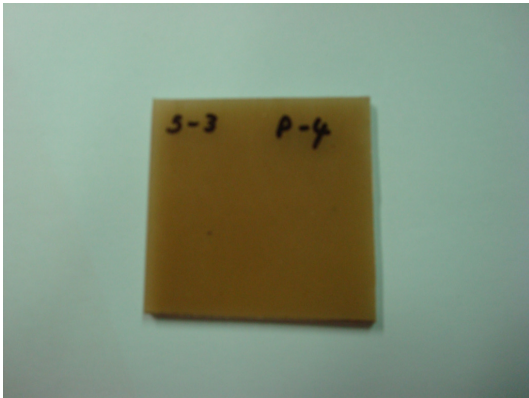
(b- after composting)



(c-before composting)



(c- after composting)



(d-before composting)



(d-after composting)

Figure 6.11 Home composting observations of PLA and its blends with starch and glycerol

Pictures taken before and after composting trials were compared to understand the composting ability of the blends and the virgin material. Composted PLA samples shown in figure 6.11 (a) have not shown any visible sign of degradation to the naked eye after exposing to the composting environment for three months. However, PLA/starch blends clearly initiated degradation as shown in figure 6.11(b). Furthermore, glycerol noticeably promoted the degradation of the PLA/starch blends as can be seen in 6.11(c) and (d). A lot of cracks were initiated and the samples were about to disintegrate at the 5% glycerol level. Two reasons can explain this phenomenon. Firstly, the glycerol plasticised the starch and most of the OH groups were exposed, and therefore moisture could easily accessed OH groups leading to the degradation. Secondly, glycerol itself has a high affinity for moisture, and this could lead to a faster degradation than the blend without glycerol. The effect of the glycerol concentration on the composting cannot be deduced because the composted samples with higher glycerol levels have not been found in the bin either due to fragmented pieces being displaced in the working compost bin or disappearance due to complete degradation. The PLA in the large pellet form has exhibited a higher rate of degradation than the blend with the small particle size PLA, at the same glycerol level. When the pellet size was large, the PLA and starch blend did not lead to a better dispersion, as demonstrated by the other blend properties. This poor dispersion generated a coarse structure with the isolated starch granules that had not mixed with the PLA, resulted in easy accessibility for moisture and other microorganisms, leading to the accelerated degradation.

6.7 Chapter summary

The glycerol was incorporated into PLA and wheat starch blends and the properties were investigated. The small particle size PLA assisted better mixing between PLA and starch to promote the blending. The results also suggested that the T_g of the PLA/starch blend can be reduced with increasing glycerol concentration. It was also observed that the flexibility of PLA/ starch blends can be enhanced with the addition of glycerol to the blend with a noticeably higher energy absorption before fracture upon impact. The morphology shows a better dispersion between PLA and starch in the presence of glycerol. The FTIR spectroscopic analysis was performed, and the results infer that some degree of interaction

between PLA and starch in the presence of higher glycerol levels. Home composting of the blended materials can evidently be accelerated by starch as well as by glycerol. However, glycerol did not facilitate the processing of the blends under conventional polymer processing conditions or exhibit the utmost degree of properties due to the migration to the surface at the processing temperatures. Nevertheless, there was an improved plasticization effect when glycerol was added and there may be an improved coupling effect depending on the mixing techniques, time and processing conditions. The experimental results demonstrate that enhanced material properties are achievable with the controlled blending of PLA and starch.

CHAPTER SEVEN

***RESULTS AND DISCUSSION
OF THE WORK WITH
NATURAL RUBBER LATEX***

7 The influence of natural rubber latex on PLA and wheat starch processing and their blend properties

In the current chapter, the issues and satisfactory outcomes of the experimental work conducted and outlined in chapter 3 are presented with regard to the blends prepared with the material codes and their compositions recorded in table 3.5, during the processing of the PLA and wheat starch blends in the presence of natural rubber latex additive, described in section 3.3.4.

The natural rubber latex, which has been obtained from a natural source, a rubber tree, was employed in this study. This white, sticky, free-flowing milky fluid obtained from the rubber tree has been long known to mankind. More precisely, it is a stable colloidal dispersion formed by metabolic processes occurring in the plant. It is a longstanding material which has been used for vast applications including major usage in the rubber industry ever since the plant was grown in Kew gardens in London in the UK in 1875, and the eventual establishment of rubber plantations in several parts of the world including Sri Lanka in 1876 (Blackley, 1997). Unique features inherited by the material have been explored in several applications from cradle-to-grave. The white milky fluid is tapped from the tree, concentrated and preserved and then transported to many places before the ultimate usage of the end product.

Latex was chosen in this study because of the possibility of forming hydroxyl bonding and its compatibility with starch. Furthermore, latex has some inheritance long chain fatty acids that could also help the bonding with starch as well as with PLA. Moreover, one of the inheritance fatty acids in latex is stearic acid and stearic acid has shown some improved properties in the PLA and starch blends as discussed in chapter 4. All these reasons have led to the current investigation of the PLA and starch blends with natural rubber latex.



Figure 7.1 Tapping of latex from a rubber tree

7.1 Analysis of thermal stability

7.1.1 Thermogravimetric analysis

In the current study, latex was used as an additive at different levels and added to PLA and starch blends to observe how the features of latex influence the behaviour of the resultant composites. The thermal behavior of PLA and starch blends with 1, 3, and 5% latex concentration levels were studied by thermogravimetric analysis in air and in an inert atmosphere (N_2 atmosphere) and the results are revealed in figures 7.2 and figure 7.3, respectively. Pure PLA and PLA/starch blend were also studied under both atmospheric conditions as a comparison and the results are shown in the same figures.

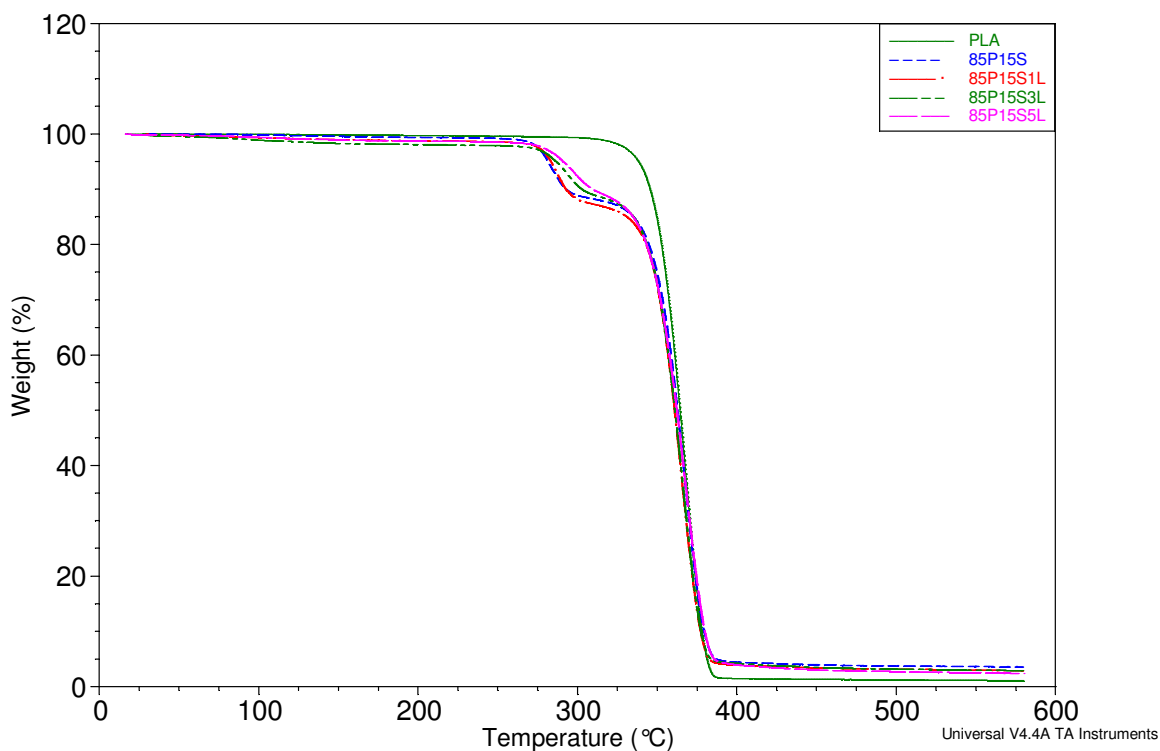


Figure 7.2 TGA curves of the pure PLA, PLA/starch blend, PLA/starch blends with different latex levels in air.

According to these results, PLA has shown no weight loss below 325⁰C, however, blends with starch have reduced this temperature stability to approximately 275⁰C. In view of the stability of PLA, any apparent reduction in stability in the blends below 300⁰C is attributed to the starch via degradation of components of starch around this temperature as discussed in previous chapters. Apart from the influence of starch, no significant affect is observed from latex towards the stability of the prepared blends from the TGA thermograms in both air and N₂ atmospheres and therefore the blends would have been stable during processing at the temperatures that are required.

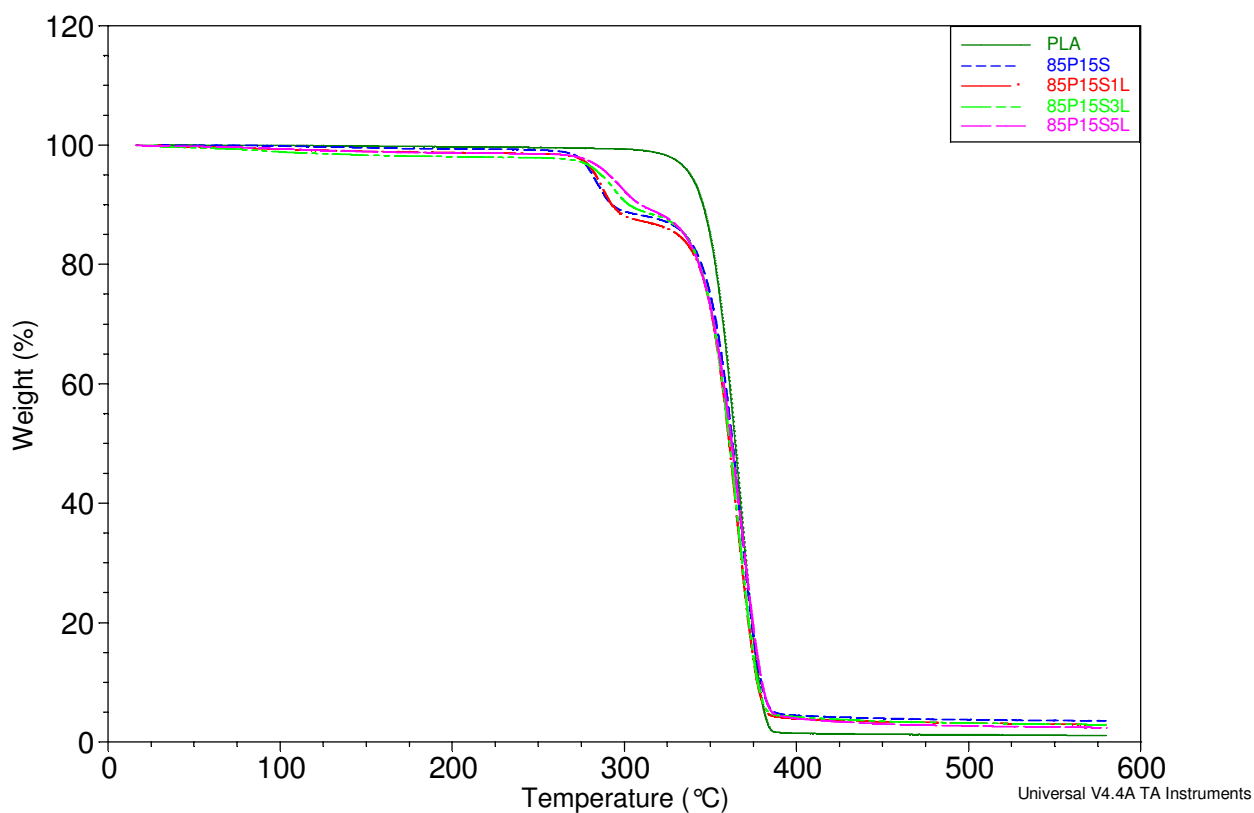


Figure 7.3 TGA curves of the pure PLA, PLA/Starch blend, PLA/starch blends with different latex levels under a N₂ atmosphere.

Further studies on TGA were carried out on the same blends in a N₂ atmosphere with an isotherm at 180⁰C for 30 minutes and the results are recorded as an overlay in figure 7.4. Due to many reasons, there could be occasions when the material may have the long residence time in the barrel of the extruder or the injection moulding machine before processing. In such situations, degradation of the material is a crucial concern. To fulfill this criterion, the aforementioned experimental part has been carried out to see the occurrence of any weight loss of the materials within a longer period of exposure at a higher temperature. An insignificant weight loss, less than 1%, was observed in all blends around 200⁰C, but PLA remained stable up to the temperature of 300⁰C even when the isotherm was applied for 30 minutes.

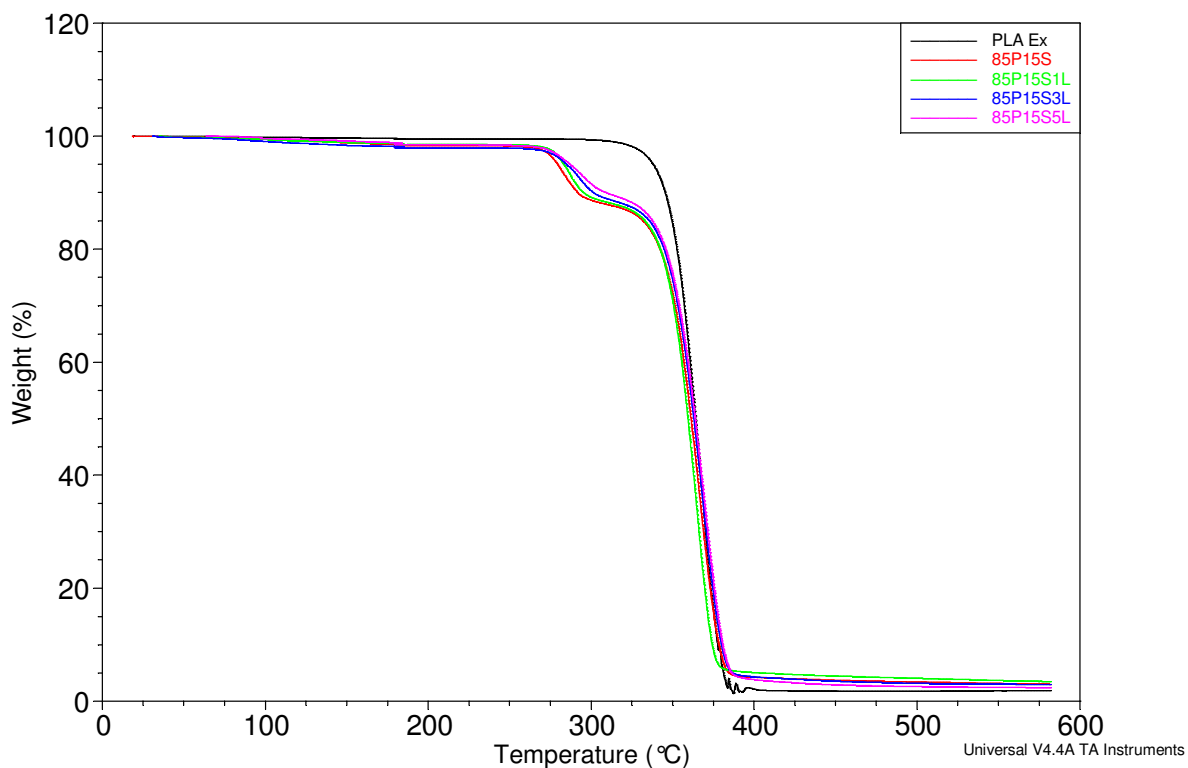
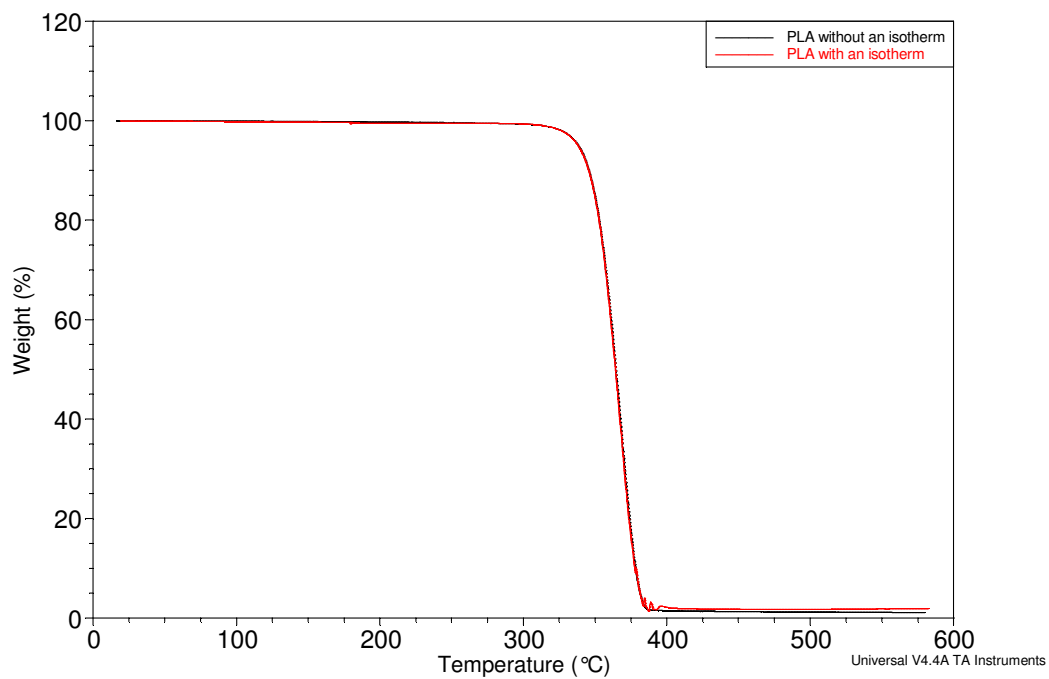


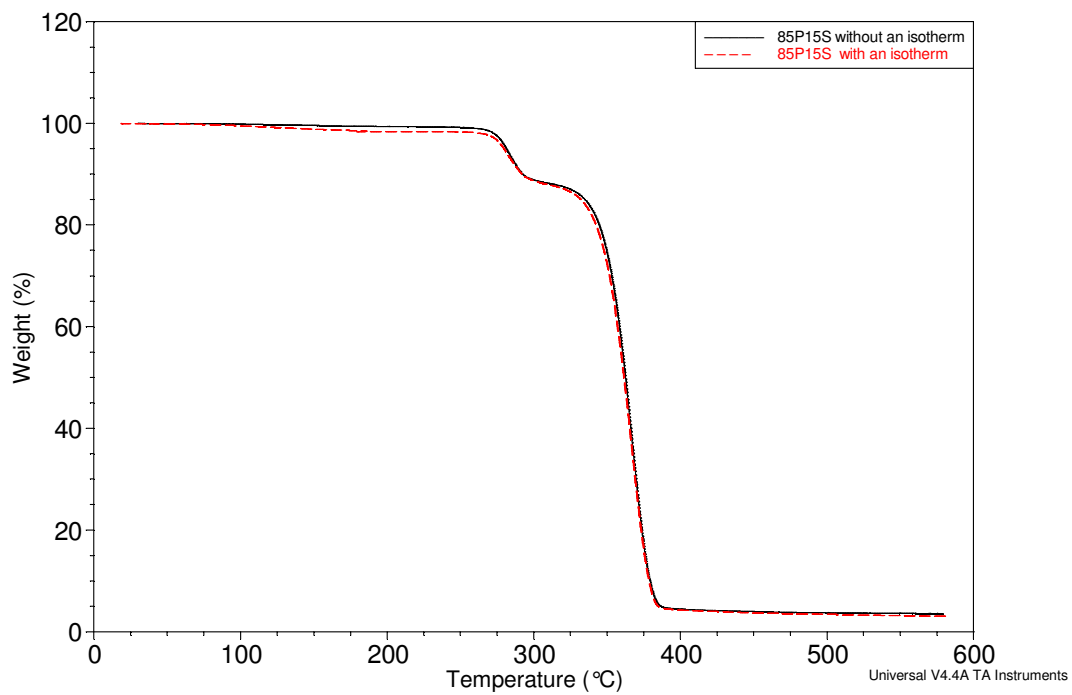
Figure 7. 4 TGA curves of the pure PLA, PLA/starch blend, PLA/starch blends with different latex levels under N₂ atmosphere with an isotherm at 180⁰C for 30 minutes.

Figures 7.5 (A), (B), (C), (D) and (E) illustrate a weight loss comparison of the materials with and without an isotherm at 180⁰C for 30 minutes in the thermogravimetric analyzer for further clarification on the isothermal stability.

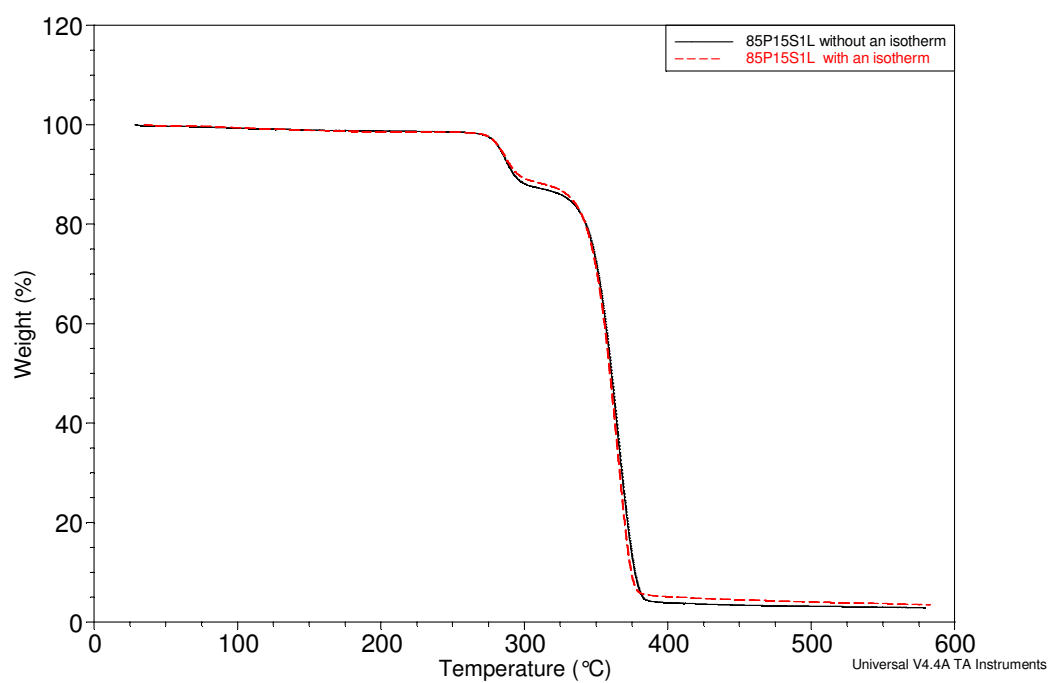
(A)



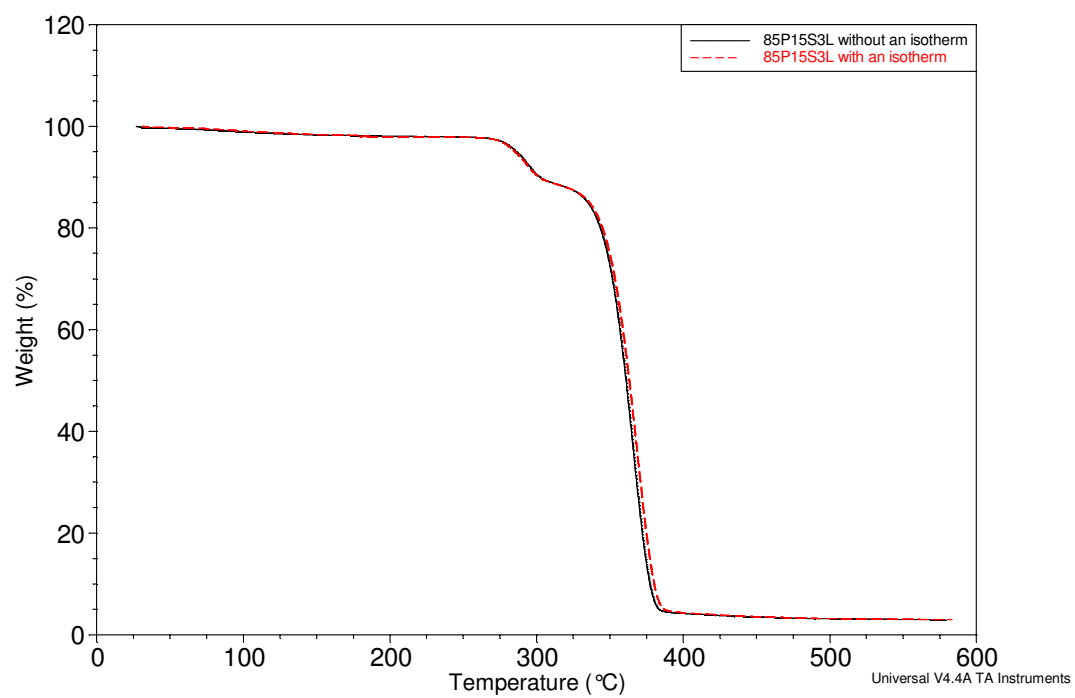
(B)



(C)



(D)



(E)

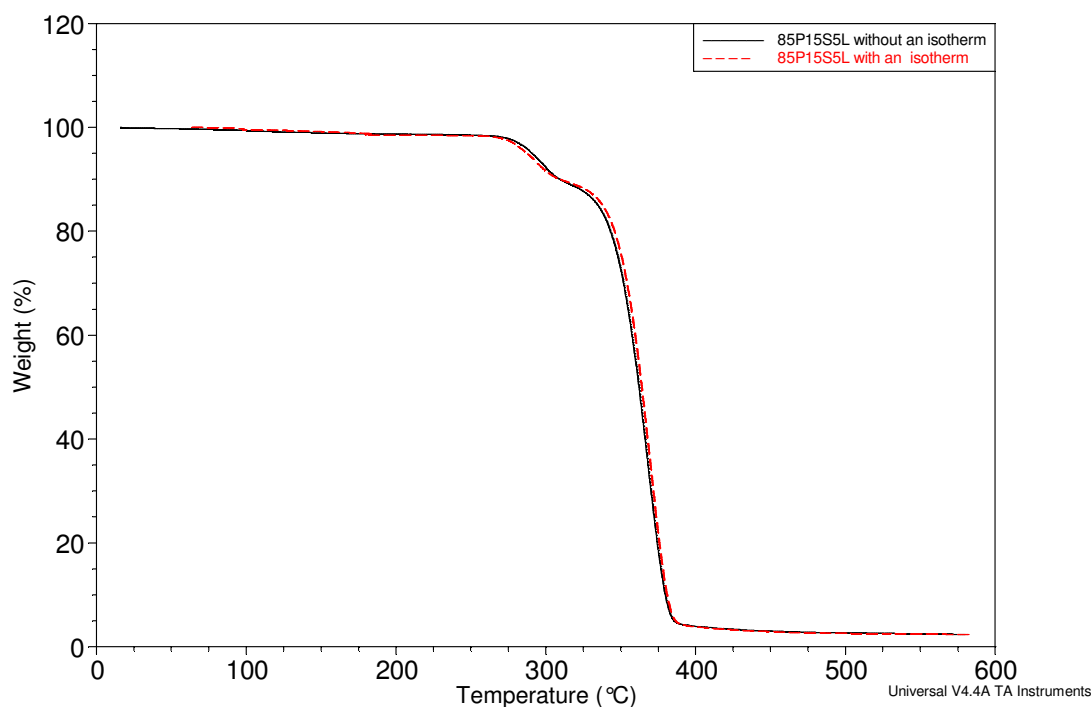
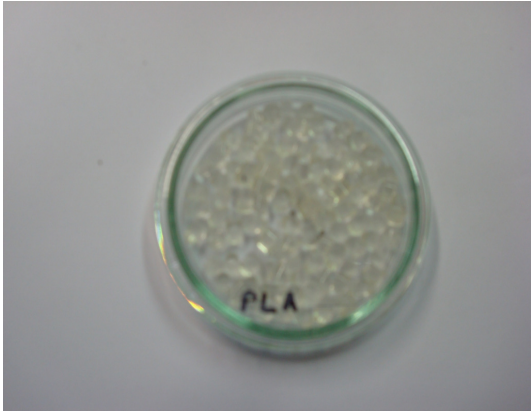


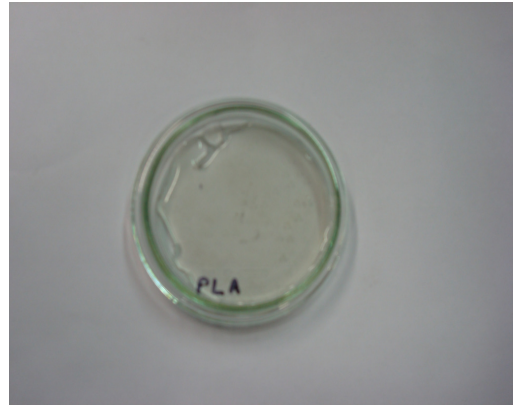
Figure 7.5 Weight loss comparison with isotherm and without isotherm at 180⁰C for 30 minutes in the thermogravimetric analyser (A) PLA (B)85P15S (C) 85P15S1L (D) 85P15S3L and (E) 85P15S5L.

7.1.2 Conventional oven heating

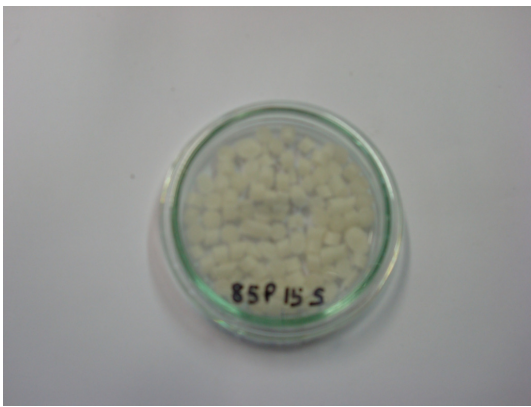
Furthermore, the temperature sensitivity of the blends upon heat treatment and their appearance were investigated by heating the materials in a conventional oven. All the prepared blends, virgin PLA and also the latex were investigated by heat treatment. The pure PLA and all blends of PLA/starch/latex were subjected to a temperature of 180⁰C for 30 minutes and were visually inspected before and after the heat treatment and the observations are presented in figure 7.6. The left column with A_b, B_b, C_b,..... etc. indicate all material photographs taken before heat treatment and the right column with the specified A_a, B_a, C_a,..... etc designate the corresponding material photographs taken after heat treatment.



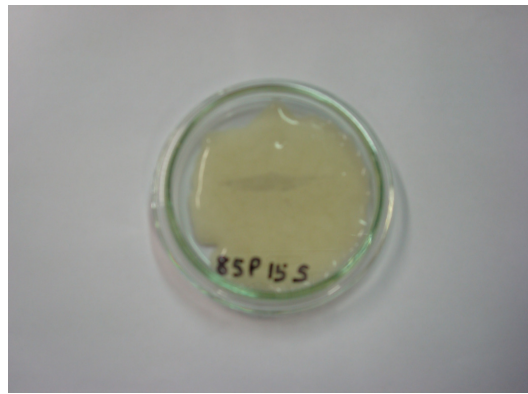
(A_b)



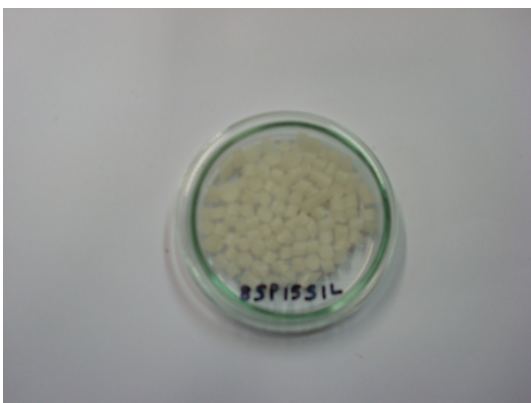
(A_a)



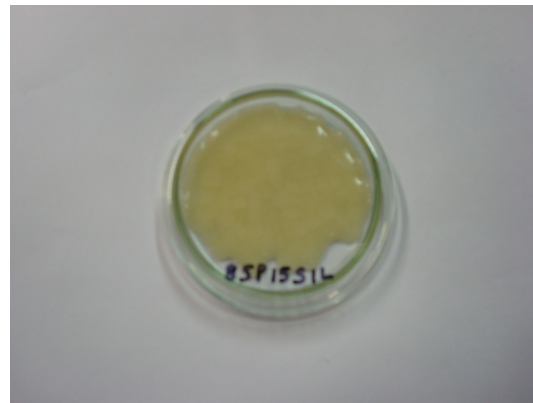
(B_b)



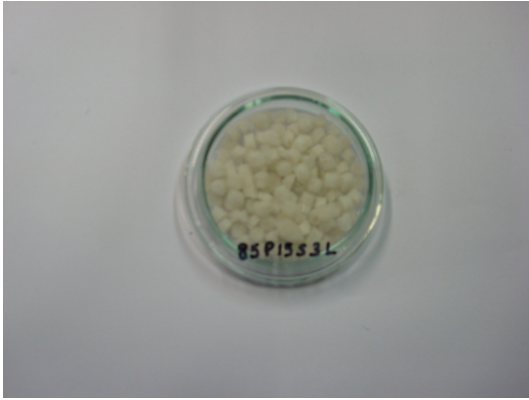
(B_a)



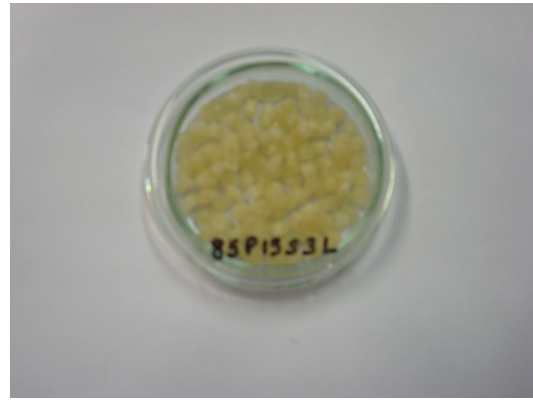
(C_b)



(C_a)



(D_b)



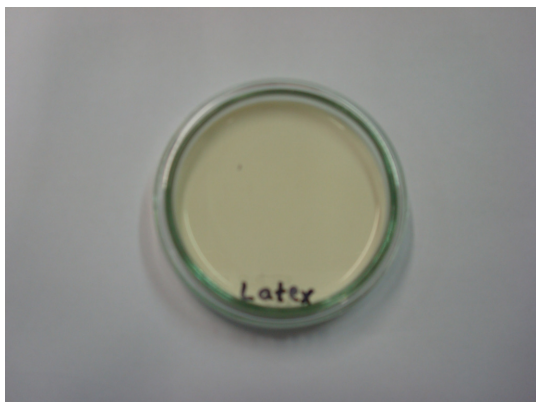
(D_a)



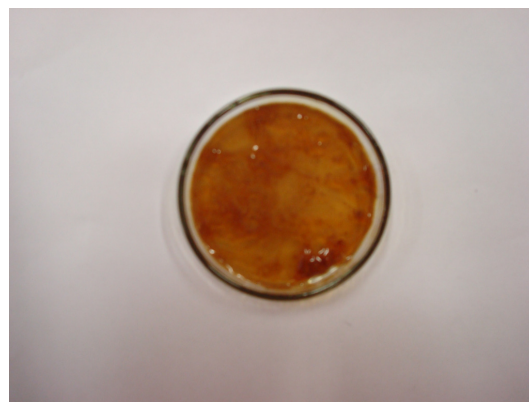
(E_b)



(E_a)



(F_b)



(F_a)

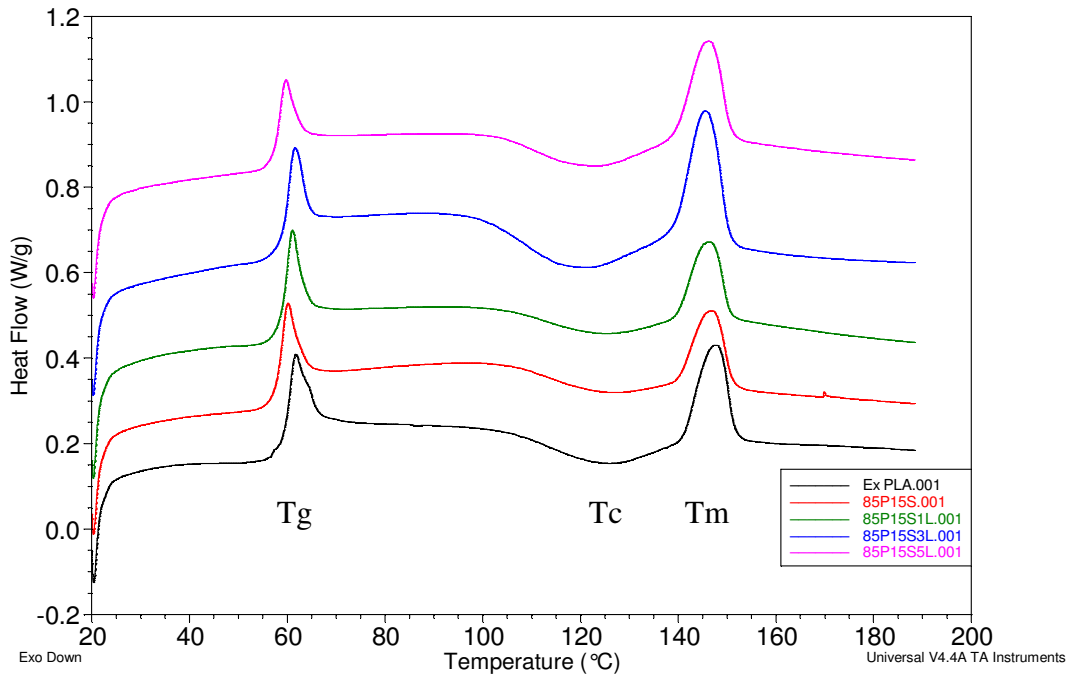
Figure 7. 6 Observations of the blends upon heating the materials in a conventional oven at 180⁰C temperature for 30 minutes (A) Extruded PLA (B) 85P15S (C) 85P15S1L (D) 85P15S3L (E) 85P15S5L (F) Latex

The appearances manifested in figure 7.6 designated that no discolouration had taken place in the materials even after heating at 180⁰C for 0.5 hr in the conventional oven. The PLA exhibits transparency (figures 7.6 A_b and A_a) while the starch demonstrates opacity (figures 7.6 B_b and B_a). However, latex has turned to a native brownish colour of the rubber when it is heated as is clearly shown in Figure 7.6 (F_a). This colour change has been imparted to the blends with latex, as can be seen in figure 7.6 (C_a), (D_a) and (E_a). Therefore it can be concluded that the colours of the blends are certainly due to the brownish colour of the latex (mainly rubber) at this temperature.

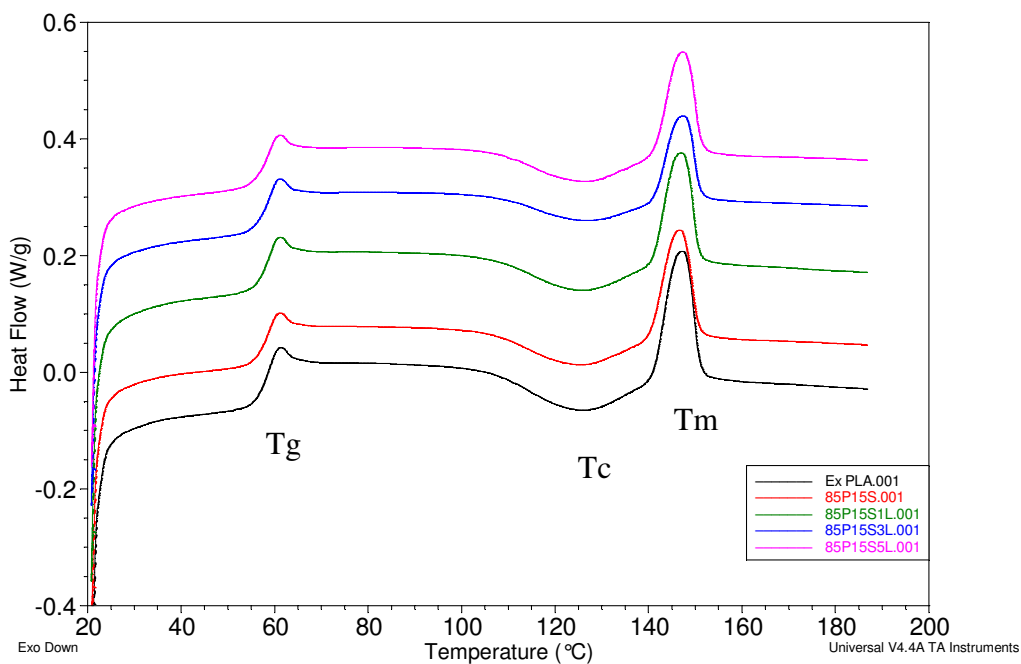
7.2 Differential scanning calorimetric analysis

The DSC thermograms of the blends were obtained and these are shown in figures 7.7(a) and (b). As shown in the schematic diagrams, the thermograms exhibit a glassy to amorphous transition around 60⁰C and this is assigned to T_g. In the first heating cycle, all blends and pure PLA have shown an enthalpy relaxation although it has partially disappeared after eliminating the thermal history in the second run. The blend preparation process involves heating and shearing in the extruder and rapid cooling in a water bath. The

enthalpy relaxation that occurred during melting in the first run was thought to be the result of relaxation of stress-distorted entanglements formed during rapid cooling. Therefore, the current protocol ensures heating to 190°C which will erase all the previous thermal history.



(a)



(b)

Figure 7.7 Thermal behaviour of pure PLA, PLA/Starch blend, PLA/starch blend with different latex levels (a) in the first cycle of the heat/cool/heat run, and (b) in the second cycle of the heat/cool/heat run.

A broad exothermic peak shown in pure PLA and the blends on the high temperature side of T_g have been assigned to crystallization and endothermic peaks around 145°C are ascribed to melting. The glass transition temperature somewhat decreased but no changes in the crystallization or melting temperatures were observed, indicating no crystalline integrity in the materials in the new thermal history, as shown in figure 7.7(b). However, changes of the peak shapes with more prominent crystallization and melting peaks indicated that the size distribution of the crystallites changed in the new thermal history. A 1994 study by Tolstoguzow (cited in (Arvanitoyannis et al., 1997) has reported that interactions in a blend system of transpolyisoprene (TPIP)/ starch/water and/or polyol, are mainly owing to starch/ water or starch/polyol, whereas TPIP is not involved. Therefore, any plasticization resulting in a decrease in T_g may be due to the plasticization of starch through the moisture content in the latex, creating highly mobile regions.

7.3 Rheological properties

Viscosity is an important property of a molten plastic (fluid) and describes its internal resistance to flow and may be thought of as a measure of fluid friction which is the force resisting the relative motion of solid surfaces. It is very important to investigate this rheological property by studying the ability of plastic materials to flow and hence the processability by conventional processing and it is of fundamental interest of this study. The oscillatory measurements conducted on pure PLA at temperatures of 150⁰, 160⁰, 170⁰ and 180⁰ C are shown in figure 7.8. The PLA data obtained below of 170⁰C show a fairly high viscosity at the lower frequencies with zero shear viscosities around 9, 6 and 3 kPa s. All the oscillatory measurements at the different temperatures exhibit clear Newtonian Plateaus and the data at 180⁰ C shows the low shear thinning at high frequencies and hence facilitate the processing by injection moulding.

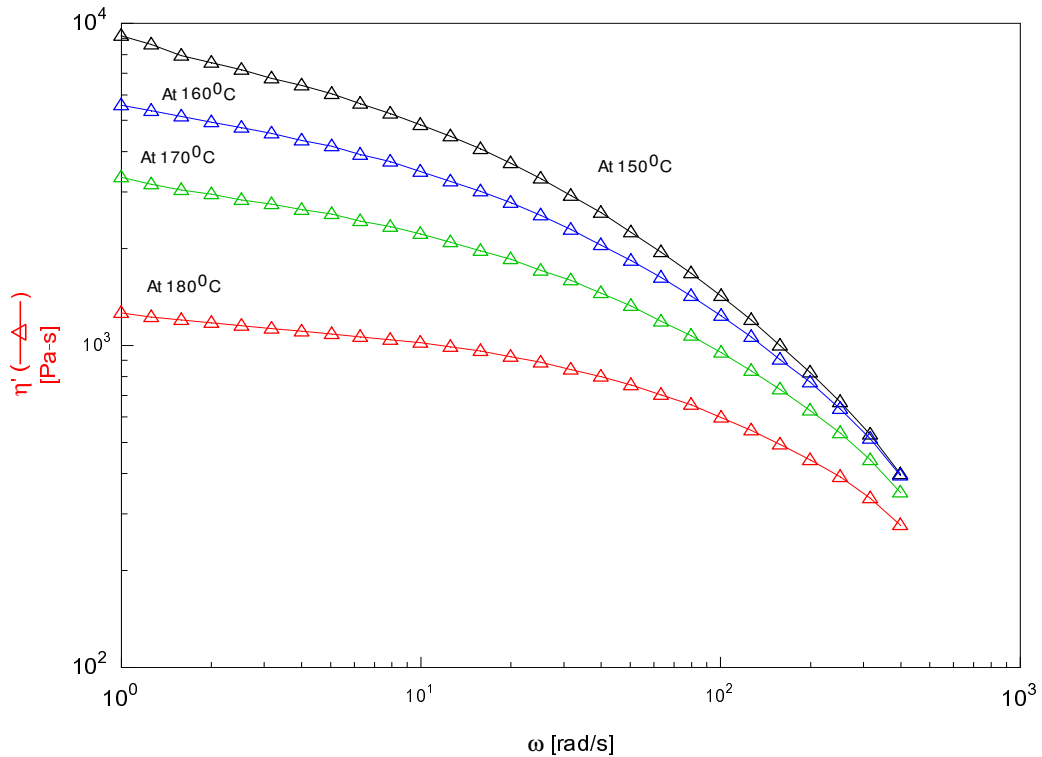


Figure 7.8 Variation of viscosity of PLA at different temperatures

The viscosity variations of other blends by oscillatory shear experiments were conducted concurrently with PLA at temperatures of 160⁰C, 170⁰C and 180⁰C and the data are recorded in figures 7.9, 7.10 and 7.11. All the blends, at the investigated temperatures have shown the similar flow behaviour upon increasing frequency with clearly defined Newtonian regions. The starch viscous behaviour is very different from that of PLA and is highly shear thinning, which is very typical of highly entangled or branched polymers. The blend of PLA/starch showed an increased viscosity with a similar behaviour by capturing the benefit of PLA. As a result, all the blends with starch have exhibited a clearly defined Newtonian region within the investigated shear rate range. Similar viscous behavior has been reported elsewhere (Huneault & Li, 2007), for the rheological properties of corn starch PLA blends. The results are also in agreement with the previous work (Xie et al., 2007) reporting on an increased melt viscosity of blends with starch content. Nakason *et al* (Nakason et al., 2004) also reported that the incorporation of starch increased the viscosity of the ENR/cassava starch blends and shear thinning at high shear rates exhibited the pseudoplastic behaviour. Furthermore, similar to the non modified PLA/starch blend, PLA/starch blends with added latex also demonstrated higher viscosities than pure PLA. The possibility of promoting blend viscosity owing to the rubbery character of latex has also clearly been revealed. It is important to point out that the influence of high molecular weight starch and branched and entangled amylopectin and amylose in starch have acted beside the latex to increase the blend viscosity. Moreover, in its origin, latex is a highly viscous dispersion of rubber particles. Therefore inclusion of latex in starch would explicitly increase the viscosity of the mixture resulting in an increase of viscosity of the blend. However, increasing the latex concentration results in an increase in the concentration levels of the other constituents in latex mainly water, thereby plasticizing the starch and resulting in a decrease in the viscosity as shown in blends with 5% latex.

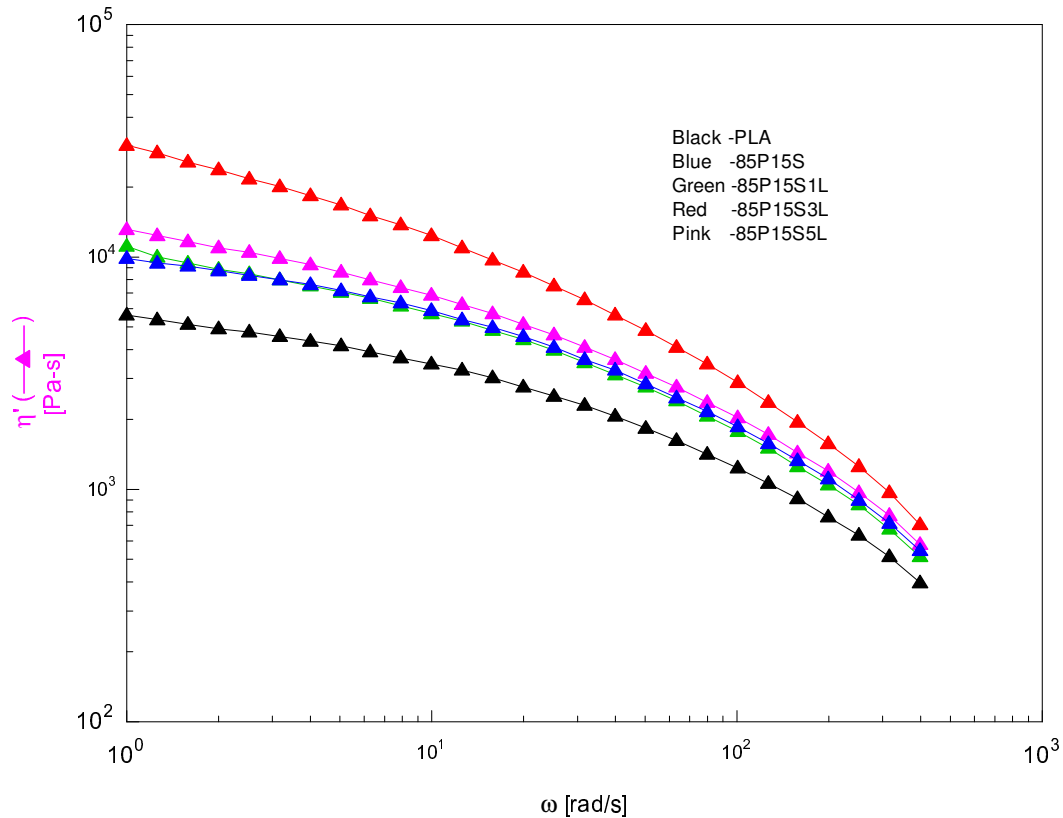


Figure 7.9 Variation of viscosity with different blend types at 160⁰C temperature

Latex mainly consists of a total solid content which accounts for dry rubber as the major constituent together with other minor constituents and water. However, 1 and 5% latex in the blend showed similar behaviour, whereas 3 % latex in the blend showed a higher viscosity than the other two percentages. There exists an optimum level of latex, in the range of 3% and 5% that raise the viscosity in the blend. Higher latex levels than the optimum level could have led to the hydrolysis of starch caused by higher levels of its other constituents, thereby decreasing the viscosity. Similar to pure PLA, initial viscosities of all blends at 180⁰C were reasonably low and stable at higher frequencies, but the final material viscosity remained in an acceptable range and was therefore chosen for injection moulding with the anticipation of facile processing.

