

Novel Bio-Composites Based on Whole Utilisation of Wheat Straw

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By

Lei Zhao

School of Engineering & Design

Brunel University

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Abstract

This thesis reports research work in the development of biocomposites based on whole utilisation of renewable wheat straw for industrial applications. The concept of “whole utilisation” is based on a previous work on a novel twin-screw extrusion technology for processing of feedstock in wheat straw reinforced bio-composites. It demonstrated that straw raw material could be restructured into a feedstock with cellulose fibre finely dispersed in the non-cellulose matrix, which can be utilised as a bonding phase without having to be removed as in conventional processes to extract the cellulose. The whole straw can thus be utilised to avoid waste of materials and the negative impacts to environment associated with the extraction process.

Raw wheat straw in this research was prepared in three ways: size reduction through mechanical milling, pre-treatment by aqueous NaOH solution and deep preparation with aqueous NaOH solution soaking followed by extrusion fractionation. Prepared wheat straws were processed into varieties of forms according to the applications. They were hot-compressed into self-reinforced composite with good flow ability and also processed through extrusion and compression moulding to compound with other biopolymers as good filler. The relationships of processing parameter and property, as well as formulation and property were established for each form of product, which provides a key understanding of the whole development circle of an end product.

Through this research, scientific and technical problems has been addressed in materials formulation/processing, product design/manufacturing, enhancement of functionality/ performance as well as economical/environmental assessment so as to develop a series of cost-effective bio-composites and products, which satisfy diverse technical and environmental performance requirements in the industrial sectors across packaging, horticulture, building/construction and shooting sports.

Key words: *wheat straw, extrusion, biocomposites, material science, processing technology*

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Abbreviations and acronyms

ASTM	= American Society for Testing and Materials
BSI	= British Standards Institution
DEFRA	= Department for Environmental Food and Rural Affairs
DSC	= Differential Scanning Calorimetry
EN	= European Norm
FTIR	= Fourier Transform Infrared Spectroscopy
HGCA	= Home Grown Cereal Authority
ISO	= International Organisation for Standardisation
L/HDPE	= low/high density polyethylene
NNFCC	= National Non-Food Crops Centre
PAH	= polycyclic aromatic hydrocarbon
PCL	= Polycaprolactone
PDLA	= Poly-D-lactide
PET	= Polyethylene terephthalate
PGA	= Polyglycolic acid
PHA	= Polyhydroxyalkanoate
PHB	= Polyhydroxybutyrate
PHBV	= Polyhydroxybutyrate valerate
PHH	= Polyhydroxyhexanoate
PHV	= Polyhydroxyvalerate
PLA	= Polylactic acid
PLLA	= Poly-L-lactide
PP	= Polypropylene
SEM	= Scanning Electronic Microscopy
TGA	= Thermal Gravity Analysis
WPC	= Wood Plastic Composite

Chapter 1 Introduction

1.1 Background of the research

Wheat straw, as a by-product of wheat production, is an annually renewable, low-cost and abundant source of natural fibre in the UK with great potential to be utilised as industrial feedstock for manufacturing cost-effective bio-composites (DEFRA, 2004). Many attempts have been made to extract cellulose from wheat straws for papermaking or for partial substitution of wood fibre in fibreboard products. These techniques are largely based on pulping of straw followed by washing and bleaching operations. The extraction process requires high-energy input during the processes and results in large quantities of complex effluent, which can be very costly to treat. Highly reactive halides produced from the use of chemicals such as chlorine and the use of sulphur-based chemicals can cause both air and water pollution. Cellulose fibre, starch and other carbohydrates can escape from pulping waste streams adversely affecting flora and fauna in receiving waters. Suspended organic solids from pulping can cause an increase in water turbidity and opacity which can be detrimental for photosynthetic organisms, increase anaerobic respiration, and the rate of decomposition. Thus, the utilisation of straw with the fibre extraction as an industrial material has largely been restricted by a lack of low environmental impact processing technologies for the mass production of low-cost and acceptable quality industrial feedstock.

Wheat straw, as the primary side-product of wheat grain, is estimated to be 5 to 7 million tonnes produced annually in the UK. The tonnage of wheat straw annual traded is only 50,000-80,000 at about £25-30/tonne for baled straw. This price has already incorporated the costs for baling, local transport, storage and loss of the soil conservation value of straw from land (Koduah, 2004). If straw is to be used as an industrial feedstock for manufacturers, then additional costs are likely to include pre-processing (e.g. chopping) and other conversions (e.g. fractionation, compounding with additives and pelletising) to provide a feedstock comparable to that for other polymers. Transportation and storage costs to manufacturers using a straw-based feedstock in pellet form are expected to be similar to those for traditional polymers. Pre-processing by chopping is estimated to increase the cost (from simple baled straw) by about 100%, but costs for conversions are

more difficult to estimate at this stage. However, even if a 400% increase is assumed (to account for energy, equipment and additives), the price of the feedstock would still be as low as £125-150/tonne compared with ~£300-500/tonne for starch, ~ £1000/tonne for polymers and ~£2000-3000/tonne for biopolymers (DEFRA, 2006a). It is obvious that low cost will be a significant advantage for wheat straw feedstock over conventional polymers and biopolymers which will be the driving force of the potential increase in demands for industrial use.

The strength of cereal straw fibres is relatively low compared with some fibres such as flax and hemp. Although this restricts their use as effective reinforcements in high-performance composites, wheat straw fibre has acceptable strength and can be used as a key feedstock in a wide range of bio-composites for many of the high volume & relatively low-tech applications identified below.

A feasibility study has been carried out based on the findings in