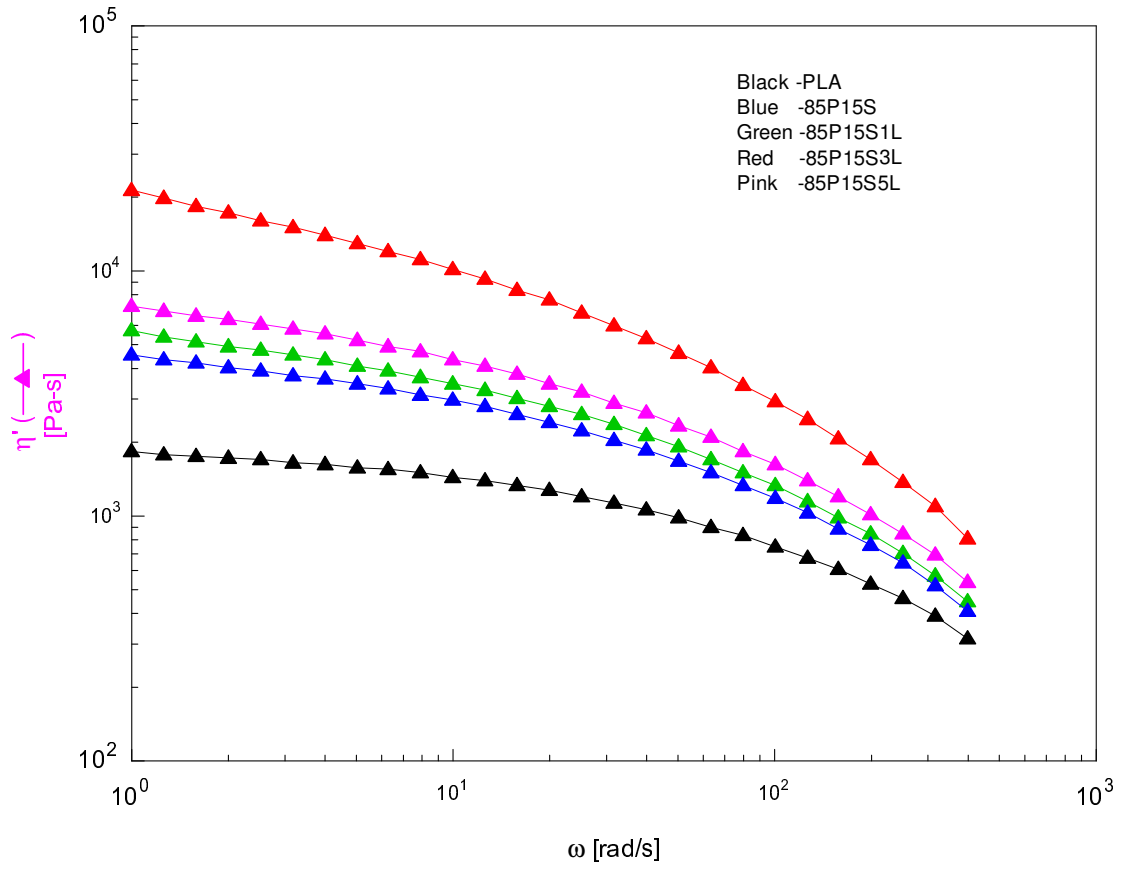


Figure 7.10 Variation of viscosity with different blend types at 170⁰C temperature

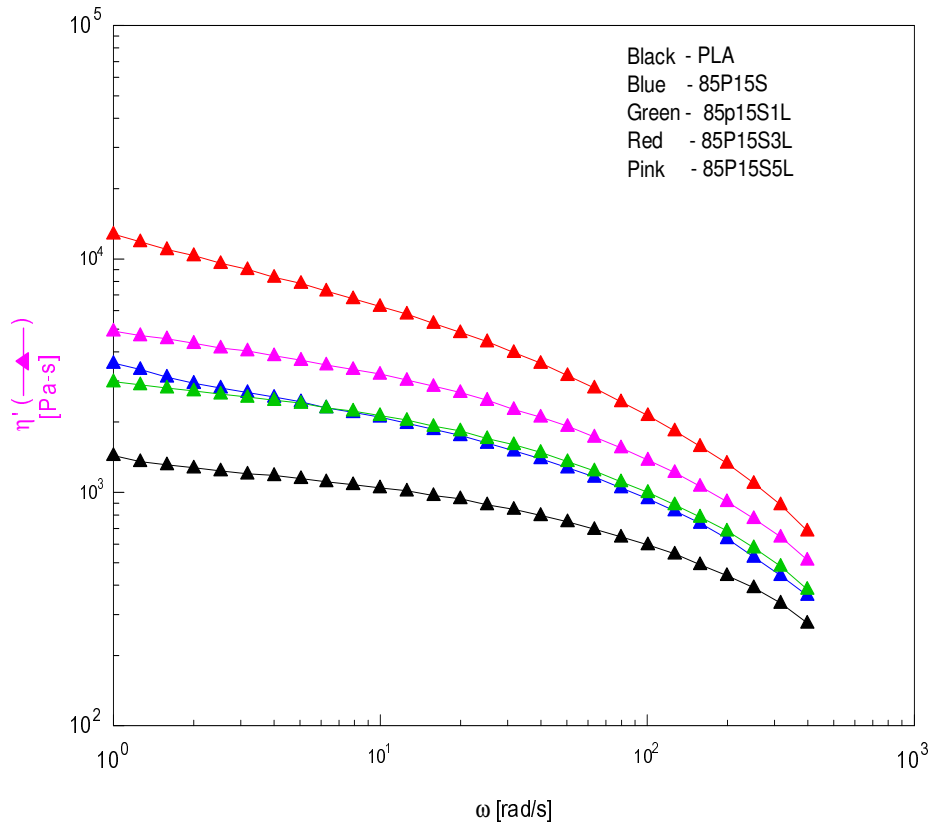


Figure 7.11 Variation of viscosity with different blend types at 180⁰C temperature

The storage modulus (E') and loss modulus (E'') were also derived from the graph and the results are illustrated in figures 7.12 and 7.13 respectively. According to the results, all the blends and the PLA tend to follow the same pattern of variation in storage modulus and loss modulus at increasing frequency. However, PLA shows the lowest values whereas the blends with 3% latex show the highest values indicates that in the presence of latex, energy absorption and heat dissipation of the blend increases. Similar to the viscosity, the PLA and starch blend and the blend with 1% latex show similar modulus properties.

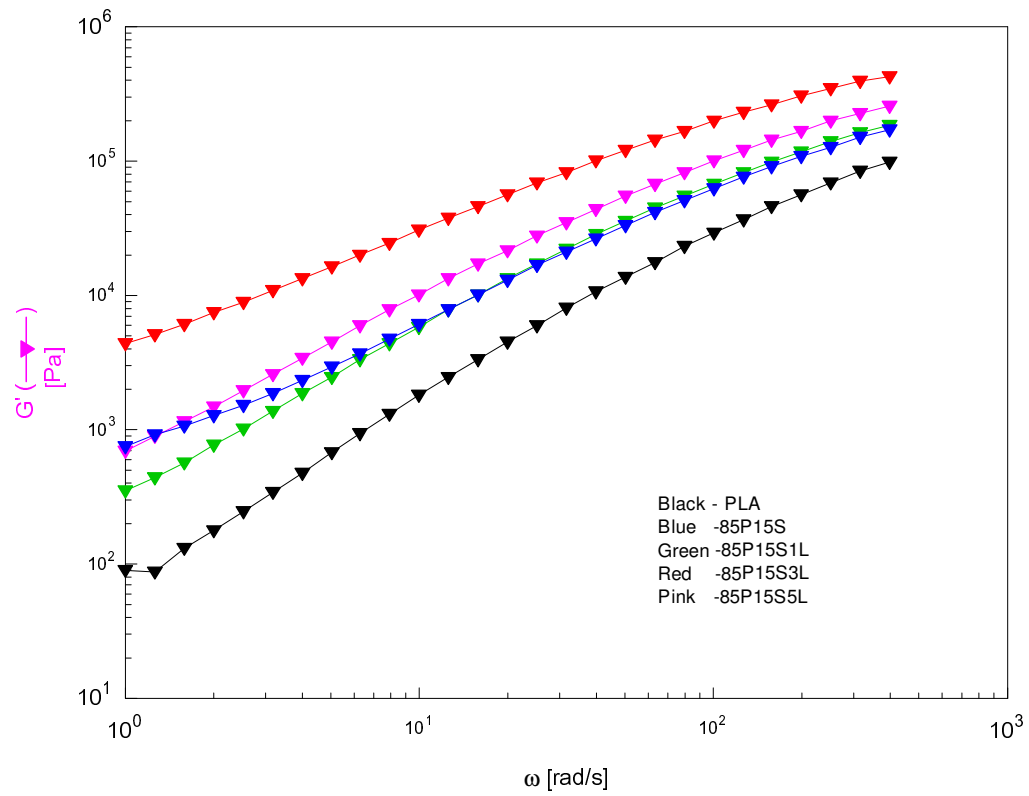


Figure 7.12 Variation of storage modulus with different blend types at 180°C temperature

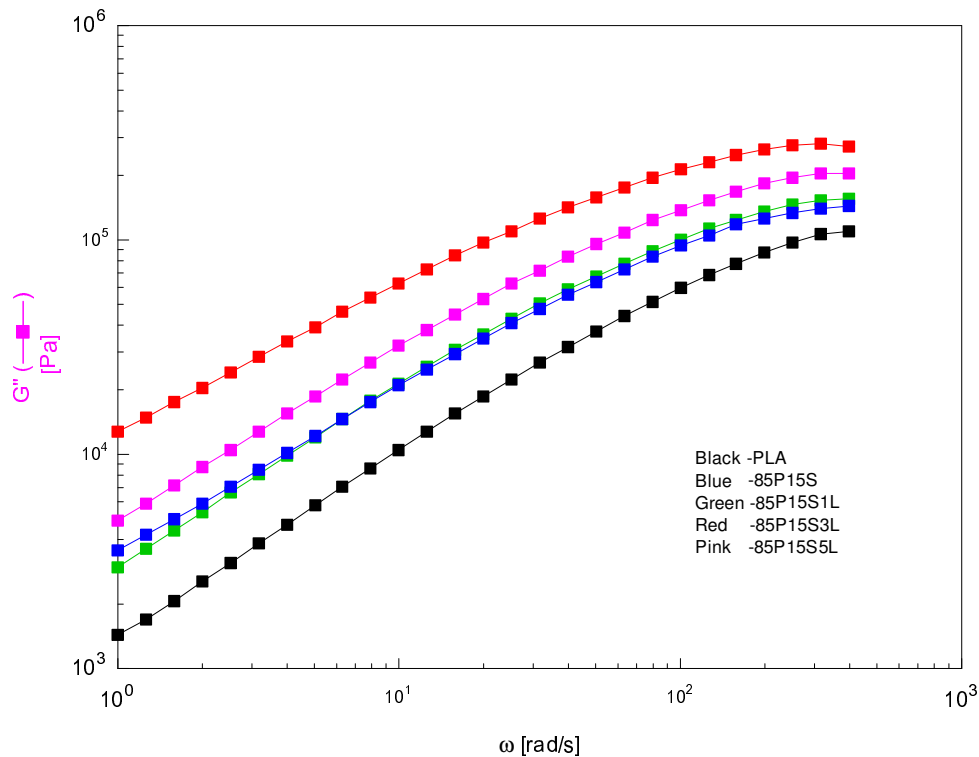


Figure 7.13 Variation of loss modulus with different blend types at 180⁰C temperature

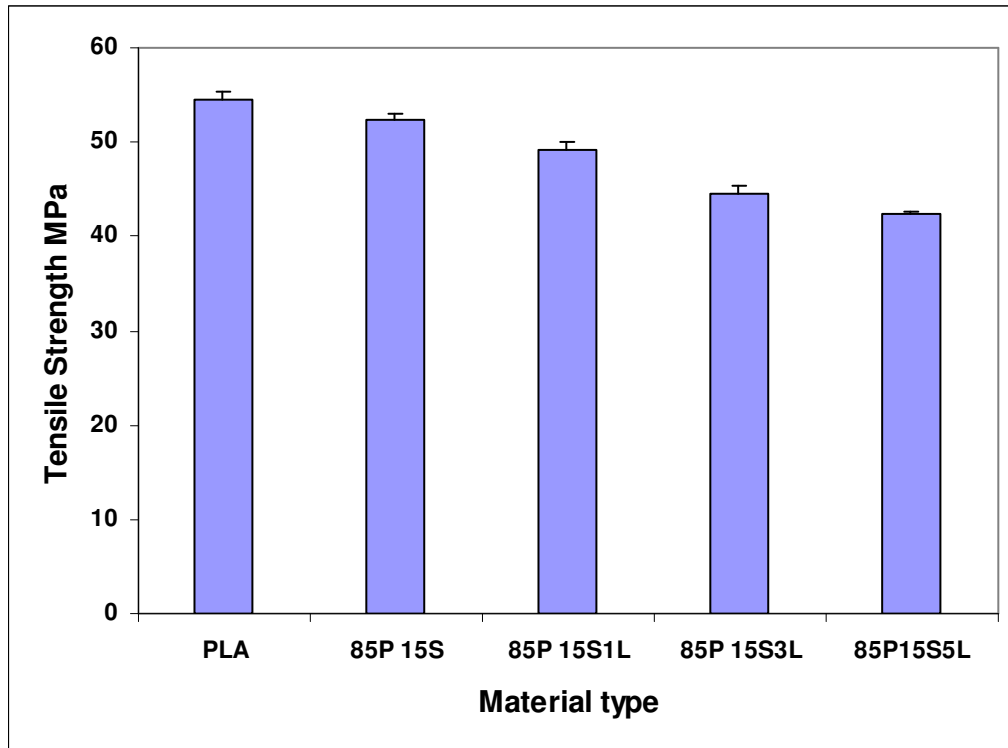
7.4 Measurements of Mechanical Properties

7.4.1 Stress- strain behaviour

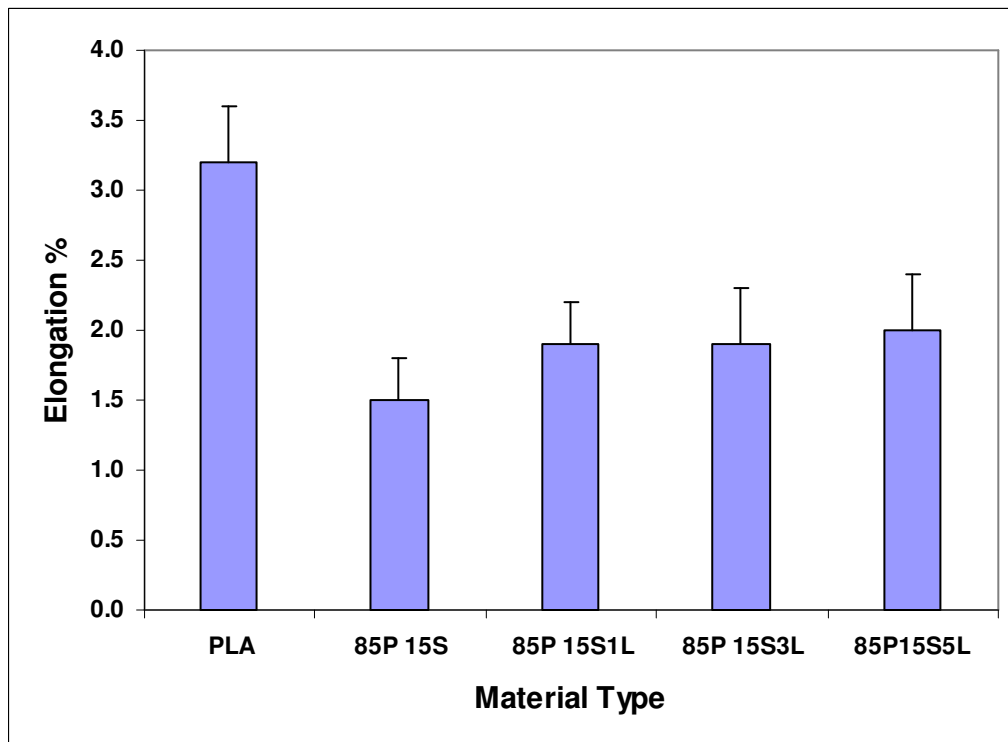
Latex is a stable colloidal dispersion of rubber with minor non rubber constituents such as long chain fatty acids and proteins, which actually provide stability to the latex medium (Silva & Walpalage, 2009) and the mechanical properties of the latex filled PLA/starch blends actually depend on many factors, among the most important ones are the extent of dispersion and interfacial strength.. The tensile measurements were performed on the latex dispersion filled blends and calculated by the average of 5 samples and the results are presented in figure 7.14. As shown by the results, the tensile strength of the blends

progressively decreased with the incorporation of starch and latex to the PLA matrix, but the strength remained at an attractive level with the latex. The elongation of pure PLA is notable although the starch/PLA blend has halved the elongation of the PLA. The latex has shown a positive effect towards the elongations at break of the PLA/wheat starch blend, showing around a 20% increase and the less brittle behaviour than the PLA/wheat starch alone, with the small implication with regard to the latex level. As reported by Wu *et al*, (Wu et al., 2004) the natural rubber exhibits an extremely high, more than 700 %, elongation at break. Therefore, it can be assumed from the results that the inherited rubbery nature of the colloidal dispersions of rubber particulates in latex would have contributed towards the increased elongation of PLA/starch/latex blends.

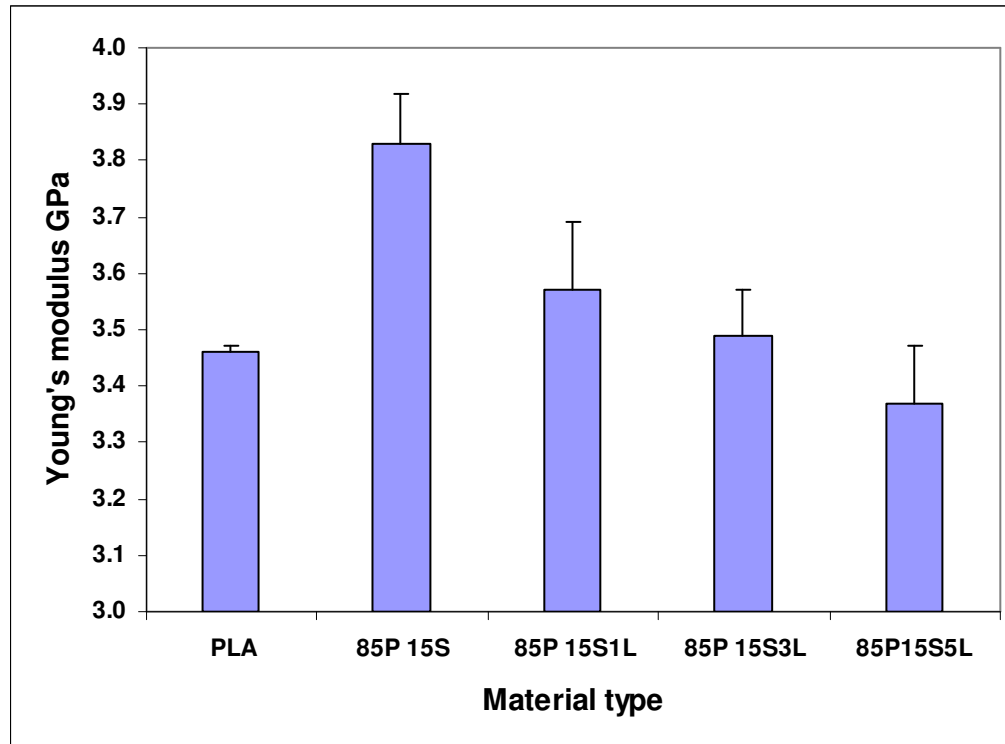
The Young's modulus of the PLA/starch illustrated in figure 7.14(c) clearly shows the double the modulus value of pure PLA. The 1% and 3% latex addition to the blend had crucial effects, although all the latex levels in the blends have induced softening, as shown by the corresponding decrease in the Young's modulus. 1% latex had a less pronounced decrease, but subsequent addition further reduced the modulus. The 1% and 3% latex levels maintained a considerable modulus level above the modulus of pure PLA. It is noticed that the addition of latex to the starch and PLA blends has not revealed satisfactory improvements in terms of the blend properties. In the current study, starch, latex and PLA were directly blended to make the investigated blend. The polar surface, high melting point and large particle size of starch as well as PLA made it difficult to finely disperse the latex in the PLA and starch matrix. Therefore, the incorporation of latex with direct blending would have resulted in moderate properties. In a previous study, Wu et al (Wu et al., 2004) also reported that the direct blending of starch and rubber could result in deterioration of the mechanical properties of vulcanizates. Furthermore, it can be suggested that the higher shearing action and temperature during the extrusion destroyed the stability of the latex dispersion leading to the coagulated latex, which has hindered its potential to improve the blend properties. This suggestion can be supported by the mechanical stability of latex reported elsewhere (Pendle, T.D. and Gorton, A.D.T., 1978).



(a)



(b)



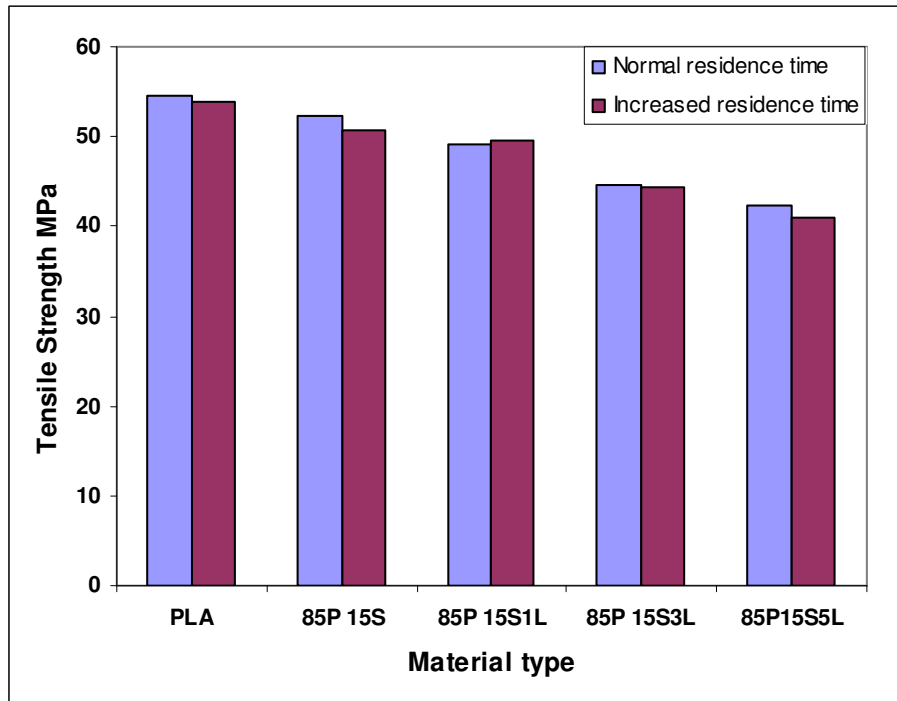
(c)

Figure 7.14 The variation of tensile properties of pure PLA, PLA/Starch blend, PLA/starch blend with different latex levels (a) Tensile strength (b) Elongation, and (c) Young's modulus.

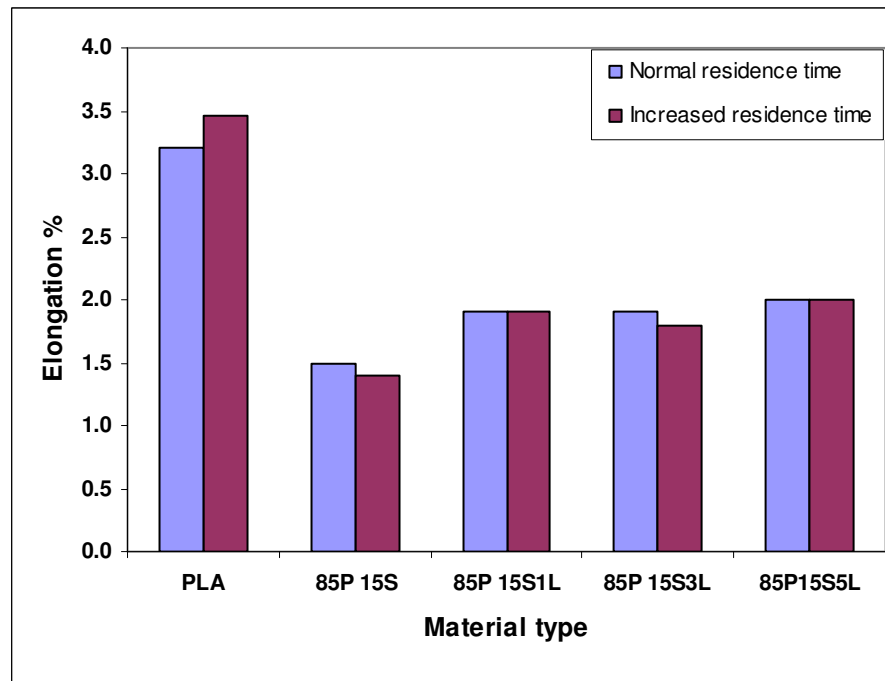
7.4.2 Measurements of increased residence time

The measurements of tensile properties of the same blends were also performed after the material was subjected to an increased residence time in the injection moulding machine. Moulding of the dumbbell specimens were carried out by increasing the cycle time of the injection moulding by 1 ½ times the normal cycle time of the moulding process as explained in chapter 3, section 3.5.1. The average results of the stress-strain behaviour of 5 samples were plotted against material type and compared with normal residence time as shown in figure 7.15. The tensile strengths of the materials after exposing them to processing temperatures at longer times exhibited no significant failure. The elongation of the blends decreased or remained the same although the increased in the PLA as can be seen in figure 7.15(b). However, Young's moduli have increased in almost all blends and in PLA with the higher proportion of the increment in the blends with latex as illustrated by

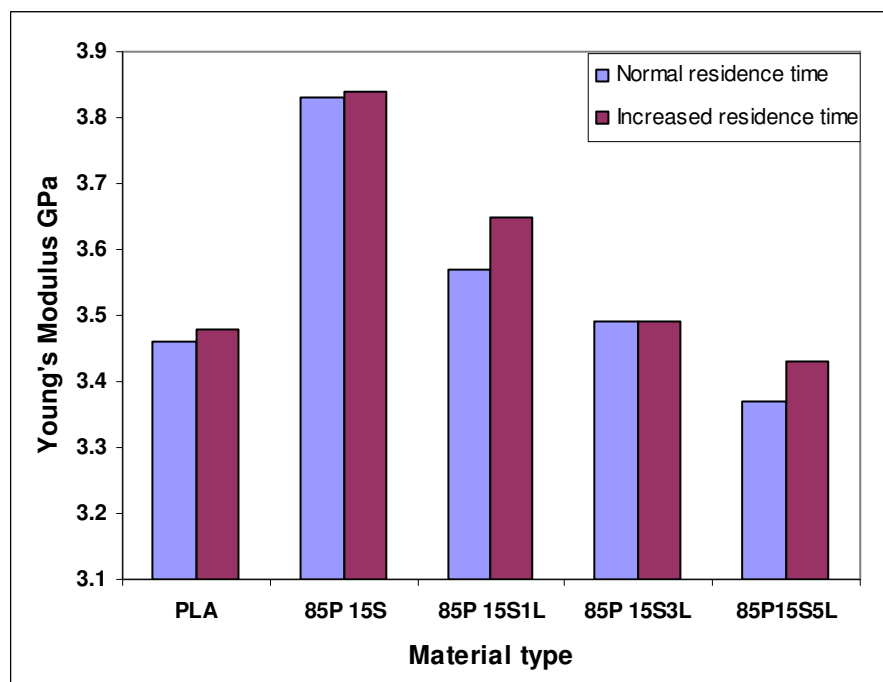
figure 7.15(c). During the longer exposure to heat, latex can undergo crosslinking resulting in higher stiffness in the blend, and this would have contributed to the high modulus for the corresponding longer exposed blends with latex.



(a)



(b)



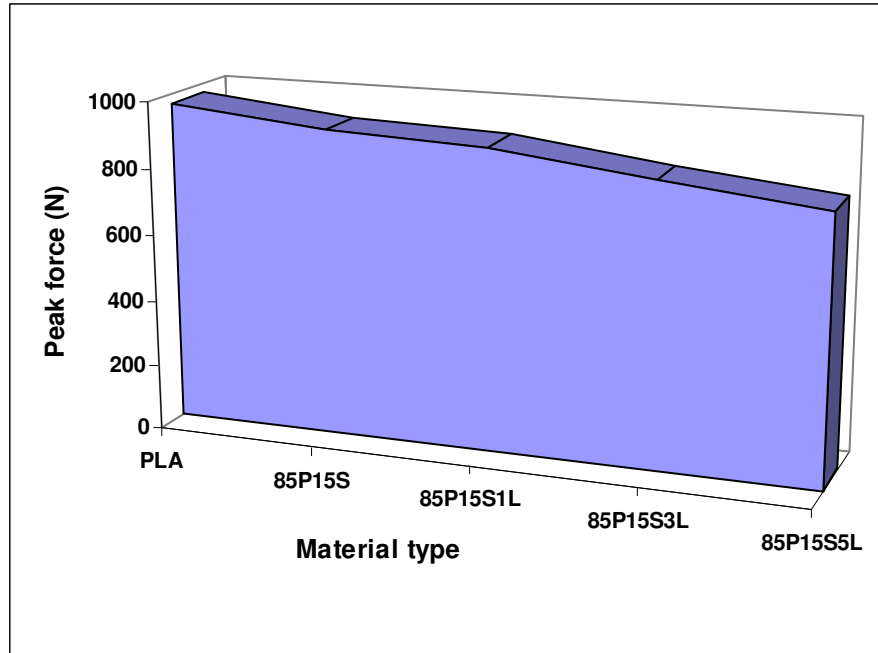
(c)

Figure 7.15 The variation of tensile properties of pure PLA, PLA/starch blend, PLA/starch blend with different latex levels for an increased residence time during injection moulding (a) Tensile strength (b) Elongation, and (c) Young’s modulus.

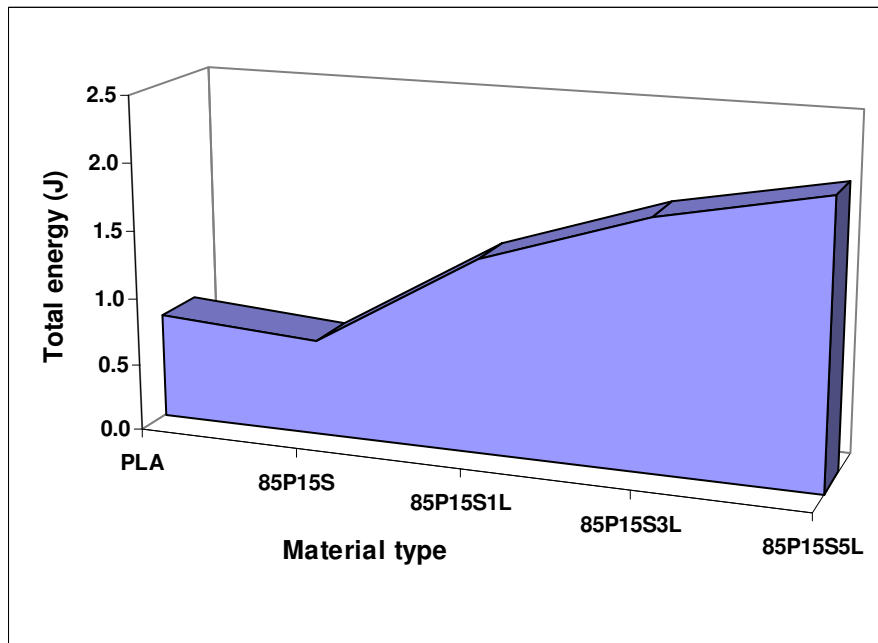
7.4.3 Measurements of instrumented drop weight technique

This advanced and most modern technique of measuring impact behaviour of a polymer is performed under a wide range of variables such as energy, temperature and impact velocity. The method provides complete details of the impact event, from the initial contact to the final failure of the test specimen, monitoring the relative force vs time curve on its data acquisition system. Results of the technique performed on the blends with latex under a constant impact velocity were plotted by taking the average of six samples. The figures 7.16(a) (b) and (c) respectively show the relative force, total energy and deformation of the blends plotted against the material type. The peak force of all blends gradually decreased after starch and latex addition. Both the PLA and PLA/starch blend demonstrated the similar energy absorption, however, starch contributed to a reduced deformation in the PLA/starch blend as seen in the figure 7.16(c). In contrast, the amount of energy absorbed

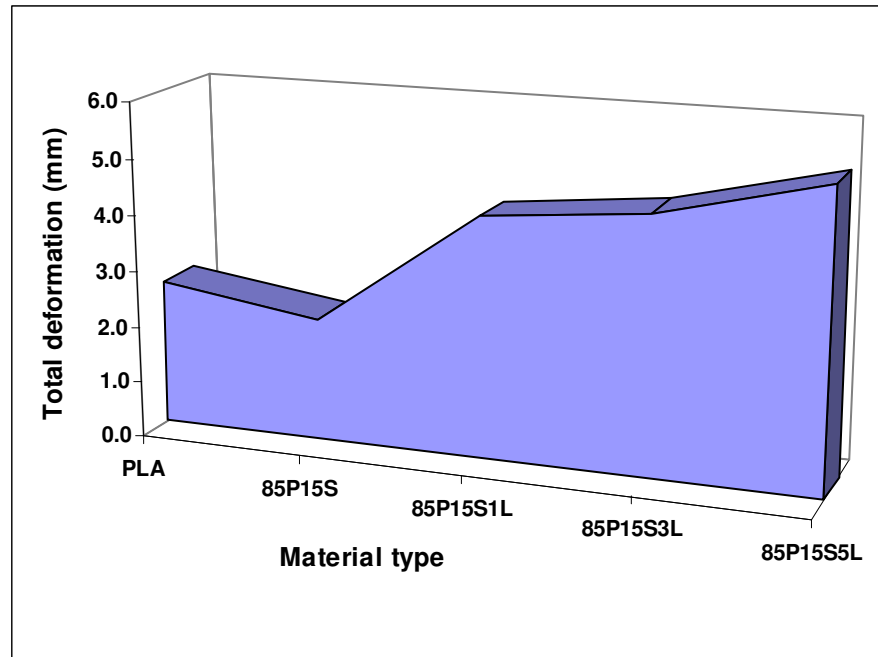
by the materials during fracture largely increased in the presence of latex and the blend materials show the highly increased deformation compared with PLA and PLA/starch.



(a)



(b)



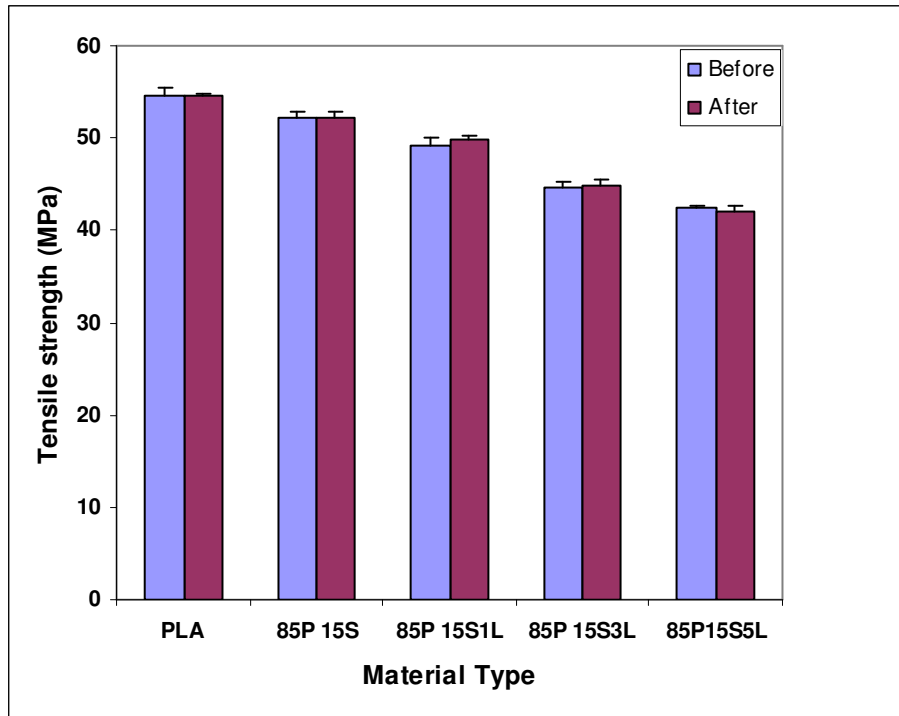
(c)

Figure 7.16 The variation of impact properties of pure PLA, PLA/starch blend, PLA/starch blend with different latex levels (a) Peak force (b) Total energy, and (c) Total deformation.

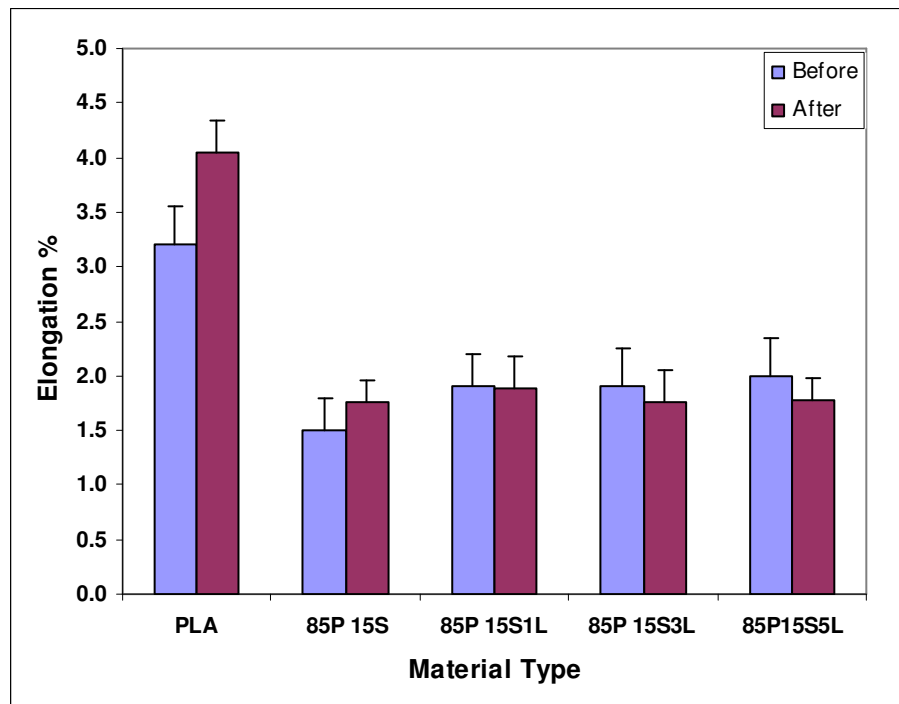
7.5 Effect of storage on mechanical properties

It is noteworthy that materials which exhibit remarkable mechanical properties could demonstrate a range of different properties depending on the time dependent phenomena called physical ageing. Physical ageing is an inherent characteristic of the amorphous phase of semi-crystalline polymers. The general notion of free volume which is actually not occupied by the polymer is usually associated with physical ageing. The aforementioned free volume of the polymer can influence physical and mechanical properties such as shrinking, brittleness and stiffness of the polymer (Hay, 1995; McGonigle et al., 2000). The effect of physical ageing on tensile properties and impact behaviour were investigated after 90 days storage and reported in this study as a comparison with the initial values. Figure 7.17 represents the measurements of the tensile strength, elongation and modulus of the aged and unaged samples as can be seen in (a), (b) and (c) respectively. The blends and PLA did not show significant changes in strength, nevertheless, the modulus decreased

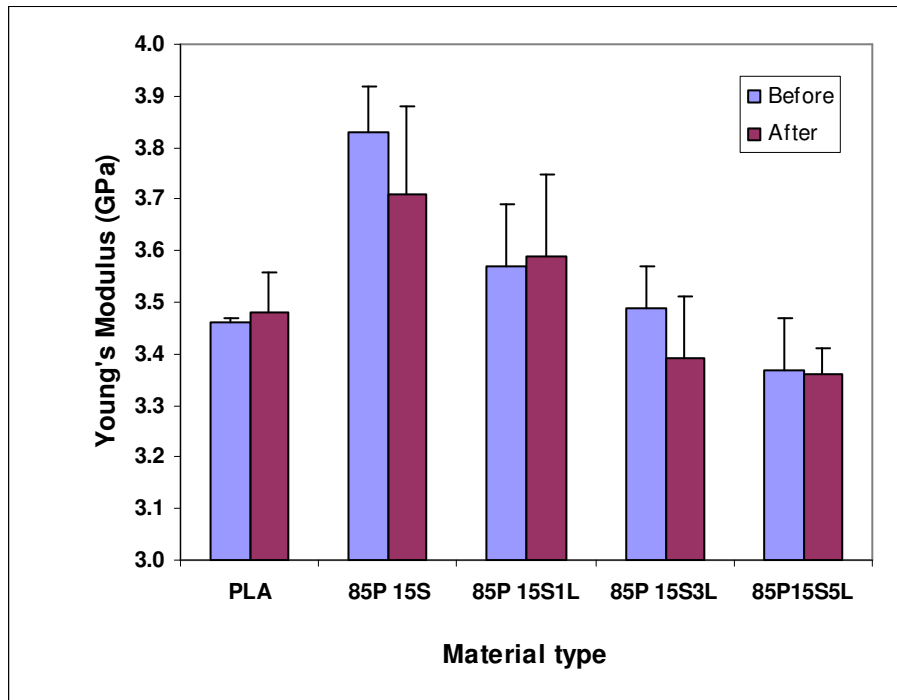
after 90 days storage. The elongation of PLA considerably increased, whereas the blends with latex remained the same or decreased.



(a)



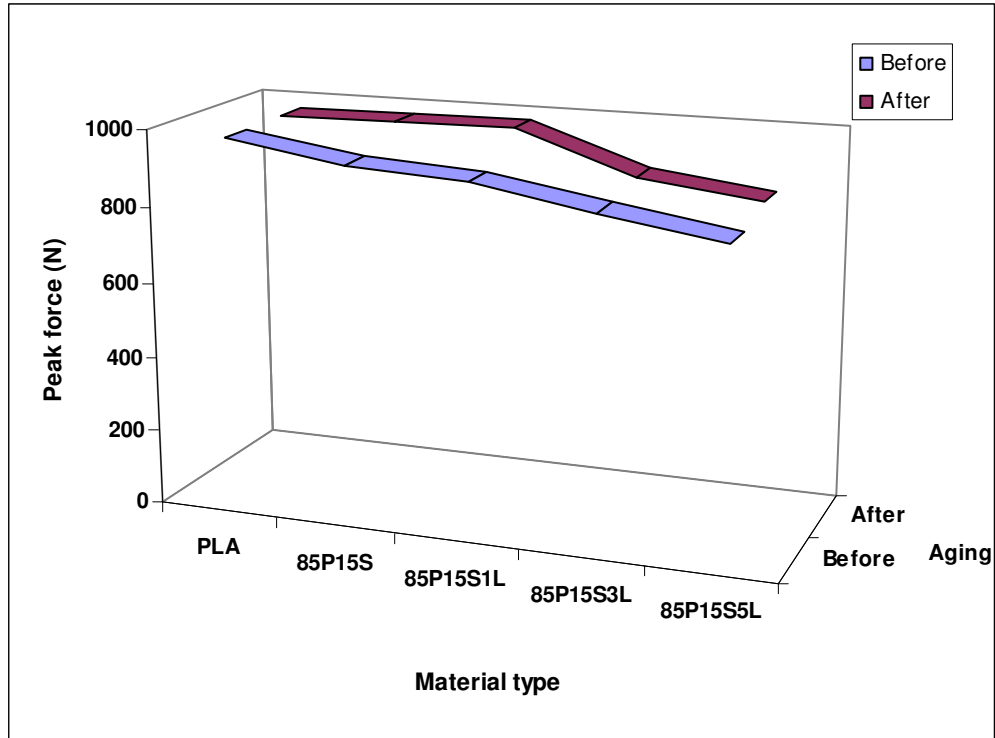
(b)



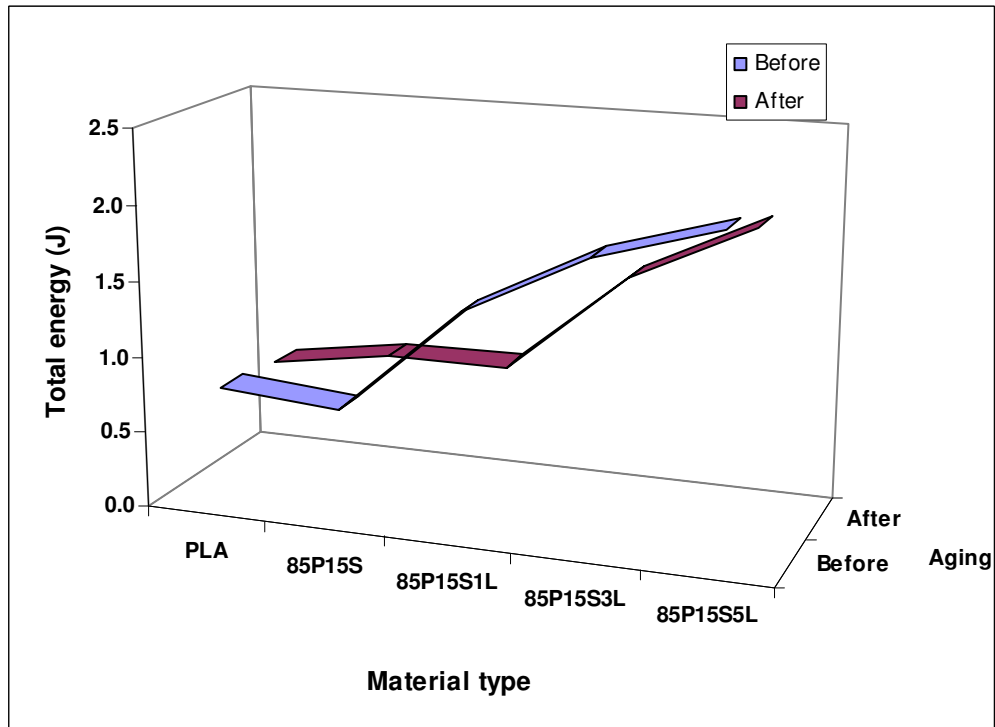
(c)

Figure 7.17 Comparison of tensile properties of pure PLA, PLA/starch blend, PLA/starch blend with different latex levels after 3 months aging (a) Tensile strength (b) Elongation, and (c) Young's modulus.

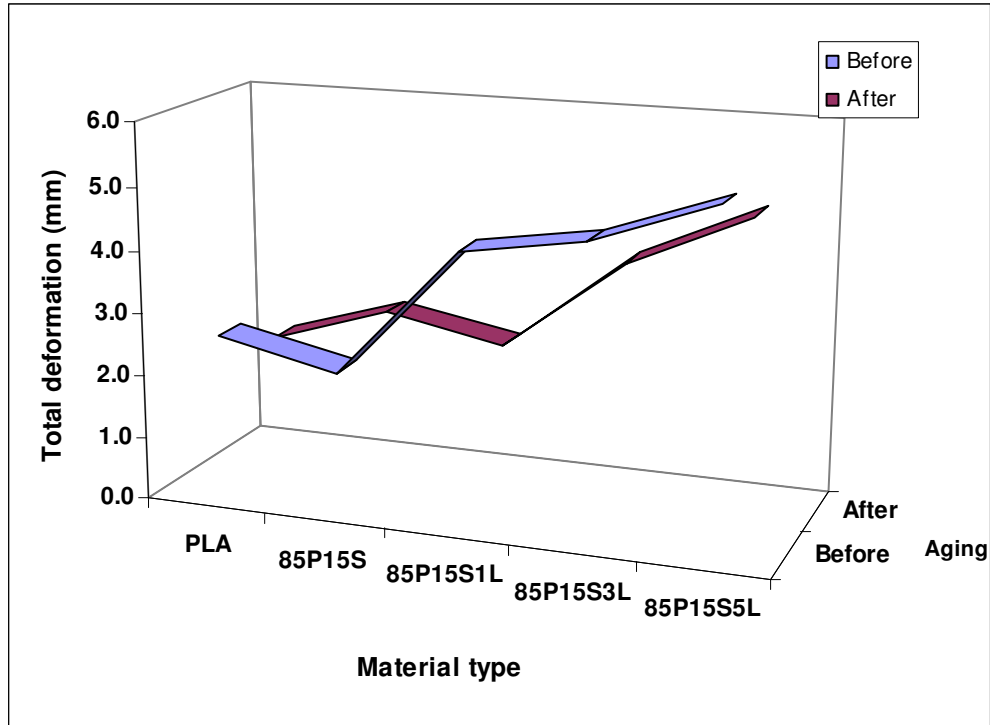
The effects of physical ageing on the impact properties were investigated after 3 months storage at 21⁰C and reported in this study as a comparison with the initial impact behaviour. Figures 7.18 (a) and (b) illustrate the measurements of the peak force and total energy respectively. Each graph represents a comparison of the properties of aged and unaged samples. The PLA and all blends revealed an enhanced peak force after 3 months. The highest peak force was attained by the blend with 1% latex. There could be a maximum latex limit between 1% and 3% that can give the highest peak force. The total energy absorption and deformation of the materials shown in figures 7. 18 (b) and (c) increase in the PLA and PLA/starch blends without latex but decrease in the blends with latex after 90 days storage.



(a)



(b)



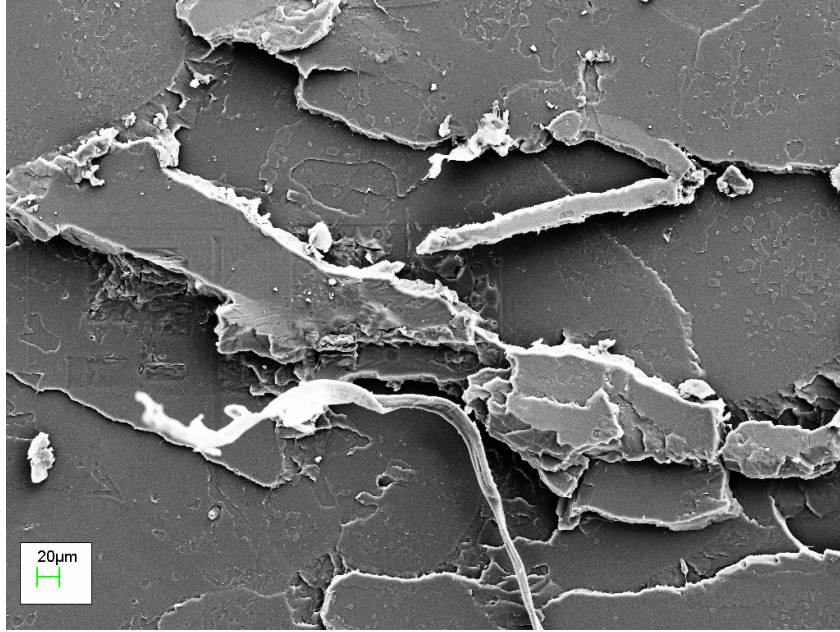
(c)

Figure 7.18 Comparison of impact properties of pure PLA, PLA/starch blend, PLA/starch blend with different latex levels after one year storage (a) Peak force (b) Total energy, and (c) Total deformation.

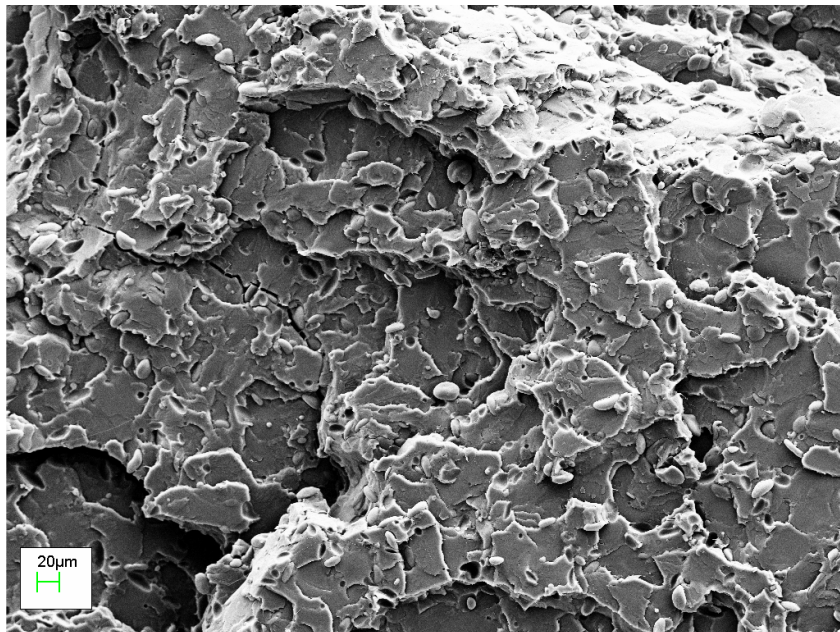
7.6 Analysing microstructure

Scanning electron microscopy provides important information of the materials that can be used to explain the morphology of the materials and their blends. Therefore, SEM micrographs were obtained of the tensile fracture surfaces of PLA (Figure 7.19 a), PLA/wheat starch blend (Figure 7.19 b) and PLA/wheat starch /latex blends (Figure 7.19 c, d, e). The fractured surface of the PLA was smooth but the PLA/starch/latex was rough and undulated similar to the characteristic of a rough fracture. In the PLA/starch blend, two phases can be seen, some starch granules were pulled out and voids have been created as can be seen in the figure 7.19 (b). The observation is more prominent with 1% latex as a lot of aggregated granules and voids have been clearly formed (figure 7.19 (c)). Furthermore, the size of the starch particles in the PLA/starch composite in the presence of 1% latex appears to be almost the same as that of the starch granules in the PLA/starch blend. The results reflects the fact that the shearing force exerted by the extrusion during blending is

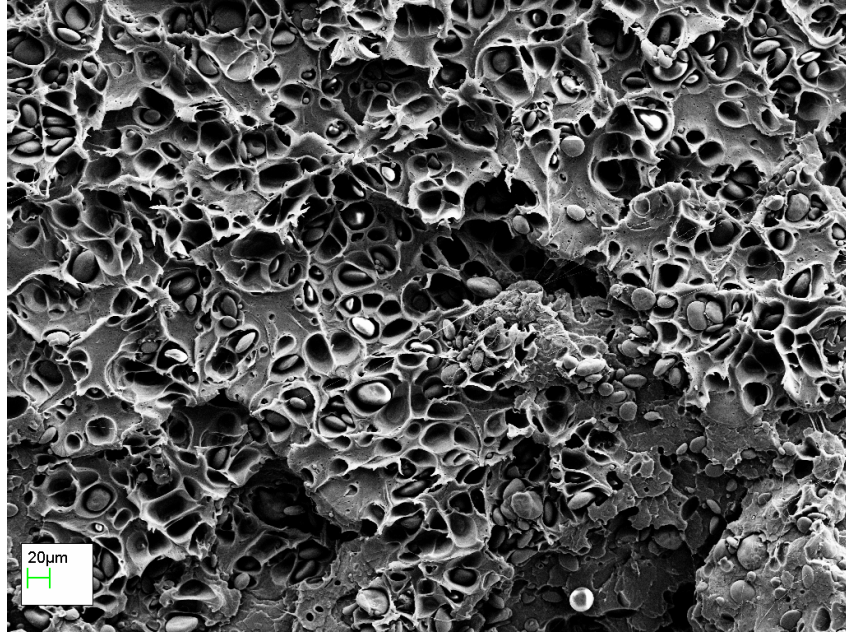
not adequate to break the starch particles, due to the large number of hydrogen bonds and high cohesion energy. This observation suggests that the direct blending protocol of starch and latex which was employed in the current study was unsuccessful and did not lead to a fine dispersion. Additionally, some apparent voids with a similar size as the starch particles are left on the fracture surface of the composites (figure 7.19c and), which also suggests that the interfacial interaction between the starch and latex is weak. A micro-composite with large, dispersed particles, that resulted in a significant separation was reported elsewhere (Wu et al., 2004) with direct blended starch and rubber. Nonetheless, some fibrous material was clearly observed at higher magnifications as shown in picture in figure 7.19(c'). Moreover, at higher latex levels, the granules were not distinguished and the starch could have gelatinized and lost its structure because of the moisture in the latex. A vital role is played by the distribution of water in the starch granule, which ultimately affects the starch properties. Wang and coauthors (Wang, Sun & Seib, 2002a) have reported that starch could be gelatinized even leading to a detectable T_g, which is undetectable for dried starch, and is readily observed at 28⁰C for 20% moisture in starch. The report is consistent with the results reported by Ke et al (Ke, Sun & Seib, 2003) on starch gelatinization in the presence of water. At latex levels above 1%, a larger proportion of other non rubber constituents in latex including water could have gelatinized starch. The smoother morphology in the SEM pictures shown in figure 7.19 (d) (e) could be caused by starch gelatinization. However, a starch continuous phase is difficult to discern with the latex where a starch granular form is still visible. The authors of a previous study on corn starch and natural rubber latex (Carvalho et al., 2003) have also reported the limitation of latex in the blend due to phase separation.



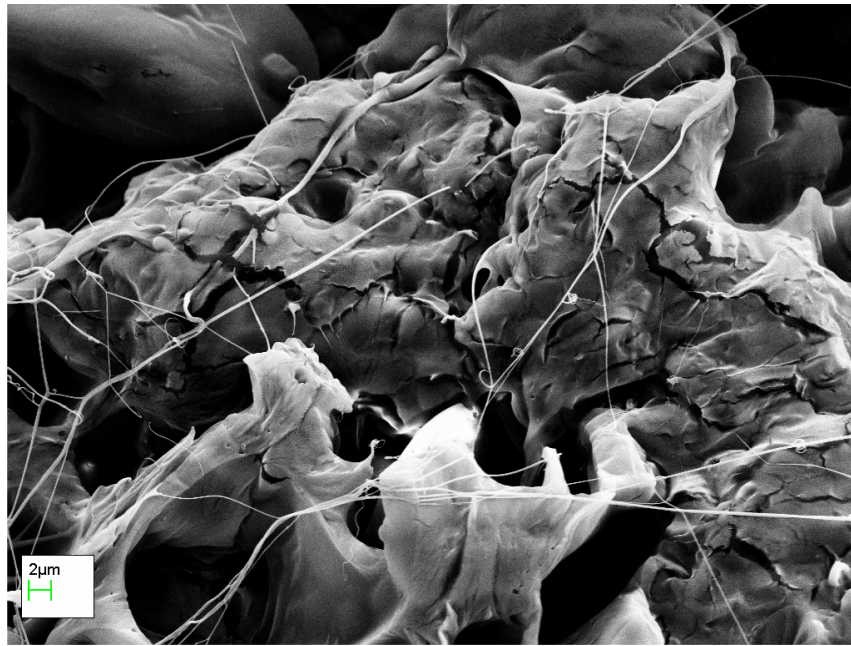
(a)



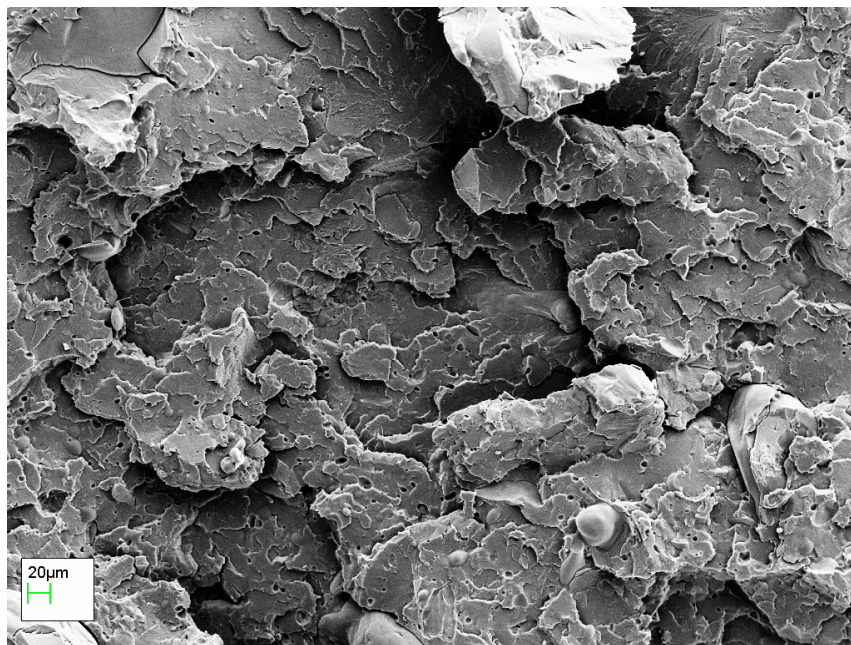
(b)



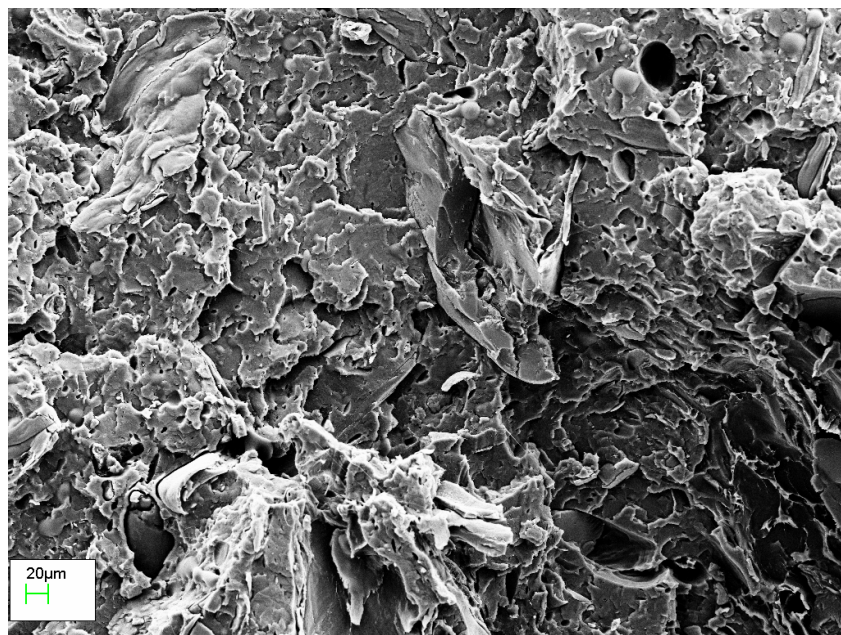
(c)



(c')



(d)



(e)

Figure 7. 19 SEM studies of pure PLA, PLA/starch blend, PLA/starch blend with different latex levels (a) PLA (b) 85P15S (c) 85P15S1L (d) 85P15S3L, and (e) 85P15S5L.

7.7 Vibration pattern

FTIR spectroscopy has become one of the most important tools for the characterization of polymers as it provides qualitative and quantitative structural details of polymers such as their chemical nature, steric order, physical arrangement, intermolecular forces, lamellar thickness, orientation etc. Interpretation of the technique is based on the concept of the energy of the molecules. The energy of a molecule can be separated into various contributions and is represented by

$$E = E_{el} + E_{Vib} + E_{rot}$$

E_{el} = motion of electrons

E_{Vib} = vibration of the atoms and atomic groups

E_{rot} = rotation of entire molecule

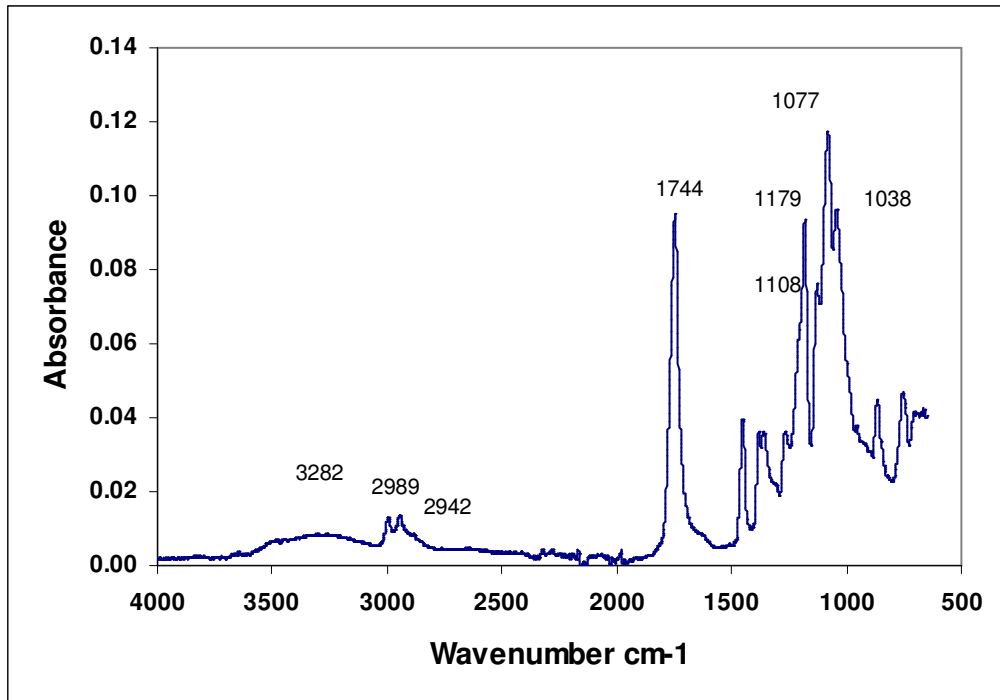
The energies of these motions differ considerably in the order of $E_{el} > E_{Vib} > E_{rot}$ ((Siesler & Holland-Moritz, 1980). A molecule can interact with electromagnetic radiation when the Bohr's frequency relation $\Delta E = h\nu$ is fulfilled, where

ΔE = Energy difference between two levels

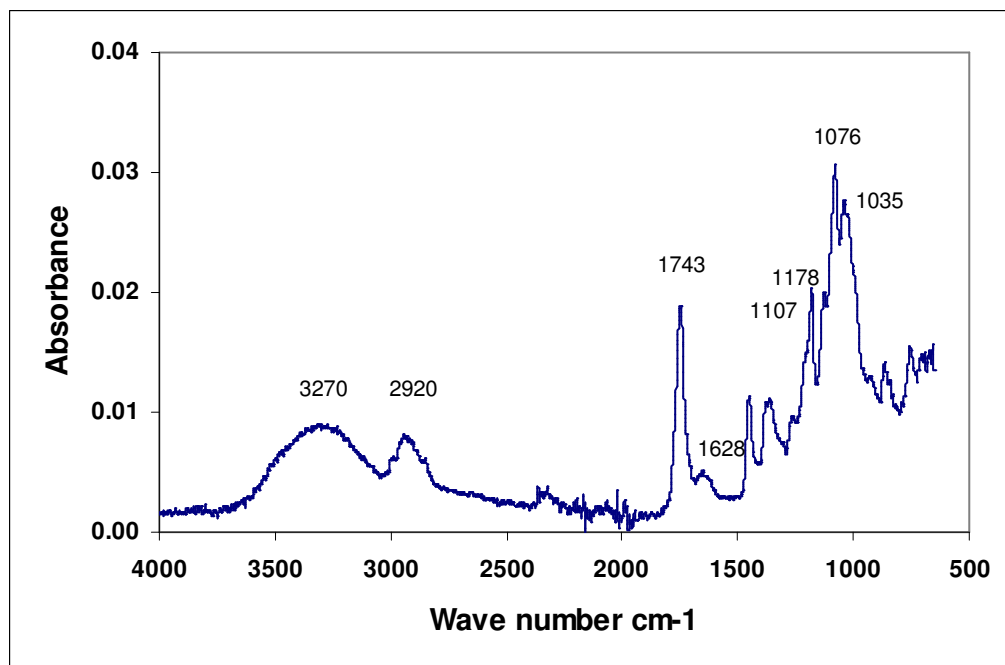
h = Planck's constant

ν = frequency of the absorbed radiation

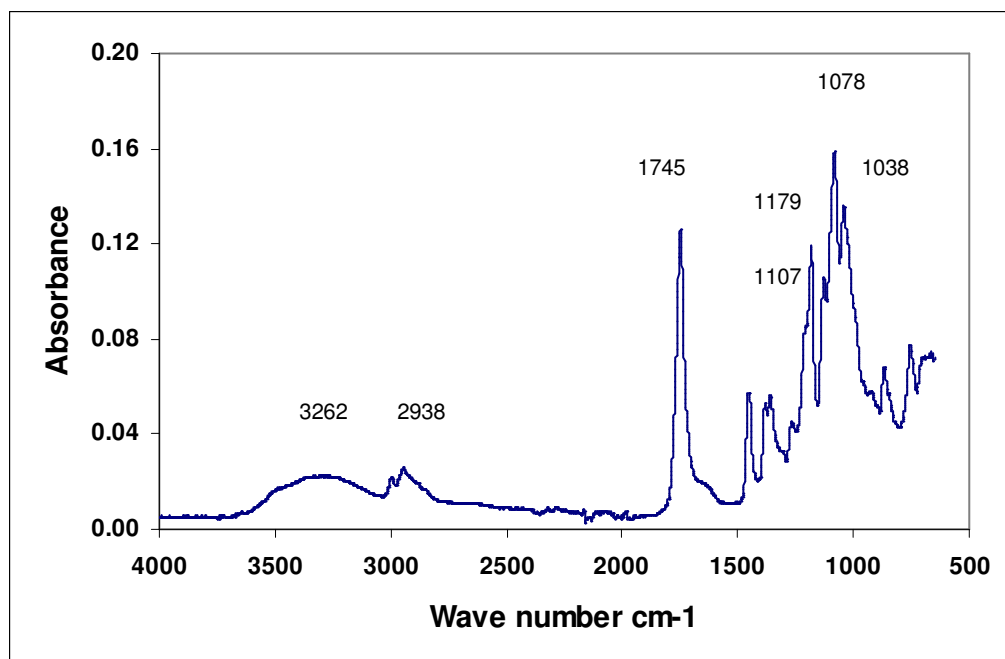
Similar to polymers, the technique can also be used for polymer blends to identify their interactions of the components and provide information about the behavior of the polymer blends. Therefore, FTIR spectroscopy measurements were conducted on the PLA/starch blends in the presence of latex. Figure 7.20 presents the FTIR spectra obtained for PLA starch blends with latex as a function of the latex concentration.



(a)



(b)



(c)

Figure 7. 20 FTIR spectroscopic analysis of PLA/starch blend with different latex concentrations.

The strong PLA carbonyl stretching absorption peak at about 1745 cm^{-1} has moved to a lower wavenumber after blending with starch and latex. The OH band shown at around 3490 cm^{-1} for PLA has clearly changed to a broader band which is typically shown between 3000 and 3500 cm^{-1} (Park et al., 2000) for all the blends. Furthermore, this OH band has shifted to lower wave numbers in the presence of latex. Moreover, a clear doublet after the OH peak in the PLA has adjoined with a broad OH peak of the PLA/wheat starch blend, which is observed at 2989 and 2942 cm^{-1} . The doublet has turned into a triplet with the highest peak wavenumber changing to 2920 cm^{-1} for blend with 3% latex, and 2938 cm^{-1} to blend with 5% latex. It is also noticeable that there is a shoulder peak appearing around 1628 cm^{-1} after strong carbonyl peak in the blends with 3% and 5% latex. Even though there are some peak shifts in the FTIR spectra, some of the shifts in particular, for example the carbonyl group shift is very small, and the most noticeable changes are seen in the OH groups. It can be inferred from the observed results that there is little interaction within the polymers in the investigated blends.

7.8 Chapter summary

PLA and wheat starch blends were prepared with natural rubber latex, and the decomposition and thermal behaviour, flow behaviour, tensile and impact properties, microstructure, infrared spectra were analysed. In general, the latex has shown some positive effects in the PLA/ starch blends, however, weak interactions were exhibited in the total tri-blend system. A lack of a fine dispersion of the latex in the blend has had a negative effect on the properties. Moreover, other constituents in the natural latex medium, in particular water, have affected the ultimate blend properties. Therefore, further investigations need to be carried out with latex, such that latex needs to be brought to a more dehydrated state before mixing with the blend. On the other hand, the mixing mechanism, indeed, needs to be improved before any critical conclusion can be made on latex. Nonetheless, the natural rubber latex, utilized within the scope of the current study showed attractive properties to the blend system. But, due to some practical limitations, further studies have not been carried out with latex in this research. Instead, the investigation was concentrated on the use of an aliphatic acid with the PLA/wheat starch blends. Adipic acid integrated with a blend of PLA and starch was carried out followed by the property investigation. The results of the study are explored and presented next in chapter 8.

CHAPTER EIGHT

***RESULTS AND DISCUSSION
OF THE INVESTIGATION
WITH ADIPIC ACID***

8 The effect of adipic acid on the properties of PLA and wheat starch blends

This chapter is mainly focused on the discussion of the formulated results of the experimental work carried out according to the description given in chapter 3, on the blends prepared and listed in table 3.6, for the investigation of the impact of adipic acid on the properties of PLA and wheat starch blends described in section 3.3.5. The adipic acid, which is also known as 1,6 hexanedioic acid, is an organic compound having molecular formula of $C_6H_{10}O_4$ with two active carboxylic acid functional groups at the two ends of the molecular chain. From the industrial perspective, adipic acid is the most important dicarboxylic acid, mainly as a precursor for the production of nylon. Apart from its' main use, it has been used in the medical industry and also as a flavour ingredient and gelling agent in the food industry. To consider how this compound affects a biodegradable polymer like PLA and its blends with starch, it was compounded with PLA and starch and the properties were investigated.

8.1 Investigation of thermal behaviour and stability

8.1.1 Thermogravimetric analysis

Biomaterials are very sensitive to temperature and therefore the stability during processing at elevated temperatures is technically very important. Figure 8.1 presents the thermograms of pure PLA, PLA/starch blend, PLA/starch blends with different adipic acid concentrations in an air atmosphere. All the blends and pure the PLA were also studied using TGA in the N_2 atmosphere to investigate the effect of the atmospheric condition on the stability and the results are showed in figure 8.2. The weight loss measurements given in figure 8.1 indicate a firmly stable plateau for the PLA below $300^{\circ}C$, and the other blends show about a 1% weight loss around $200^{\circ}C$. The stability is then maintained up to $275^{\circ}C$ at which, considerable weight loss is observed. The initiation of the weight loss around $275^{\circ}C$ in the blends is undoubtedly due to the starch, which starts losing weight at this temperature as reported in the previous chapters. Nonetheless, there is no significant weight

loss observed in the starch or the additive at very early stages of heating. Although the blends have exhibited a small weight loss, the stability remains in an acceptable range. The influence of the inert atmosphere on the weight lost, shown in figure 8.2 illustrates a similar behaviour to the weight loss of the PLA, however, PLA/starch without AA exhibits a steady plateau up to 275⁰C. The loss of weight around 1-2% in the blends with AA is also evident, which has slightly accelerated upon increasing the AA concentration. These observations clearly demonstrate some impact of air atmosphere on the starch stability.

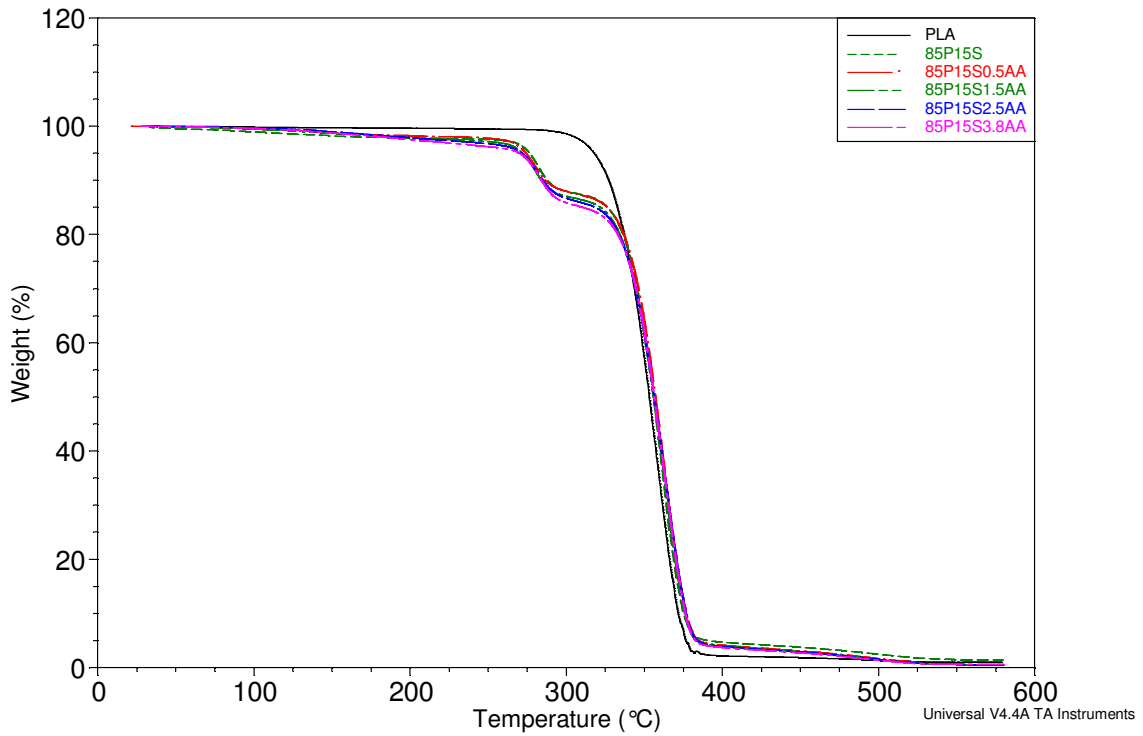


Figure 8.1 TGA thermograms of the pure PLA, PLA/starch blend, PLA/starch blends with different adipic acid concentrations in air.

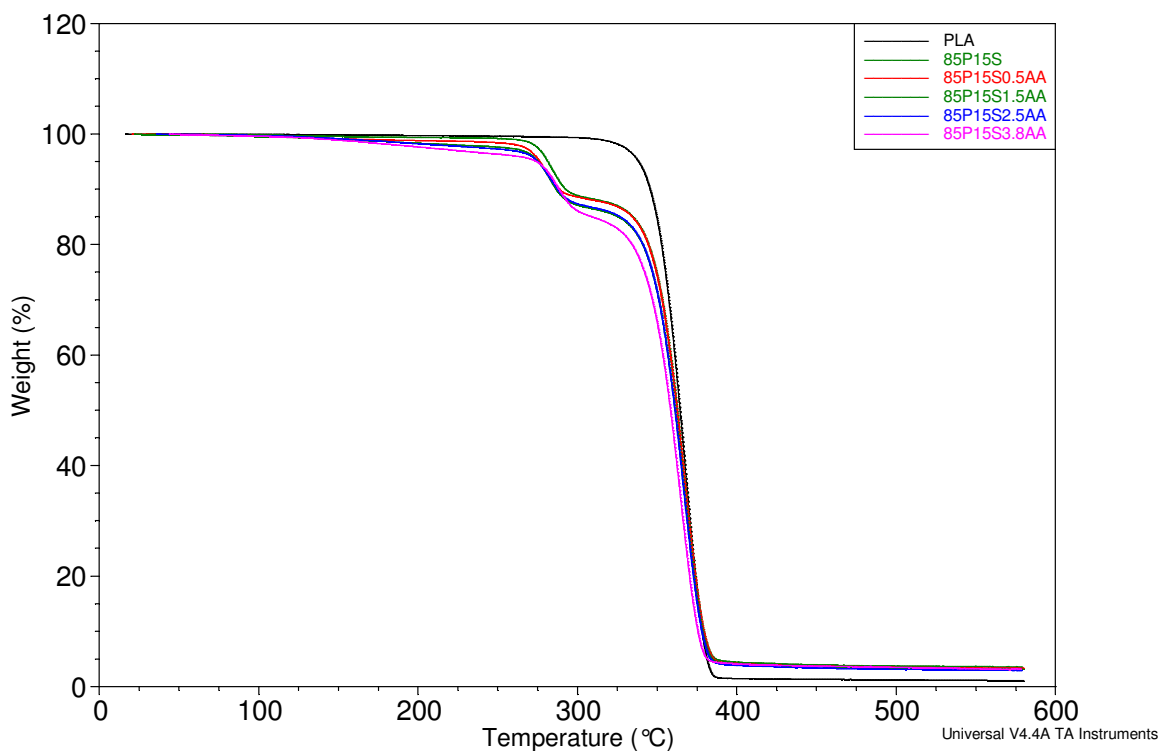


Figure 8.2 TGA thermograms of the pure PLA, PLA/Starch blend, PLA/starch blends with different adipic acid concentrations in N₂ atmosphere without an isotherm.

The stability of the material upon the extended residence time in a processing barrel due to unexpected difficulties during actual processing is also crucial to note and to mitigate any weight loss due to these reasons. Such an assumption was made during the TGA investigation by having an isotherm at 180⁰C for 30 minutes and the weight loss was observed. Figure 8.3 demonstrates the TGA thermograms of the pure PLA, PLA/starch blends with and without AA obtained at an isotherm of 180⁰C for 30 minutes. These results demonstrate a small weight loss in the blends, around 2-3%, at the isothermal temperature and it is only noticeable at high AA concentrations. It is well known that AA can hydrolyse starch to produce short chain polymers that would have reduced the weight at lower temperatures than their expected degradation temperature. Nonetheless, this decrease is considerably low and one would have assumed that the materials remained in the acceptable range without any negative effect when the material was processed.

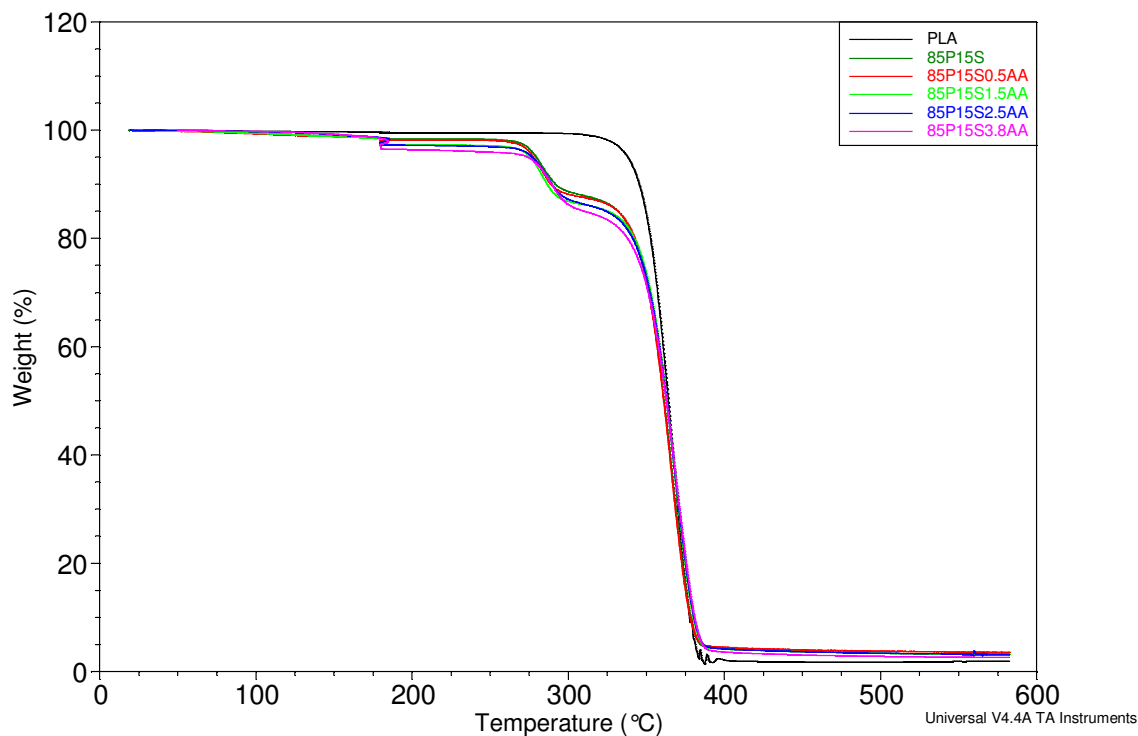
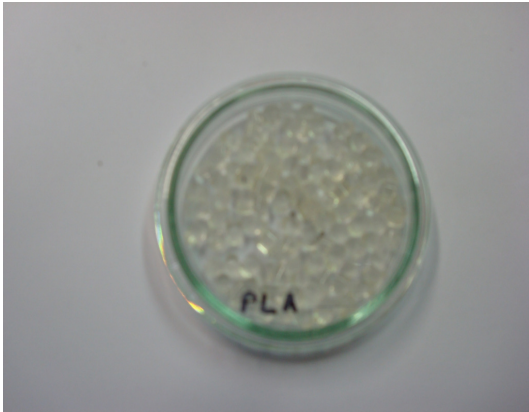


Figure 8.3 TGA thermograms of the pure PLA, PLA/Starch blend, PLA/starch blends with different adipic acid levels in N₂ atmosphere with an isotherm at 180⁰C for 30 minutes.

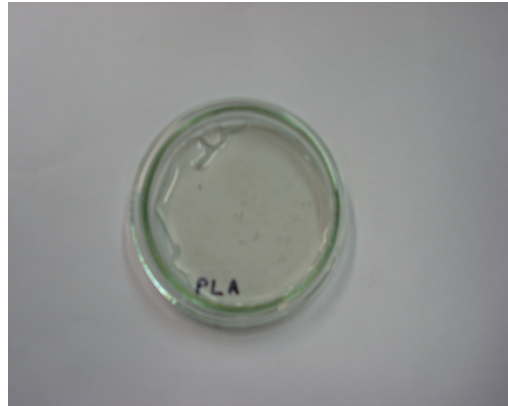
8.1.2 Observations of conventional oven heating

Given in figure 8.4 are the observations of pure PLA and formulated blends, before and after heat treatment, in a conventional air circulating oven, at 180⁰C for 30 minutes. Observations of the pictures in figure 8.4 appear to be an apparently clear melt for the pure PLA, and mostly opaque melts for other blends. The opaque colour imparted in the blends with starch and adipic acid during blend preparation has become prominent after heating at 180⁰C for 0.5 hour in a conventional oven. It is apparent that the colour of PLA/starch blend becomes more noticeable with increasing AA levels. However, from the odour

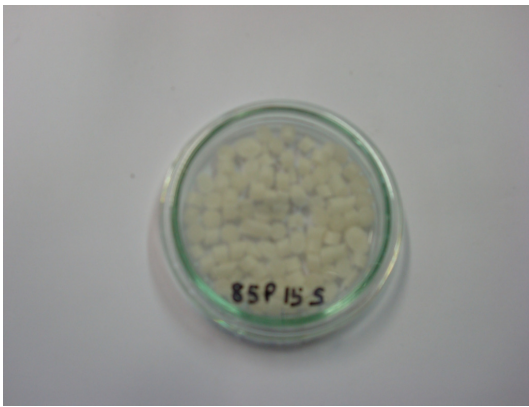
released and the appearance of the heated samples, it can be inferred that these samples appear to be not-degraded and exhibit their natural colours due to the hydrolysis of the starch by AA. These observations indicate that all the processed materials show no sign of degradation but chain scission is possible due to AA.



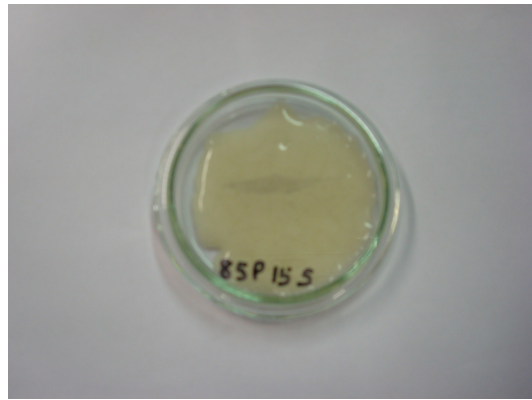
(A-Before)



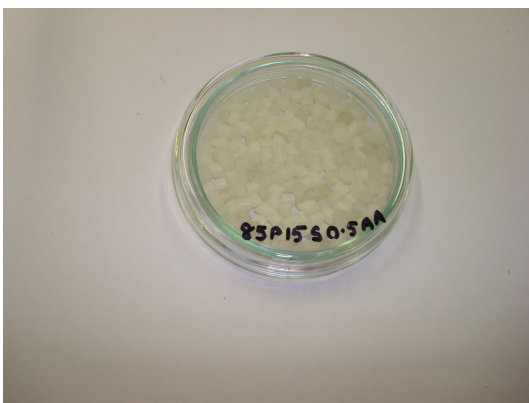
(A-After)



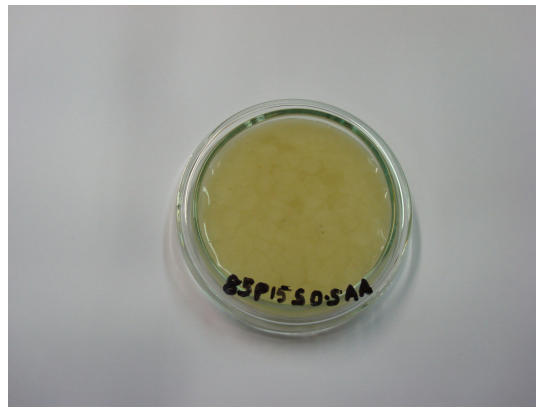
(B-Before)



(B-After)



(C-Before)



(C-After)



(D-Before)



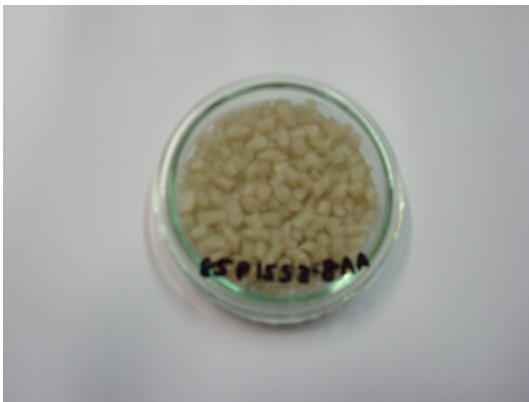
(D-After)



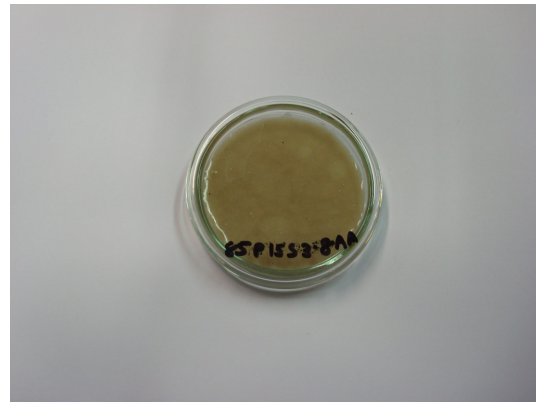
(E-Before)



(E-After)



(F-Before)

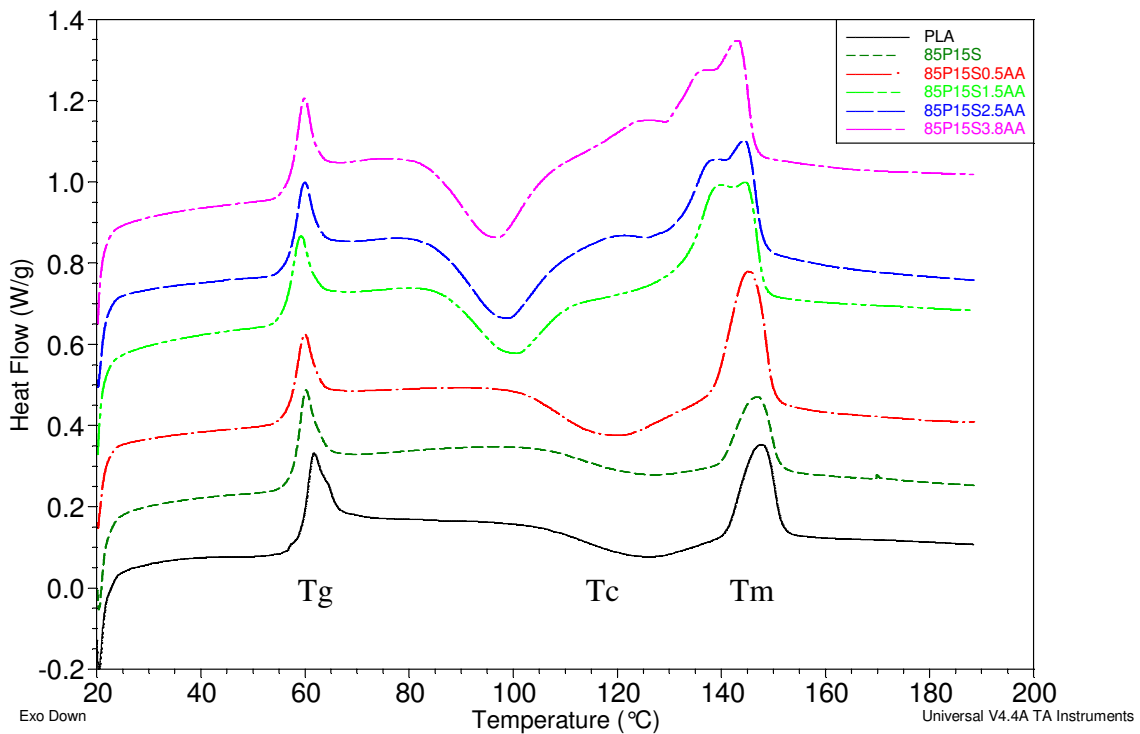


(F-After)

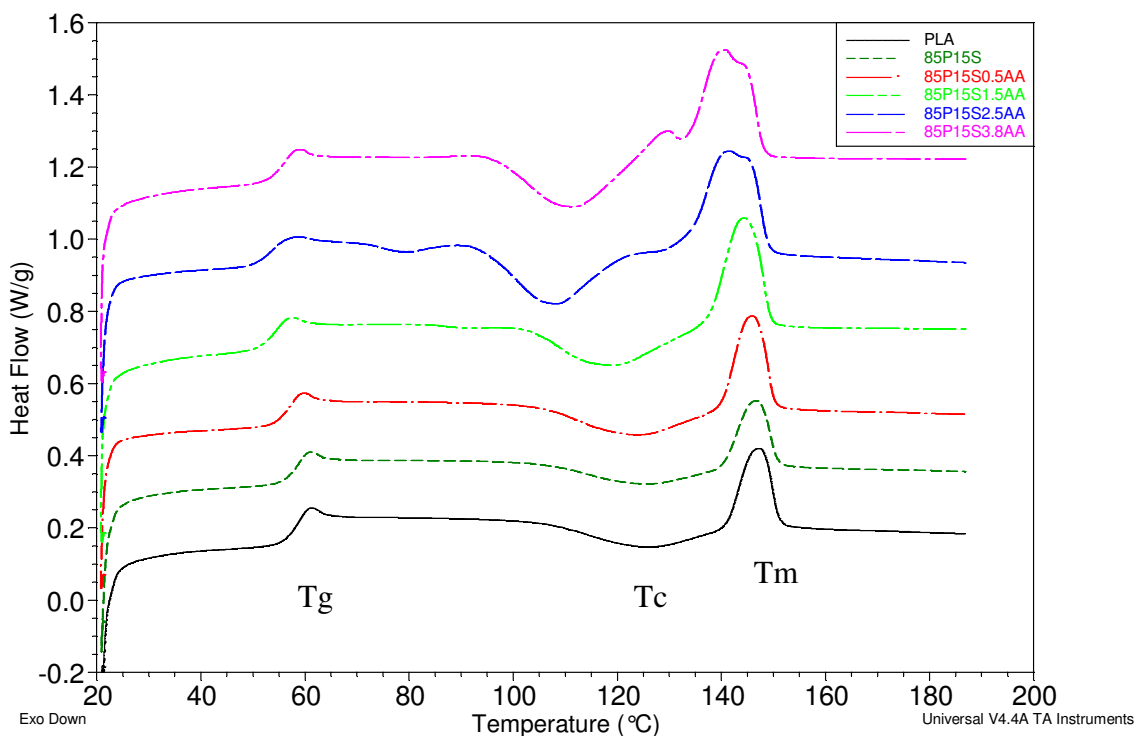
Figure 8.4 Observations of temperature sensitivity of the blends upon heating in a conventional oven at 180°C temperature for 30 minutes (A) PLA (B) 85P15S (C) 85P15S0.5AA (D) 85P15S1.5AA (E) 85P15S2.5AA (F) 85P15S3.8AA

8.1.3 Differential Scanning Calorimetry

The T_g , T_c and T_m are equally important for material processing as these temperatures demonstrate the phase transitions of a material and can be found by differential scanning calorimetry. The DSC measurements demonstrate the thermal behaviour of raw PLA and other prepared blends as given in figures 8.5 (a) and (b). The T_g and the enthalpy relaxation of the blends derived from figure 8.5 (a) are illustrated in figure 8.6. The first and the second heating cycles exemplified in figure 8.5 show a T_g at about 60°C and a temperature decrease accordingly with an increasing adipic acid concentration up to 1.5% in the blend. The AA level at and above 2.5% exhibits a slightly increasing trend in the T_g , as can be seen in figure 8.5.



(a)



(b)

Figure 8.5 Thermal behaviour of pure PLA, PLA/Starch blend, PLA/starch blend with different adipic acid concentrations (a) in the first cycle (b) in the second heating cycle of heat/cool/heat method.

The blends and the raw PLA show higher endothermic enthalpy recovery peaks around T_g in the DSC scans. An endothermic enthalpy relaxation near T_g is attributed to a secondary molecular reordering in the amorphous phase of the semicrystalline polymers (Niaounakis, Kontou & Xanthis, 2011). This is a time dependent process and known as the physical ageing of the material and relates with the free volume of the polymer. The enthalpy relaxation can vary with time because the mobility of large segments of polymer chains is controlled by the free volume of the polymer (Wang, Sun & Seib, 2003).

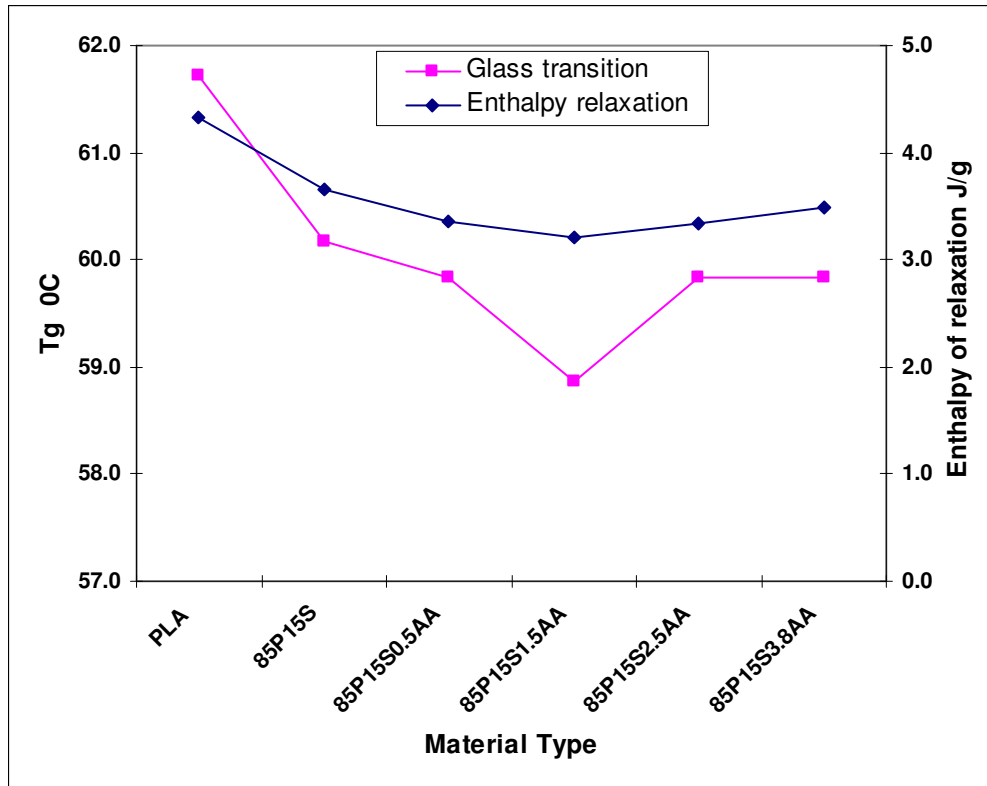


Figure 8.6 The glass transition temperature and excess enthalpy relaxation of PLA and blends

A broad peak around 125⁰C, assigned for the crystallisation of pure PLA also changed significantly in the presence of adipic acid in the blend. This change is not prominent at the 0.5% AA level, however a major change has occurred at the adipic acid \geq 1.5% levels. The melting temperature of about 145⁰C has also been altered and the shape of the peak is modified and split at the higher AA levels. In the second heating run, the transformations at all the temperatures of T_g , T_m and T_c has emerged similar to the first heating cycle, but no substantial endothermic peak shown at the T_g to indicate physical ageing of the blends. This investigation clearly demonstrates the thermal history of the materials.

8.2 Flow behaviour

The melt viscosity of materials under shear conditions has both scientific and commercial importance and therefore, the rheological properties of PLA and PLA/ starch blends with and without AA were measured by parallel plate rheometer tool. Figure 8.7 presents the viscosities of the PLA/starch blends with different AA levels and PLA/starch blend without AA. Figure 8.7 also presents the oscillatory measurements of pure PLA as a control, which exhibits a clear Newtonian behaviour. All the other blends also exhibit distinct Newtonian regions. It is noted that the dependence of viscosity on the shear rate of the PLA/starch blend without AA shows the highest zero viscosity, which is more than two fold greater compared to that of pure PLA. The AA has reduced the blend viscosity progressively and the 1.5AA blend viscosity is relatively close to the viscosity of the pure PLA. The blends with 2.5 AA and above, the oscillatory measurements show a significant decrease in the blend viscosities. It is important to point out that the higher molecular weight and larger polymer segments restrict the molecular mobility and hence influence the blend viscosity. The molecular weight of native starch is about 50×10^6 g/mol (Divers et al., 2004) and is comparatively 100 times higher than the molecular weight of most established polymers (Xie et al., 2007) and it has resulted in a high viscosity in the PLA/starch blend. However, the AA has clearly hydrolysed some of these bulky starch polymer chains to smaller chains thereby reducing the viscosity of the blends as clearly demonstrated in figure 8.7. The molecular weight reduction and the resultant low viscosity due to the hydrolysis of the polysaccharide chains (cleavage of ether moieties) catalysed by carboxylic acid was also reported by Carvalho and coworkers (Carvalho et al., 2005).

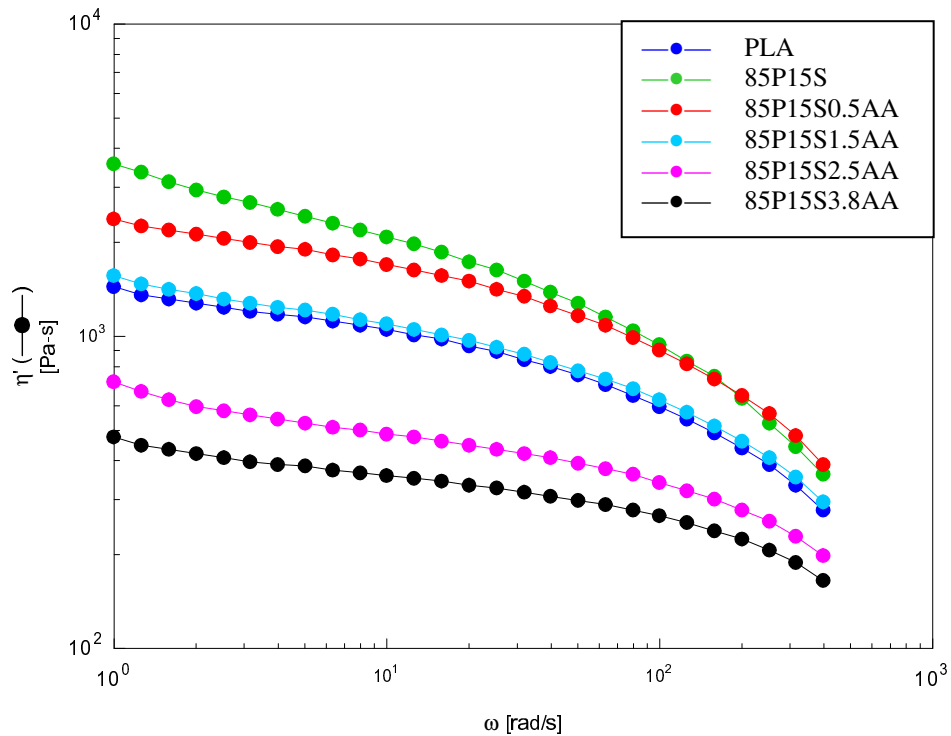


Figure 8.7 The viscosity of the different blends as a function of frequency at 180⁰C temperature

The storage modulus (G') and the loss modulus (G'') were also derived from the graphs and the results are presented in figures 8.8 and 8.9 respectively. According to the results, all the blends and the PLA tend to follow the same pattern of variation in the storage modulus and loss modulus upon the increasing frequency at 180⁰C. This is because, in the presence of an acid, most of the gelatinisation of starch proceeds at room temperature. The starch gelatinization in formic acid has also been reported at very low temperatures elsewhere (Divers et al., 2004). The blend with 3.8 AA has shown the lowest storage and loss moduli values, whereas the blend without an additive has shown the highest modulus value. The observation suggests that the PLA has higher energy absorption and heat dissipation than the blends. Similar to the viscosity, the pure PLA and PLA/starch blend with 1.5 AA showed relatively similar modulus properties. However, at 0.5AA level, the polymer chains become more independent as a result of destruction and therefore the slope is slightly larger

than the PLA/starch blend. Moreover, at the 1.5 AA level, the slope is slightly decreased and a further reduction in the slope of G' at higher adipic acid levels is evidence of a more cooperative behavior of the polymer chains resulting from their progressive loss of structure. However, at higher frequencies, all the blends deviate from the different behaviours and follow the same pattern. This corresponds to a flow behaviour in which the macromolecules are very mobile and have few interactions with each other at higher frequencies. It can also be concluded that the macromolecules exhibit a more independent behaviour due to chain scissions owing to the hydrolysis leading to a higher mobility at the higher temperature.

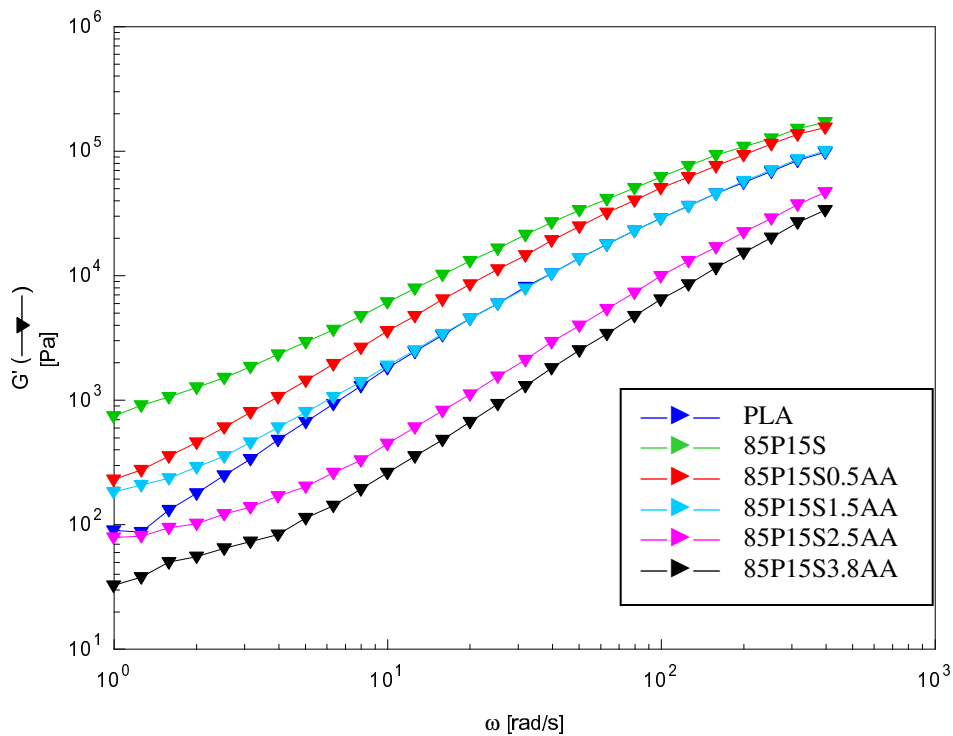


Figure 8.8 Variation of storage modulus of different blends as a function of frequency at 180°C temperature

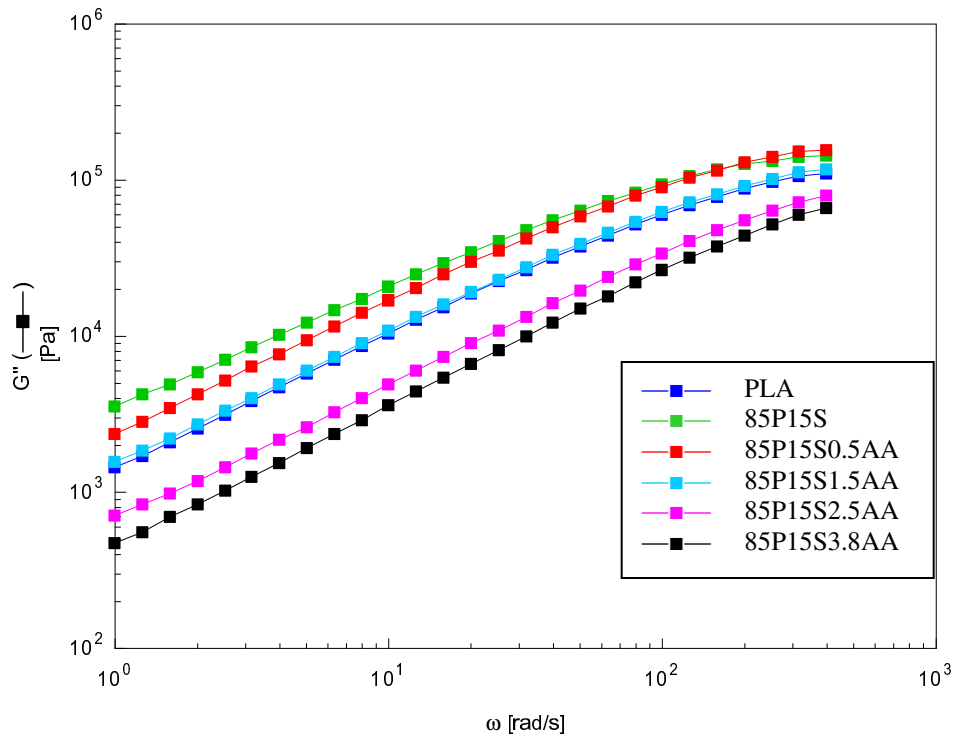


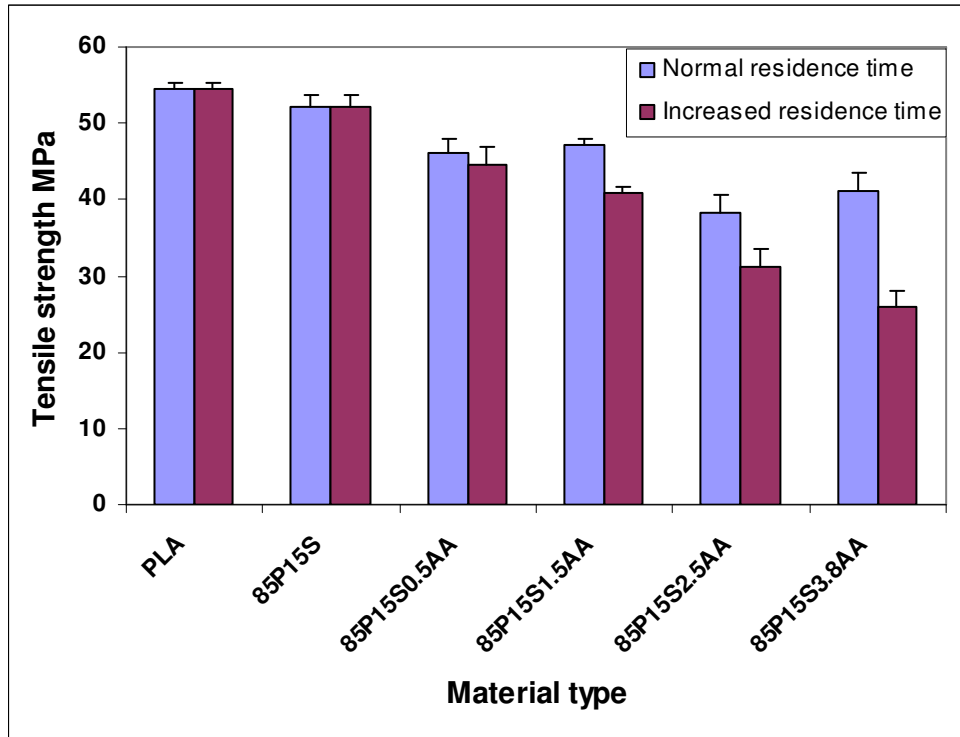
Figure 8.9 Variation of loss modulus of different blends as a function of frequency at 180°C temperature

8.3 Mechanical properties

8.3.1 Measurements of tensile properties of normal and increased residence time

Measurements of the tensile properties were performed and the average of 5 samples was calculated and the results are given in figure 8.10. The results in figure 8.10 also presents the tensile properties of the same blends after the pellets were subjected to an increased residence time in the injection moulding machine and defined as increased residence time. As can be seen by the results, the tensile strength of the blends in figure 8.10(a) progressively decreased with the incorporation of starch and AA at the normal residence time apart from the 85P15S1.5AA sample. These observations indicated that the reaction

responsible for the macromolecular fragmentation was not due to mechanical shearing, but, instead, to the action of the added carboxylic acid. However, the strength of the blends up to the 1.5AA level, maintained an encouraging high range.



(a)

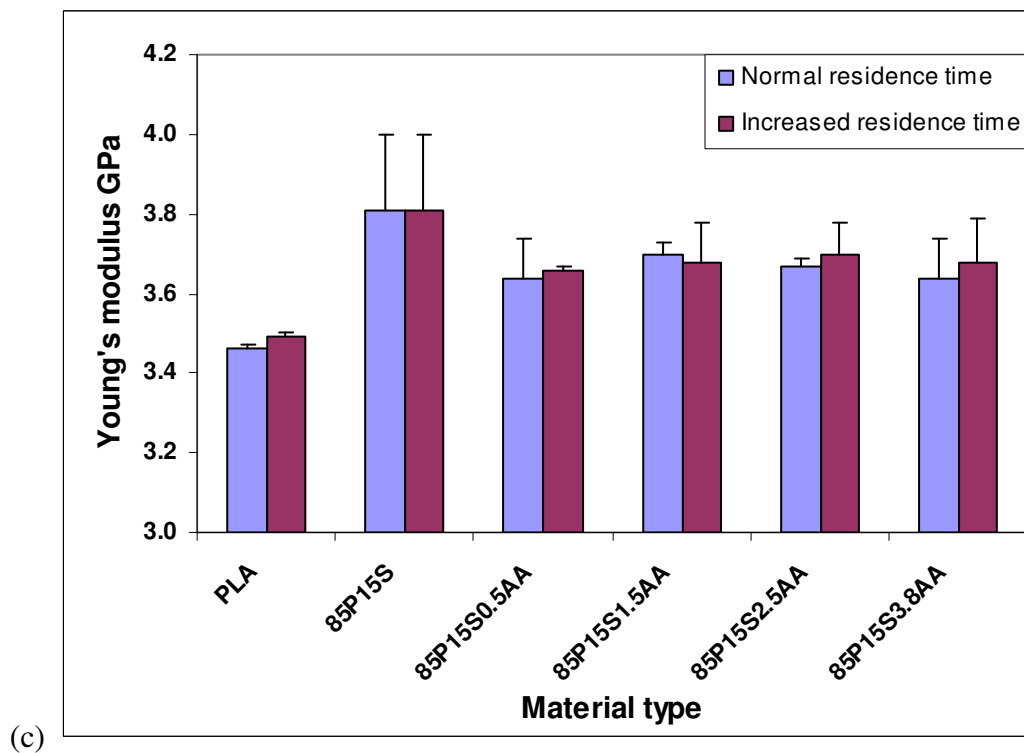
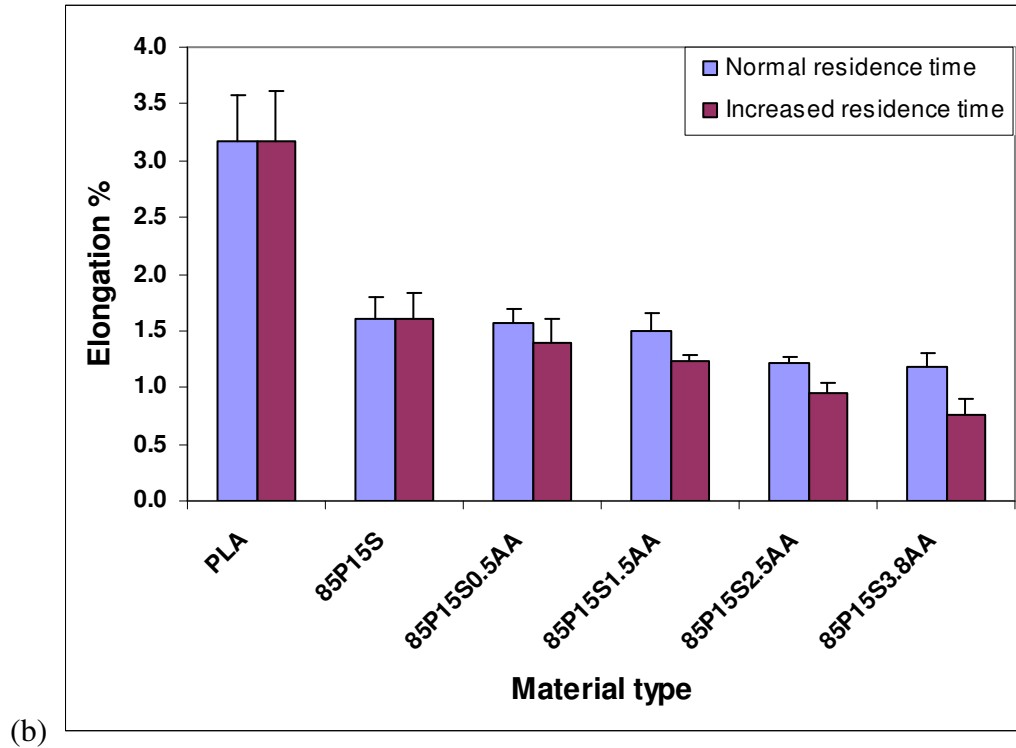


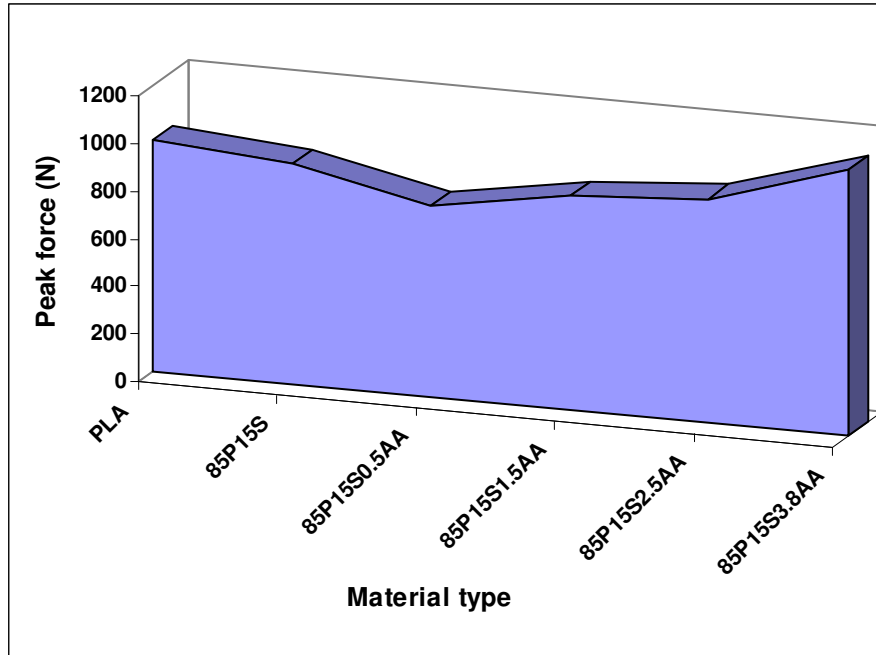
Figure 8.10 Evaluation of tensile properties of pure PLA, PLA/Starch blend, PLA/starch blend with different AA levels at normal and increased residence time during injection moulding (a) Tensile strength (b) Elongation (c) Young's modulus

Similarly, the results presented in figure 8.10 (a) showed that the materials exposed to an increased residence time in the barrel also reduce their strength significantly in the presence of all levels of AA. But, the PLA and PLA/starch blend without AA remained the same. In the presence of the AA, short chains are produced and owing to the molecular mobility facilitated by time, the crystalline domains would have been disturbed or destroyed resulting in a low strength. Moreover, the elongation of the pure PLA was halved in the PLA/starch blend due to the starch addition and further reduced upon the incorporation of AA. The negative effect from the starch is more prominent than the effect from the AA. The elongation of the samples prepared with increased residence time in the barrel followed the same decreasing pattern described above in the strength. These results revealed a very poor approach of the AA towards the elongation of the PLA/starch blend. The Young's modulus of the PLA/starch blend illustrated in figure 8.10(c) clearly shows increased modulus value compared to that of pure PLA. Both the starch and the PLA have contributed towards the Young's modulus of the blend. The blends with AA also show a higher Young's modulus than that of pure PLA but lower than the PLA/wheat starch blend owing to the hydrolysis of the starch caused by the AA. Furthermore, an elevated time at the processing temperature has further raised the Young's modulus values in almost all the blends except for the PLA/starch, which remained the same. The Young's modulus of pure PLA also increased due to the fact that the increased mobility of the polymer chains favouring crystallisation at the increased residence time in the barrel. The similar behaviour is also exhibited in the blends, probably due to the hydrolysis of the starch caused by the AA resulting in some PLA chains to be more relaxed to move than in the PLA in the PLA/starch blend. This situation would have facilitated localised plastic deformation in the blends thereby increasing the elasticity.

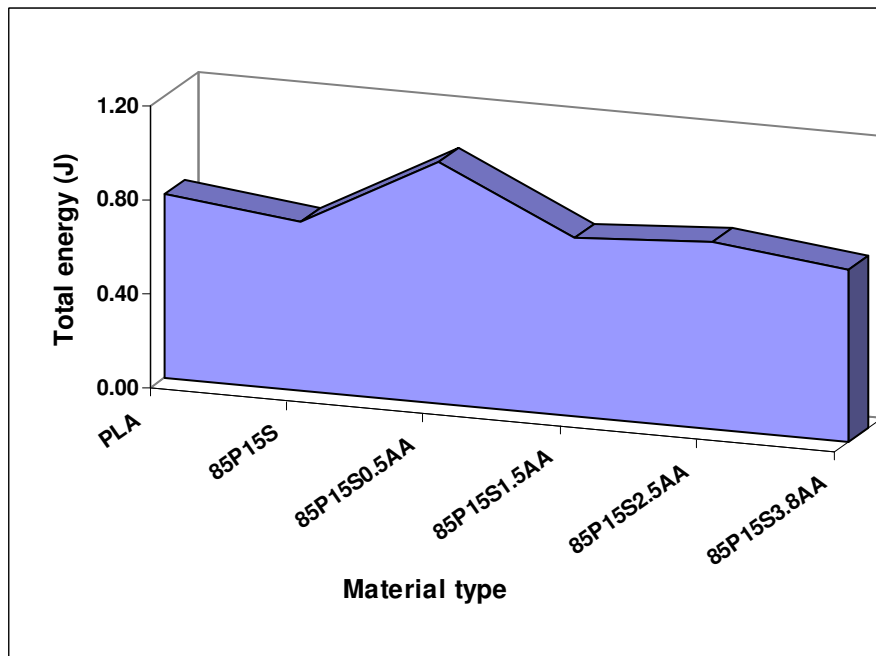
The peak force and the total energy absorption of the blends investigated by the drop weight technique are presented in figures 8.11 (a) and (b) respectively. The peak force tends to decrease with the starch as well as with the addition of a small quantity of AA such as 0.5%. However, the AA showed a positive influence by progressively increasing the peak force of the blends at and above the 1.5 AA level in the blends. The PLA/starch blend

having 0.5AA exhibited lowest peak force, whereas the 3.8AA level in the blends displayed the highest peak force. On the other hand, the energy absorption and also the deformation, which is nearly the mirror image of energy absorption, showed a maximum at 0.5AA level and showed a decreasing propensity towards increasing AA levels. According to the results, there is a possibility to exist an optimum energy absorption level between 0.5AA and 1.5 AA levels. Similarly, a minimum peak force in between these two AA levels is also possible.

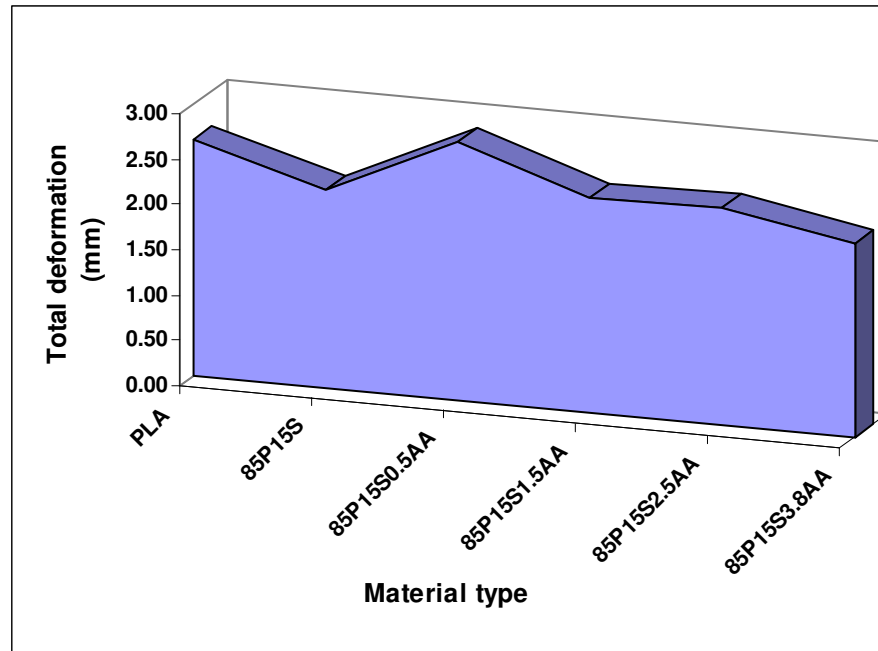
According to Moreno and Leever (Moreno & Leever, 2004), the law of mixtures suggest that the total toughness of the blend is controlled by the material that mostly contributed to the total volume. However, for the fracture resistance of the biodegradable multiphase systems, this does not always appear to be true. The presence of AA in the current study, starch can undergo hydrolysis resulting in some H bonds being broken within the starch granule. The acid modification of starch can preferentially attack the amorphous section with complete disintegration and a limited disintegration of the crystalline regions (Whistler, BeMiller & Paschall, 1984). It is also possible that the long PLA chains can breakdown to some extent by the AA, which can directly or indirectly influence the crystalline domains within the blends resulting in a lower peak force. The resultant effect would have altered the existence of the polymer network, ensuring some changes to a certain extent. Consequently, the acquired new pattern would have contributed to the rise in energy absorption. At the higher adipic acid concentrations, hydrolysis is prominent and also some crystallization taking place as confirmed by DSC, resulting in a high peak force and the low energy absorption to the blend.



(A)



(B)



(C)

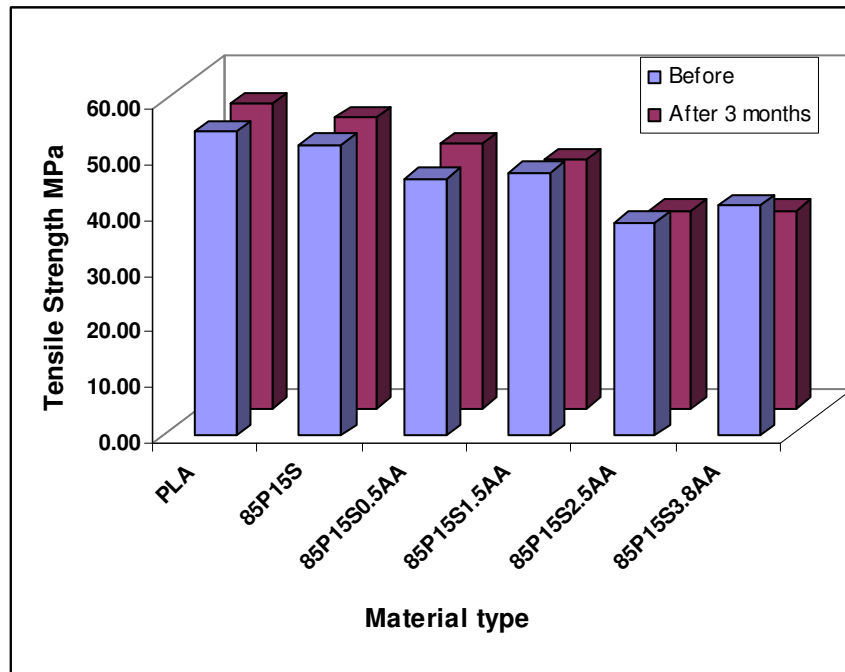
Figure 8.11 The variation of impact properties of pure PLA, PLA/starch blend, PLA/starch blend with different AA concentrations (A) Peak force (B) Total energy (C) Total deformation

8.4 Concept of physical ageing on mechanical properties

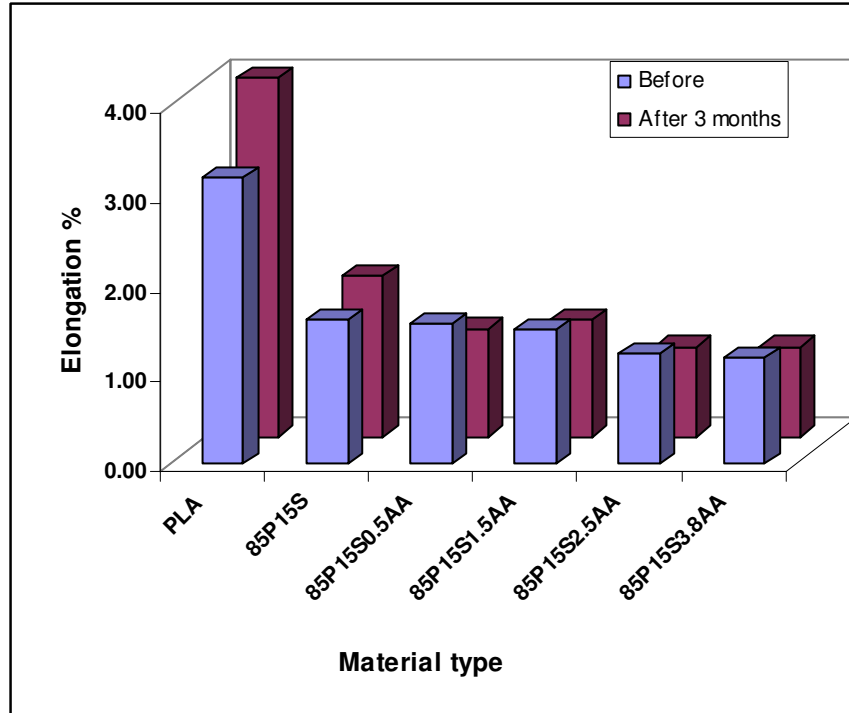
8.4.1 Measurements of tensile properties of the blends

It is important to note that some materials which show notable mechanical properties could weaken and demonstrate substantially different properties when they are aged, as a result of the time dependent phenomenon called physical ageing. Therefore, it was interesting to investigate the mechanical stability of the PLA and the blends because of its great importance for most applications. As reported in the previous chapter under section 7.5, the amorphous phase of partially crystalline polymers inherently exhibit this characteristic and the general concept of free volume is usually associated with the physical ageing. A previous study (Hay, 1995; McGonigle et al., 2000) has reported that the free volume can influence shrinking, brittleness and stiffness of the polymer. The effect of the physical ageing on the tensile properties and impact behaviour were investigated and reported in this

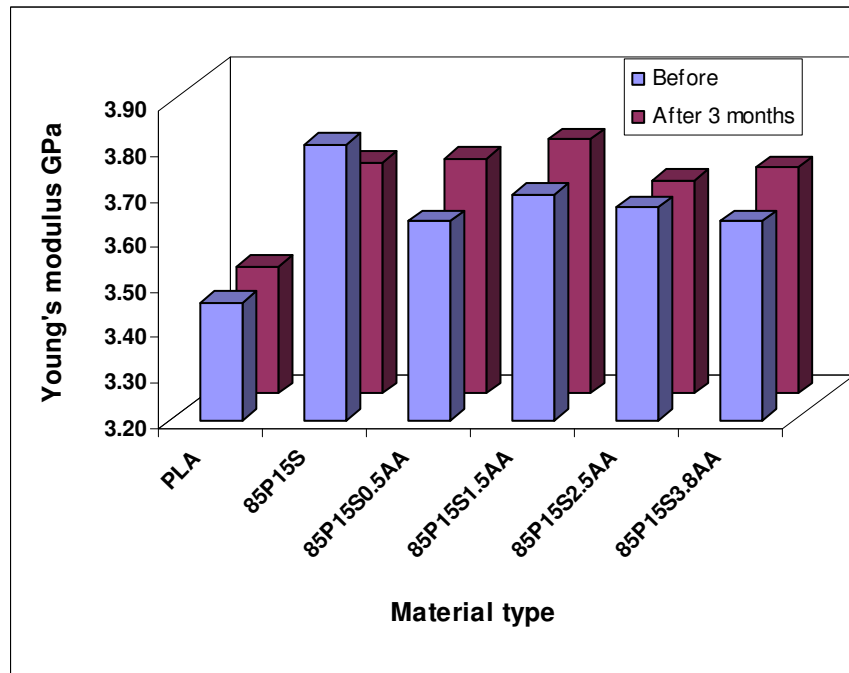
study in comparison with the initial properties. Figures 8.12 represent the measurements of the tensile strength, elongation at break and Young's modulus of the aged and unaged samples as can be seen in (a), (b) and (c) respectively. The PLA, PLA/starch and PLA/starch with 0.5AA demonstrate a slightly improved strength upon 3 months ageing, whereas the blends with the higher AA levels remained almost the same. The elongation of the PLA significantly increases, and some increase is also shown in the PLA/starch blend. However, all the blends with AA have demonstrated a cutback in the elongation after 90 days storage. Young's modulus of all the blends and pure PLA increased except for the PLA/starch blend without an additive.



(a)



(b)

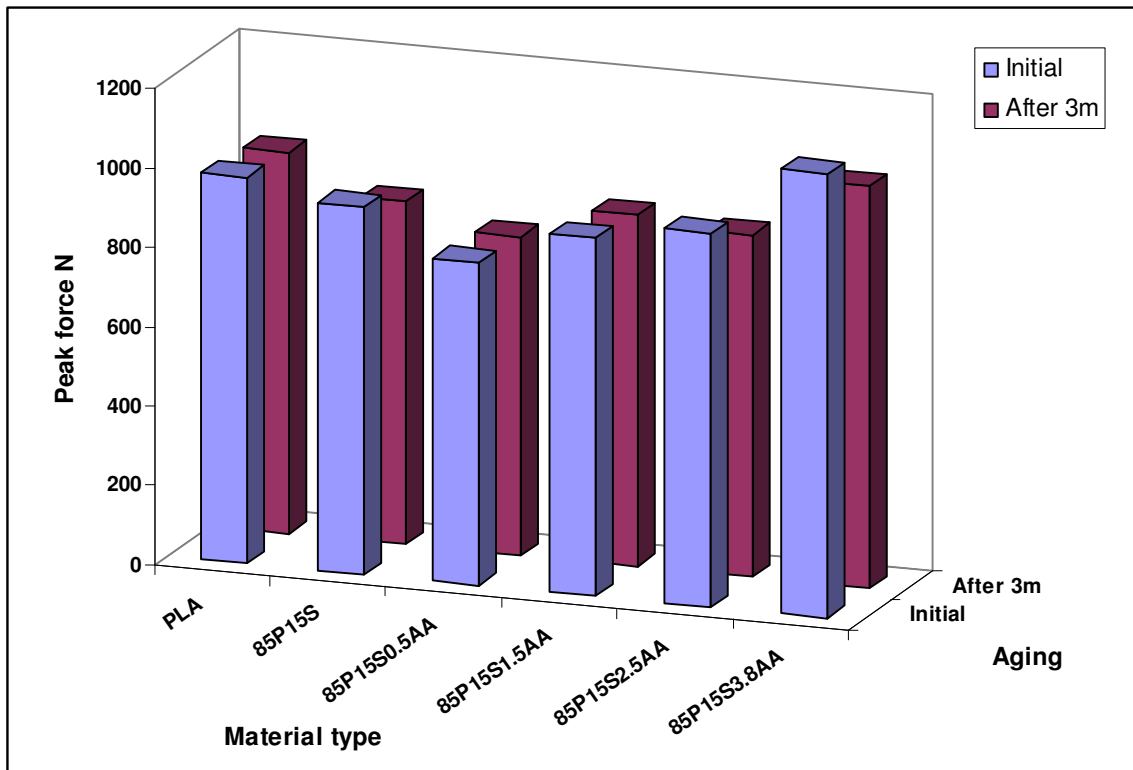


(c)

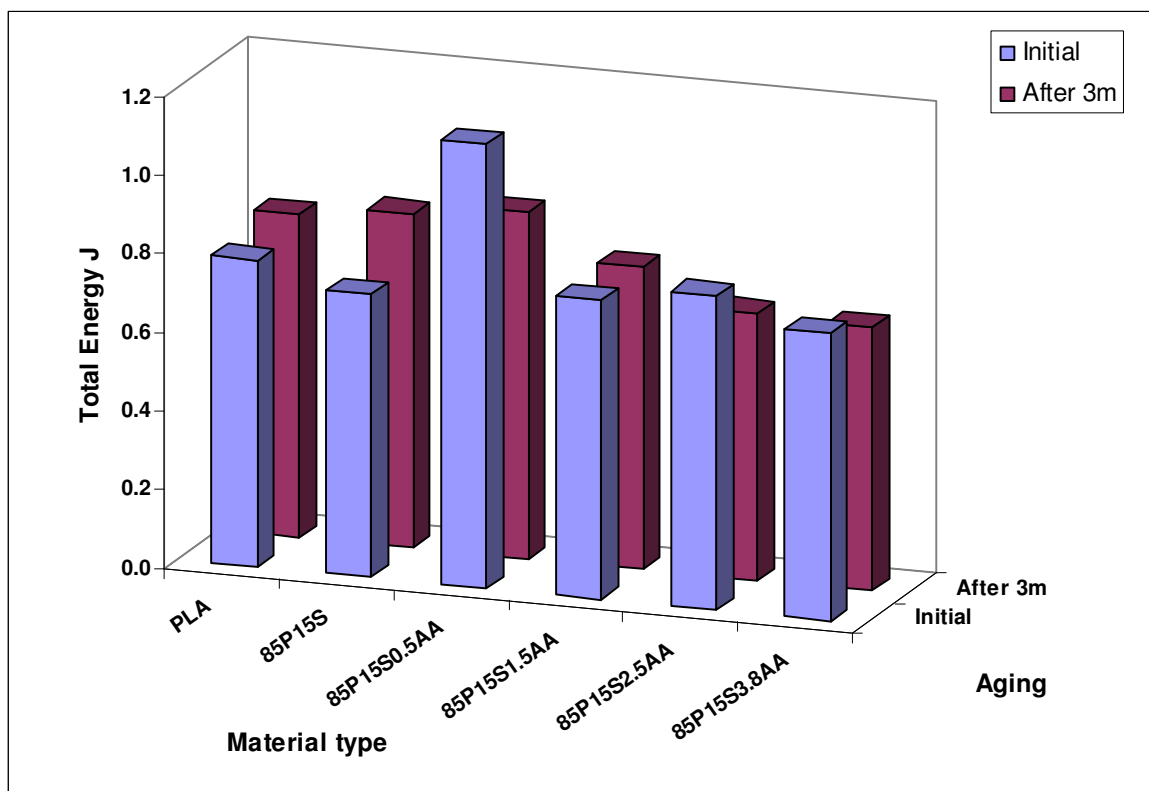
Figure 8.12 Comparison of the variation of tensile properties of pure PLA, PLA/Starch blend, PLA/starch blend with different AA concentrations before and after 3 months ageing (a) Tensile strength (b) Elongation (c) Young's modulus

8.4.2 Measurements of impact behaviour of the blends

The service life of the article and the product safety and liability is closely related with the impact property and therefore is an important property of the plastics. The effect of physical ageing on the peak force and the impact energy absorption were investigated and measurements were compared with the initial values. Figures 8.13 (a) and (b) present the aged and unaged measurements of the peak force and impact energy absorption by the materials respectively. The PLA and PLA/starch with 0.5AA and 1.5AA demonstrate a slightly improved peak force upon 3 months ageing but higher AA levels show a reduced peak force. The PLA and PLA/starch showed an increased level of energy absorption, which can be ascribed to the change in free volume. The blends with AA have exhibited cutback in the energy absorption after 90 days storage except for blend with 1.5AA. These results can be credited to the hydrolysis that has mostly taken place in the presence of the AA, which has produced short chains, thereby resulting in decreased ability of energy dissipation.



(a)



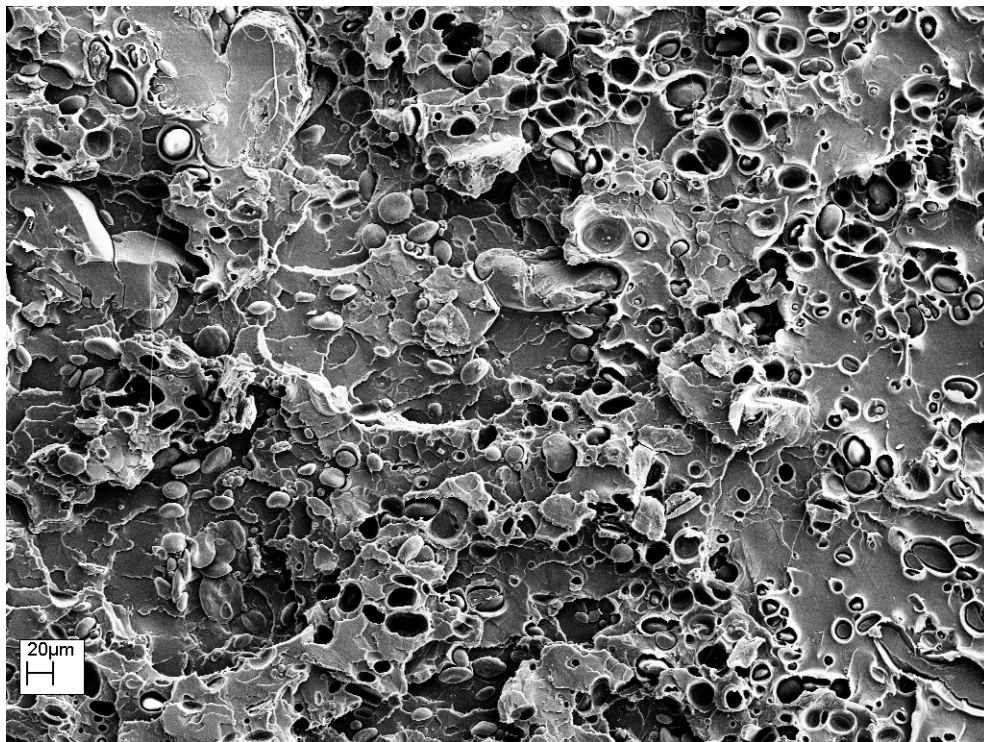
(b)

Figure 8.13 Comparison of impact properties of pure PLA, PLA/starch blend, PLA/starch blend with different AA levels after 9 months storage (a) Peak force (b) Total energy

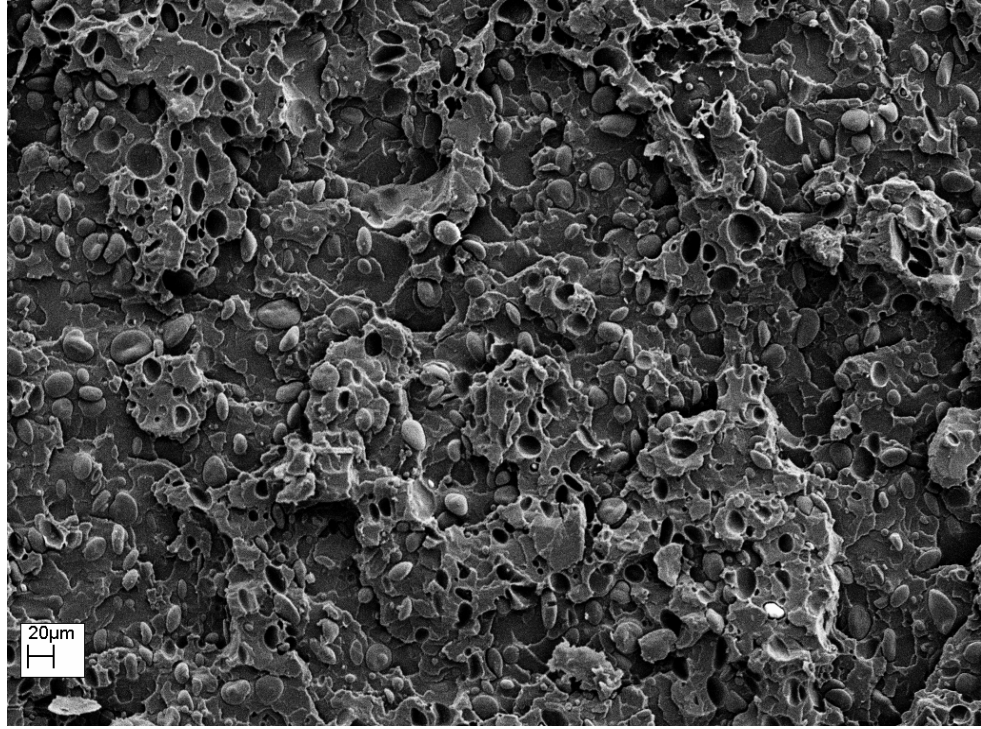
8.5 Morphology of the blends

Many properties of polymer blends are controlled by the morphology, especially the mechanical properties of the blend systems. On the other hand, the morphology, which shows miscibility of the polymers within the blends also provides the better understanding to interpret its failure and therefore is of practical importance of the current study. The morphology of the PLA/starch blends with AA was studied on fractured surfaces of the dumbbell specimens and the observations are explored in figure 8.14. The pictures shown in figures 8.14 illustrate the morphology of the PLA/starch blend with 0.5AA (a) and (b), (c) and (d) exhibit the morphology of the blends with 1.5AA, 2.5AA and 3.8AA respectively. The fracture surface of the PLA/starch blend is visibly coarse compared to the

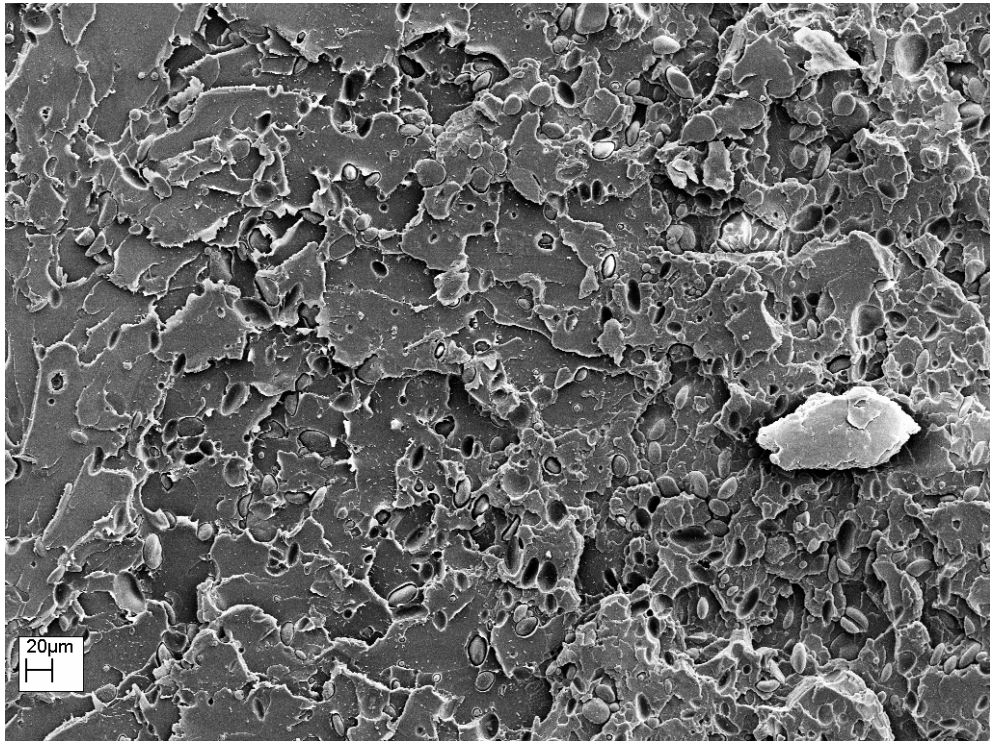
pure PLA, figure 7.19 (a). In addition, in the SEM micrograph of the PLA/starch blend with 0.5AA, two phases with aggregated starch granules can clearly be observed, which increased further at the 1.5AA level. It appears that most of the starch granules are obviously not hydrolysed and some of the starch granules are removed from the fracture surface and voids are created (figures. 8.14 a and b). Moreover, the interface between the starch and PLA is clearly observable at these AA levels, pointing to a poor interfacial adhesion between the two phases.



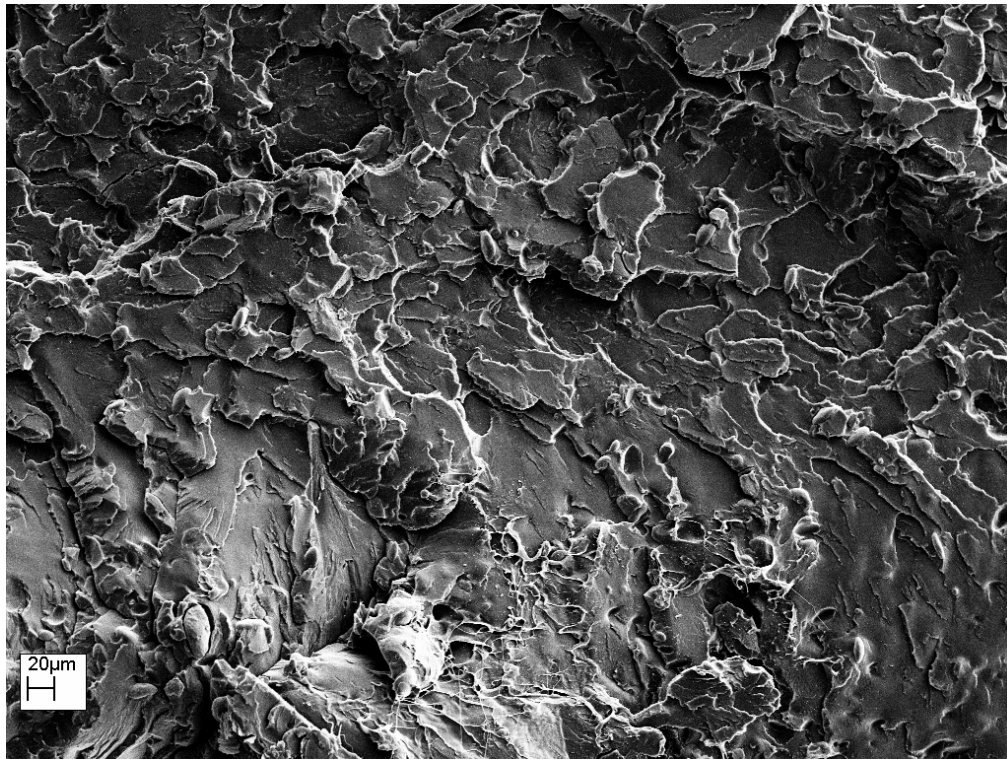
(a)



(b)



(c)



(d)

Figure 8.14 SEM studies of pure PLA, PLA/starch blend, PLA/starch blend with different AA concentrations (a) 85P15S0.5AA (b) 85P15S1.5AA (c) 85P15S2.5AA (d) 85P15S3.8AA

According to Whistler (Whistler, BeMiller & Paschall, 1984) when the starch is treated by an acid, the starch aggregates and forms larger granules, this phenomenon is clearly observed in the blends with 0.5 AA and 1.5AA. However, the fracture surface become smooth at the increasing level of AA, and most of the starch granules were destroyed at 2.5 AA with very low number of residual starch granules leading to a starch continuous phase at 3.8AA level. This is because the high AA can accelerate the fragmentation and dissolution of the starch granules. Moreover, as reported by Wang (Wang et al., 2007) the decrease in viscosity of the blends can increase the dispersion and decrease the interfacial tension between the starch and PLA blends. This result is in agreement with the decrease the viscosity reported in section 8.2 and attributed to the resulting highly dispersive and compatible PLA/starch blend at higher AA levels. Furthermore, a previous study carried out by Gunaratne and Corke (Gunaratne & Corke, 2007) also reported the disruption of

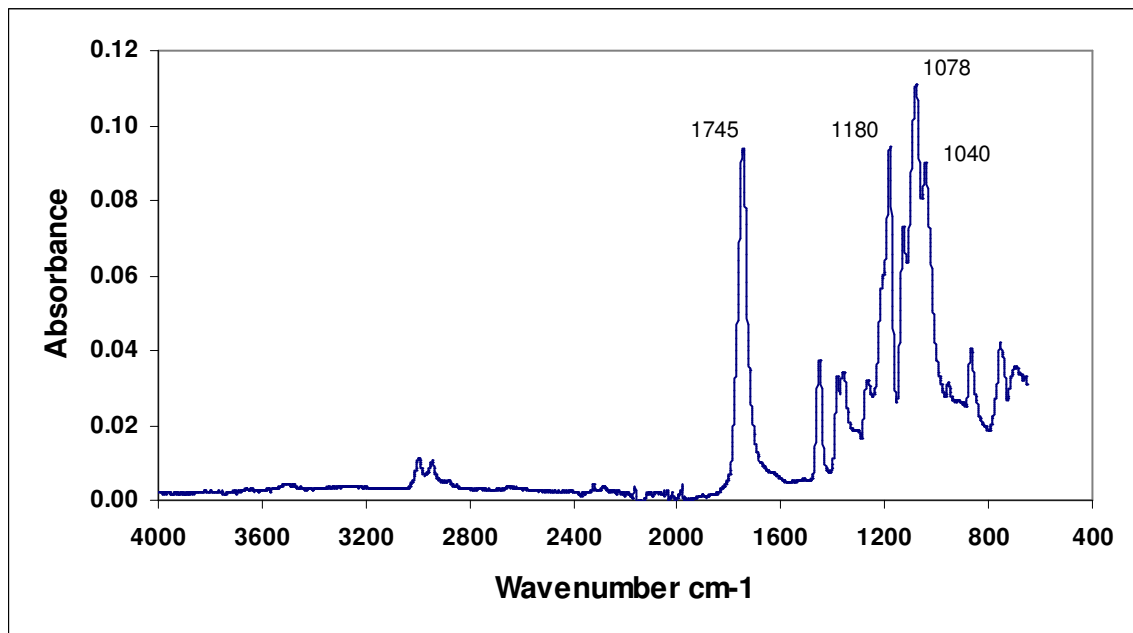
hydrogen bonding between neighboring starch polymer chains by acid, which could increase the swelling ability of starch granules at low acid concentration and decrease swelling power with greater erosion of the amorphous region at a higher concentration of acid.

8.6 FTIR spectra

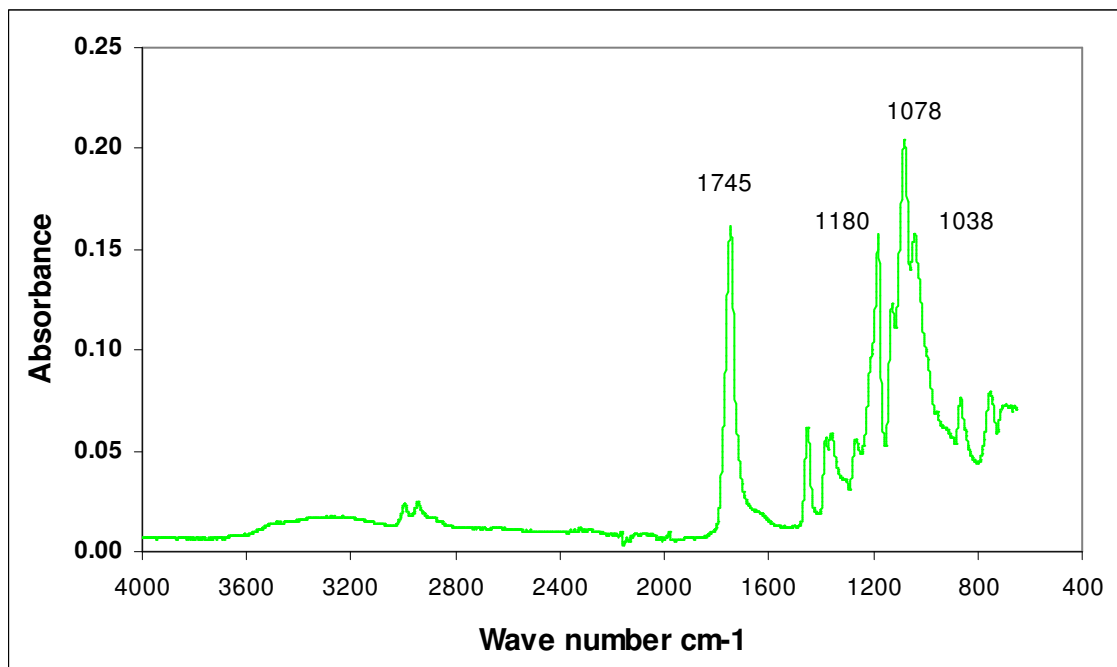
FTIR spectroscopy is one of the most important techniques currently in practice for polymer characterization. The degree of variation or deviation in structural information of the polymers from its original state can be identified by different vibration patterns. This technique can lead to identify their interactions between polymers in a polymer blend. Therefore, FTIR spectroscopy measurements were performed on the PLA/starch blends in the presence of AA to investigate how the adipic acid alters the vibration pattern in the blend. Figure 8.16 presents the FTIR spectrums obtained for the PLA/starch blends as modified by the adipic acid. The vibration pattern of virgin PLA illustrated in figure 8.16(a) clearly shows a strong carbonyl stretching absorption peak at about 1746 cm^{-1} together with -C-O- in -CH-O- at 1180 cm^{-1} and a triplet for -C-O- in -O-C=O at 1127 cm^{-1} , 1078 cm^{-1} , 1040 cm^{-1} . The hydroxyl peak projecting at about 3400 cm^{-1} is not clearly evident in pure PLA. However, in the blend of starch and PLA, this O-H peak becomes more prominent with a broader band between 3000 cm^{-1} and 3500 cm^{-1} due to the abundance of hydroxyl groups available in amylose and amylopectin fractions of starch. As a result of incorporation of starch into the PLA matrix, no other changes are observed in the vibration pattern of the blend, as can be seen by figure 8.16(b). The blends with the AA also demonstrate a similar vibration pattern and no significantly noticeable peak shifts exhibit, although there are some shifts in the FTIR spectra. Nevertheless, a small shift is also visible in the carbonyl peak from 1746 cm^{-1} to a lower wave number only at higher AA levels.

However, the results reported in figure 8.16 (d), (e) and (f) with adipic acid show a peak split in the strong carbonyl peak, although it is not profoundly noticed at 0.5AA level. The carbonyl peak shows a small shoulder appearing at about 1692 cm^{-1} at the level of 1.5 AA

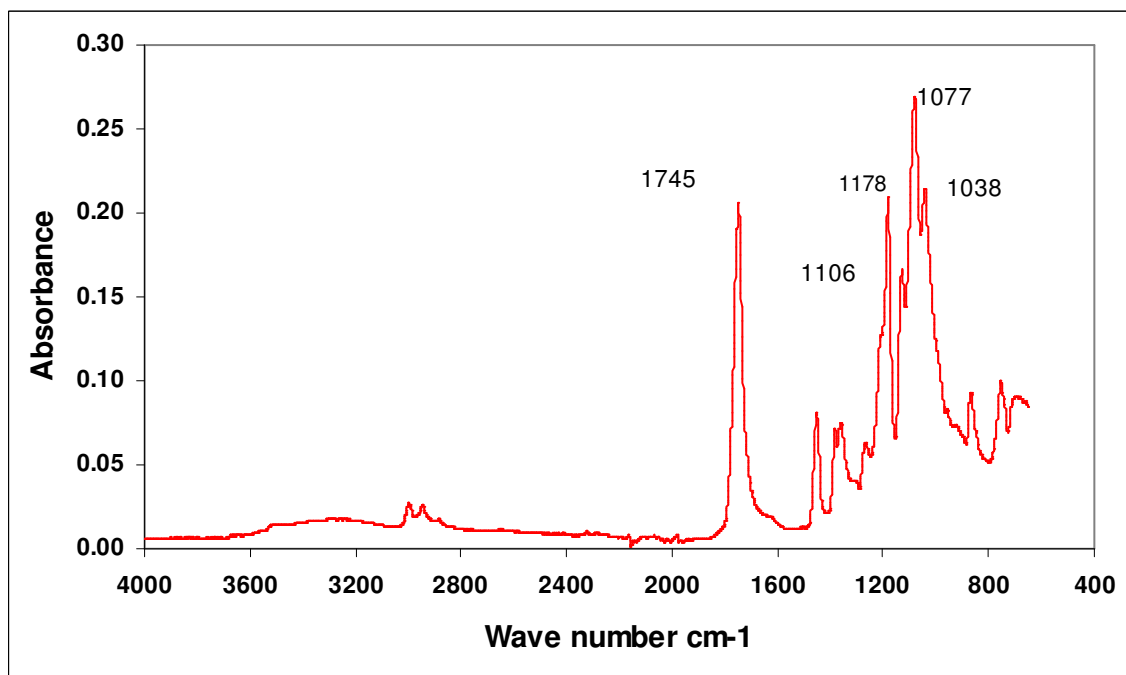
and then becomes a clear peak at about 1696 cm^{-1} wave number at higher AA levels. There could primarily be two explanations for this observation. Firstly, it can be inferred from the observation that there is very little involvement from the carbonyl group towards the interaction within the polymers in the investigated blends, at higher AA levels. Secondly and more precisely, the ester linkage within the PLA polymer chain would have hydrolysed in the presence of the higher AA. This inference can be further supported by the presence of a large crystallization peak originated due to a short polymer chains as observed by DSC and lower the tensile strength reported at the higher AA levels.



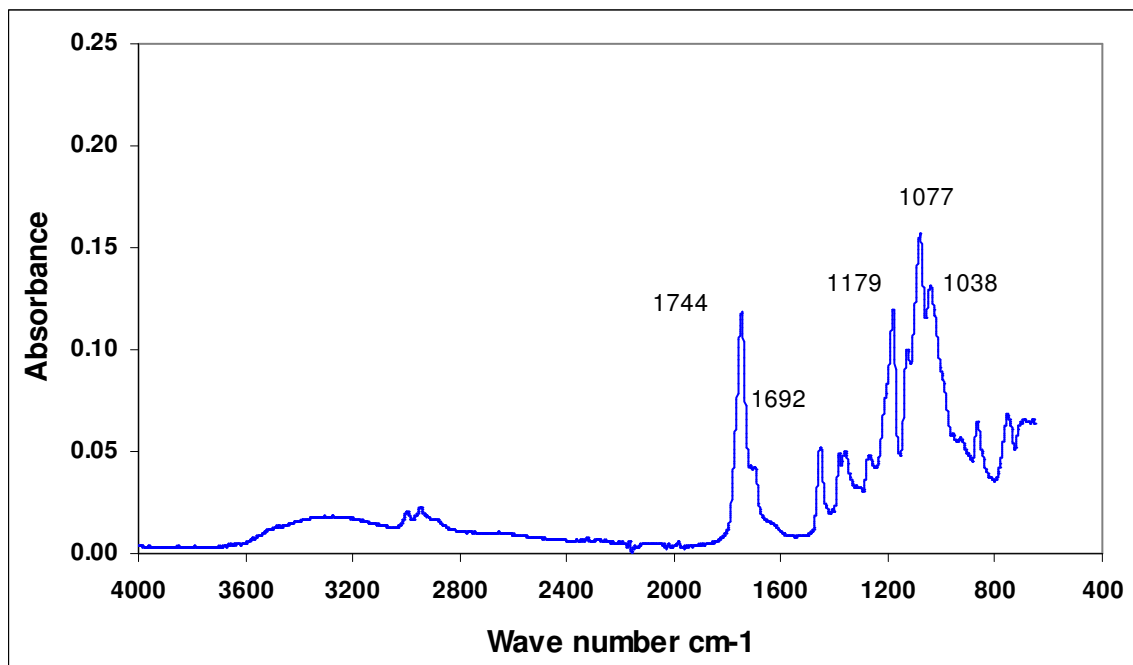
(a)



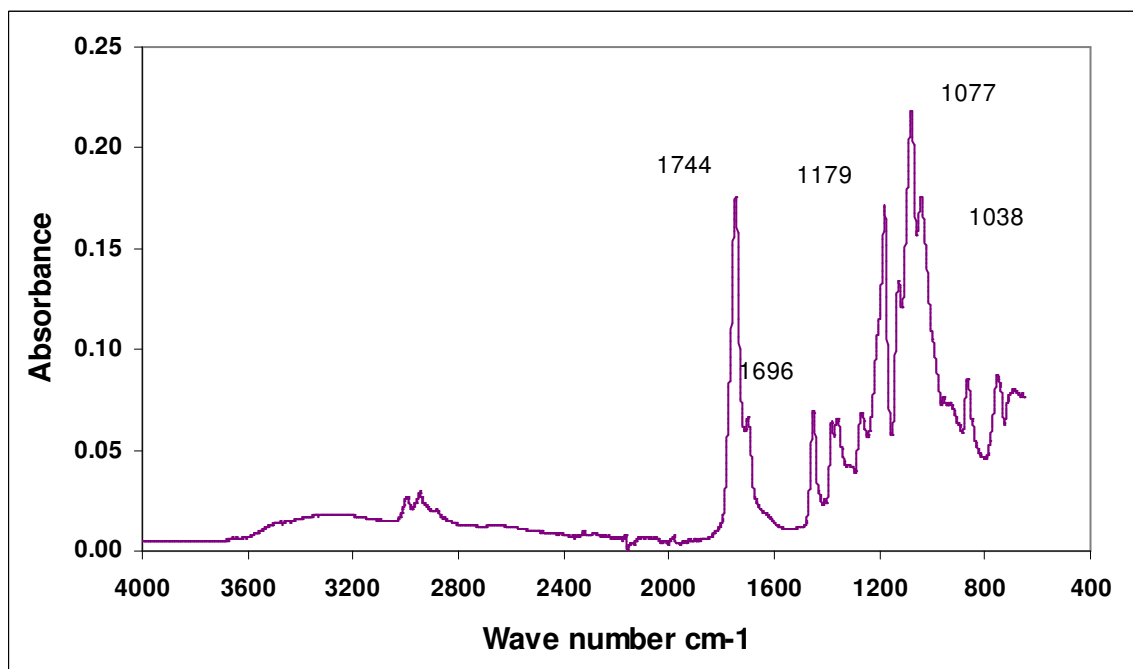
(b)



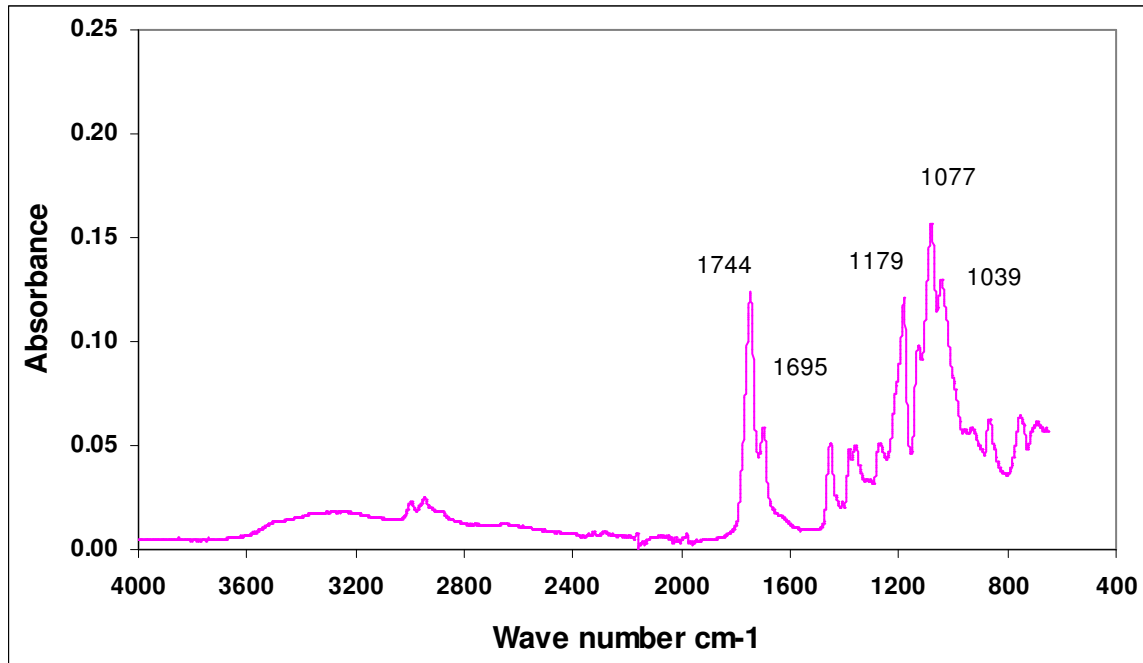
(c)



(d)



(e)



(f)

Figure 8.15 FTIR studies of pure PLA, PLA/starch blends with different AA concentrations (a) PLA (b) 85P15S (c) 85P15S0.5AA (d) 85P15S1.5AA (e) 85P15S2.5AA (f) 85P15S3.8AA

8.7 Chapter synopsis

Polymer blends were prepared with PLA and wheat starch in the presence of adipic acid in search of desirable properties. The decomposition in air and N₂ atmospheres and thermal behaviour, flow behavior, tensile and impact properties, effects of increased residence time and ageing on mechanical properties, microstructure and FTIR spectra were analysed. The AA has shown some positive as well as negative effects towards the properties of the PLA/starch blends. The tensile strength and modulus were attractive, although the elongation was compromised. Although AA destructured the internal H-bonding in the starch by opening some opportunities for functional groups to interact in the tri blend, the system exhibited weak interactions. The results have also shown some suspected hydrolysis of the ester linkage in the PLA polymer chains at the higher AA levels. As the elongation was

strongly forfeited, the blend became very brittle. However, the low AA levels exhibited some attractive properties in the tri blend system though they need further improvements.

In chapter 5, initial study with impact modifier explored some improved properties with PLA, though it did not align with the PLA/starch blend. The particle size and the starch quantity were the major drawbacks encountered during processing. Therefore, further efforts have been undertaken to inquire the possibility of incorporating the impact modifier to the PLA /starch blend system with reduced particle size of PLA and the ratio of starch in the blend, before the PLA/starch blends were prepared. Impact modifier and pistachio nutshell powder was incorporated with the blends and the properties were investigated. The results are explored in chapter 9 together with some discussions.

CHAPTER NINE

***RESULTS AND DISCUSSION
OF THE WORK WITH
THE IMPACT MODIFIER***

9 Bioimpact modifier and pistachio nutshell blended with PLA and wheat starch

Chapter nine reports results of the experimental investigation carried out according to the description given in chapter 3 about the blends prepared and listed in table 3.7, to scrutinize the outcomes of the impact modifier and pistachio nut shell powder on the properties of the blends prepared with PLA and wheat starch as described in section 3.3.6.

9.1 Thermal behaviour and material stability

9.1.1 Thermogravimetric analysis

Temperature plays a vital role in material stability, particularly on biomaterials and hence temperature sensitivity during processing is very important. Due to the sensitivity of the technique to decomposition, thermogravimetric measurements were used to characterize the material stability throughout their processing at elevated temperatures. Preliminary experiments were conducted in air and N₂ atmospheres in order to study the degradation behaviour of the pure material and prepared blends. Figures 9.1 and 9.2 present the thermograms obtained of pure PLA, PLA/starch blend, PLA/starch blends with IM at an air and an inert atmosphere respectively. The weight loss measurements given in figure 9.1 indicate firmly stable plateau for PLA below 300⁰C temperature and the other blends with the starch showed a weight loss initiation around 275⁰C. As reported in the previous chapters, the instigation of weight loss around 275⁰C in the blends is certainly due to the loss of weight by the starch in the blend at this temperature. Nonetheless, there is no significant influence from starch or additives upon the loss of weight at the very early stages of heating, and the stability of the final materials remains in an acceptable range. The influence of inert atmosphere on weight loss, shown in figure 9.2 illustrates a similar behaviour in PLA and its blends.

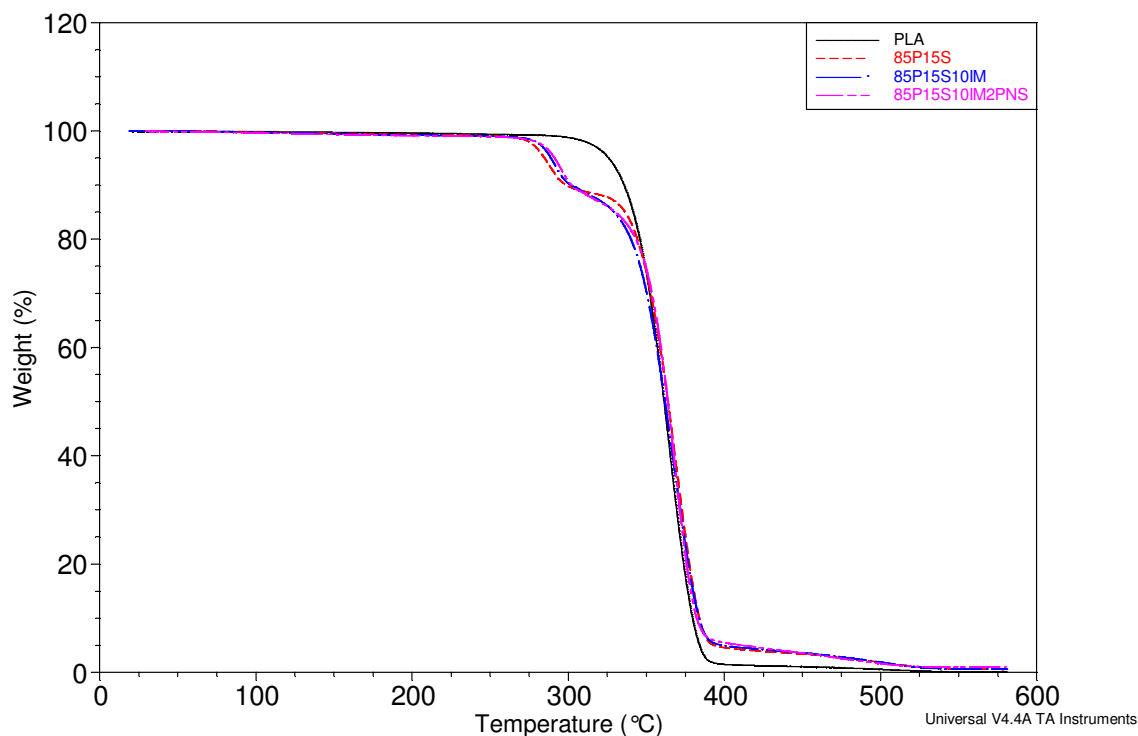


Figure 9.1 TGA analysis of the blends with impact modifier in air

Thermogravimetric analyses were also conducted on the same batch of materials with a slightly different protocol in order to identify the material stability because material may be forced to stay in the moulding barrels for a longer period than its theoretical expectation. Therefore, the effect of long exposure time of the material at processing temperature was investigated with the use of TGA. The decomposition patterns were investigated by heating the raw materials and blends with an isotherm at 180⁰C for about 30 minutes and the results are presented in figure 9.3. The decomposition behaviour with an isotherm is similar to the decomposition pattern observed without an isotherm and no weight loss was observed before 275⁰C. It can be concluded with these observations that longer exposure times do not contribute to decomposition at early stages, but there could be some penalties in mechanical properties.

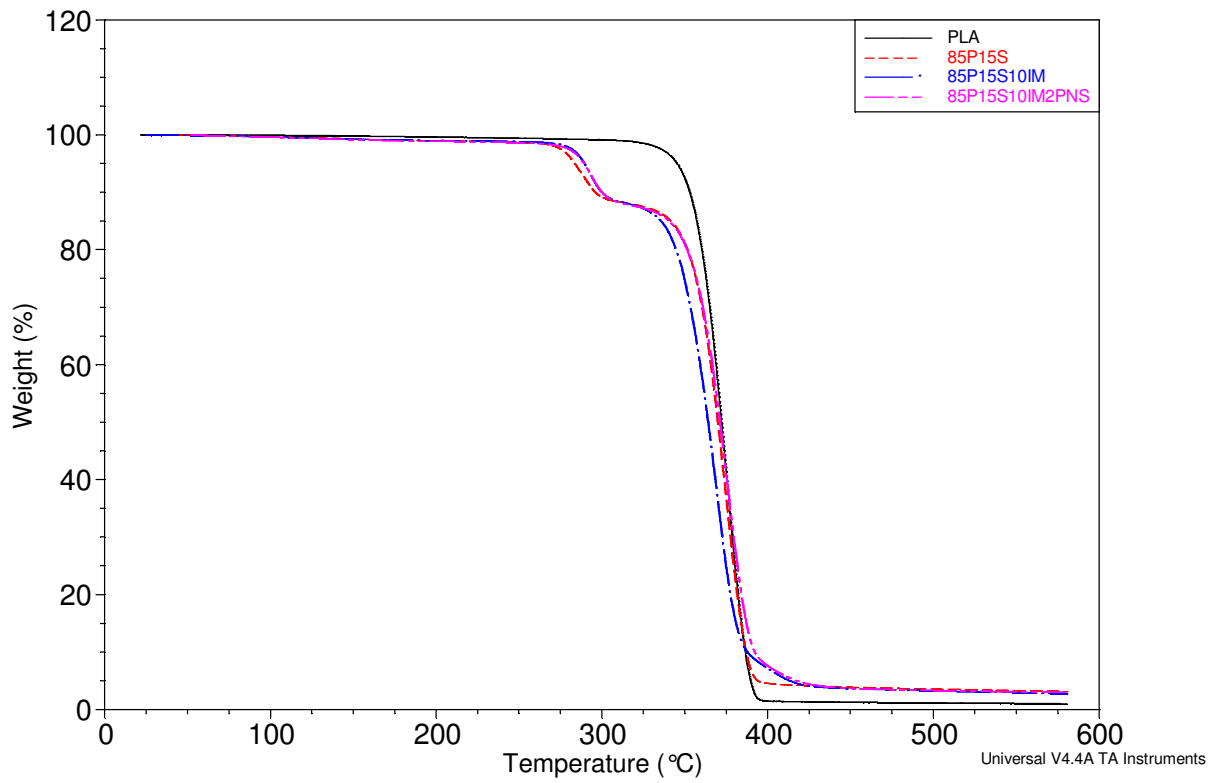


Figure 9.2 TGA analysis of the blends with impact modifier in N₂

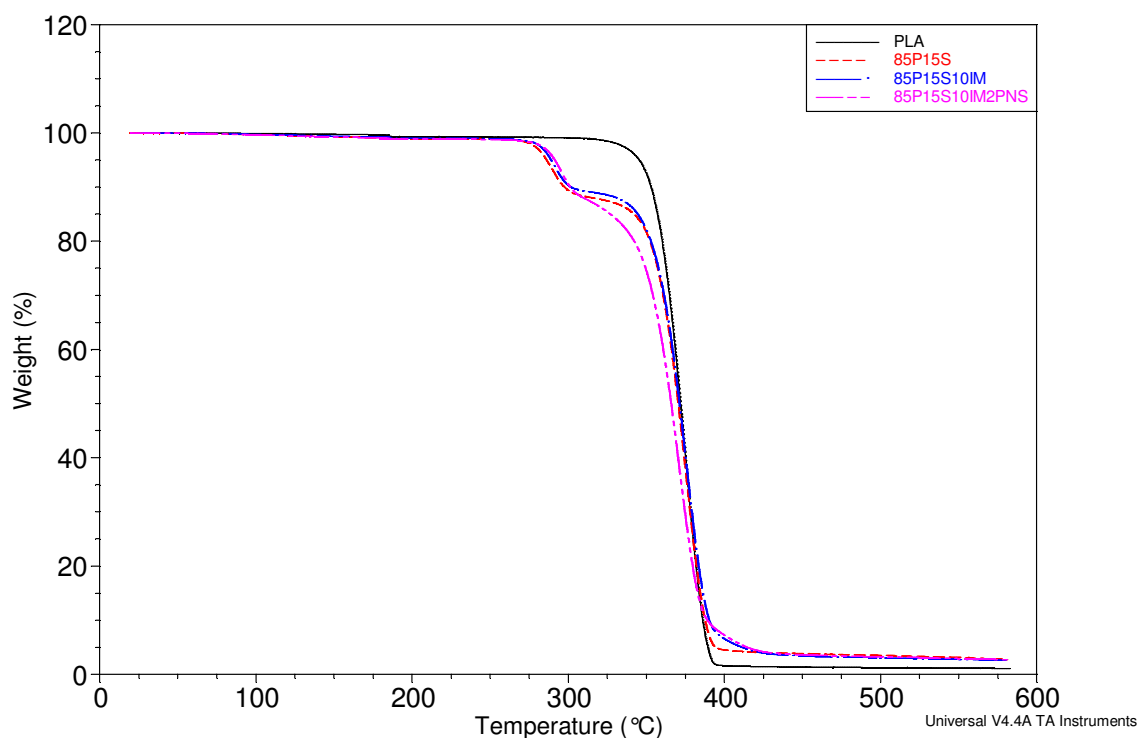


Figure 9.3 TGA analysis of the blends with an isotherm at 180⁰C for 30 minutes in N₂

9.1.2 Heat treatment in a conventional oven

The observations of formulated PLA/starch blend with IM, examined by heat treatment in a conventional air circulating oven at 180⁰C temperature for 30 minutes, are given in figure 9.4. The pictures on the left hand side illustrate the appearance of the pellets before the materials were subjected to the heat treatment and on the right hand side after the heat treatment. According to visual observation, the appearance of the PLA is a transparent melt as presented in figure 8.4 (A) in chapter 8. However, the opaque colour imparted in the blends with the starch has become vaguely visible in the blends of PLA/starch and PLA/starch/IM after heating at 180⁰C for 0.5 hour. The IM is a typical MBS core-shell rubber modifier, in which styrene and methyl methacrylate are graft polymerized onto polybutadiene (PB) or styrene-butadiene rubber (SBR) particles. The addition of MBS

does not sacrifice its transparency (Zhou et al., 2006). This statement is further established by the observations made during the investigations reported in the chapter 5 with PLA/IM blends. However, the pellets of PLA/starch/IM appear to be more whitish than PLA/starch pellets. Moreover, it is also noticeable that the colour of the heated PLA/starch/IM blend is darker than the corresponding PLA/starch blends and the appearance becomes more brownish. It can be concluded that the IM which is an acrylic core-shell of a methacrylate-butadiene-styrene (MBS) copolymer, indeed melts around this temperature has imparted a slight brownish colour to the blend. The observation is further confirmed by the observation reported for the rubber latex under similar conditions, which resulted in the brownish colour under section 7.1.2 in chapter 7. Nevertheless, the odour and the appearance of the exterior of the heated samples support the inference that the samples appear to be not degraded and exhibit their natural colours upon heating.

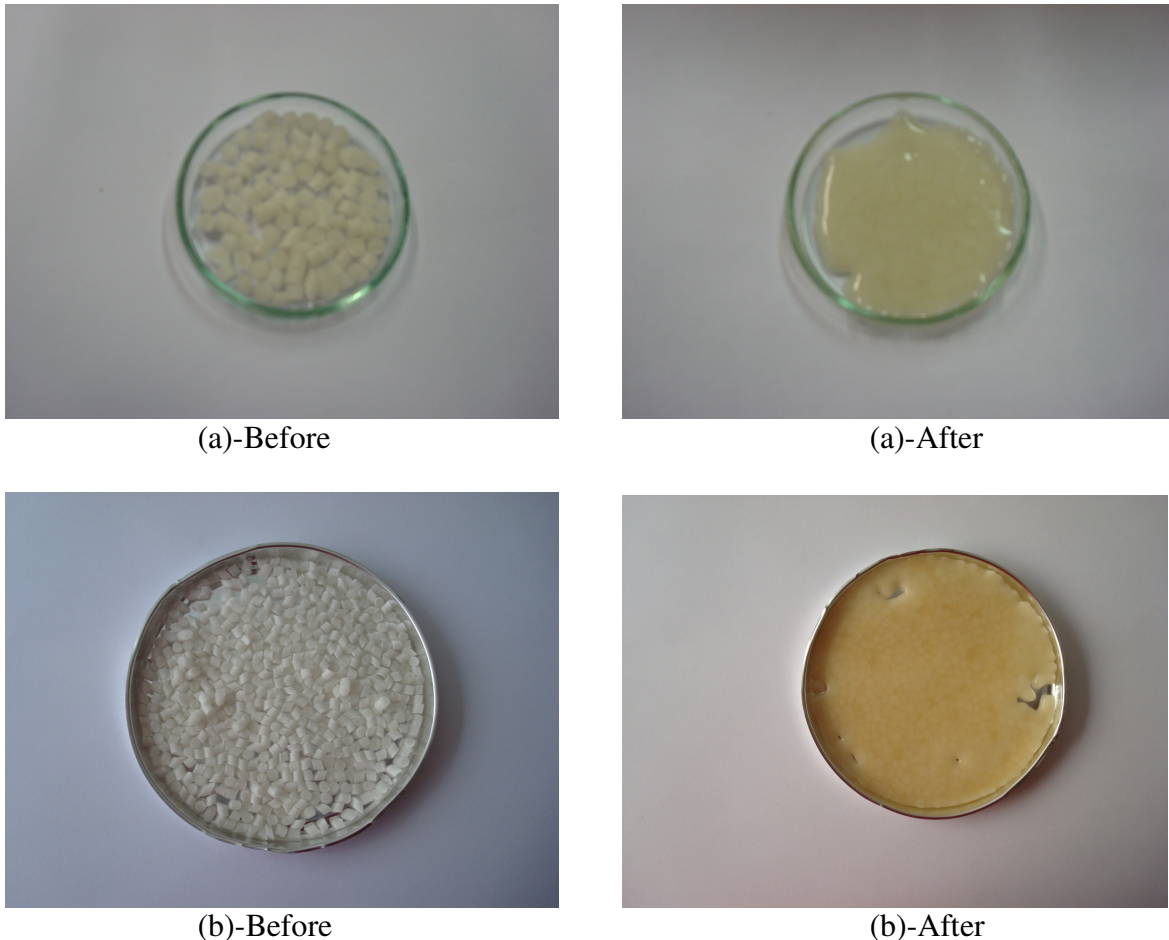


Figure 9.4 Observation of the blends upon heating the materials in a conventional oven at 180°C temperature for 30 minutes (a) 85P15S (b) 85P15S10IM

9.1.3 Differential Scanning Calorimetry

The prepared blends were further analysed by differential scanning calorimetry because important measurements of a material such as glass transition temperature T_g , melting temperature T_m and crystallization T_c can be observed. The DSC measurements showing the thermal behaviour of the raw PLA and the other prepared blends, investigated according to the methodology given in chapter 3, section 3.7 are given in figure 9.5. The experiment was carried out to erase any thermal history of the materials, and the measurement was made during the second heating cycle as presented in figure 9.5. The results show the T_g at about 60°C and no influence on the T_g , T_m or T_c temperatures are observed with the IM. Although polybutadiene in MBS has the T_g around -80°C (Granel & Tran, 2002), it has not utilized towards a reduction in T_g of the tri blend system.

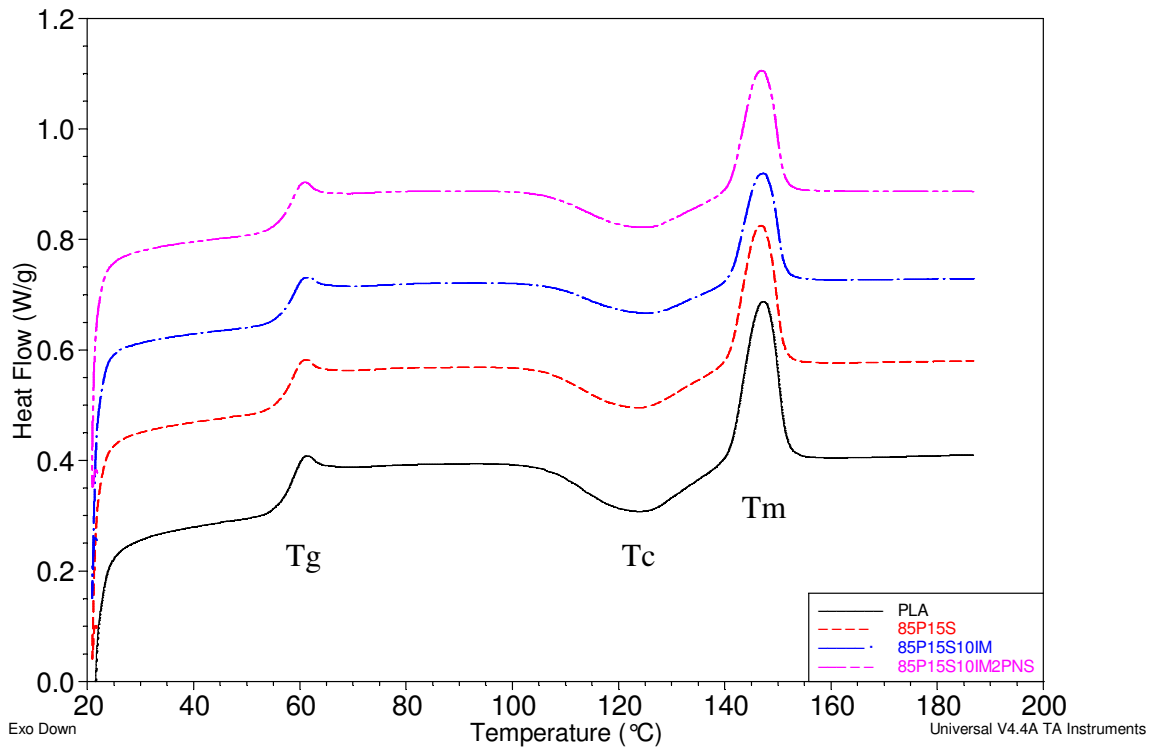


Figure 9.5 DSC analysis in the second heating cycle

However, the size of the exothermic crystallization peak of PLA and blends noticed around 125⁰C has become smaller with the starch as well as with the IM and it has been confirmed by the reduction in the area of endothermic melting peak. In a previous study, the changes of a peak shape have been reported as an illustration of the change in size distribution of the crystallites (Qi et al., 1993). The change of fusion enthalpy, ΔH , for the blend with PLA/starch/IM was slightly smaller than those of the PLA and PLA/starch blend. The difference reflects a small divergence between the crystallinity. As evidently reflected by the results, the MBS core-shell further reduced the crystallization of the PLA/starch blend. This might have happened owing to the polymer chains of the PLA being encapsulated within the core and affecting the polymer phase continuity.

9.2 Rheology of the blends

The flow behaviour of a polymer is very susceptible to changes in the chain structure, therefore practically important for the processing in the current study. Figure 9.6 presents the viscosity of PLA, PLA/starch and PLA/starch/ IM at a temperature of 180⁰C. The PLA data was obtained as a control from the oscillatory measurements and used to assess the effect of molecular weight when starch and additives are added. The PLA exhibits the clear Newtonian plateau with a zero shear viscosity of 1.2 kPa s. The viscosity of the blends with the starch and impact modifier is significantly higher than that of the PLA. These blends also demonstrate a clearly defined Newtonian region but the zero viscosity is up to 2.3 kPa s. It is well known that the molecular weight of starch is comparably larger than many conventional polymers. Accordingly, increased blend viscosity could be attributed to the high molecular weight of starch, which has been reported as many times larger than the molecular weight of other conventional polymers (Xie et al., 2007).

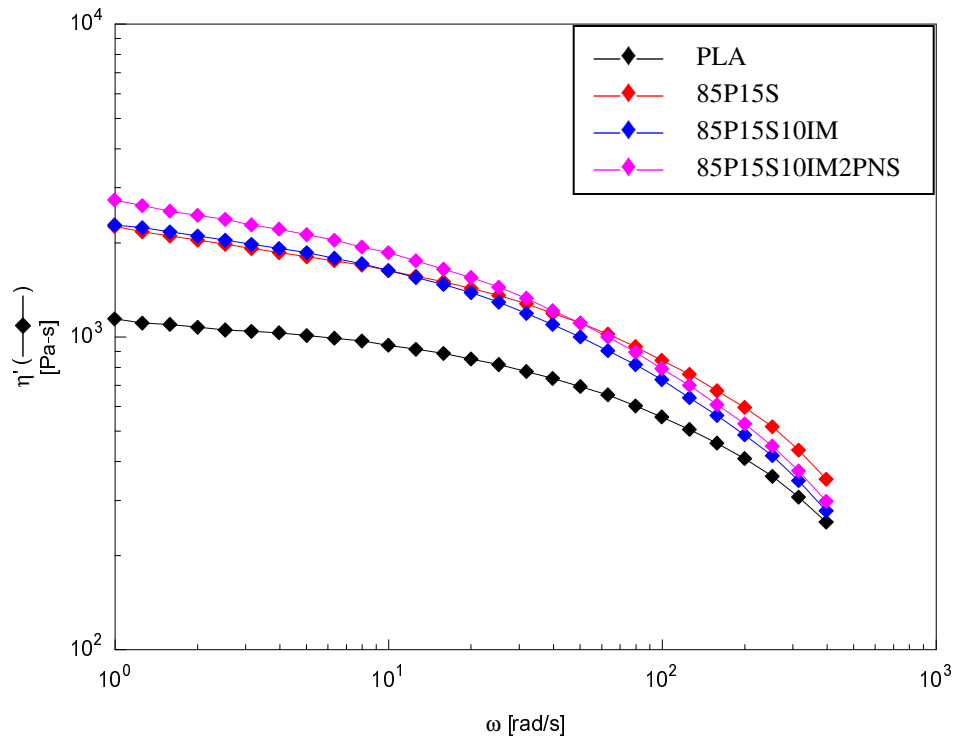


Figure 9.6 Viscosity of different blend types at 180°C temperature

However, there is no noticeable contribution towards blend viscosity by impact modifier compared with starch though pistachio nut shell powder has shown small increment at initial frequencies. Even though IM is a rubbery MBS core-shell, the concentration of the IM that was employed in the study is sufficient to control the blend viscosity at the same level as the viscosity of the PLA/starch blend. It is also important to note that pistachio nut shell powder has acted as a filler and has increased the blend viscosity. Moreover, PNS belongs to lignocellulosic type materials (Yang & Lua, 2006) which consist of cellulose, hemicellulose and lignin that had contributed for higher molecular weight apart from starch thereby increasing blend viscosity.

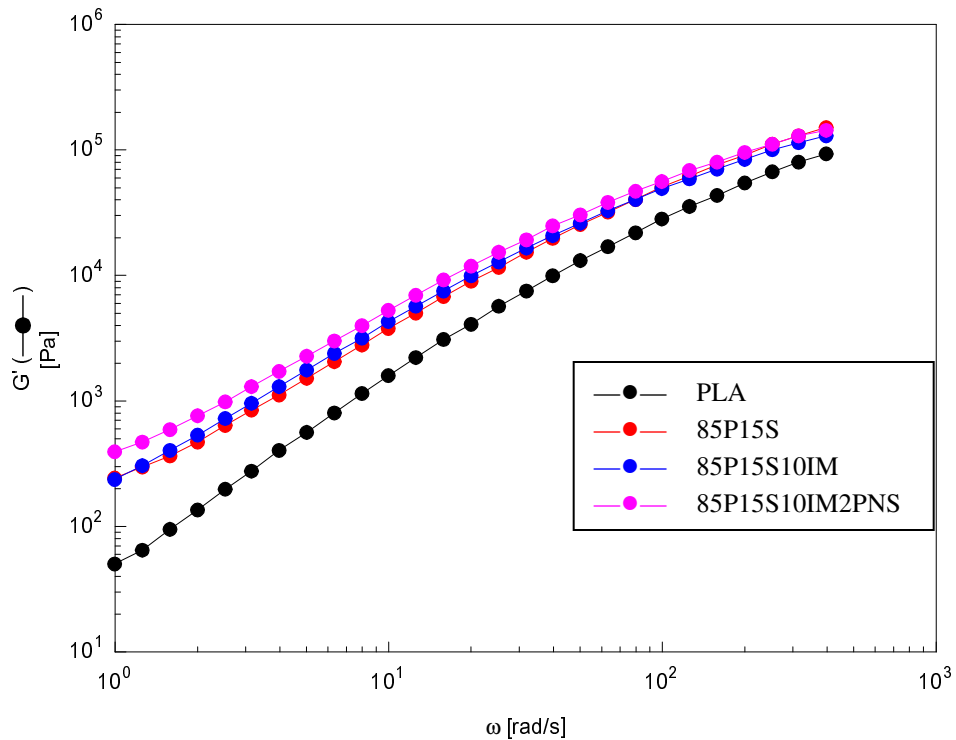


Figure 9.7 Storage modulus G' of different blend types at 180°C temperature

The storage modulus (G') and loss modulus (G'') were also investigated during oscillatory measurements and the results are presented in figures 9.7 and 9.8 respectively. This effect was investigated to consider energy absorption and heat dissipation. According to the results, all the blends and the PLA tend to follow the same pattern of variation in the storage modulus and the loss modulus at increasing frequencies. The PLA exhibited the lowest modulus whereas the blend with pistachio nut shell powder showed the highest storage modulus. Similar to the viscosity, the PLA/starch blend and PLA/starch/IM blend showed relatively similar modulus properties. Due to the flow behavior in which the macromolecules are very mobile at 180°C , particles tend to be very independent and have not much association with each other.

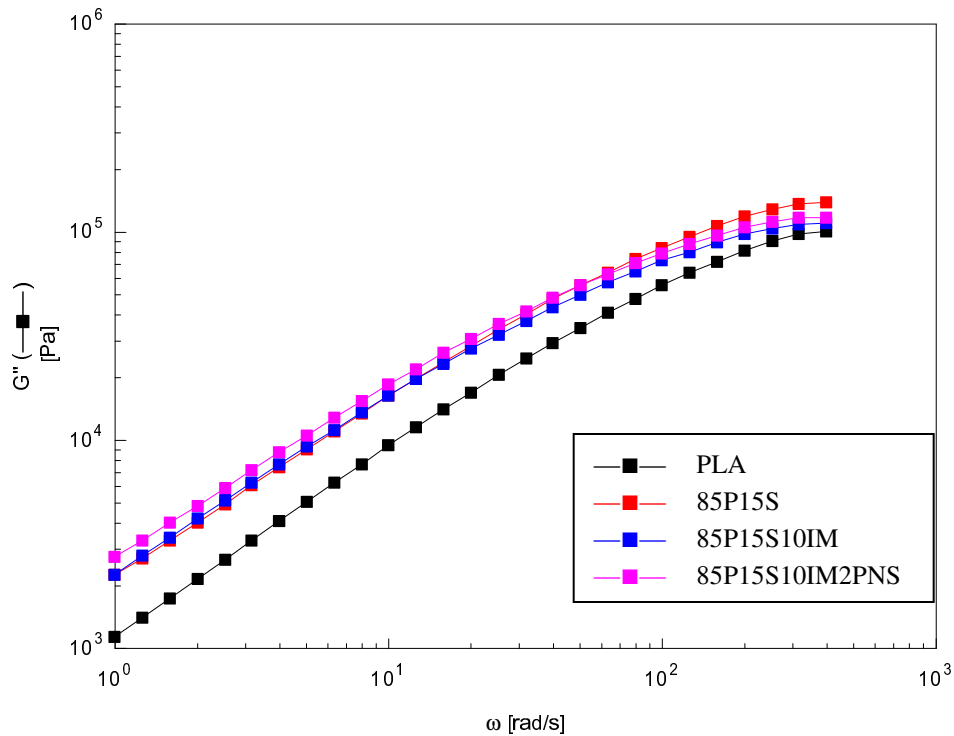


Figure 9.8 Loss modulus G'' of different blend types at 180⁰C temperature

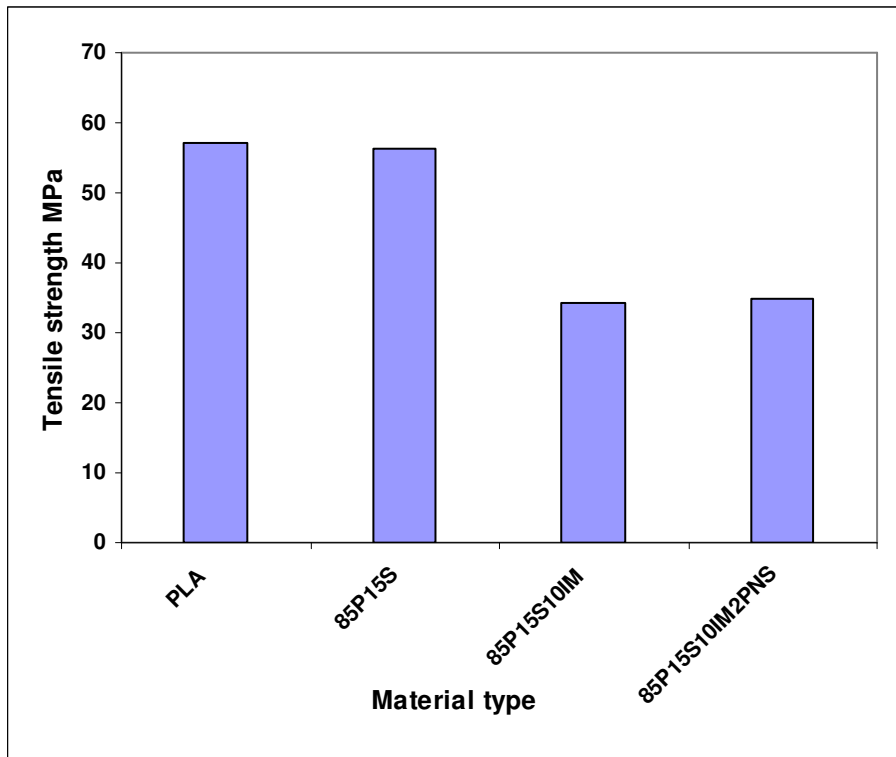
9.3 Mechanical properties of the blends

9.3.1 Tensile test properties

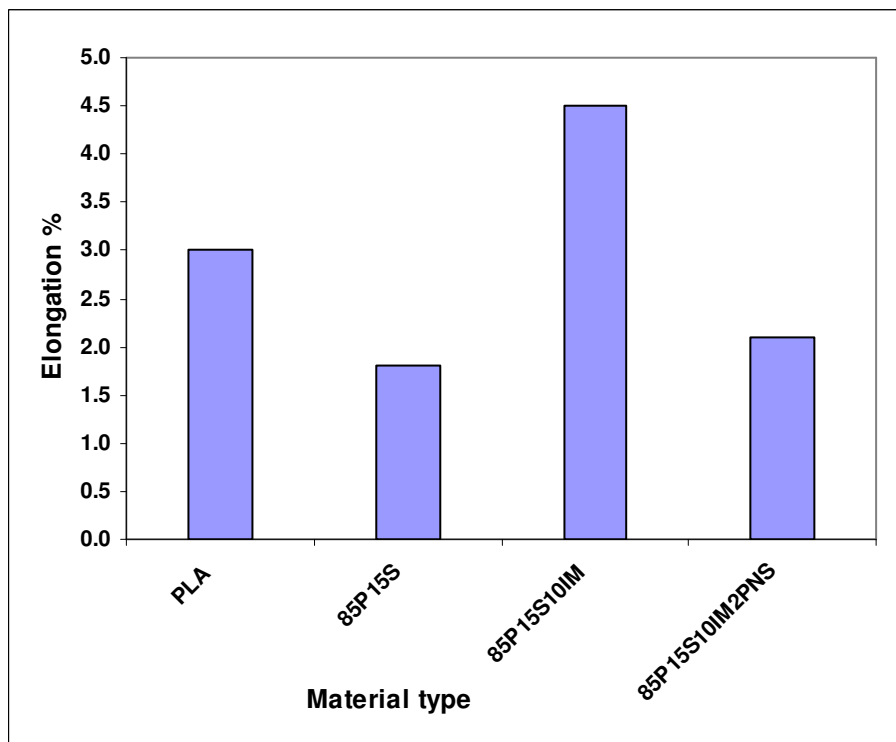
The mechanical properties of polymeric materials mostly dominate the selection criterion of the materials and thus are decisive in applications. The measurements of the tensile properties were performed and calculated by an average of 5 samples according to the standard and the results are reported in figure 9.9. As shown by the results, the tensile strength of the PLA and PLA/starch blend demonstrated approximately identical values but the strength of the blends decreased with the incorporation of the IM powder. The results can be attributed to a loss of crystallinity of the PLA in the blends as ascribed by the DSC analysis due to the structure and the nature of the core-shell. The core-shell structure has a rubbery cavity or a core part covered by a glassy shell. The polymers tend to adsorb and

entrap on to the core with the support of the glassy shell. The new arrangement would lead to low crystalline domains owing to the lack of opportunity to align the polymer chains. It has also been reported that a reduction in tensile strength is to be expected in the presence of core-shell structured latexes because of their soft rubbery cores (Sun et al., 2010). However, the noticeable reduction reported is not expected just based on the dispersion of MBS core-shell alone but is also likely related to the interfacial adhesion of the IM in the PLA and starch blend. It is obvious that a poor compatibility between phases will also lead to a greater loss in strength.

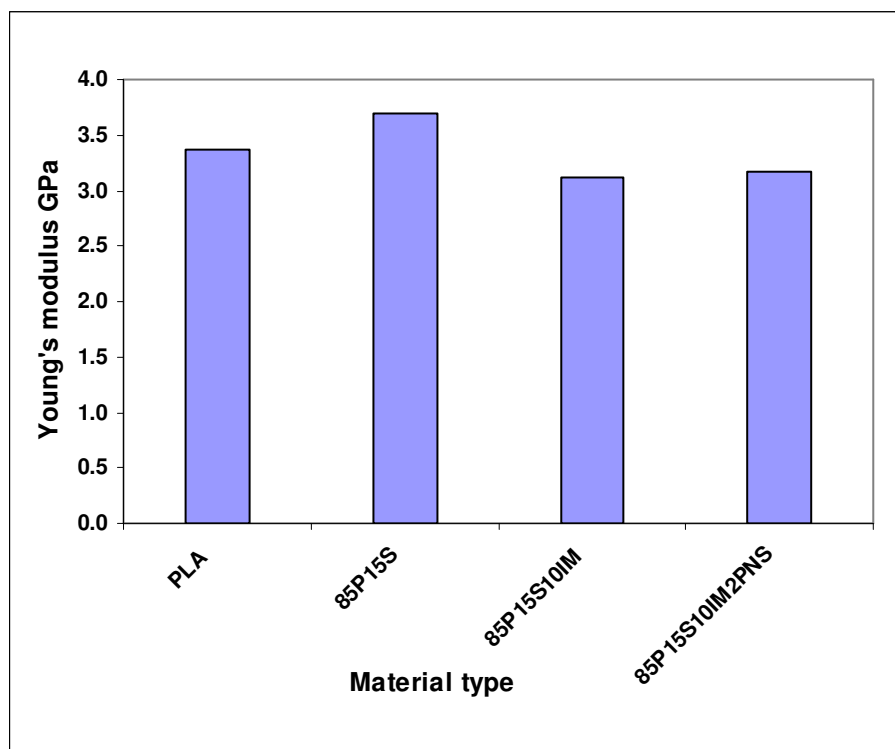
Nonetheless, these results were obtained by incorporating a considerably large amount of IM and there are possibilities to obtain desirable strengths by controlling the IM levels in the blends. Furthermore, this conclusion can be drawn because of the reported results in chapter 5 on the study carried out with a lower level of IM than the work reported in this chapter. According to the results reported in chapter 5, even at the high starch loading such as 30% with a low concentration of IM than the current study, tensile strength was maintained at an attractive level. However, the properties of the blends presented in chapter 5 are not directly comparable with the current study due to differentiations in compounding and the particle size of the materials. Therefore, further studies need to be carried out in this area with conditions applied in the current study to rectify supporting evidence. Moreover, results elucidated no significant effect from the pistachio nut shell powder as both PLA/starch/IM and PLA/starch/IM/PNS blends have surprisingly exhibited very similar tensile strength values. But the PLA/starch/IM/PNS blend however exhibit a slightly higher tensile strength value than the PLA/starch/IM, although it is not noticeable in figure 9.9 (a). The observation has also confirmed by the higher ΔH_c reported in the DSC analysis for the PLA/starch/IM/PNS than the PLA/starch/IM blend. The main components of pistachio nut shell are cellulose, hemicellulose and lignin and it has been shown that the PNS has 60% cellulose and nearly 13% acid insoluble lignin (Apaydin-Varol, Pütün & Pütün, 2007). The reason behind the slightly higher tensile strength in the PLA/starch/IM/PNS blend is that the possibility of the PNS particles to compete together with the PLA and starch for the core-shell. This arrangement leaves the PLA chains out of the rubbery core and maintained the PLA crystalline domains.



(a)



(b)



(c)

Figure 9.9 The tensile properties of pure PLA, PLA/starch blends (a) Tensile strength (b) Elongation (c) Young's modulus

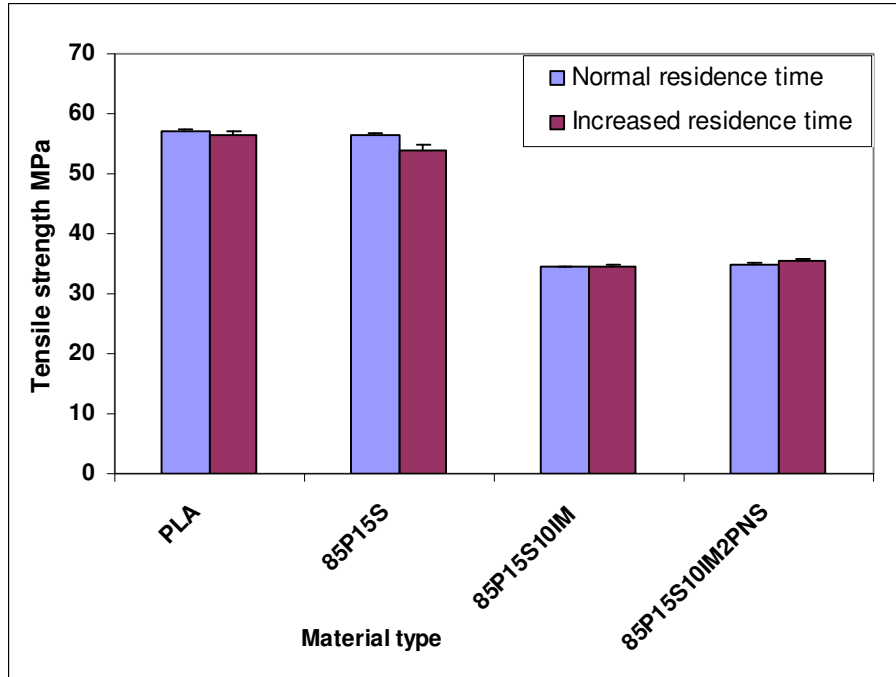
The elongation at break of the PLA/starch blend is notably reduced to nearly half of the original elongation of the PLA in the presence of the starch in the blend. The results have shown a remarkably constructive effect by IM, which has increased the elongation of the PLA/starch blend by nearly 2.5 fold with respect to the blend without the IM and 50% compared to pure PLA. The results clearly demonstrate that the acrylic core shell IM have massively contributed to impart the rubbery nature to the PLA and starch blend. The reported large increment is attributed to the MBS core-shell, which could adsorb PLA and/or starch to the rubbery core and more likely to relate to the better interfacial adhesion between the tertiary phases. Nevertheless, the ability of IM to increase the elongation at break was hidden by the PNS in the blend of the PLA/starch/IM/PNS, which has a lower elongation than the PLA/starch /IM blend. But the blend maintained higher elongation than the corresponding PLA/starch blend owing to the competing effect of PNS discussed

above. The Young's moduli illustrated in figure 9.9(c) clearly reveal that PLA has high Young's modulus. The results also demonstrate that elasticity decreased resulting in a high modulus in the PLA/starch blend due to rigid starch. Blending with the core-shell structured latexes has the potential advantages for improving impact resistance, but hopefully is not at the expense of losing the original properties. The Young's modulus reported for PLA/starch/IM blend is lower than PLA/starch blend as well as the PLA but the IM could maintain the modulus of the PLA at a reasonably high level as can be seen in figure 9.9(c). The results also demonstrate that the blend with the PNS has a slightly higher Young's modulus than PLA/starch blend, which is appropriate with the filler effect of the PNS in the PLA/starch/IM/PNS blend.

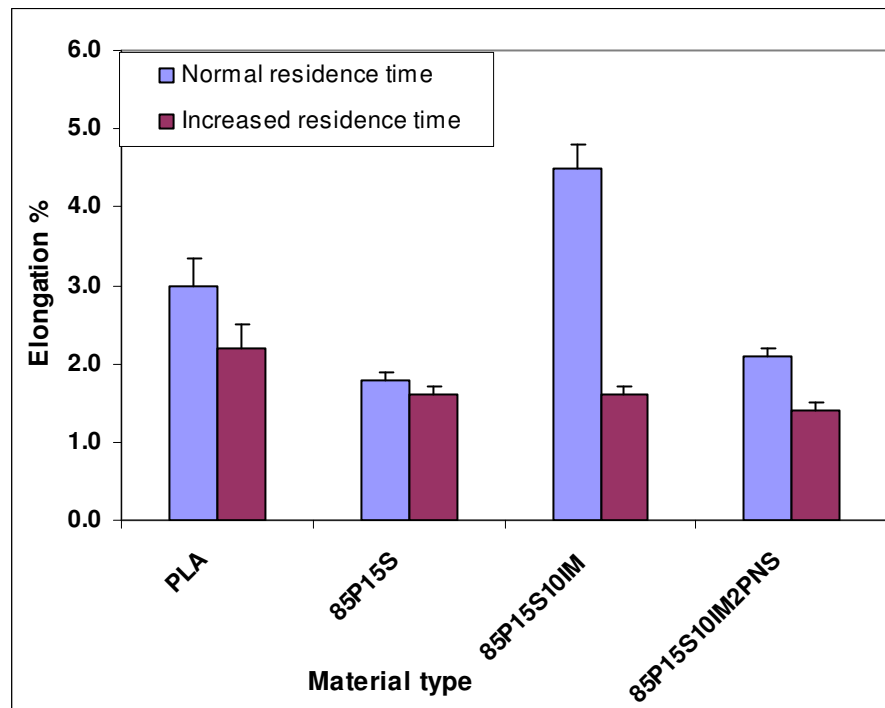
9.3.2 Measurements of an increased residence time on tensile properties

The automated injection moulding processes can occasionally undergo obstructions during moulding, and some delays in the actual injection moulding process may occur. Under these mitigating circumstances, the materials remain in the barrel for a longer period of time and extended exposures of the material at the elevated temperatures could dramatically influence the mechanical properties of the final product. The aforementioned consequence is fundamentally and technically very important and therefore, tensile properties of the same blends were performed after the material was subjected to increased residence time in the injection moulding machine. Moulding of the dumbbell specimens was carried out by increasing the cycle time of the injection moulding by twice the normal cycle time of the moulding process as explained in chapter 3, section 3.5.1. The average results of 5 samples of the stress-strain behaviour were calculated according to the BS EN ISO 527 standard, plotted against material type and compared with normal residence time as shown in figure 9.10. As illustrated by the results, the tensile strengths of all the blends and the PLA after they were exposed to a longer residence time at the processing temperatures exhibited no change except for the PLA/starch which exhibited a small reduction in strength. However, the elongation at break of the PLA and blends has shown substantial decrease where PLA/starch/IM blend has most extensively been affected. The

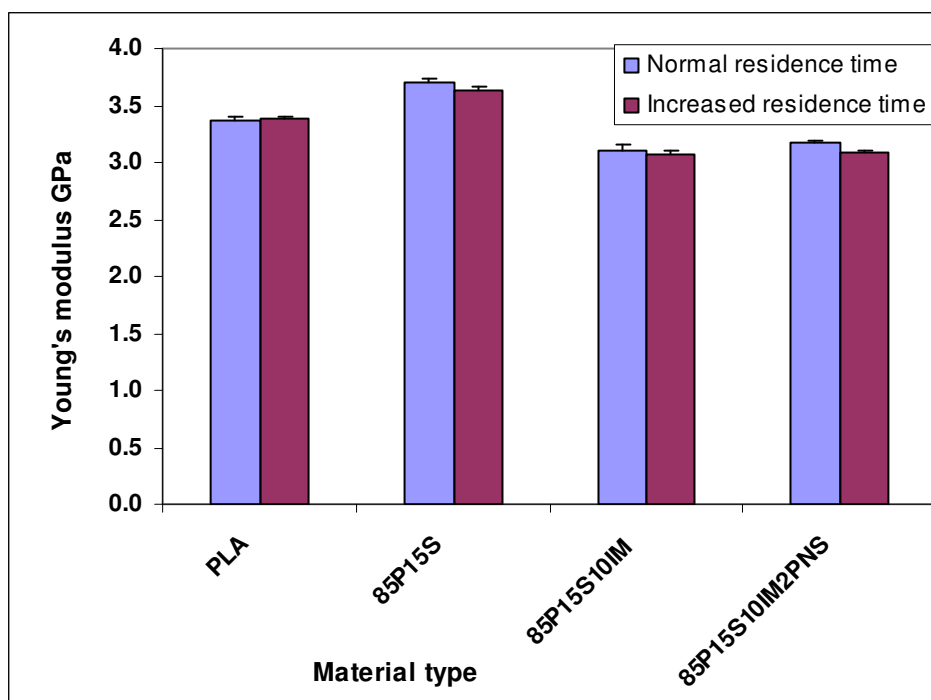
Young's moduli at normal residence time and the increased residence time of almost all the blends and PLA remain approximately similar as illustrated by figure 9.10(c).



(a)



(b)



(c)

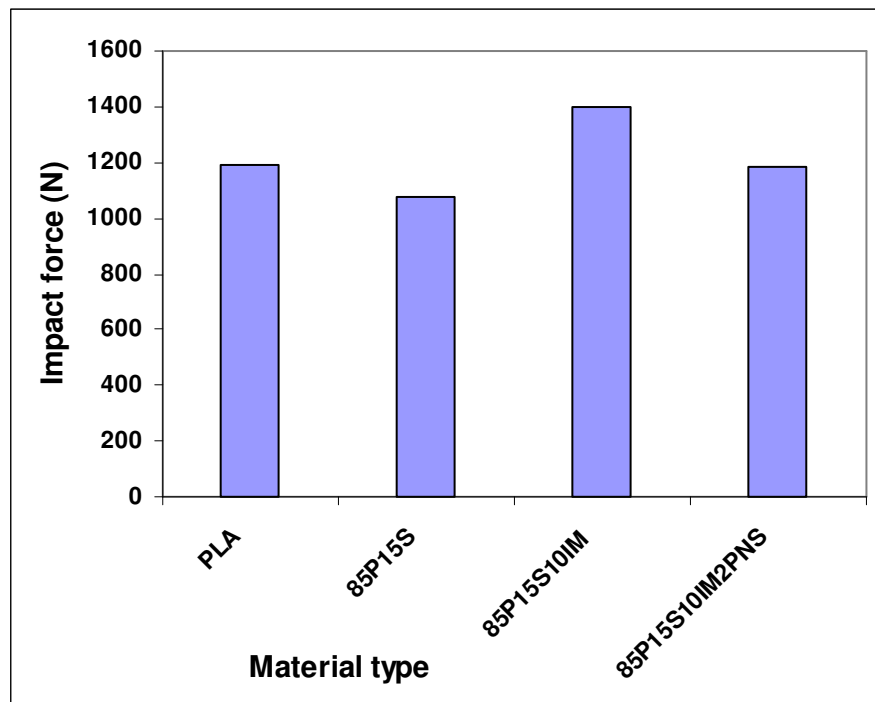
Figure 9.10 The tensile properties of pure PLA, and its blends with IM at increased residence time during injection moulding (a) Tensile strength (b) Elongation (c) Young's Modulus

When the polymers were exposed to a longer residence time at high temperatures, the polymer chains in the melt move more and there could be motions in the polymer segments as well. As a result there could be a greater deformation in the polymer melts than its initial state. Therefore, the dumbbell specimens prepared from these melts have different arrangement and the arrangement would not favour further extension, under the stress-strain investigation and could lead to a lower elongation at break. In the blends of PLA/starch/IM, it can infer that the MBS core-shell has mostly deformed from its original internal structure due to the longer exposure time in the barrel. As a result of the deformation, its original potential to adsorb the chains into the core part has destroyed thus resulting in a massive reduction in the elongation at break in the blends.

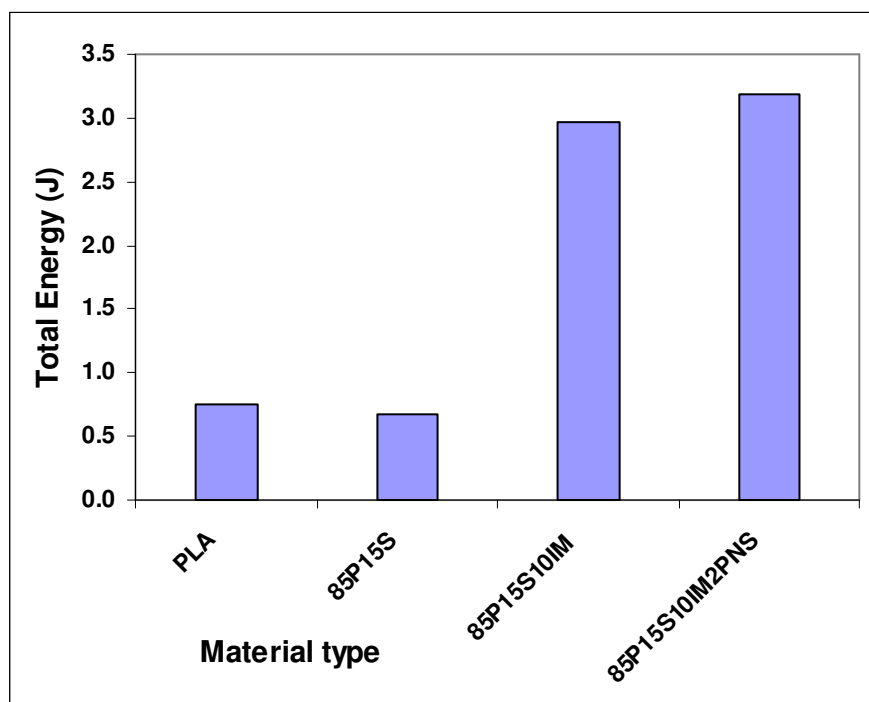
9.3.3 Impact properties

Semi-crystalline polyesters are considered as semi-ductile polymers but these polymers are brittle at ambient temperature. This problem can efficiently be overcome by the incorporation of a rubbery polymer phase, resulting in an increase of its toughness (Granel & Tran, 2002) . The blends were prepared with IM and the peak force and total energy of the blends investigated by dart drop technique are presented in figure 9.11 (a) and (b) respectively. The peak force of pure PLA is around 1200 N and it has clearly decreased in the PLA/starch blend with starch addition. But the PLA/starch/IM blend exhibited the higher impact force than those of the PLA/starch and pure PLA. The PLA/starch/IM /PNS blend demonstrated the lower peak force than the PLA/starch/IM but higher than PLA/starch blend with approximately similar impact force of that of pure PLA.

The PLA continuous phase is disturbed in the presence of starch as discussed before and the reduction in crystalline domains took place, thereby resulting in a lower impact force. The starch also behaved as a stress concentrator and therefore no energy dissipation within the blend and resulted in a lower energy absorption in the PLA/starch blend.



(a)



(b)

Figure 9.11 Impact properties of pure PLA, PLA/starch blends (a) Impact force (b) Total energy

However, IM in the PLA/starch/IM blend has shown a greater impact force than the PLA and the PLA/starch. The rubbery core of a core-shell modifier provides resistance to impact, whereas the glassy shell provides rigidity and compatibility to the polymer matrix (Si et al., 2007). The shell functions as the layer that physically binds the matrix to the rubber core. The rubber particles act as stress concentrators, and relieve the hydrostatic tension by cavitation processes and produce the more extensive matrix deformation (Liu et al., 2009) plastics. The deformation mechanism usually depends on the morphology of the modifier. In the presence of a good interfacial adhesion between the modifier and matrix, enhanced impact properties are provided. A phase separation is possible if the two phases repel each other and the interface could be very weak and fail under any kind of mechanical or thermal stress. Compatible polymer blends have a strong interface that permits the stress to transfer across it successfully. The greater energy absorption reported in figure 9.11 (b) for PLA/starch/IM and PLA/starch/IM/PNS exhibits the key efficiency and compatibility

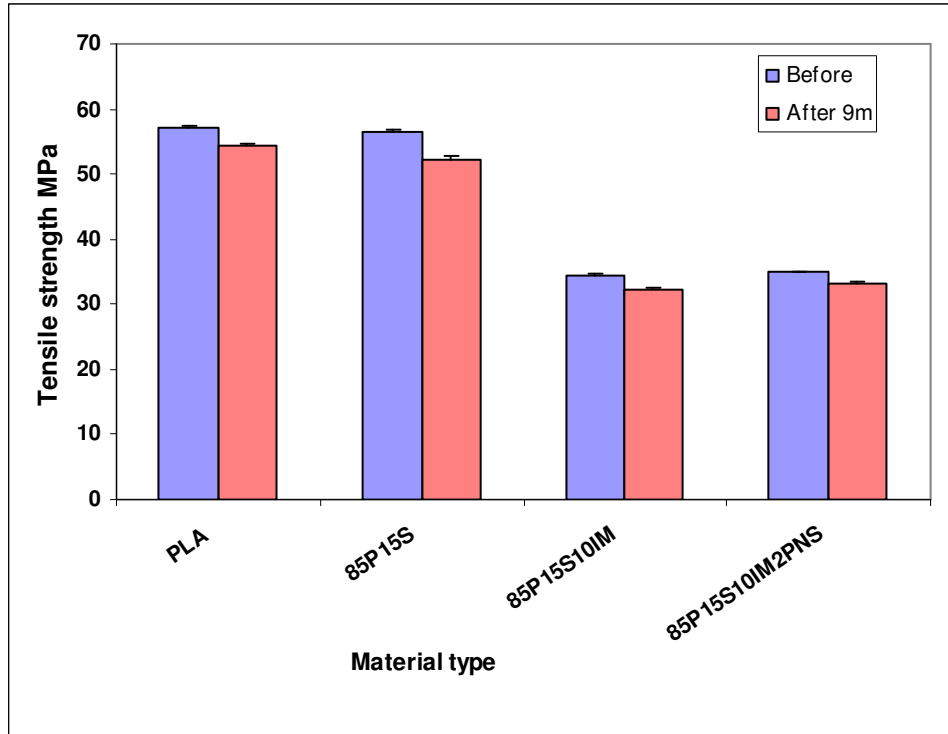
of the MBS core-shell with the PLA/starch blend. Substantially enhanced impact properties were also reported on a study of inherently brittle PLA with the biostrength impact modifier elsewhere (Cygan, Sing & Seshadri, 2007).

9.4 Measurements of ageing studies

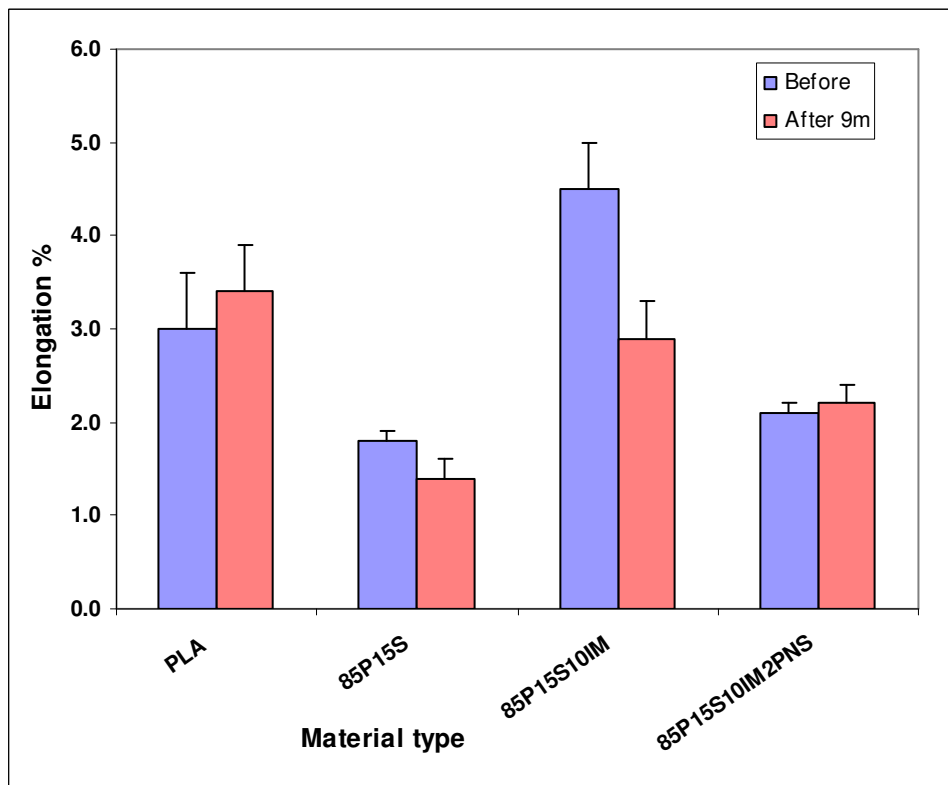
9.4.1 Tensile properties

When a polymer is cooled from its melt, the molecular chain becomes frozen if the temperature is below its T_g . The polymer exist in a nonequilibrium state, at temperatures near the solidification of the melt, the free volume will reduce spontaneously toward an equilibrium thermodynamic state, resulting in a reduction in enthalpy (Wang, Sun & Seib, 2003). This phenomenon is a time dependent process and referred to as physical ageing. The free volume of the polymer can vastly influence its physical and mechanical properties (Hay, 1995; McGonigle et al., 2000). Therefore, it is very vital to understand that the physical ageing parameter can strongly influence the internal structure and behaviour of the polymers exhibiting significant changes in mechanical properties. The effect of physical ageing on tensile properties and impact behaviour were investigated after 9 months storage and reported in this study as a comparison with the initial properties. Figure 9.12 represents the measurements of the tensile strength, elongation at break and Young's modulus of the samples aged for 9 months and unaged samples as can be seen in (a), (b) and (c) respectively. The blends and PLA have shown a reduction in the strength due to the phenomena of physical ageing, nevertheless, the Young's modulus has slightly increased upon 9 months storage. The elongation at break of PLA has considerably increased whereas in the other blends the elongation remained the same or decreased.

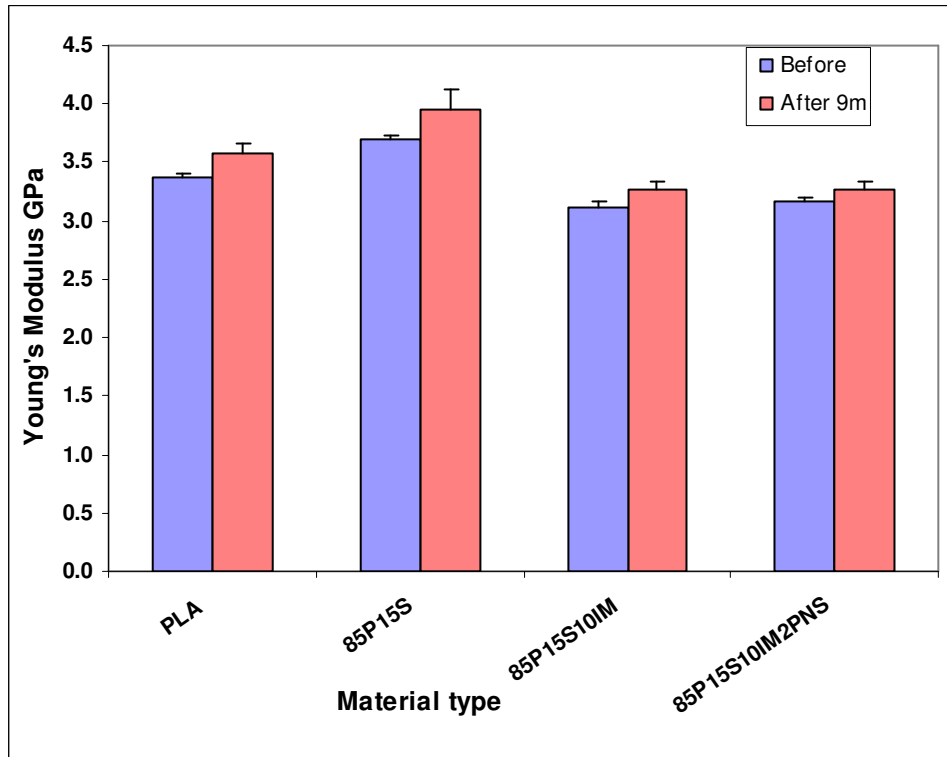
The origin of physical ageing associated with free volume and controls the molecular mobility of large segments of the polymer chains. Due to the molecular mobility of the polymer segments, the unoccupied volume will reduce, so that their orientation gradually changes with the elapsed time. Consequently, the polymer attains a new arrangement which in turn influences the mechanical and electrical properties (Van Turnhout et al., 1977).



(a)



(b)



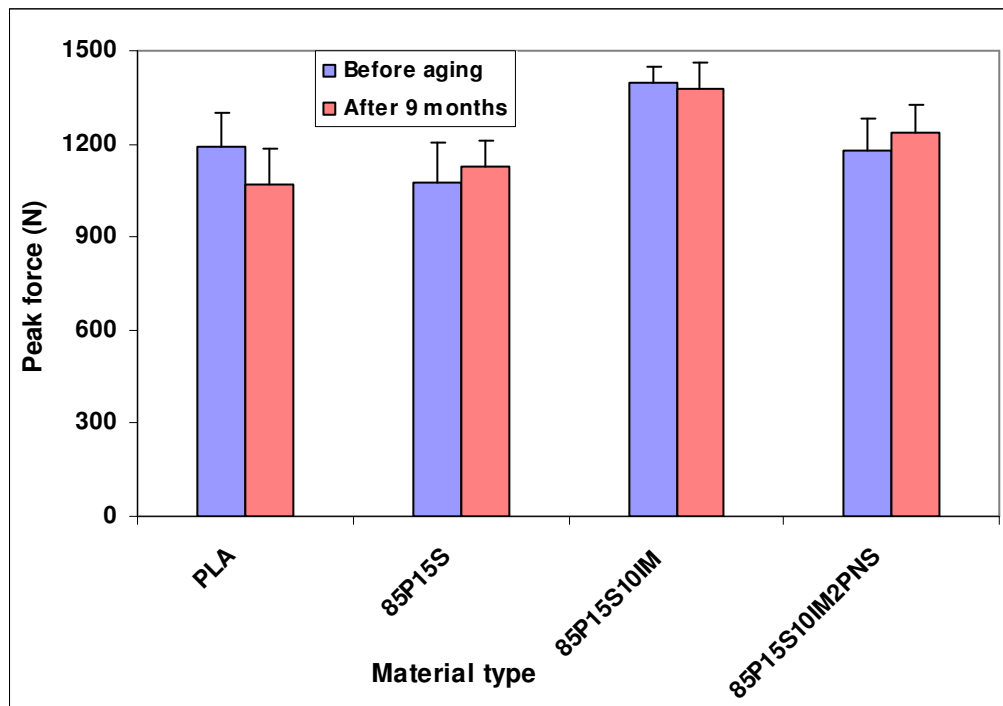
(c)

Figure 9.12 Comparison of tensile properties of pure PLA, PLA/starch blends with IM after 9 months storage (a) Tensile strength (b) Elongation at break (c) Young's modulus

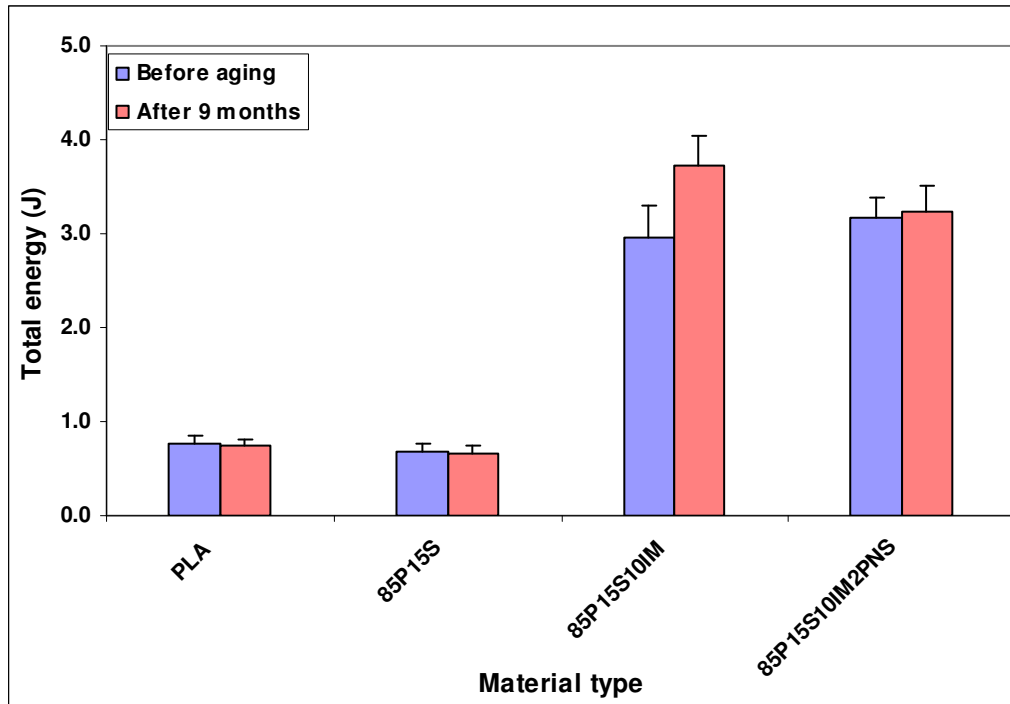
All the investigated blends including pure PLA have shown a low tensile strength after storage due to this molecular mobility resulting in a free volume reduction. As a result of this new arrangement in polymer chains, the PLA has exhibited a higher elongation at break than its original capacity. However, the PLA/starch and PLA/starch/IM have demonstrated a substantially lower elongation at break than initial values. In the PLA/starch blend, the bulky starch has evidently controlled the mobility of the polymer segments. The massive reduction in the elongation at break of the PLA/starch/IM is not only due to the starch but also attributed to part of the mobility of the polymer segments. The segments could either have caused desorption from the core-shell, or reduction in free volume of MBS core-shell owing to the physical ageing have defeated its original control. As the polymer ages, it becomes more glass-like and hence becomes stiffer and more brittle (Van Turnhout et al., 1977). The results of all the blends and PLA agree with this phenomenon with the elapsed time.

9.4.2 Impact behaviour

Ageing studies were further extended, impact properties were also investigated by drop dart method after 9 months of storage under room temperature conditions. Figure 9.13 (a) and (b) illustrates the measurements of the variation of the peak force and the total energy absorption with regard to the material type respectively. The effect of ageing is reported in this study as a comparison of the initial peak force and total energy absorption and each graph represents comparison of the properties of the aged and unaged samples. As shown by figure 9.13 (a), PLA/starch and PLA/starch/IM/PNS blends have revealed a slightly enhanced peak force after 9 months storage while the PLA has shown the lower peak force and the PLA/starch/IM remains almost the same as before ageing. The total energy absorption by the materials after 9 months storage, exposed in figure 9.13(b) is 25 % higher for the PLA/starch/IM blend compared with no ageing whereas the PLA, PLA/starch and PLA/starch/IM/2PNS blends remains the same.



(a)



(b)

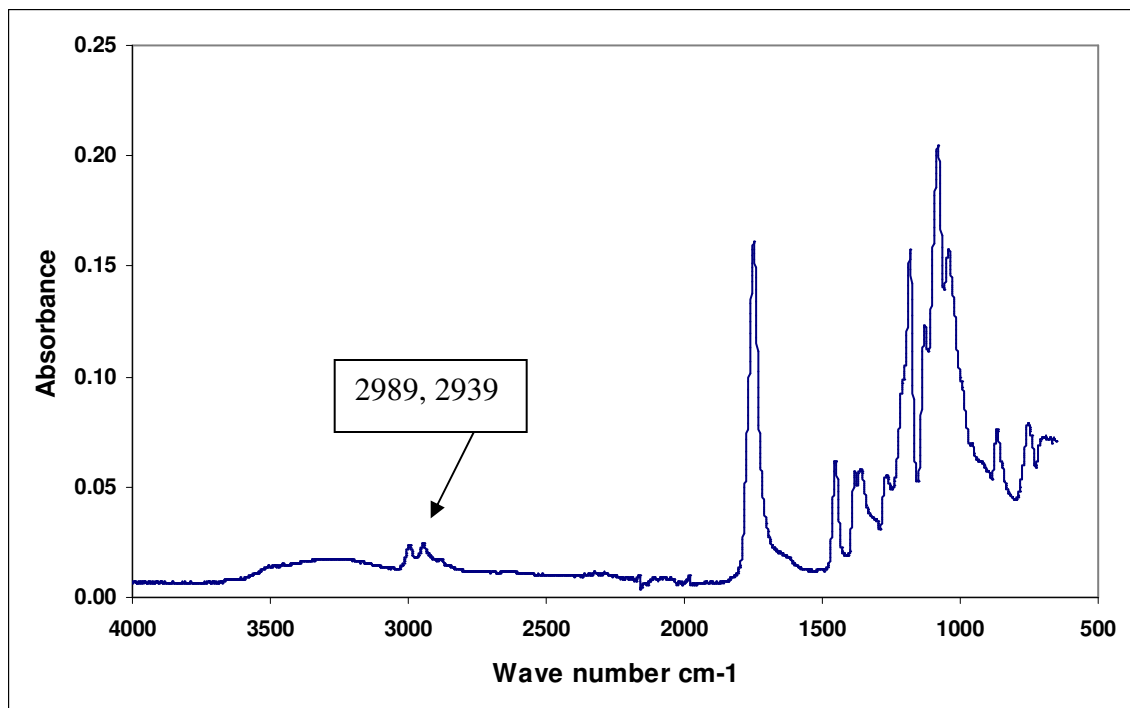
Figure 9.13 Comparison of impact properties of pure PLA, PLA/starch blends with IM after 9 months storage (a) Peak force (b) Total energy (c) Total deformation

As time elapsed, segmental motions occur in the polymer chains to attain an equilibrium state. Consequently, the free volume reduces as more and more segments occupy these unoccupied areas. In this new arrangement, more segments could have physically bound to the rubber core in the presence of the IM facilitating an extensive matrix deformation resulting in a higher impact resistance than in their original resistance. However, the PNS has prevented the IM efficiency to a considerable extent, and exhibits a little higher impact resistance than original upon physical ageing.

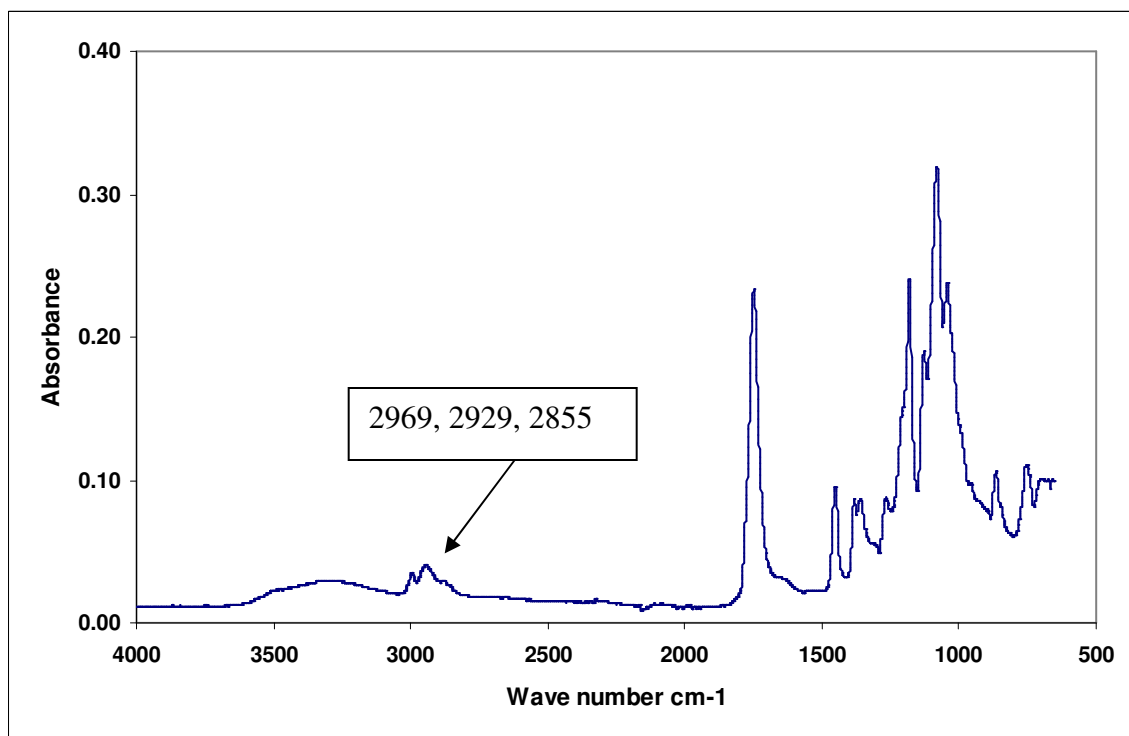
9.5 Vibration pattern in the IR region

As reported in the previous chapters, the appreciable transformations that take place in the FTIR spectra can demonstrate immiscibility or miscibility of blends upon the addition of each component. In addition to what has been said, IR spectra of the blends can also reflect a distinct chemical interaction such as hydrogen bonding or the dipolar interaction between

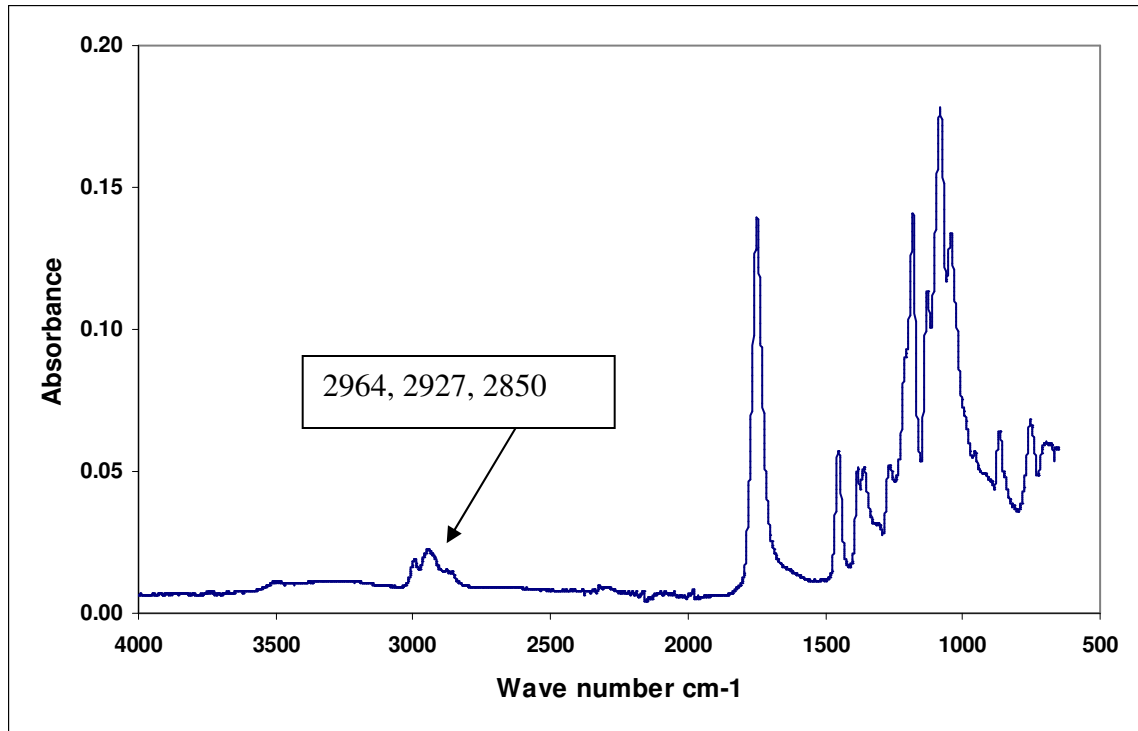
the chains of the different polymers if they are compatible, by means of band shifts and broadening. Therefore, FTIR analyses of the prepared blends were carried out according to the protocol described in chapter 3 and the vibrational spectra present in figure 9.14. The vibrational spectra illustrated in figures 9.14 (a) (b) and (c) are for the blends of PLA/starch, PLA/starch/IM and PLA/starch/IM/2PNS respectively. The strong carbonyl stretching peak of PLA at about 1746 cm^{-1} wave number can apparently be observed in all the blends without any deviation in the peak position. The triple peaks at the 1125, 1078, and 1040 cm^{-1} wave numbers for pure PLA as well as for the PLA/starch blends which are responsible for the -C-O- stretching in the -O-C=O has slightly changed. The peak at 1125 cm^{-1} has changed to 1127 cm^{-1} while the peak at 1140 cm^{-1} changed to 1139 cm^{-1} and the 1078 cm^{-1} peak remained in the same position. Furthermore, the -C-O- stretching of the -CH-O- shown at about 1180 cm^{-1} for the PLA as well as for PLA/starch blend remained without any change in the peak position. According to these observations, the results obviously suggest that the carbonyl group does not participate in forming a new bonding, but the -CH-O- group could moderately partake. However, a noticeable change around the 3000 cm^{-1} wave number is clearly observed in the blends with the IM. The doublet which is observed around the 2989 and 2939 cm^{-1} wave numbers has changed to a triplet at 2969 cm^{-1} and 2929 cm^{-1} with a small shoulder peak at 2855 cm^{-1} for the blend of PLA/Starch/IM and 2964 cm^{-1} , 2927 cm^{-1} and 2850 cm^{-1} for the blend with PLA/Starch/IM/2PNS. These peaks are usually associated with C-H stretching of starch material and the changes imply that some of the H in the starch was involved in the bonding. These results together with some of the changes observed in -C-O stretching of CH-O group in PLA can suggest that some moderate bonding between these two materials are possible in the presence of the IM.



(a)



(b)



(c)

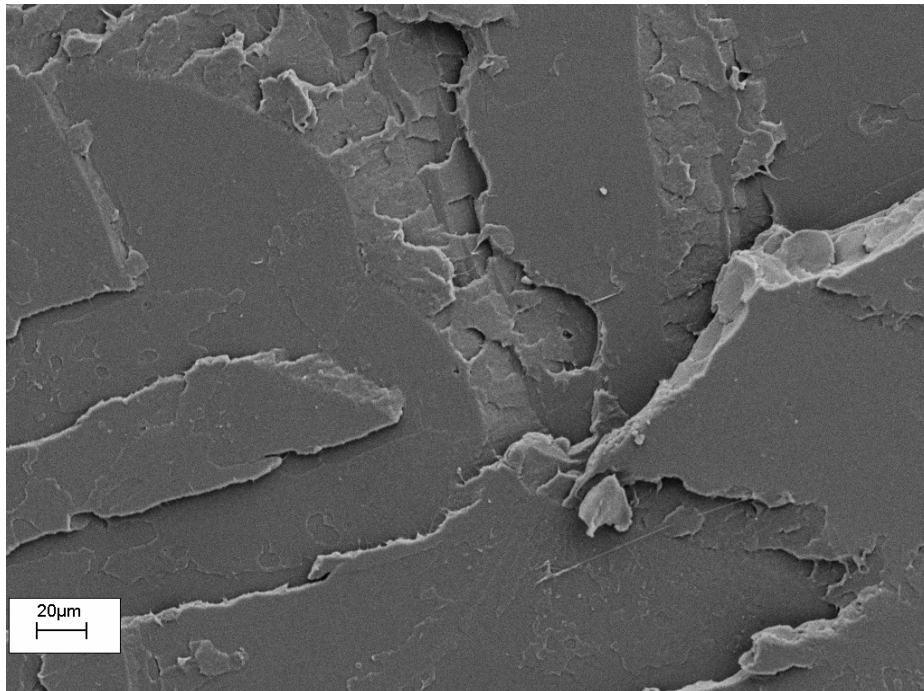
Figure 9.14 FTIR studies of pure PLA, PLA/starch blend, PLA/starch blend with IM (a) 85P15S (b) 85P15S10IM (c) 85P15S10IM2PNS

9.6 Scanning electron microscopic analysis

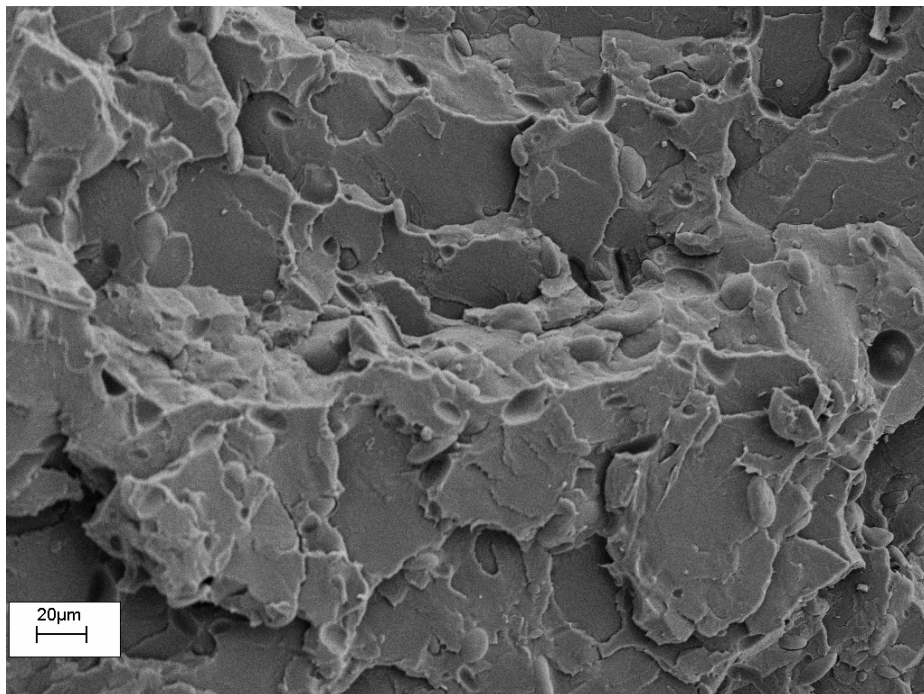
Morphology of the blend is another characteristic feature, usually investigated with the use of scanning electron microscopy technique and used to deduce vital information whereby elucidating its properties. The investigation of the morphology was performed and SEM micrographs have been obtained of the tensile fracture of PLA (Figure 9.15a), PLA/wheat starch blend (Figure 9.15b), PLA/wheat starch /IM blend (Figure 9.15 c) and PLA/wheat starch /IM/2PNS blend (Figure 9.15 d). As described in the previous chapters, the fractured surface of PLA was smooth and PLA/starch was coarse and it can also be seen from the SEM micrographs of the PLA and the PLA/ wheat starch blends. In the PLA/wheat starch blend, some starch granules were clearly observed, some voids have been left after the granules were pulled out as shown in the SEM, figure 9.15(b). Conversely, for PLA/starch/IM blends, an undulated and rough surface was exhibited,

which is a characteristic of a rough material fracture. However, the SEM micrographs of these blends surprisingly illustrated some larger granules which were pulled out and pores have been created as can be seen in the figures 9.15 (c) and (d). The particles were larger in size and was prominent than in the PLA/wheat starch blend. The IM which was incorporated into the PLA/starch blend is a core-shell copolymer. Copolymers tend to migrate to the surface by forming continuous layer around each particles thereby reducing interfacial tension coefficient (Aji & Utracki, 1996). In a core-shell, the core is usually a rubbery particles and shell or the outer layer is a glassy polymer, which functions as a layer that physically binds the matrix to the rubber core (Liu et al., 2009).

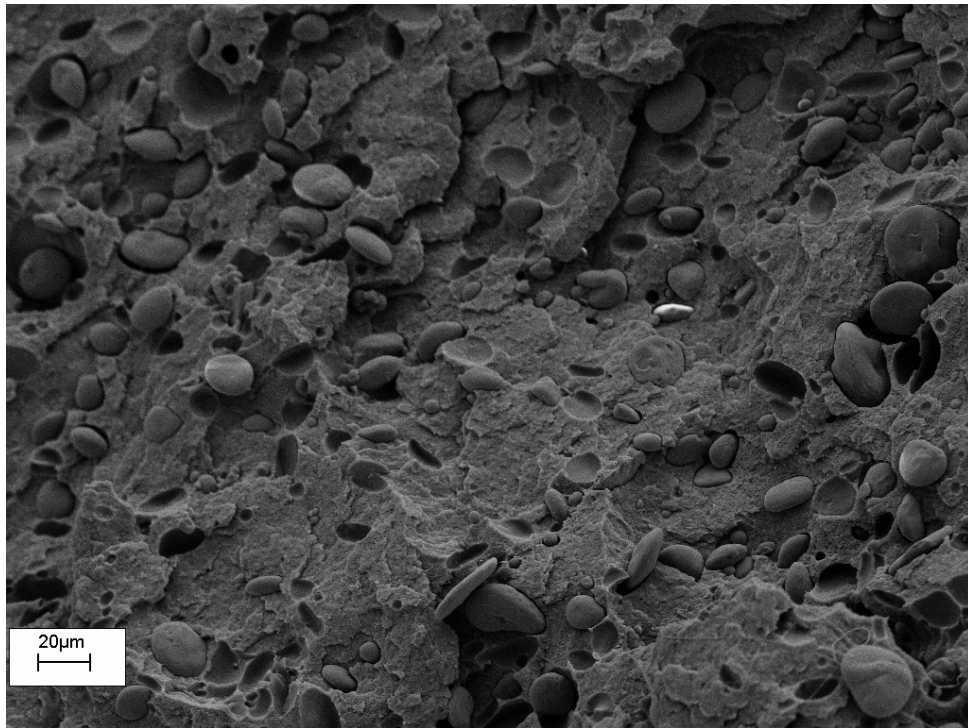
Compared to the surface of PLA/starch binary blend, the blend with the IM shows a multi porous surface with the nonuniform distribution of the cavity size as shown in Figure 9.15(c). A very similar phenomenon can be observed for the PLA/starch/IM PNS blend as shown in figure 9.15 (d). This suggests that blends based on the IM have large aggregates of the IM particles because of some incompatibility between the starch and the shell of the core-shell. As starch consists of amylopectine and amylose which are bulky polymers, there could be steric restrictions for the shell of the polymer to form a continuous layer that bind the starch with the core. On the other hand, due to the structural arrangement of the core-shell, starch granules could have clustered without binding to the core. The structural arrangement of clustered starch particles or aggregated core-shell polymers would have attributed for the larger particle sizes in the SEM micrographs.



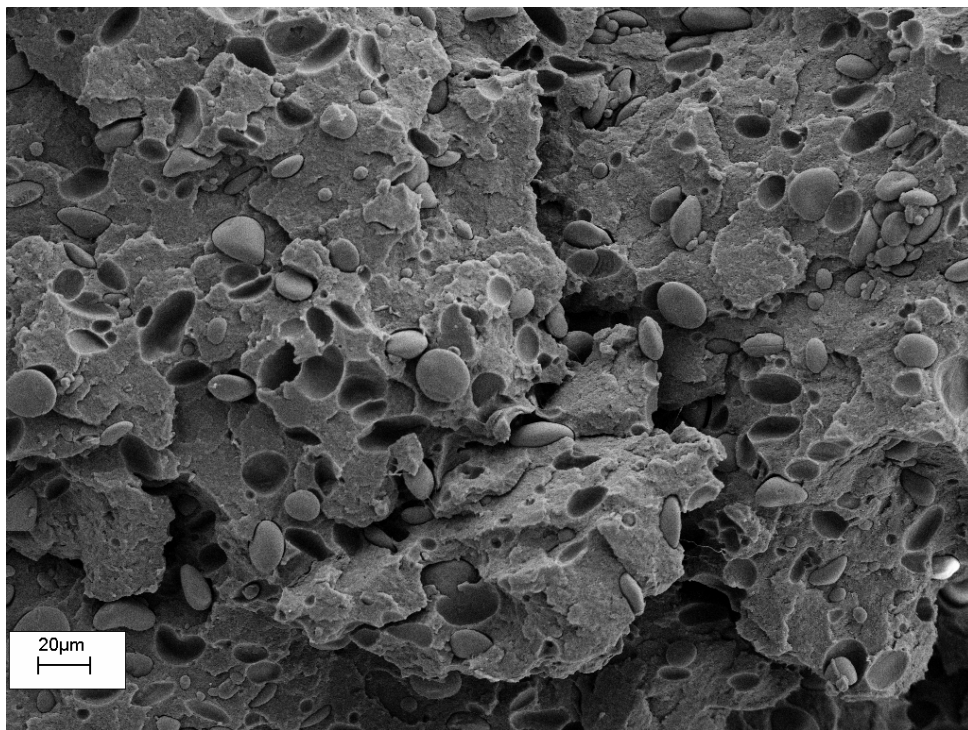
(a)



(b)



(c)



(d)

Figure 9.15 SEM studies of pure PLA and PLA/starch blends with IM (a) PLA (b) 85P15S (c) 85P15S10IM (d) 85P15S10IM2PNS

9.7 Water absorption measurements

The major constituents in starch, amylose and amylopectin consist of a plethora of hydroxyl groups. Moreover, PLA itself consist of reactive hydroxyl functional groups. Therefore both polymers could exhibit a high susceptibility towards water. However, it has been reported in the previous study that PLA is hydrophobic whereas starch is greatly hydrophilic (Wang, Sun & Seib, 2001). Therefore, the water absorption of PLA, PLA/starch blends and blends with the IM is of another interest in the current study. The study of water absorption with higher starch loading is reported in chapter 5. The results in chapter 5 have shown that PLA absorb water at a lower level than starch. Figure 9.16 exhibits the water absorption of the PLA, the PLA/starch blend at low starch loading and the PLA/starch blends with the IM. The PLA and the other blends show a high rate of water absorption in the first week of storage and eventually the absorption rates decrease and in the PLA it levels off at less than 1% water absorption. The other blends show an increasing propensity towards water absorption even after 35 days of immersion in water. The highest water accumulation was observed in the blends with the PNS whereas the lowest water accumulation in the PLA samples. The reason behind the observation is that, beside the starch, the hydrophilic components of the pistachio nut shell such as cellulose and hemicellulose have additionally contributed to a higher percentage of water absorption. However, the PLA/starch and the PLA/starch/IM show very similar water absorption rates. The IM appears to be neutral in the water absorption according to the results explored in figure 9.16. The results reported in chapter 5 demonstrated that the high starch loading can increase the water absorption rate as well as the absorption percentage. It can be inferred from these results that the starch has the potential in controlling water absorption in the starch PLA blends.

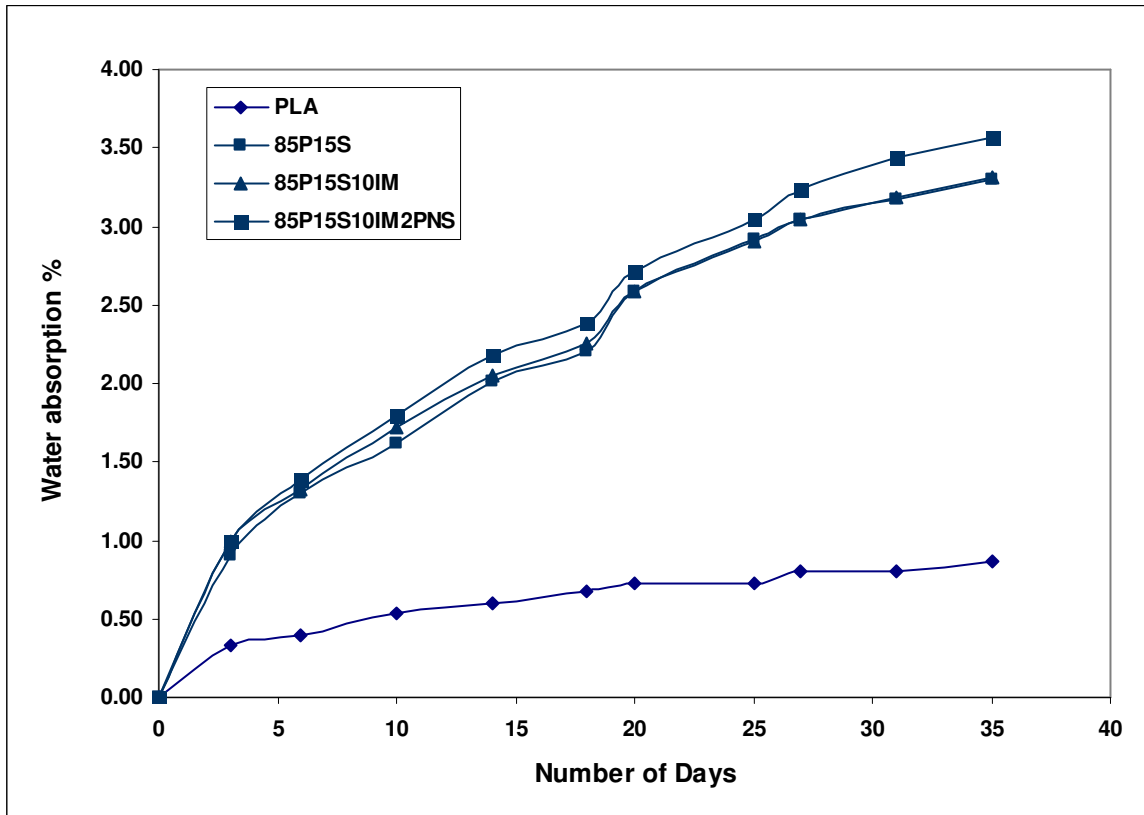


Figure 9.16 Water absorption measurements of PLA and its blends with starch and impact modifier

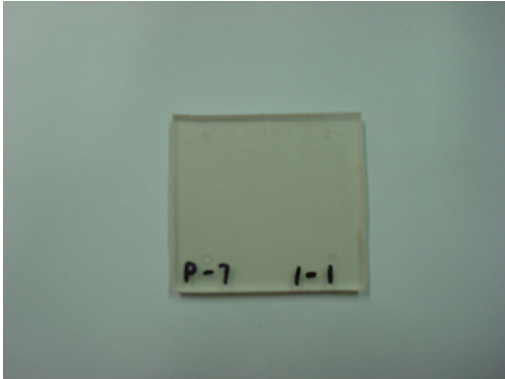
9.8 Home composting trials

Beside recycling, incineration, and composting, the leading method of packaging waste disposal worldwide is landfill. As a result, valuable space is defeated and the generation of greenhouse gases and contaminants have become harmful environmental issues. Therefore, methods such as reuse, recycling or composting are highly encouraged as a way of reducing packaging waste disposal. However, analysis of 2007 RECOUP report (www.recoup.org), by Tarverdi (Tarverdi, 2010) has pointed out that the cost involved for recycling is extremely high to the reprocessor, of which half of the cost was associated with sorting and cleaning. As such, there exist some limitations in recycling, and it is always advised to minimize sorting and cleaning in the process. Furthermore, there are more

limitations to physical recycling, if packaging materials are soiled with foods or other biological substances. In such situations, one of the promising alternatives of reducing biodegradable waste stream is by composting. Subsequent disposal of biodegradable polymers are expected to undergo complete degradation for example, to carbon dioxide under aerobic conditions such as composting and methane under anaerobic conditions such as landfill and anaerobic digestion together with other elements that may present in the materials (Davie & Song, 2006). However, landfill of biodegradable polymers could be another critical issue as it generates methane and therefore not recommended. As biopolymers are increasingly used in many applications now including food, pharmaceutical and consumer goods packaging, one of the widely spread methods for disposal of packaging waste could be composting provided that, governments, commerce and especially consumers support and embrace this substitute. The composting technique follows the natural concept of the biodegradation and breakdown of massive waste in small scale by a treatment method known as 'slow-stack'. The controlling protocol of controlled biological decomposition of organic waste in the 'backyard composting' process is explained in the chapter 6 under section 6.6.

The plastic packaging including single use plastic goods have become real issues that are vastly contributing to landfill and thus needs immediate consideration. Promoting home composting can immensely reduce these waste collected by municipal councils for landfills and can reduce cost involved in the process by many ways. To instigate the home composting process, the plastic waste requires to be biodegradable. Therefore, the investigation of the home composting trials of the blend, developed by amalgamating completely biodegradable raw materials, is a vital requirement and is of the practical importance in the present communication. Given in figure 9.17 are the pictures of the home composting trials of the samples carried out in a working home composting environment at London borough of Harrow. The average temperature of the compost pile was observed to be 45⁰C. The pictures given in the left side of the figure 9.17 demonstrate the appearance of the samples before the composting treatment and pictures shown in the right side exhibit appearance after they were composted. The pictures taken of the PLA and shown in figure

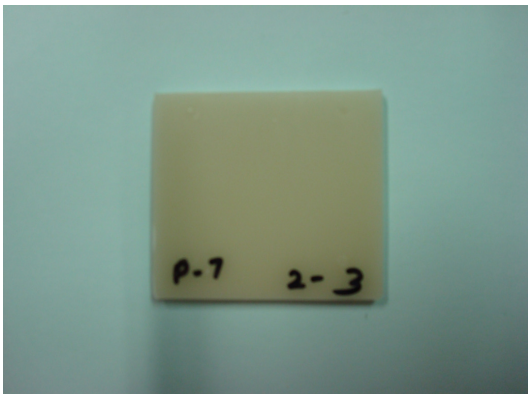
9.17 (a) do not illustrate any apparent sign of degradation after they were buried in the composting bin for 90 days.



(a) -Before



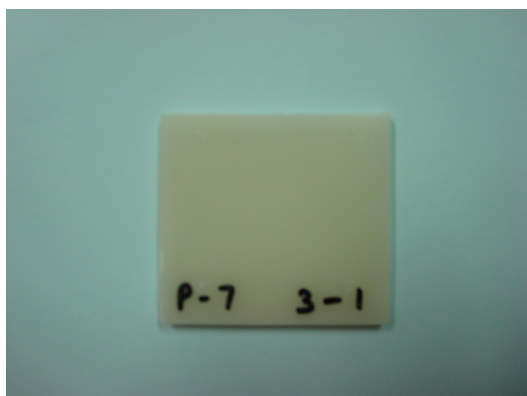
(a) -After



(b) -Before



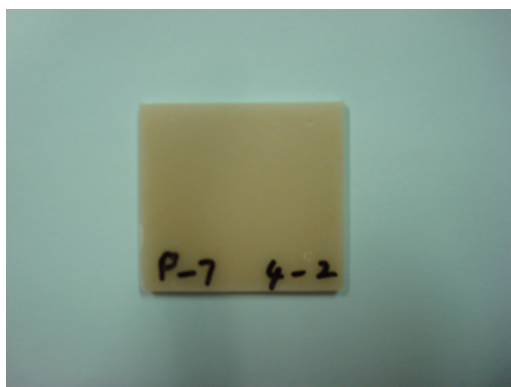
(b) -After



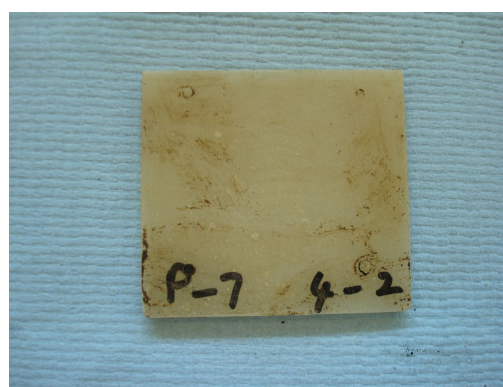
(c) –Before



(c) -After



(d) –Before



(d) -After

Figure 9.17 Home composting observations of PLA and its blends with starch and impact modifier (a) PLA (b) PLA/starch (c) PLA/starch/IM (d) PLA/starch/IM/PNS

It is important to note that in order to satisfy the biodegradation, certain material properties are necessary beside the environmental conditions. The rate of biodegradation not only depends on the raw material but also on the chemical structure, geometry and essentially on the thickness of the final article (Szegda, 2009). It has also been reported that PLA can be hydrolyzed into smaller molecules such as oligomers, dimers, and monomers in a composting environment after 45–60 days at higher temperatures around 60 °C (Tokiwa & Calabria, 2006). The hydrolysis and molecular weight reduction of PLA is schematically shown below.

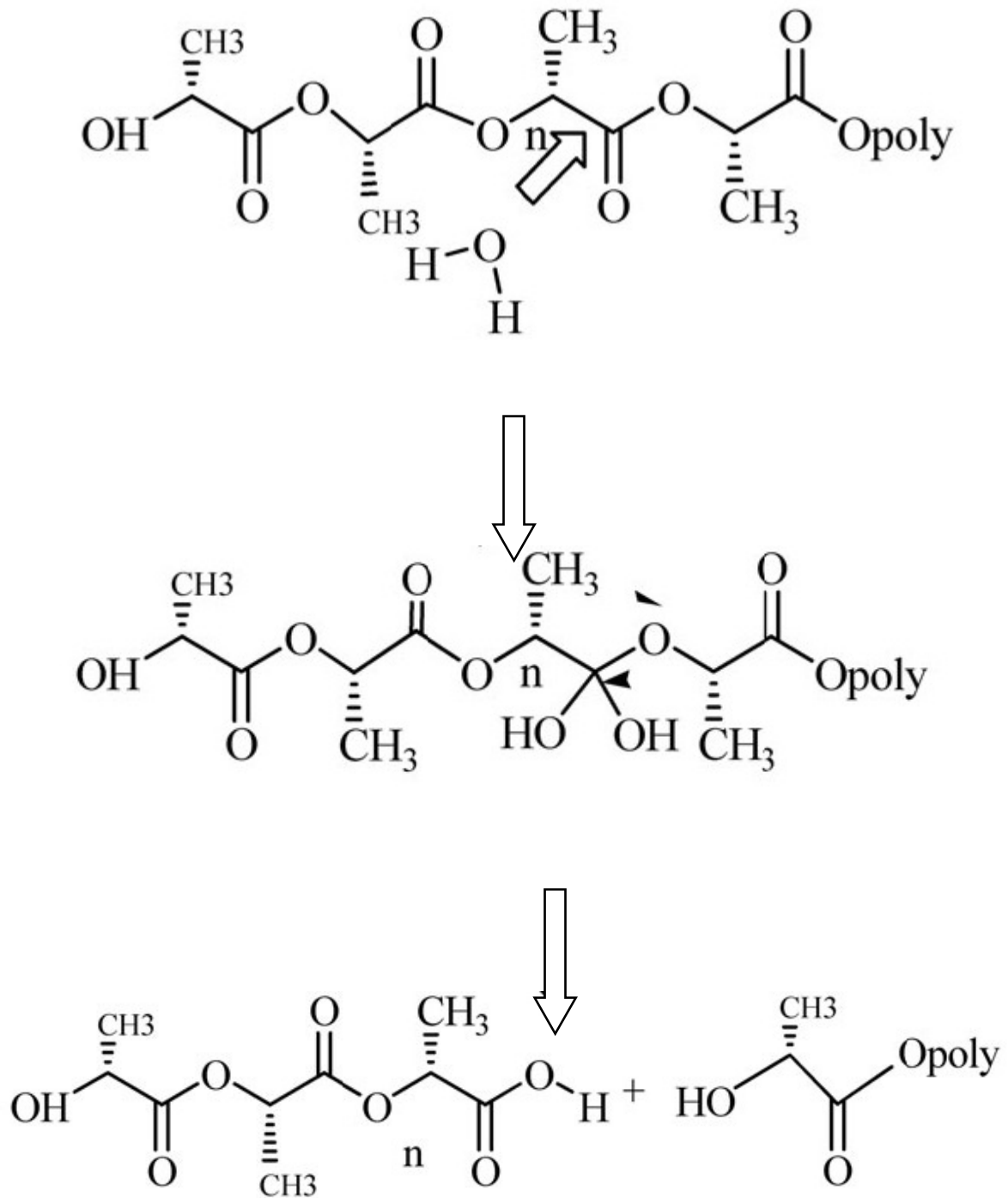


Figure 9.18 PLA hydrolysis leading to smaller molecules (courtesy, (Kale, Auras & Singh, 2007))

These smaller molecules are then further degraded into CO_2 and H_2O by microorganisms in the compost. Moreover, the exposure conditions such as moisture, pH and temperature can

be categorized as factors affecting the rate of degradation. Water or moisture can greatly affect the biodegradation of polymers as water is needed for microorganisms to grow and reproduce. Therefore, in a moisture rich environment, more microbial activity should lead to faster polymer degradation than the environment without moisture. On the other hand, since hydrolysis plays a fundamental role in the biodegradation of PLA and starch, the hydrolysis reactions should increase, which produces more chain scission reactions and increases the available sites for microorganisms to attack.

Furthermore the rate of hydrolysis reactions can also be altered by the pH, since reactions can be either acid or base catalyzed (Kale et al., 2007). For example, it was found that the hydrolysis rate of the PLA capsules was slowest at a pH of 5.0 and increased in more acidic and more alkaline solutions (Auras, Harte & Selke, 2004). The pH of the exposure environment can change as a result of degradation products such as water-soluble lactic acid from the PLA. Changes in the pH affect not only the rate of hydrolysis, but also the growth of microorganisms. Temperature is another significant factor in controlling the polymer biodegradation since both hydrolysis reaction rates and microbial activity increase as temperature increases; however, if temperatures are too high, microbial activity decreases or even stops.

The current study doesn't comply and cannot be compared with the previous studies of the composting of PLA (Kale, Auras & Singh, 2007) carried out on bottles and deli-containers which disappeared after 30 days of composting mainly due to the sample thickness, beside the exposure conditions. Because of the higher thickness of the sample, the exposure of most of the polymer chains to the environment is restricted. However, the degradation of PLA/starch blend demonstrate in figure 9.17 (b), shows some initiation of the degradation within 90 days exposure in the compost bin. The colour has changed and some holes were created in the injection moulded impact test specimen after 90 days exposure. Accelerated biodegradation has also been reported elsewhere with starch based materials (Vikman, Iitiivaara & Poutanen, 1995). Conversely, the blends with the IM have not shown any sign of degradation leading to a similar observation to that of the PLA. It can be inferred that in the blends with the IM, the PLA and starch are entrapped within the core-shell and locate

hindered from the direct exposure to the environment, which has prevented the reach of microorganisms and moisture to the polymer chains thereby preventing accelerated degradation. As this is a very primary investigation, final conclusions cannot be made on the composting. This observation could be different on the actual plastic products made from the new composite based on the product thickness and exposure conditions.

9.9 Chapter summary

The biostrength impact modifier and PNS were incorporated into PLA and wheat starch and the processing was conducted by the lab-scale extruder and injection moulding machines. The decomposition in air and N₂ atmospheres, thermal behaviour, and flow behavior were investigated. Moreover, tensile and impact properties, the effect of increased residence time and ageing on mechanical properties, microstructure, vibration pattern, water absorption and home composting were also carried out and the results analysed. Particularly, in the presence of the IM, the blends of PLA/ starch have shown desirable properties compared to that of blends without IM or pure PLA. The blends were stable for the processing temperatures and no critical changes were observed in the thermal behaviour compared to that of the pure material. An attractive elongation at break resulted although the tensile strength was forfeited to a certain level, which can, however, be controlled depending on the IM concentration. Nevertheless, Young's modulus of the PLA/starch blend in the presence of the IM was comparable to that of the PLA. Moreover, an increased residence time in the barrel has not affected the tensile strength and Young's modulus of the tri blend but the elongation has significantly affected.

One of the most important properties of plastics, which relates to the service life of the article, and involves increasingly essential product safety and liability, is the impact properties, and these samples displayed noticeable impact properties in the presence of the IM. Furthermore, the mechanical properties on ageing were also satisfactory for the new blend. Water absorption of the blends was comparable to the PLA/starch blend and much higher than pure PLA. Overall the results presented attractive properties in the tri blend

systems, which can be easily adopted by the plastic industry for the development of injection moulded products within the scope of applications such as dry food packaging or cosmetic packaging.

This is the final piece of the research work of the current communication and the attention is then drawn to align an overall conclusion of the entire work in chapter 10 together with some future directions, which can be meaningfully expanded for future research based on the current research work.

10 CHAPTER TEN

CONCLUSION

10.1 Conclusions of the overall results of the current communication

This chapter draws conclusions from the complete research study carried out, reflects on the contribution to the knowledge made during the current investigation and also presents recommendations for future directions.

The packaging industry is a large global industry, which has gained a massive growth in the past decade, generating unreasonable plastic waste within the world. In the industrial perception, some short term working practices are exercised but a long term solution is evidently essential for the management of current legislative concerns and environmental impact. The current research communication highlights a longer term sustainable solution for plastic packaging by providing baseline formulations and processing conditions for biodegradable plastic composites.

10.2 Conclusions of the overall results

The experimental work and the results presented in this thesis gives some in-depth insight into the behaviour of the PLA and starch materials during extrusion and injection moulding processes and their properties with a wide range of additives. The material characterisation in this work during extrusion and injection moulding and the investigation of the influencing factors on the experiments were carried out in six different phases. The issues and material behaviour were then addressed for each phase separately under different chapters. The following section summarises and highlights the most improved parameters.

Firstly in the initial stage, PLA and wheat starch were blended with the MDI, SA and a combination of the MDI and glycerol additives and DSC, tensile and impact properties, morphology and water absorption were investigated. A few issues during extrusion, primarily due to the starch content were identified. Higher starch levels such as 30% resulted in adverse processing in the extruder and subsequently in the injection moulding process. The transparency of the extrudate of the PLA was lost in the blends turning them into an opaque appearance. Beside, the extruded strands with stearic acid collapsed during

the cooling process and hence produced non-uniform pellets. The methyldiphenyldiisocyanate additive resulted in a yellowish extrudate. It can be inferred from the results that starch can be incorporated into a PLA matrix at a 10% level without difficulty in processing in the presence of 2% MDI. The pellets can be used to make shaped mouldings by injection moulding. The tensile strength, elongation, and impact strength properties of this blend were similar to those of the raw PLA. Furthermore, in the presence of 10% wheat starch, the water absorption properties were similar to those of raw PLA. Glycerol and stearic acid have the ability to restore the crystallinity of the PLA and the heat of crystallization better than the MDI and hence there could be better physical properties with these two materials. Moreover, a higher glycerol level in the presence of MDI can better plasticise starch making a ductile material. Nonetheless, MDI is known as a toxic material and therefore further studies on this material have not been carried out in the current research, but more work was concentrated on environmentally friendly materials.

Two such materials produced by Arkema Inc. have been employed in the study with PLA/wheat starch, in search of desirable properties. Although the PLA pellets separated to some degree from the starch and biostrength modifiers in the powder form, composite pellets were successfully made by extrusion and shaped mouldings were made by injection mouldings for PLA/MS modifier blend and PLA/IM as well as both blends in the presence of starch. However, a starch content of 30% was found to make processing a little difficult due to the starch powder being separated from 5-6 mm diameter PLA pellets. The transparency of the PLA was sustained with both the IM and the MS, unlike in the previous study with starch more whitish appearance was induced in the blends of PLA/starch/modifier. The addition of the IM to the PLA was very successful towards the elongation at break and the impact properties, which resulted in 700% growth for the elongation and more than 50 and 300 percent increases for the impact force and energy absorption, respectively. The effect of the melt strength modifier and the impact modifier was found to be less prominent in the presence of starch. Furthermore, all the mechanical properties decreased after one year of storage, except for the GMO free PLA, which showed a higher impact force. It is also noticeable that GMO free PLA with the MS have shown a 74% growth in elongation whereas PLA with IM have showed a 70% reduction

after one year of storage. Similar to the previous study, the addition of starch has a prominent effect upon the water absorption.

The 30% starch content exhibited many negative effects towards the properties of the PLA/starch blend but 10% starch in the research study, discussed in chapter 4 has demonstrated a facile processability and therefore, the starch content was fixed to 15% for the other investigations of the PLA/starch blend properties. Glycerol in the preliminary study with MDI showed considerably attractive properties, behaving more like a plasticizer. Subsequently coupling effect of glycerol without MDI were investigated by employing different glycerol concentrations. Furthermore, the particle size of the PLA crucially affected the processing, and hence the PLA pellets were ground into small particles in a cutting mill by passing through a 1.5 mm sieve. The glycerol was mingled with wheat starch and mixed with grounded PLA and the blend was extruded, pellets were injection moulded and properties were investigated.

The small particle size of the PLA facilitated a better mixing between the PLA and starch. The results also suggested that the T_g of the PLA/starch blend can be reduced with an increasing glycerol concentration. The flexibility of PLA/starch blends enhanced with the addition of glycerol to the blend, with a noticeably higher energy absorption upon impact blow. The morphology showed better dispersion between PLA and starch in the presence of glycerol. The FTIR analysis also infers some degree of interactions between the PLA and starch in the presence of glycerol. Home composting of the blends have shown an accelerated rate due to the starch as well as to the glycerol. However, glycerol did not facilitate the processing of the blends using conventional polymer processing equipment due to its migration and evaporation at the processing temperatures. Nevertheless, the blends have shown an improved plasticization effect in the presence of glycerol and there may be an improved coupling effect primarily depending on the mixing technique and time and the processing conditions.

Further investigations of the reduced particle size of PLA and wheat starch blends were carried out with natural rubber latex, and the decomposition and thermal behaviour, flow

behavior, tensile and impact properties, microstructure, and bond vibrations by means of FTIR spectroscopy were investigated. The latex has shown some encouraging effects in the PLA/starch blends, however, it exhibited weak interactions in the total tri-blend system. The lack of a fine dispersion of the latex in the blend lead to a depression of the properties. Moreover, other constituents in the natural latex medium, in particular water, have affected the ultimate blend properties. Therefore, further investigations need to be carried out with latex, such that the latex is in a more dehydrated form before mixing with the blend. On the other hand, the mixing mechanism, indeed, needs to be improved before any critical conclusion can be made on latex. Nonetheless, the natural rubber latex, utilized within the scope of the current study exhibited attractive properties to the blend system. Among certain practical limitations, further studies have not been carried out with latex in this research. However, further analysis was carried out with PLA and wheat starch blend systems in the presence of a mild aliphatic acid. The adipic acid was incorporated into the blend of PLA and starch before the blend properties were investigated.

A blend was prepared with PLA and wheat starch by hydrolyzing the starch at different concentrations of adipic acid in search of desirable properties. The temperature sensitivity of the blends in air and N₂ atmosphere, transition temperatures, flow behavior, tensile and impact properties, effect of the increased residence time and aging on mechanical properties, microstructure and vibrational properties were analysed. The AA has shown some positive as well as negative effects towards the properties of the PLA/ starch blends. The tensile strength and modulus were attractive although elongation was compromised. Although AA destroyed internal the H-bonding in the starch by creating opportunities for the functional groups to interact in the tri blend, the system exhibited weak interactions. The results exhibited some hydrolysis of the ester linkages of the PLA polymer chains at higher AA levels. At the expense of the elongation, the resultant blends became very brittle. However, low AA levels exhibited some attractive properties in the tri blend system with very similar properties to the commercial PLA. Although the impact strength was improved, the flexibility of the strand was not satisfactory.

The initial study with the impact modifier discussed in chapter 5 explored some good properties with the PLA, especially the flexibility of the strand, though it was hindered in the the PLA/starch blend. The particle size and the starch quantity were the major drawbacks encountered during processing. Efforts were then taken to investigate the possibility of incorporating an impact modifier to the PLA /starch blend system with reduced particle size of the PLA and reduced quantity of the starch in the blend, before PLA/starch blends were prepared. The impact modifier and pistachio nutshell powder were incorporated into the blends, the decomposition in air and N₂ atmospheres with and without an isotherm, thermal behaviour, and flow behavior were investigated. Moreover, tensile and impact properties, the effect of increased residence time and the aging on the mechanical properties, microstructure, vibration pattern, water absorption and home composting were also analysed. Encouragingly, the presence of an IM in the blends of PLA/ starch has shown desirable properties compared to those of the blends without an IM or pure PLA. The blends were stable for the processing temperatures and no critical changes were observed in thermal behaviour compared with the pure material. An attractive elongation at break resulted although the tensile strength was compromised to a certain degree, which can however be controlled depending on the IM concentration. Nevertheless, Young's modulus of the PLA/starch blend in the presence of the IM was very much comparable to that of the PLA. Moreover, an increased residence time in the barrel has not affected the tensile strength and Young's modulus of the tri blend but the elongation has been significantly affected.

One of the most important properties of the plastics, the impact property, which relates to the service life of the article, and involves increasingly essential affairs of product safety and liability, was noteworthy for the blends in the presence of IM. Furthermore, the mechanical properties after time elapsed were also satisfactory for the new blend. Water absorption of the blends was comparable to the PLA/ starch blend and 3% higher than pure PLA. The overall results exhibited some attractive properties in the tri blend system, which can be easily adopted by a plastic industry for development of injection moulded products within the scope of applications such as dry food packaging or cosmetic packaging.

By developing all formulations and processing conditions of the biodegradable materials and their blends, the current research was undertaken to tackle the environmental impact of petroleum based polymers by implementing the new blend for packaging industry. Furthermore, new streams of applications generating revenue can be found for PLA and starch blends. Moreover, home composting can be stimulated with PLA and starch blends in the presence of certain additives, which in turn reduce municipal solid waste generation for collection for landfills.

10.3 Potential biodegradable blend from renewable resources to oil based polymers

PLA is the only commercially available *honourary bioplastic* material in large scale that has suitable physical and mechanical properties. Therefore, PLA is the only viable biodegradable alternative to petroleum based polymers for food packaging or the cosmetic packaging industry. By combining PLA granules with starch and processing under conventional processing conditions, the researcher has established fundamental formulations to develop an affordable biodegradable composite from sustainable materials with the ultimate goal of adopting into sustainable and environment friendly packaging material.

10.4 Development of novel PLA-starch based composites

All the blends of the PLA and starch investigated using a range of additives in the current communication were successfully extruded into pellets and injection moulded.

Processing of the blends was smooth except for the blends with stearic acid and higher concentrations of glycerol.

Material stability during processing temperatures was very satisfactory for all the blends.

Mechanical properties have been compromised in most of the blends but impact behaviour was noticeable for almost all the blends.

Observations made on the increased residence time suggest that the blends with impact modifier additive are stable even at double the cycle time of the injection moulding.

The preliminary study was a success and proved that it is viable to produce environmentally friendly affordable PLA-starch composite pellets for injection moulding. A foundation has been laid and formulations have been established for biodegradable composite pellets with different additives.

10.5 Recommendations for future directions

The current research study can be extended and materials can be improved and a further understanding can be gained in the future in the following aspects.

Chapter 9: Following my recommendation of using biostrength impact modifier with PLA and starch, future research can focus to conduct injection moulding trials and thermoforming trials for actual products with the established blend. Furthermore, research can be conducted on different modifier concentrations under current conditions to identify optimum levels of the modifier that is necessary to provide a compromise between both strength and the flexibility to required extent. Moreover, different concentrations of starch can be incorporated into the PLA matrix with the scope of a new stream of applications and further reducing the cost of the blend. Biodegradation in terms of home composting trials can be conducted on thinner samples or actual products by injection moulding the established blend as well as the blends to be developed. The LCA analysis is also required for the established blend before any conclusion of the cost is made on the PLA and starch blend.

Chapter 8: The established blend of PLA and starch with 1.5% AA can be used for thermoforming and injection moulding trials to develop actual products. Moreover, different starch loadings can be investigated with the PLA matrix in the presence of 1.5% AA concentration to obtain desirable properties with a higher starch content. Samples made according to real life scenarios (actual product thickness) can be employed for biodegradation studies to be conducted under home composting conditions.

Chapter 7: Latex can be incorporated into PLA and starch blends in a more dehydrated form to investigate the material properties. Different mixing methodologies can also be employed. Degradation of the blends at different weathering conditions can be examined.

Chapter 5: Different concentrations of modifiers need to be investigated with PLA matrix to obtain the optimum properties of PLA. Biodegradation study can be conducted on the biomodifiers and the PLA blend.

Chapter 4: The mechanical properties of PLA, starch and MDI blends can be further investigated in the presence of glycerol as a general alternative to petroleum based polymers or non-food packaging applications. The investigation can be further extended to biodegradation studies under home composting or industrial composting conditions to investigate the resulting compounds for MDI breakdown. However, research studies are not encouraged on “environmentally friendly” PLA and starch with harmful MDI due to its toxicity, which would also lead to damage to the overall environmentally friendly concept.

10.6 Contribution to knowledge

Of all work of the current research, particular aspects that are the original contribution to the present-day knowledge include:

- The processing of low cost composites based on starch and PLA materials with high MDI levels and glycerol, stearic acid suitable for laboratory scale extrusion and injection moulding, and the investigation of the thermal and mechanical properties.

- The processing of low cost composites of PLA and starch materials with biostrength modifiers by extrusion and injection moulding by exploring their thermal behaviour and mechanical properties.
- The incorporation of the natural rubber latex into PLA and starch composite and processing of the resultant blend by conventional extruder and injection moulding machinery to produce low cost composites with desirable properties.
- The blending of low cost starch material with PLA in the presence of adipic acid and processing under laboratory scale extrusion and injection moulding followed by examination of thermal and mechanical behaviour, rheology, and ageing upon mechanical properties.
- Biobased materials are very sensitive to temperature and their properties are vastly differing, leading to degradation. Therefore isothermal conditions were used at the processing temperatures and the TGA was carried out. This showed some weight losses of the blends at 180⁰C temperature. As such, percentage weight loss at processing temperatures can be assessed prior to actual injection moulding process.
- Some mitigating circumstances during actual mass scale production conditions lead the materials to remain in the injection moulding barrel for a longer period of time than expected, thus some delays in the actual injection moulding process may occur. These extended exposures of material at the elevated temperatures could dramatically influence the mechanical properties of the final product. The consequence is fundamentally and technically very important and therefore, tensile properties of the same blends were performed after the material being subjected to the increased residence time in the injection moulding machine. As such, the feasibility of the mechanical property loss of the material can be evaluated and its processability and the maximum time the material can retain its initial properties can be identified. As the processability improves, utilization of the material improves and the concept can be used to reduce the waste.

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APPENDICES

Appendix A: Paper published in the Plastic Rubber Composite Macromolecular Engineering, 2011

Appendix B: Abstract and the poster presented at the Bioplastic Conference 2009, Loughborough University, UK

Appendix C: Poster presented at the Graduate School Poster conference 2009, Brunel University - Vice Chancellor's prize

Appendix D: Abstract and the poster presented at the Global Plastic Environmental conference, Florida USA – 2nd Place

Appendix E: Poster presented at the Graduate School Poster conference 2010, Brunel University - Vice Chancellor's prize
ResCon 2010, Brunel University -3rd Place

Appendix F: Abstract and the poster presented at the Annual Technical Conference 2011, Boston, USA

Appendix G: Injection moulding operating conditions and temperature profile of the dumbbell specimens

Appendix H: Injection moulding operating conditions and temperature profile of the plaques

Appendix I: consist of figures obtained from thermal gravimetric analysis of the materials and weight loss comparison with time of each material between with and without isotherm at 180⁰C for 30 minutes

**Appendix A: Paper submitted to Plastic Rubber Composite
Macromolecular Engineering 2011**

Incorporation of wheat starch and coupling agents into poly(lactic acid) to develop biodegradable composite

K. Manjula Dilkushi Silva, K. Tarverdi, R. Withnall and J. Silver

Composites of poly (lactic acid) (PLA)/wheat starch and PLA/wheat starch/methyldiphenyldiisocyanate, were prepared and characterised in this study. The effects of incorporating different coupling agents on the physical properties and morphology of the composites were studied. Extrusion technology and injection moulding techniques were used to prepare standard tensile and impact test pieces. Tensometry was used to investigate the tensile properties of the composites and impact testing using falling weight technique was used to investigate impact strength. To investigate the thermal behaviour of the composites, differential scanning calorimetry was employed. Water absorption properties of the composites were also investigated. Scanning electron microscopy was used to investigate the morphology of the composites. Starch can be incorporated in a PLA matrix at 10% level without difficulty in processing by extrusion followed by injection moulding to make shaped mouldings in the presence of MDI. With 10% wheat starch and 2% MDI, blends of wheat starch/PLA can reach the tensile strength, elongation, impact strength properties of raw PLA. In the presence of 2% MDI and 10% glycerol, blends of PLA and starch make an entirely flexible material.

Keywords: Poly(lactic acid), Wheat starch, Composites, Glycerol, Processing

Introduction

The use of synthetic polymer based composites in packaging has continuously increased over the last 20 years which has resulted in an increased emission of CO₂ and carbon footprinting. It has also resulted in the deposition of large volume of plastic waste either in landfill or municipal waste recovery sites, where sorting and recovery are consuming energy and money. Plastics can be recycled rather than being buried but limitations exist with different types of plastic products. Combining of plastic products with natural systems which would reduce the environmental impact of the plastics would be a promising solution.

There is less use of alternative materials derived from renewable resources as they do not match the performance of commodity polymers and have a higher cost. Incorporation of starch into biodegradable polymers such as polylactic acid(PLA),¹⁻¹¹ poly-ε-caprolactone,¹²⁻¹⁵ and poly-hydroxybutyrate,¹⁶⁻¹⁸ gives composites which have been studied as promising alternatives to petroleum based polymers. Both PLA and starch derived from crops are completely biodegradable. Therefore the composites of these polymers can be considered as biodegradable. However, composites of hydrophobic PLA and hydrophilic starch do

not have the processing and mechanical properties¹⁻⁵ that are exhibited by fossil fuel derived polymers. Efforts have been taken to improve mechanical properties of PLA and starch blends by incorporating compatibilizers such as MDI,¹⁹⁻²² maleic anhydride,²³ decyl maleate,²⁴ triethyl citrate,²⁵ sorbitol,²⁶ glycerol,²⁷ combination of maleic anhydride and acetyl triethyl citrate²⁸ and aliphatic isocyanates.²⁹ Of them, MDI was the most effective coupling agent and it has considerably improved the strength of the PLA/starch blend at the 0-5% MDI level by hot mixing followed by compression moulding.¹ However, processing of PLA/starch composites has not been developed sufficiently for it to be adopted by industry.

In this work, coupling agents and mixtures of these coupling agents have been employed to process the blends with conventional polymer processing equipment to investigate their thermal behaviour and to improve the compatibility between PLA and wheat starch. Wheat starch³⁰ is one of the most utilised starch sources in the UK and its mechanical properties have been reported to be relatively superior to other starches.³¹ Composites of PLA and wheat starch were prepared with compositions of 90:10 and 70:30 (w/w). Coupling agents such as MDI at higher levels, glycerol at lower levels, and stearic acid (SA) have been incorporated and the blends have been extruded and injection moulded for the investigation of the thermal behaviour, mechanical properties, microscopic morphology and water absorption properties of the composites.

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Experimental

Materials

Wheat starch (Maritima 200 BA) was purchased from Food Ingredient Technology Ltd, Great Grimsden, UK. PLA (LACTY 1012) polymerised mainly from L-lactic acid was obtained from Shimadzu, Inc., Kyoto, Japan. Methylphenylthiocyanate, a yellowish brown liquid was obtained from Bayer AG, Leverkusen, Germany. Glycerol with 98% purity was obtained from Fisher Scientific, Loughborough, UK as a colourless liquid. General purpose reagent grade SA with 97% purity and a melting point of 67–69°C was obtained as a white powder from BDH Laboratory supplies, England.

Preparation of blends

Wheat starch was dried in an air circulating oven at 120°C for about 2 h. Dried wheat starch and PLA pellets, dried overnight at 60°C, were premixed in an airtight polyethylene (PE) bag at PLA/starch weight ratios (w/w) of 90:10. The MDI, glycerol and SA were added to the blend as 2 wt-% based on 100 parts of the starch/PLA blend. All the blends, with and without coupling agents, were then mixed and kept for 2–3 h in an airtight PE bag before extrusion. MDI was added to all the other blends as 2 wt-% based on 100 parts of dried starch and PLA total weight. According to the material safety data, MDI is harmful by inhalation or through skin and eye contact and therefore the material was handled with suitable safety precautions. A safety glass, face mask and a pair of gloves were worn when handling the material for personal protection and also processing was carried out under adequate ventilation and exhaust system.

PLA/starch/MDI/glycerol blends were prepared by adding 2, 5 and 10 wt-% glycerol based on 100 parts of PLA/starch blend. Wheat starch and PLA were premixed at PLA/starch weight ratios (w/w) of 90:10 and 70:30 at ambient conditions. MDI was added and the mixtures were well mixed and stored in airtight PE plastic bags for ~1 h. The blends without MDI were prepared in the same way. Then they were extruded in a lab-scale co-rotating twin screw extruder (BHS 30, Bredel Machinery Ltd, Luton, UK), which has a screw diameter of 30 mm and length to diameter ratio of 25:1, through a strand die with a 6 mm diameter at a temperature profile of 150°C (feed inlet) and 185°C for the other zones, including the zone nearest to the die. The screw speed was fixed at 80 rev/min⁻¹. The extruded rods were pelletised into small pellets using a Bredel pelletiser (B306, Bredel Machinery Ltd). Samples were dried and stored in airtight PE bags at ambient temperature until they were analysed. Pure PLA was treated under similar conditions. Blends of PLA/starch/MDI were prepared with weight ratios 90:10:2 and 70:30:2 and left overnight in airtight PE bags and extruded under the same conditions. Material compositions of the blends and their identification codes are listed in Table 1.

Tensile testing

Pure PLA and the blends were dried overnight at 60°C and injection moulded into tensile test bars according to BS EN ISO 527 using a DEMAG injection moulding machine (D60NCH, DEMAG, Schwab, Germany). The moulded specimens were then labelled and pre-conditioned at 50% relative humidity and 23°C at least for 24 h before testing. The tensile strength and

elongation at break were determined with a Zwick tensiometer (SMART PRO, Zwick Roell, UK) according to BS EN ISO 527 with a crosshead speed of 5 mm min⁻¹ and a 50 mm gauge length. Five replicates were tested for each treatment.

Impact testing

Dried pure PLA and the blends of prepared composites were injection moulded into plaques according to BS EN ISO 6603 using a DEMAG injection moulding machine (D150 NC III-K, DEMAG). The moulded specimens were then cut into 65 × 65 mm squares using a bench saw, labelled and pre-conditioned at 50% relative humidity and 23°C at least for 24 h before testing. The impact strength was determined by the falling weight technique with a Fractovis Plus impact tester (Model 7520, CEAST, Pianezza, Italy) according to BS EN ISO 6603.

Morphology

The microstructures of the blends were observed with a scanning electron microscope (SEM; Zeiss Super 25, Carl Zeiss AG, Oberkochen, Germany). Each specimen from a broken tensile test bar was mounted on an aluminium stub, and the fractured surface was coated with gold particles with a sputter coater (Polaron desk sputter coater, Quorum Technologies, East Sussex, UK) before observation.

Thermal properties

Differential scanning calorimetry (DSC) was used to determine the thermal properties. The test was carried out using a DSC Q2000 series instrument (TA Universal analysis, TA Instruments Inc., New Castle, DE, USA) according to ASTM Method D 3417-83. About 4–10 mg of each sample was sealed in an aluminium pan, with an empty sample pan being used as a reference in all cases. The thermal history of a sample was erased by heating it from 20 to 190°C at a rate of 10°C min⁻¹, holding it at 190°C for 10 min, and then cooling it to 20°C at the same rate. The thermal behaviour was recorded by the reheating of the sample from 20 to 190°C at the same rate. The heat of fusion (ΔH_f) and heat of crystallisation (ΔH_c) were determined. The heat of fusion of 100% PLA was set to 93.6 J g⁻¹ (Ref. 11) and the crystallinity of PLA in the blend was calculated. The DSC test was carried out two times for each sample to fine calculation of data and reported DSC data were 38% reproducible.

The degradation behaviour of the materials was determined by thermogravimetric analysis (TGA Q500 series, TA Universal analysis, TA Instruments Inc.). A small amount of material was placed in a clean platinum pan and heated from room temperature to 500°C at a heating rate of 10°C min⁻¹.

Table 1. Material codes and composition

Sample	PLA% (w/w)	Starch% (w/w)	Additive% (w/w)
PLA	100	0	0
C8000	90	10	0
303402	70	30	0
C8002SA	90	10	2 MDI
303402SA	70	30	2 MDI
C8002GG	90	10	2 Glycerol
C8002SA	90	10	2 Nicotinic acid
C8002M30	90	10	2 MDI / 2 Glycerol
C8002M30	90	10	2 MDI / 4 Glycerol
C8002M100	90	10	2 MDI / 10 Glycerol

Water absorption

Injection moulded standard tensile test bars were used for the water absorption test. They were dried at 50°C for 24 h and cooled to room temperature. The dried specimens were immersed in distilled water at ambient temperature for specific intervals, removed from the water, fixed with tissue paper to remove excess surface water, and then weighed. Three replicates from each blend were tested. The water absorption was calculated on a dry basis as follows:

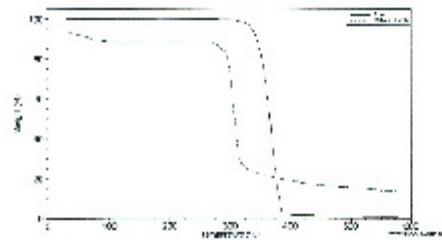
$$\text{water absorption \%} = \frac{\text{wet weight} - \text{dry weight}}{\text{dry weight}} \times 100$$

Results and discussion

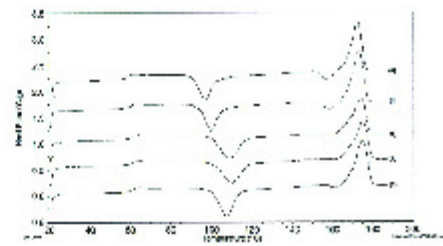
Thermal behaviour

Table 1 shows the prepared blend materials and their material codes and the TGA data are presented in Fig. 1 which shows the degradation pattern of PLA and wheat starch. Figure 2 shows the DSC thermograms exhibiting the thermal behaviour of raw PLA and the blends of wheat starch and PLA with various coupling agents, and the DSC data are summarised in Table 2. The DSC thermograms evidently showed that the glass transition is at about 60°C and an exothermic peak after the glass transition is assigned to cold crystallisation.^{21,22} The glass transition temperature (T_g) and the melting temperature (T_m) of PLA and the blends have not been significantly affected by the type of coupling agents but the crystallisation temperature (T_c) differed by approximately 10°C for glycerol and stearic acid. Furthermore, the extent of crystallisation of PLA was affected greatly by starch as well as by the coupling agents. Upon addition of wheat starch to PLA, the crystallinity of PLA was reduced by 12%. Granular starch existing as concentric growth rings²³ might have disturbed the continuous PLA phase and its molecular motion¹ thus reducing crystallinity. The addition of MDI has slightly increased the degree of crystallinity as a result of interfacial interaction between the starch and PLA in the 10S90P2M blend.

Wheat starch and PLA blends with glycerol and SA coupling agents have lowered the crystallisation temperatures (100 and 97°C respectively) compared to raw PLA (107°C), as can be seen from Table 2. This decrease in T_c suggests that the small, disordered crystals are formed.²¹ As a result of the effect of glycerol and SA in the blend, chain slippage would have been enhanced during extrusion thus favouring crystallisation. Furthermore, the extent of the discontinuous phase



1 TGA analysis of PLA (solid line) and wheat starch (dashed line)



a PLA; b 10S90P; c 10S90P2M; d 10S90P2G; e 10S90P2SA

2 DSC thermograms of PLA and wheat starch-PLA blend with and without different coupling agents

between PLA and starch might have been reduced in the blend by increasing chain flexibility which would allow molecular motions thus shifting the crystallisation temperature to lower levels. According to Wang and coworkers,¹² bonding interactions between starch and PLA restrict the molecular slippage during mechanical shearing and thereby accelerate the crystallisation. Therefore, it is possible that glycerol and SA promoted bonding between starch and PLA.

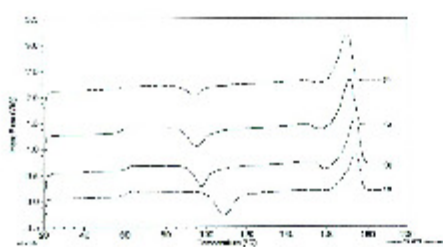
Such interactions, in the form of hydrogen bonds or ester linkages, would have controlled the slippage of chains at the interface during mechanical shearing and favoured fragmentation of PLA to enhance the number of short chains in the blend. An increased percentage of these short chains consequently supports crystallisation lowering the crystallisation temperature of the blends and giving rise to large melting peaks.

The results demonstrate that wheat starch has decreased the ΔH_m and ΔH_c of the raw PLA. In the presence of MDI, the heat of fusion and ΔH_c exceed those of the starch and PLA blend. However, glycerol and SA have restored the heat of fusion of the blends but further reduced ΔH_c .

Cold crystallisation depends on the internal structure present at the time of crystallisation and not on external constraints²⁴ and it is apparent that coupling agents as well as the starch have altered the internal structure of the blend. Incorporation of starch has produced a discontinuous phase in the whole blend and resulted in lower ΔH_c , ΔH_m and crystallinity. However, blends with MDI having active difunctional groups have decreased the discontinuity by promoting interfacial interaction between starch and PLA. Therefore, the crystallinity of the blend with MDI is higher than that of the blend without MDI. Stearic acid and glycerol^{12,25} might have plasticised the starch molecules by leaching out smaller amylose molecules with hindered O-H groups in the wheat starch to the starch granule surface.

Table 2 Crystallisation and melting properties of raw PLA and PLA-wheat starch blends with different coupling agents

Sample	T_g , °C	ΔH_c , J/g	T_m , °C	ΔH_m , J/g	Crystallinity, %
PLA	107.57	26.55	175.02	38.04	40.6
10G90P	110.04	24.94	175.17	32.81	37.9
10S90P2M	109.00	26.21	174.12	33.72	35.4
10S90P2G	99.83	21.13	173.24	38.23	42.6
10S90P2SA	100.01	20.43	172.53	37.47	40.0

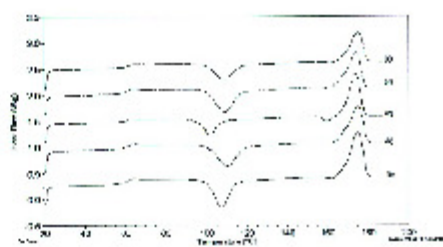


a 10S90P2M; b 10S90P2M2G; c 10S90P2M5G; d 10S90P2M10G
 3 DSC thermograms of wheat starch/PLA/MDI blends with various glycerol levels

resulting in increased molecular mobility of the chains. As a result of this liberation and exposure of the O-H groups of sugar molecules at the surface, increased interactions with other molecules might have favoured an increase in entanglements. Free ends of such molecules might have hindered molecular motions. On the other hand, plasticised starch could have been entrapped in the PLA matrix in an ordered pattern or formation of bonds between starch and PLA in the presence of glycerol and SA might have supported molecular fragmentation thus increasing crystallinity as discussed above. It is also noted that re-crystallisation has taken place in the presence of glycerol and SA. The re-crystallisation suggests that the small, disordered crystals have eventually changed into more ordered crystals.

Differential scanning calorimetry thermograms of wheat starch/PLA blends with MDI and different glycerol levels are presented in Fig. 3 and the DSC data are summarised in Table 2. According to the data, all three temperatures T_g , T_m and T_c have shifted to lower levels with an increasing percentage of glycerol compared to the blends without glycerol. It is apparent that the ΔH_f has decreased but the heat of fusion has increased with increasing glycerol level in the blend. With 10% glycerol, the ΔH_f has been reduced more than 60% with respect to the blend without glycerol. The cold crystallisation and heat of crystallisation are very sensitive to chain orientation. In the absence of the molecular orientation, crystallisation is a slow process²² and therefore there is a possibility that the polymer remains in its amorphous state. According to these results, the decrease in the ΔH_f with increasing glycerol level is due to the better plasticisation of starch and hence increases the chain flexibility in the blends.

Furthermore, an exothermic peak near to the melting peak is observed with glycerol in the blend due to re-crystallisation taken place in the blend. Increased chain mobility in starch incurred by glycerol and amylose which have been liberated from the granules could have made more stable crystals. Most probably, the glycerol penetrated throughout the granule and randomly



a PLA; b 10S90P; c 30S70P; d 10S90P2M
 4 DSC thermograms of wheat starch/PLA blends with and without MDI

packed amorphous amylopectin chains interlocked between crystalline amylopectin chains²³ have increased the free volume increasing the mobility of the amorphous lamellae. This arrangement could have favoured crystallisation. Also, amylopectin double helices within the crystalline lamellae could have taken up favourable crystalline arrangement. However, these peaks get smaller with increasing glycerol content. It is assumed that the decrease in crystallisation has taken place due to the better plasticisation of amylopectin as well as the amylose molecules in starch with higher glycerol¹⁹ content in the presence of MDI causing molecular entanglement rather than crystallisation. Therefore, there is no increment in crystallisation observed towards increasing glycerol level from 2 to 10% in the blends.

The summarised DSC data of wheat starch/PLA blends with and without MDI are presented in Table 4 and the relevant thermographs are shown in Fig. 4. There is no significant difference at the melting temperatures of the blends and PLA but the crystallisation temperatures are different. The blend 30S70P without MDI shows unusual results having very low T_c and low ΔH_c . It is believed that the blend has absorbed moisture and as a result the starch has been plasticised. The resulting molecular orientation might have favoured crystallisation thus reducing T_c . The presence of an exothermic peak (see Fig. 4) near the melting peak is a result of re-crystallisation. It is well known that in the presence of water, starch molecules undergo re-crystallisation. Compared to 10S90P blend, MDI in the 10S90P2M blend has increased ΔH_c as a result of formation of urethane linkages^{1,24} between isocyanate and OH groups. Consequently, chain flexibility is restricted due to the steric hindrance of benzene rings in the MDI. Crystallinity of PLA is reduced as expected with increasing starch due to the scattered dispersion of starch in the base matrix.

Mechanical properties

The appearance of the tensile test bars of only PLA and wheat starch/PLA blends with and without MDI prepared

Table 3 Crystallisation and melting properties of wheat starch/PLA/MDI blends with various glycerol levels

Sample	T_g , °C	T_m , °C	ΔH_f , J g ⁻¹	T_c , °C	ΔH_c , J g ⁻¹	Crystallinity, %
10S90P2M	60.2	174.00	25.21	174.13	37.12	31.4
10S90P2M2G	60.2	173.89	17.76	173.67	35.63	39.0
10S90P2M5G	58.24	173.82	17.01	173.43	35.60	39.4
10S90P2M10G	57.85	174.25	9.80	170.23	37.07	39.9

by injection moulding are different from each other. Tensile test specimens of only PLA are transparent but with the inclusion of starch the clarity of the specimen has changed. The blend containing 10% starch has slight opacity but the blend containing 30% starch has much higher opacity. Furthermore, yellowish brown MDI has colored the dumbbell specimens turning them light yellow in the 10S90P2M blend. The appearance of the tensile bars of the blend 30S70P2M is almost dark brown and also seems to be degraded. It is apparent that the clarity of the PLA is reduced with the incorporation of starch and MDI.

Tensile strength and elongation at break of the sample 3 and sample 5 in Fig. 5 under ambient conditions decreased with increasing starch levels compared with those of only PLA. However, MDI, in the blend of 10% starch was capable of restoring the strength of raw PLA. Furthermore, elongation, which has decreased by almost 38% in the blend 10S90P has been reduced to 30% in the blend 10S90P2M. The Young's modulus was lower than raw PLA and starch/PLA blends indicating lower stiffness in the blend. The 30S70P blends with and without MDI show poorer properties than raw PLA. From its appearance, the 30S70P2M blend seems to be non-uniform as a consequence of starch overheating during extrusion and degradation due to the difficulty in uniform feeding. The blend 10S90P2M material showed properties similar to those of PLA, except for the Young's modulus.

Low strength and elongation at break when starch is incorporated into the PLA matrix is due to the distribution of continuous phase of PLA by starch granules. These starch granules might have acted as stress concentrators initiating cracks in the material. When MDI is incorporated into the 10S90P blend, the strength has increased by 4% with respect to the starch/PLA blend. It is apparent that the interfacial adhesion between PLA and wheat starch has enhanced the superior properties in the blend. These results are also comparable with the results of compression moulded blends of 0.5% MDI with PLA/starch blends carried out by Wang *et al.* This study shows increased elongation in the 10S90P2M blend but it is less than that of raw PLA. It is well known that the size of the groups in the polymer relate to chain flexibility of the polymer. Therefore two phenyl groups in the MDI as well as starch might have restricted the chain flexibility of the blend resulting in lower elongation than raw PLA.

Figure 5 shows the comparison of tensile properties with respect to annealed and non-annealed conditions of samples of raw PLA and starch/PLA blends with and without MDI. There is no effect on the tensile strength of the materials upon heat treatment. It is apparent that the enhanced molecular mobility upon heat treatment was not efficient in lessening crystallinity in the blend. However, the elongation at break of the blends has slightly increased in almost all the blend samples and

Table 4 Crystallisation and melting properties of wheat starch-PLA blends with and without MDI

Sample	T_c , °C	ΔH_c , J g ⁻¹	T_m , °C	ΔH_m , J g ⁻¹	Crystallinity, %
PLA	107.07	25.05	175.02	34.04	72.6
10S90P	112.04	24.64	175.17	32.64	34.9
30S70P	101.45	24.30	174.04	33.13	35.4
10S90P2M	105.00	25.21	174.13	33.19	35.4
30S70P2M	105.41	27.46	174.97	35.87	27.6

raw PLA. Upon heat treatment, due to energy induced molecular mobility, amorphous orientation might have increased causing the material to deform. The modulus of the blends have decreased apart from that of 10S90P2M. This is consistent with the elongation results upon heat treatment. As a result of annealing, changes in the chain orientations with MDI in the blend might have increased the modulus of the 10S90P2M blend.

According to Fig. 6, the results revealed that leaving the blends overnight before extrusion has reduced the tensile properties compared to the blends processed immediately after preparation. Upon overnight storage, possible weak acetone links formed between PLA and starch might have broken or the PLA chains might have

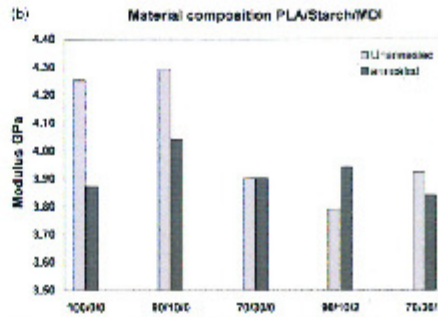
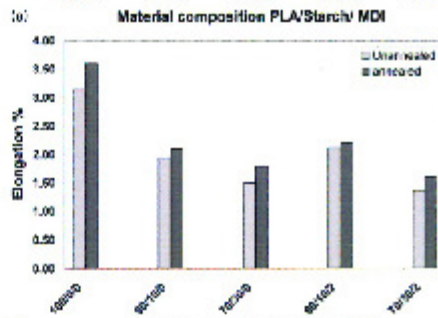
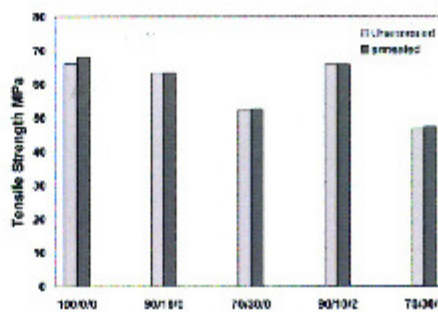
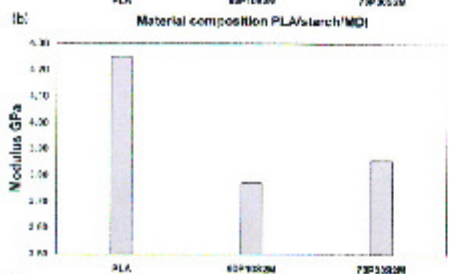
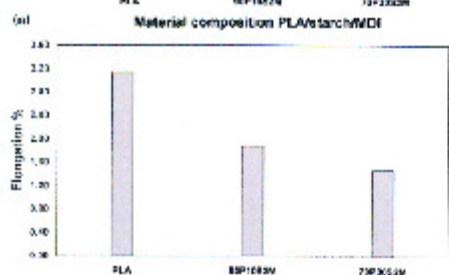
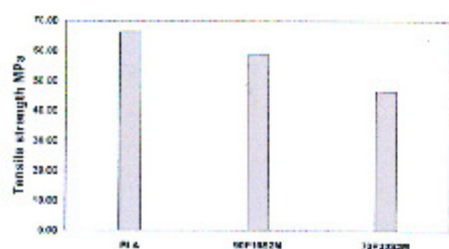


Figure 5 Variation of tensile properties of PLA, wheat starch-PLA blends with and without MDI and with and without heat treatment

fragmented to short chains resulting in poor mechanical properties. Although the short chains favour crystallisation, they decrease the strength of the material. On the other hand, if the moisture is absorbed by the blend upon prolonged exposure to the environment, this could result in hydrolysis of urethane linkages giving rise to the corresponding amine and carboxylic acid groups and resulting in poor mechanical properties of the blend.

The impact behaviour of the PLA and wheat starch/PLA blends with and without MDI is shown in Fig. 7. With increasing starch levels there is a decrease in the energy absorption in the blends. Because of the nature of the granular starch, it behaves as a stress concentrator rather than dissipator. But the blend 10S/90P2M shows energy absorption very similar to raw PLA. The starch and PLA are coupled by interfacial adhesion of MDI. Perhaps the urethane linkages which formed between starch and PLA resulted in long chains. These long chains might have crystalline regions as well as amorphous regions. These amorphous regions in the chains show better toughness behaving as shock absorbers.



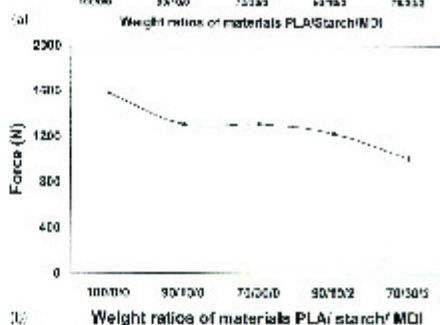
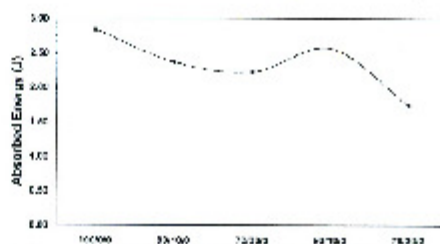
6 Tensile properties of PLA, wheat starch/PLA blends with MDI blended and left overnight before extrusion

Morphology

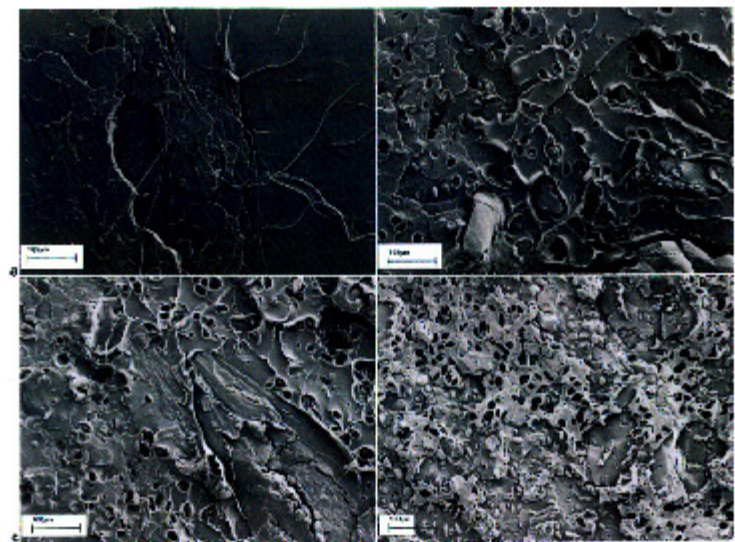
Scanning electron micrographs have been obtained of the tensile fracture of PLA (Fig. 8a), wheat starch/PLA blends (Fig. 8b and c) and wheat starch/PLA/MDI (Fig. 8d). Two phases can be clearly seen, starch granules were pulled out and voids have then been created as can be seen in Fig. 8b and c. Better interfacial adhesion of starch and PLA with MDI is observed in Fig. 8d. However, a starch continuous phase is difficult to discern with MDI whereas a starch granular form is still visible.

According to the SEM images in Figs. 8 and 9, blends with coupling agents show a better continuous phase between starch and PLA than the blend without coupling agents. It is noticeable that the continuous phase is more prominent with SA and glycerol. The blend with MDI has a continuous phase but the starch granular form is still observed and indicates that MDI does not have the plasticisation ability of starch. It is apparent from the molecular structure that glycerol and SA can plasticise starch better than MDI. However, their coupling effect upon the tensile properties has still to be investigated. Figure 9a and b shows micrographs of blends compounded with 2% glycerol and 2% SA respectively. Stearic acid shows almost the same phase appearance as raw PLA. With glycerol, small starch granules are observed in the SEM graph entrapped in PLA matrix. Both the SA and glycerol coupling agents showed better interfacial adhesion between PLA and starch from their SEM image.

Scanning electron micrographs of blends with MDI and different glycerol levels are shown in Fig. 10. The fracture surface of the blend 10S/90P2M10G was more ductile than blends with 2 and 5% glycerol. According to



7 Impact behaviour of PLA and wheat starch-PLA blends with and without MDI



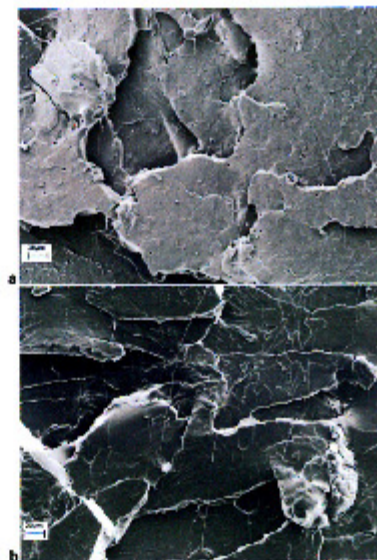
a pure PLA; b 10S90P; c 30S70P; d 10S90P2M
 8 Scanning electron micrographs of PLA, wheat starch/PLA blend with and without MDI

the SEM micrograph and the appearance of the material, with 10% glycerol, most of the starch granules have been plasticised. It is believed that starch granules exist in a form of concentric growth ring with radiating ends more randomly organised and located in the centre of the granule with non-reducing ends of amylose and amylopectin pointing outwards allowing the glucose residues to add on to extend the amylopectin chains.²² In the presence of glycerol, amylose chains can leech out to the granular surface from concentric growth ring of the granular starch.²² The small size and nature of the glycerol with high hydrogen bonding density have the ability to penetrate to reach the amorphous region of the granule. It is well understood that glycerol could have infiltrated to amorphous amylose molecular chains arrangements more than the orderly packed amylopectin crystals. A porous structure is observed in the blends in the SEM images with glycerol and the porosity increased with increasing glycerol level. In the presence of glycerol amorphous regions penetrate throughout the granule and on hydration they form continuous gel phase resulting porosity. This result is consistent with the results discussed and reported by Oates.²² The higher glycerol content at the blend shows better plasticisation of starch in Fig. 10c. The fracture surface of the materials showed ductile fracture and the material was flexible at room temperature and upon storage. However, as MDI is a toxic material, further studies will not be carried out on this area with MDI.

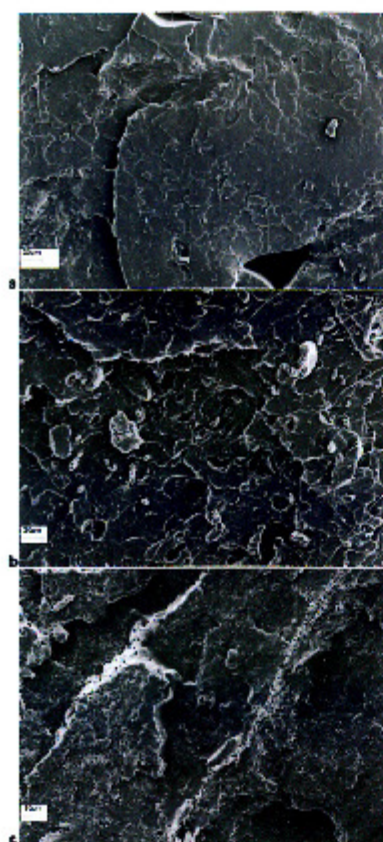
Water absorption

Starch consists of amylose and amylopectin both having an abundance of hydroxyl groups and shows hydrophilic character. However, PLA is a hydrophobic polymer. Figure 11 shows the water absorption of PLA, wheat starch/PLA blends with and without MDI. All the blends

except 30S70P2M show less than 2% water absorption. The blend without MDI having 30% starch shows 3% water absorption. The water absorption for both blends with or without MDI increased during the first two weeks and then levelled off at about 3%, Wang²³ and Ke et al.⁷



a 10S90P2G; b 10S90P2SA
 9 Scanning electron micrographs of PLA/wheat starch blends with different coupling agents

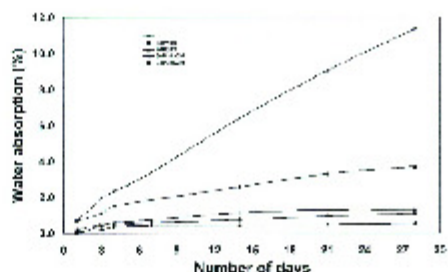


10 Images (SEM) of PLA-wheat starch blends with different glycerol levels

have also reported that water absorption gradually increased during the first 15 days before levelling off. No significant difference in water absorption occurred between the blends with and without MDI. The water absorption for raw PLA also had the same tendency as that of the blend with starch but levelled off at about 0.5%. The blend 10S90P2M shows very similar properties to PLA. These results apparently indicate that the starch content in the blend is responsible for the water absorption of the PLA/starch blends.

Conclusions

Starch can be incorporated in a PLA matrix at 10% level without difficulty in processing in the presence of 2% MDI. Pellets can be made followed by extrusion and injection moulding to make shaped mouldings. Starch was induced slightly opaque appearance. With 10% wheat starch and 2% MDI, blends of wheat starch/PLA can restore the tensile strength, elongation, impact strength properties of raw PLA. Furthermore, in the



11 Water absorption of PLA, wheat starch/PLA blends with and without MDI at different time intervals

presence of 10% wheat starch, the blend has a lower modulus than raw PLA and water absorption properties similar to raw PLA. Glycerol and SA have the ability to restore crystallinity of PLA and heat of crystallisation better than MDI and hence there could be better physical properties with these two materials. A higher glycerol level in the presence of MDI can better plasticise starch making a ductile material. MDI behaves as a coupling agent and glycerol and SA behave more like plasticisers. The coupling effect will be investigated in future work.

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Appendix B: Abstract and the poster presented at the Bioplastic Conference 2009, UK

Renewable materials for biodegradable packaging

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The development of bioplastics is of paramount importance today due to the environmental threats posed by synthetic polymer based packaging. Synthetic polymers are being used in a wide range of products, and in the last three decades they have become commonplace in our daily lives. Whilst our understanding has grown of the extent to which plastic materials increase our carbon footprint and threaten human life in other ways, it is crucial to develop alternative materials from renewable resources for packaging. The problem is that their properties are not yet comparable to polymers derived from fossil fuels. This study is being undertaken as a part of the process of improving compatibility and processability of starch and PLA blends with conventional polymer processing equipment to develop a novel packaging material.

Genetically modified organisms (GMO) free PLA and wheat starch blends were prepared and characterized in the presence of glycerol. A mixture of wheat starch and glycerol was mixed with PLA powder and extruded in a lab-scale co-rotating twin screw extruder, under low temperature profiles. Extruded strands were pelletized and injection moulded into tensile test bars and plaques. Degradation patterns and thermal behaviour were determined by Thermal Gravimetric Analysis (TGA) and Differential Scanning Calorimetry (DSC) tests respectively. The falling weight technique was employed to measure impact properties and the tensile properties were also determined. Microstructures of the blends were observed by means of scanning electron microscopy (SEM). Fourier Transform Infrared (FTIR) Spectroscopy was used to investigate interactions of the molecular components.

The thermal stability studies indicate a decrease in the maximum degradation temperature (T_{\max}) and a 5% weight loss of the blends with the incorporation of starch and glycerol. The effect from starch towards T_{\max} is higher than the effect from glycerol. The experimental data show a decrease in the glass transition temperature (T_g). Crystallization over a broad temperature range is observed in the blends above 5% glycerol and it is very prominent at higher glycerol levels in the second heating cycle. The tensile strength of the blends decreased with starch as well as glycerol but no significant difference is observed in the level of decrease with percentage of glycerol addition. The elastic modulus of the blends, progressively decrease with increasing glycerol proportion. Results show greater energy absorption with higher concentration of glycerol in the blend compared with raw PLA. The micrographs demonstrate that there is better dispersion of starch with higher percentage of glycerol. FTIR analyses show some interaction between PLA and starch in the presence of glycerol.

Mixing of PLA and starch can be improved by reducing the particle size of the PLA and the T_g of the blends can be controlled by the percentage of added glycerol, thus facilitating optimum processing conditions. It is also observed that the improvement of the tensile properties of PLA/ starch blends could be controlled by the glycerol levels used in the

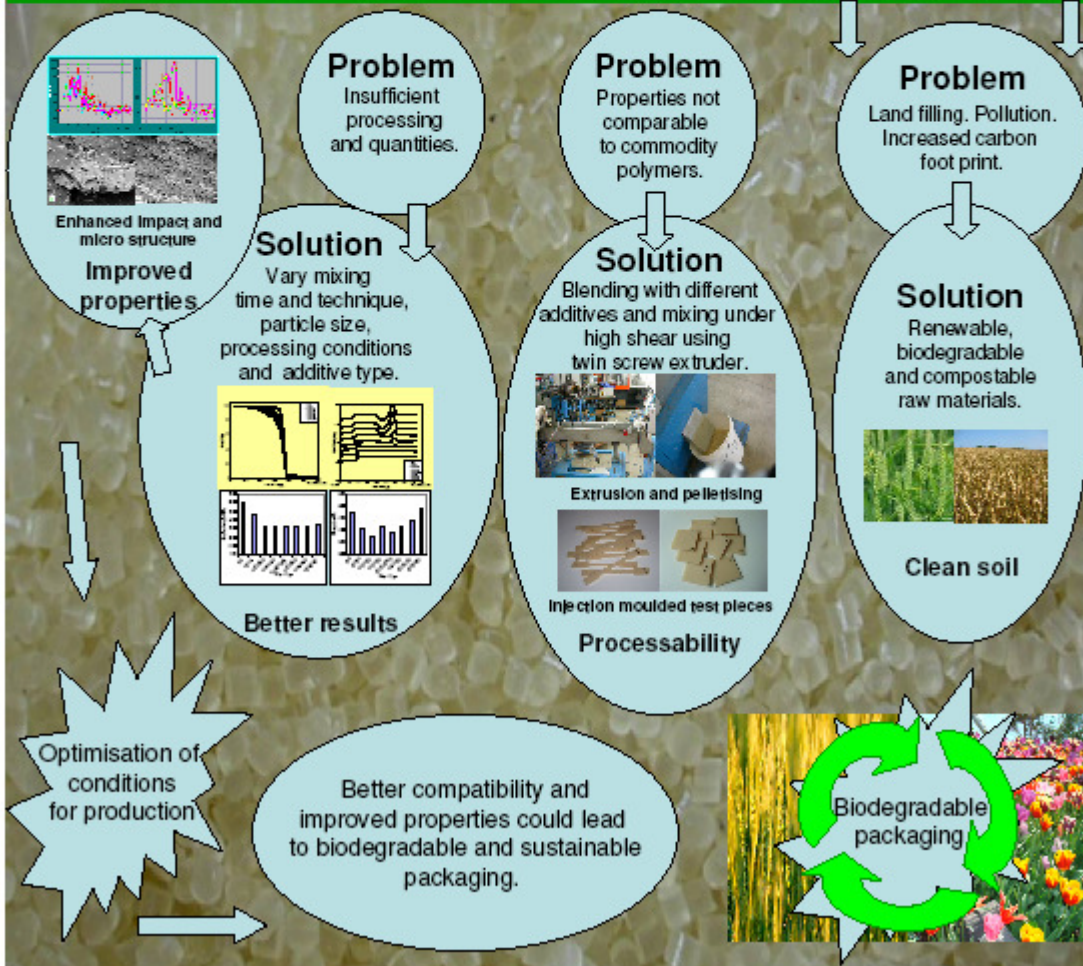
blend. Noticeably the blends with glycerol have high energy absorption and better dispersion between PLA and starch. It is early days yet, but at this stage the experimental results demonstrate that enhanced material properties are achievable by controlling the blending of PLA and starch.

Renewable materials for biodegradable packaging

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Fossil fuel based polymer packaging pose major threats to the environment and human life.
Alternative : Bioplastics for packaging: PLA and Starch.
 Eco-friendly, from renewable resources and biodegradable



Appendix C: Poster presented at the Graduate School Poster conference 2009, Brunel University - Vice Chancellor's prize

Processing and properties of materials from renewable and sustainable resources



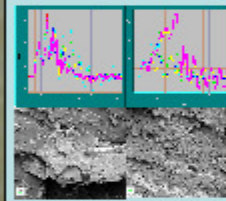
Manjula Silva, Kamik Tarverdi, Robert Withnall, Jack Silver
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Brunel University, Uxbridge, UB8 3PH, UK



Fossil fuel based polymer packaging pose major threats to the environment and human life.
Alternative : Bioplastics for packaging: PLA and Starch.
Eco-friendly, from renewable resources and biodegradable



Good heat dissipation compared to PLA or blend without glycerol. Polymer chains cohered in clustures could be exposed to the surface as a result of plasticisation. Triglyceride formation is also possible which is a good energy absorber.



Enhanced Impact and micro structure

Glycerol favoured penetration through polymer chains and amylose content in starch can leach out from its concentric growth ring thus resulting in a porous micro structure.

Conclusions
Mixing can be improved by reducing the particle size of the PLA. Tg of the blends can be controlled by the glycerol %, thus facilitating optimum processing conditions. The improvement of the tensile properties of the blends could be controlled by the glycerol levels. Noticeably the blends with glycerol have high energy absorption and better dispersion. Glycerol is a good plasticiser for starch and FTIR analysis show some coupling between PLA and starch.



Better compatibility and improved properties lead to biodegradable and sustainable packaging

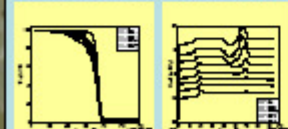
Introduction
Land filling, increased carbon foot print and pollution due to commodity polymer based packaging are major issues. Performance and processing difficulties of biodegradable materials prevented results from proving conclusive. PLA and starch have been blended with different additives [1-3]. This study is being undertaken to improve compatibility and processability of starch and PLA blends with conventional polymer processing equipment to develop a novel packaging material.

Renewable Materials



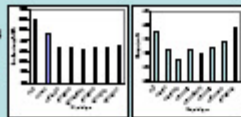
Corn and wheat fields

Results and Discussion
Pellets were successfully injection moulded. Degradation of the blends are well above processing temperature and thermal behaviour show some crystallisation. Tg is lowered making easy processing with increasing glycerol levels.

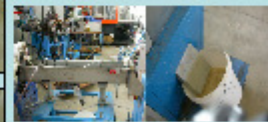


Better elongation than pure material.

Crystallization is prominent with higher glycerol levels.



Material Processing
Blending with different additives and mixing under high shear using twin screw extruder.



Extrusion and pelletising



Extruded pellets and injection moulded test pieces

Optimisation of conditions for production

References
[1] H. Wang, X. Sun and P. Seib, *J Appl Polym Sci.* 2001, 82, 1761-1767.
[2] J.F. Zhang and X. Sun, *J Appl Polym Sci.* 2004, 94, 1697-1704. [3] T. Ke, X. Sun, *Thermal and mechanical Trans of ASAE.* 2001, 44, (4), 945-953.

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Appendix D: Abstract and the poster presented at the Global Plastic Environmental Conference, Florida USA – 2nd Place

A bio-based polymer composite from renewable and sustainable resources

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Increasing awareness of green issues and environment preservation needs are pressurizing packaging materials to be eco-friendly and sustainable. As a result, scientists are working to produce biodegradable polymers as a substitute for petrochemical based plastics. It is difficult to manufacture polymers that are fully biodegradable with versatile properties. One of the typical biodegradable polymers, Polylactic acid (PLA) is being considered for various applications. PLA was first used only in biomedical applications where its bioabsorbability and biocompatibility properties were exploited. Development of methods to derive the monomer from bioconversion which leads to large scale production has enabled expansion of PLA use in many applications including packaging. However, PLA by itself does not exhibit properties that are required by the packaging industry. Efforts are being taken to develop cost effective composites by incorporating starch with PLA matrix but properties are not yet suitable for commercialization. This study is being undertaken as a part of the process of improving compatibility and processability of starch and PLA blends with conventional polymer processing equipment to develop a novel packaging material.

Genetically modified organisms (GMO) free PLA and wheat starch blends were prepared and characterized in the presence of adipic acid. Wheat starch and adipic acid were mixed with PLA and successfully extruded using a lab-scale co-rotating twin screw extruder. Extruded strands were pelletized and injection moulded into standard tensile test bars and plaques. Differential Scanning Calorimetry (DSC) tests demonstrated significant improvements in the thermal behaviour with adipic acid (AA). Crystallization over a broad temperature range is observed in the blends and it is very prominent at higher adipic acid levels. Thermal Gravimetric Analysis (TGA) gave 1% weight loss with and without isotherm at 180⁰C for 30 minutes. The heating of the blends at 180⁰C for 30 minutes show

no discolouration of the materials by visual inspection. Rheology of blends measured by parallel plate geometry demonstrated increased viscosity with the inclusion of starch with PLA, but adipic acid considerably reduces the blend viscosity and at a certain concentration equals to that of virgin PLA viscosity. However, by further increasing adipic acid levels in the blend lowered viscosity, storage modulus and loss modulus has been observed. Impact properties measured by the falling weight technique showed improved peak force on the starch PLA blend with AA, moreover, improved energy absorption and deformation were detected in the starch and PLA blends. In conclusion, it can be stated that the present experimental results demonstrate that a bio-based composite material with PLA and starch can be made with better properties.

A bio-based polymer composite from renewable and sustainable resources



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Whilst our understanding has grown of the extent to which oil-based plastic materials increase our carbon footprint, pollution and threaten human life, it is crucial to develop alternative plastic materials.

ALTERNATIVE
 Bio-plastics from renewable and sustainable resources for packaging. Eco-friendly and biodegradable.

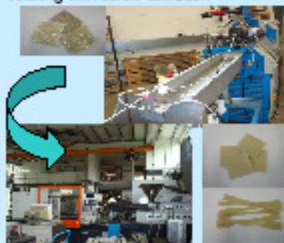
Optimisation of conditions

1. Introduction

The development of bio-plastics is of paramount importance today due to the environmental threats posed by fossil fuel based plastics. A versatile biodegradable polymer, PLA is being considered for various applications. Efforts are being taken [1-3] to develop cost effective composites by incorporating starch but results as yet, are inconclusive for commercialization. This study is being undertaken as a part of the process to improve compatibility and processability of starch and PLA blends with conventional polymer processing equipments to develop a novel packaging material.

2. Material processing

Blending with different levels of additive and mixing under high shear using co-rotating twin screw extruder.



Injection moulding

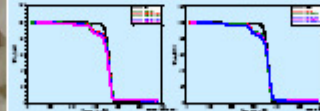
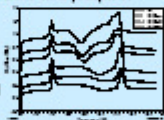
Acknowledgement

My heartfelt thanks to my supervisors Prof R. Withnall, Dr K. Tarverdi for their supervision and encouragement and also Prof J. Silver and Dr P. Allan for their continuous support.

3. Results and discussion

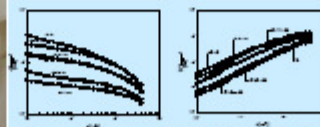
Blends were successfully extruded. Strands were pelletized and injection moulded into standard tensile test bars and plaques.

High level of crystallisation and it is prominent with high adipic acid (AA).



No degradation with and without isotherm at 180° C which is well above processing temperature.

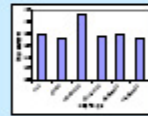
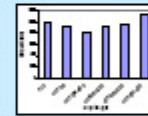
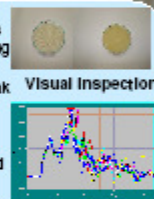
3b. Rheology - parallel plate rheometer



Adipic acid allows for easier processing by reducing the blend viscosity which at a certain level equals to viscosity of virgin PLA.

Energy absorption and dissipation are high up to a certain adipic acid level.

3c. Impact properties measured by the falling weight technique showed improved peak force on the starch PLA blend with AA, moreover, improved energy absorption and deformation were detected.



Peak force

Energy absorption

4. Conclusion

Conditions can be optimised to make a composite material with PLA and starch with better properties.

- High crystallisation
- Thermally stable at processing temperature
- Viscosity decrease resulting in easy processing
- High Impact force
- High energy absorption at low AA level
- 1.5AA show similar properties to PLA.

References

- [1] H. Wang, X. Sun and P. Seib, *J Appl Polym Sci*, 2001, 82, 1761-1767.
- [2] J.F. Zhang and X. Sun, *J Appl Polym Sci*, 2004, 94, 1697-1704.
- [3] T. Ke, X. Sun, *Thermal and mechanical Trans of ASAE*, 2001, 44, (4), 945-953.

Appendix E: Poster presented at the Graduate School Poster conference 2010, Brunel University - Vice Chancellor's prize

ResCon 2010, Brunel University -3rd Place

Solution for pollution: biodegradable and renewable materials for plastic packaging

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The environment is under threat from petroleum based polymer packaging.



Landfilling site in Deaconsfield

Problem



Eco-friendly and biodegradable materials from renewable resources for packaging



A wheat field in Norwich

Solution

1. Introduction

The major source of waste disposed in UK is landfilling. This has become a major threat to human life in many ways due to accumulation of large amount of non degradable packaging waste. These fossil fuel based polymers also increase carbon foot print and green house gas emission. Use of bio-based materials are restricted due to lack of performance and processability. Poly(lactic acid) (PLA) and starch have been studied in many ways as an alternative (1-5). This study shows processability of starch and PLA blends with an impact modifier (IM) under conventional polymer processing equipments and their improved properties.

2b. DSC analysis show decrease in crystallisation peak. No change in Tg. PLA and Starch/PLA blend show physical aging. ARES parallel plate rheometer studies show the higher viscosity in the blends with starch.

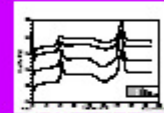


Fig.3 Thermal behavior

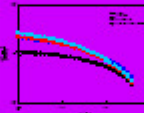


Fig.4 Viscosity

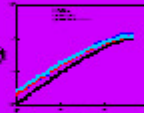


Fig.5 Loss modulus

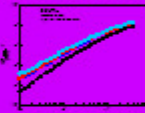


Fig.6 Storage modulus

2. Methodology/ Material processing



PLA and starch have been blended with an impact modifier. Materials were pre-blended and extruded under high shear in a twin screw co-rotating extruder through 6mm diameter die before being drawn off through a water bath. Strands were pelletised, dried and stored in airtight PE bags. Pellets were injection moulding into dumbbell specimens and plaques.

Tests - TGA, DSC, Rheology, Tensile & Impact properties, SEM, FTIR, Water absorption and Biodegradation.

3c. Tensile properties show better elongation, average strength and modulus which could be controlled by the amount of additive. However increased residence time tends to decrease elongation.

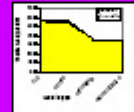


Fig.7 Tensile strength

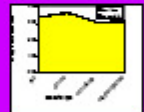


Fig.8 Modulus

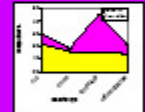


Fig.9 Elongation

Impact properties shown in Fig. 10 & 11 are remarkable with IM compared to the PLA/starch blend. Impact force and energy absorption are prominent with the modifier. Biodegradation studies and water absorption studies are being carried out. Starch has significant influence on water absorption of the blends.

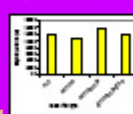


Fig.10 Impact force

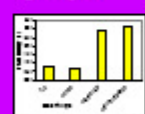


Fig.11 Energy absorption

3. Results and Discussion

3a. Pellets were made successfully by extrusion followed by pelletizing. Fig 1 & 2 show the degradation pattern of the blends in N₂ atmosphere which are well above their processing temperatures. Isotherm for 30 min at 180°C has no effect on degradation pattern.



Fig.1 Degradation

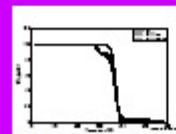


Fig.2 Degradation with isotherm at 180°C

All the blends start degradation above 270°C under air & N₂ atmosphere.

4. Conclusion

A composite material can be made by PLA and starch blend in the presence of an impact modifier. Extruded strands show completely ductile properties. Composite material show excellent impact properties, very high elongation. This material can be injection moulded to make different plastic packaging.

5. References

(1) H. Wang, X. Sun, P. Selt, *J Appl Polym Sci*, 2010, 94, 1987 - 1992. (2) J.F. Zheng and X. Sun, *J Appl Polym Sci*, 2014, 94, 1987 - 1994. (3) T. Ko, X. Sun, *Trans of ASAE*, 2001, 44, (4), 945-949. (4) K.M.D Silva, K. Tarverdi, R.Withnall, J. Silva, *Conference proceedings of GPEC*, 2010 (5) L. Jiang, *Sci Lu, J.Zheng, Macro, Mar & Eng*, 2008, 264, 301 - 306.

Acknowledgements: My thanks are due to Shara Ferris, Dr Peter Allen and also to Akema Inc. for providing impact modifier material for this study.

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Appendix F: Abstract and the poster presented at the Annual Technical Conference (ANTEC) 2011, Boston, USA.

Future plastics beyond petroleum based polymers

Amidst the concerns of plastic impact on the environment and the continuous depletion of finite fossils, environmentally benign materials are in the forefront of scientific research today. Consequently, intrinsically unique poly(lactic acid) and starch were blended with a bioimpact modifier in search of desirable properties, thereby producing an entirely flexible strand by extrusion process. Thermogravimetric analysis showed no weight loss even above the injection moulding temperature. Relatively high impact properties were demonstrated, and the results showed that the elongation at break increased by factors of 3 and 1.5 compared to those of PLA/starch blends and PLA, respectively. The tensile strength and Young's modulus of the new blends were unaffected upon extended residence time in the moulding barrel. Ageing studies of the new blend exhibited enhanced impact properties in the presence of the bioimpact modifier. Water uptake by the new blends did not differ significantly when the modifier was present, but starch made a huge difference in promoting the rate of degradation under home composting conditions.

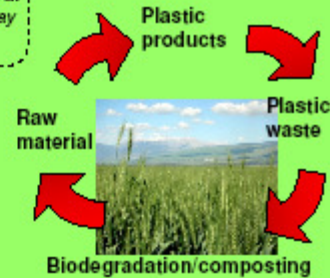
FUTURE PLASTICS... BEYOND PETROLEUM BASED POLYMERS

Graduate student: Kodikara Manjula Dilkushi Silva
Supervisors: Professor R. Withnall and Dr K. Tarverdi
Wolfson Centre for Material Processing and Centre for Display Materials, Brunel University, Uxbridge, UB8 3PH, UK



I draw attention to human attitudes and technologies that are against nature and resulted natural disasters and their harmful effects, for people to sense the impact of the plastics industry on nature. The environmental pollution, threat to the marine life, contaminated lands and floods are some of the effects mankind experiences due to the plastics industry. Therefore, without any further delay, society needs to understand how important it is to use environmentally friendly materials for your future benefit and well-being.

Nature



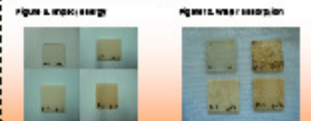
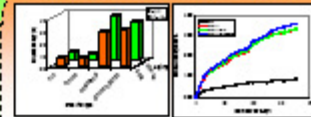
1. INTRODUCTION

Forty seven global plastics associations, including PlasticsEurope, have identified the necessity to develop solutions to marine debris globally and recently pledged to work in partnership with others without detailing any specific new initiatives[1]. However, amidst the concerns of plastic impact on the environment and the continuous depletion of finite fossils, environmentally benign materials are in the forefront of scientific research today. Many investigations have been carried out with starch and PLA in the presence of additives gained some developments in properties [2]. However, further investigations have been restricted due to unsuitability for the environment and food packaging industry [3]. The present study investigate the processing of a new blend of the PLA and starch with bio-impact modifier using the conventional polymer processing equipments, and their properties with respect to the modifier addition.

ABSTRACT

Intrinsically unique PLA and starch were blended with a bioimpact modifier in search of desirable properties, thereby producing an entirely flexible strand by extrusion process. The extrudate was analysed by means of TGA analysis and showed no weight loss at processing temperatures. Relatively high impact properties were demonstrated, and the results also showed that the elongation at break increased by factors of 3 and 1.5 compared to those of PLA/starch blends and PLA, respectively. Furthermore, the tensile strength and Young's modulus of the new blends were unaffected upon extended residence time in the moulding barrel. Water uptake by the new blends did not differ significantly when the modifier was present, but starch promoted the rate of degradation under home composting conditions.

3b. RESULTS AND DISCUSSIONS



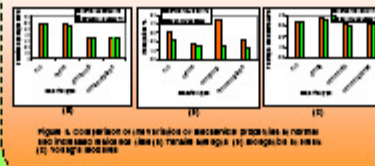
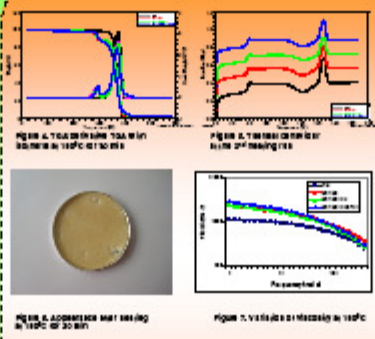
2. EXPERIMENTAL WORK

Dried PLA and starch were pre-blended with bio-impact modifier followed by mixing under high shear in a twin screw co-rotating extruder.



Extruded strand was drawn through a water bath and pelletized. Pellets were then dried and injection moulded to plaque and dumbbell specimens. TGA, DSC, tensile, impact, FTIR, composting, aging studies and water absorption were performed.

3a. RESULTS AND DISCUSSION



4. CONCLUSIONS

PLA and starch can be mixed with bio-impact modifier to make tri-blend composite pellets with following desirable properties.

- Smooth extrusion and completely flexible strand
 - Thermally stable pellets at processing temperature
 - Pellets can be injection moulded to shaped articles
 - High impact force, energy absorption and elongation at break
- However, longer exposure time in the barrel is not favourable for elongation at break.

5. FUTURE DIRECTIONS

Following the current communication, further recommendation is made to optimise properties by further investigations on

- Different starch levels in the blend system
- Different modifier concentrations

6. REFERENCES

- [1] <http://www.pnw.com/subscriber/newsmail2.html>
- [2] H. Wang, X. Sun and P. Seib, *J Appl Polym Sci*, 2001, 82, 1761-1767.
- [3] K. Manjula Dilkushi Silva, K. Tarverdi, R. Withnall and J. Silver, *Plastics, Rubber and Composites* 2011, 40(1), 17-24

ACKNOWLEDGEMENTS: Thanks are due to Arkema Inc for supplying impact modifier material for the study. My heartfelt thanks are also extended to Dr P. Ailan, Prof J. Silver and Steve Ferriss for their continuous support.

FURTHER INFORMATION: Kodikara.silva@brunel.ac.uk, robert.withnall@brunel.ac.uk, kamik.tarverdi@brunel.ac.uk

Appendix G: Injection moulding operating conditions and temperature profile for the dumbbell specimens prepared

Profile 1-blends with MDI and different additives

Profile 2-blends with biostrength materials

Profile 3- blends with glycerol

Profile 4- blends with adipic acid

Profile 5- blends with natural rubber latex

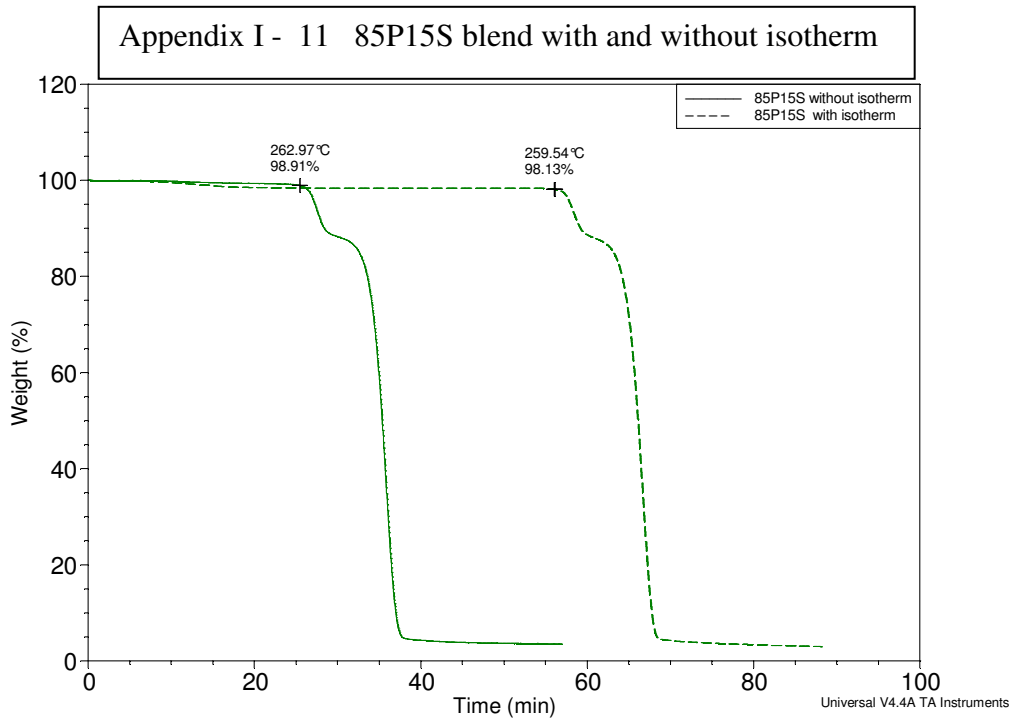
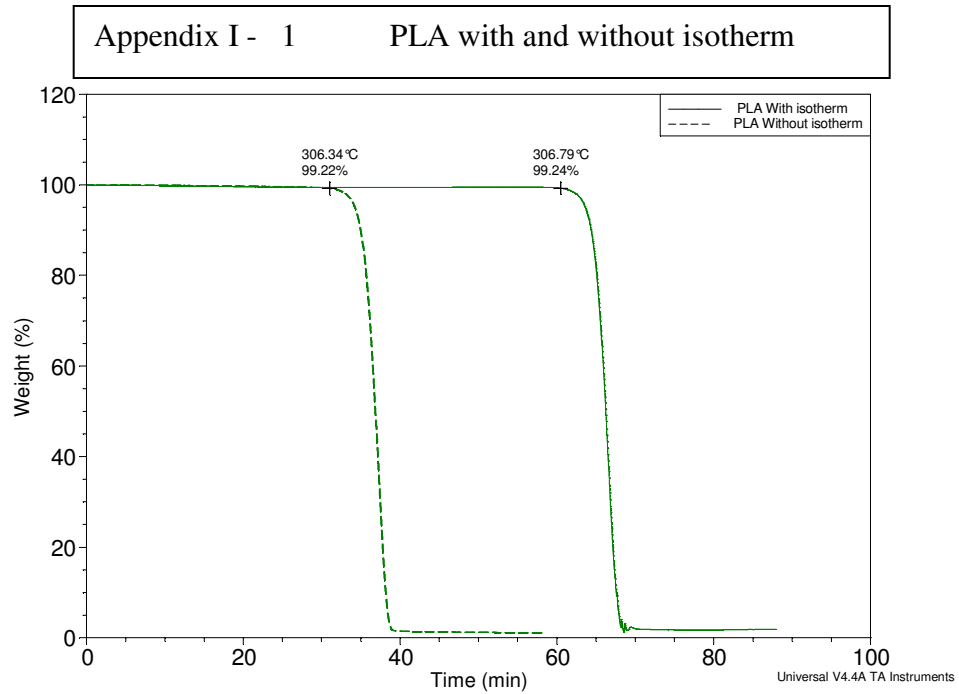
Profile 6- blends with impact modifier material and pistachio nut shell powder

Conditions	Profile 1	Profile 2	Profile 3	Profile 4	Profile 5	Profile 6
First heating zone	160 ⁰ C	140 ⁰ C	155 ⁰ C	150 ⁰ C	150 ⁰ C	140 ⁰ C
Second heating zone	170 ⁰ C	155 ⁰ C	165 ⁰ C	165 ⁰ C	165 ⁰ C	165 ⁰ C
Third heating zone	185 ⁰ C	165 ⁰ C	170 ⁰ C	180 ⁰ C	180 ⁰ C	180 ⁰ C
Fourth heating zone	185 ⁰ C	165 ⁰ C	170 ⁰ C	180 ⁰ C	180 ⁰ C	180 ⁰ C
Nozzle heating	185 ⁰ C	165 ⁰ C	170 ⁰ C	180 ⁰ C	180 ⁰ C	180 ⁰ C
Injection pressure	100 bar	120 bar	80 bar	100 bar	100 bar	100 bar
Injection time	5 Sec	5 Sec	10 Sec	5 Sec	5 Sec	5 Sec
Cooling time	30 Sec	30 Sec	60 Sec	30 Sec	30 Sec	30 Sec

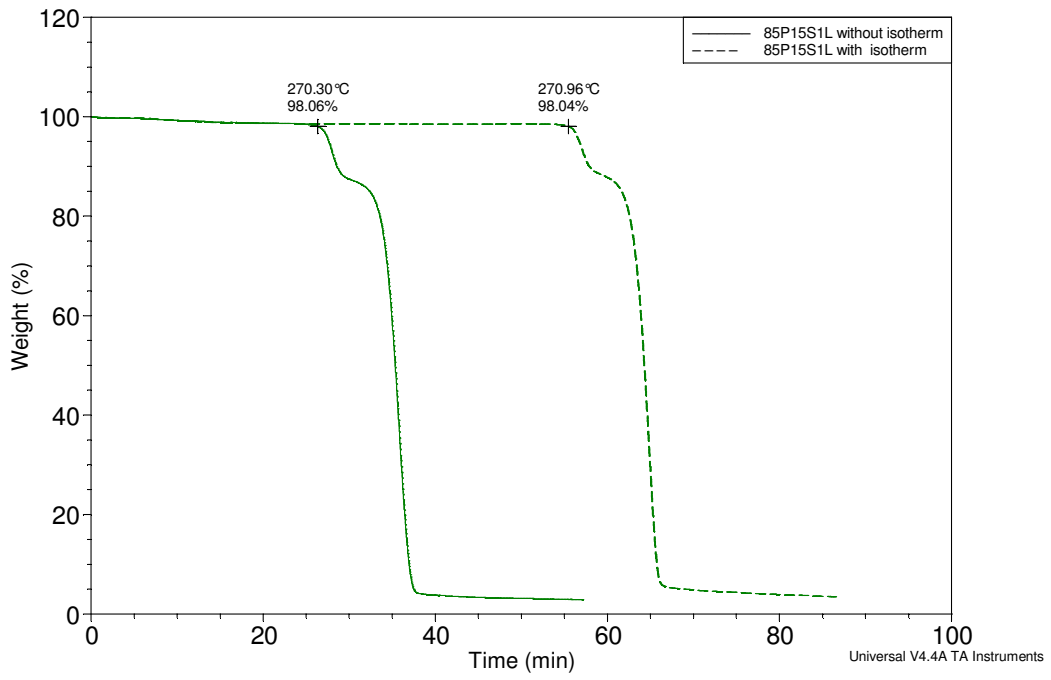
Appendix H: Injection moulding operating conditions and temperature profile for the plaques prepared from blends with MDI and other additives

Conditions	Profile 1	Profile 2	Profile 3	Profile 4	Profile 5	Profile 6
First heating zone	160 ⁰ C	140 ⁰ C	155 ⁰ C	150 ⁰ C	150 ⁰ C	140 ⁰ C
Second heating zone	170 ⁰ C	155 ⁰ C	165 ⁰ C	165 ⁰ C	165 ⁰ C	165 ⁰ C
Third heating zone	185 ⁰ C	165 ⁰ C	170 ⁰ C	180 ⁰ C	180 ⁰ C	180 ⁰ C
Fourth heating zone	185 ⁰ C	165 ⁰ C	170 ⁰ C	180 ⁰ C	180 ⁰ C	180 ⁰ C
Nozzle heating	185 ⁰ C	165 ⁰ C	170 ⁰ C	180 ⁰ C	180 ⁰ C	180 ⁰ C
Injection pressure	100 bar	120 bar	100 bar	170 bar	100 bar	100 bar
Injection time	10 Sec	10 Sec	10 Sec	10 Sec	10 Sec	10 Sec
Cooling time	30 Sec	30 Sec	50 Sec	25 Sec	30 Sec	30 Sec

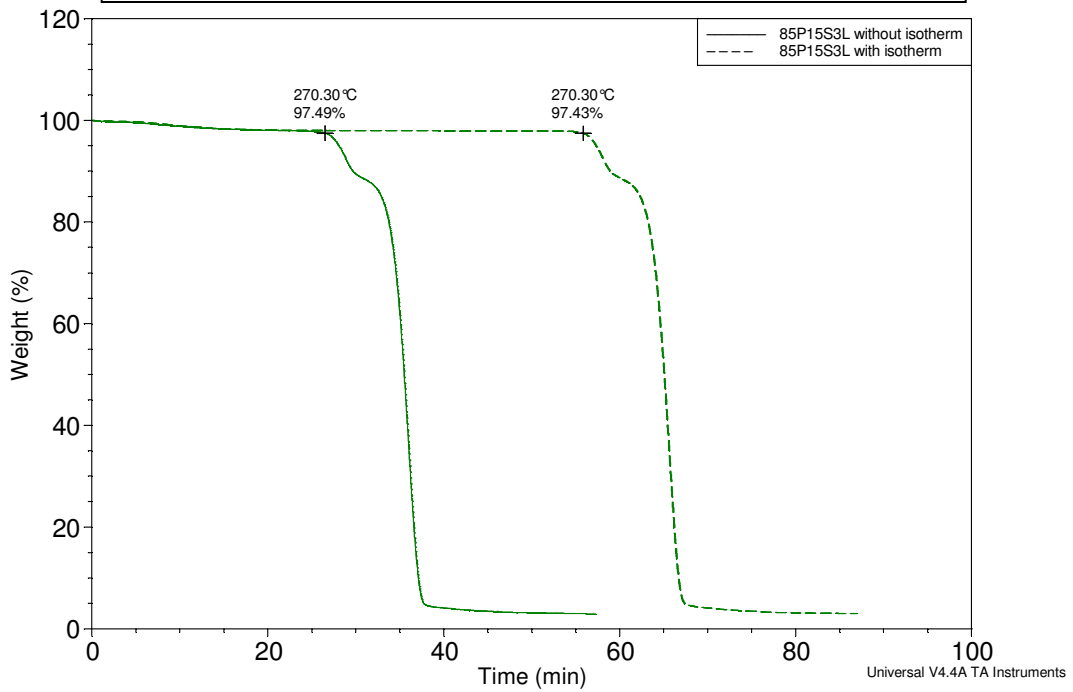
Appendix I: consist of figures obtained from thermal gravimetric analysis of weight loss comparison of each material with and without isotherm at 180°C for 30 minutes of the blends with latex.



Appendix I - 111 85P15S1L blend with and without isotherm



Appendix I - 1V 85P15S3L blend with and without isotherm



Appendix I – V 85P15S5L blend with and without isotherm

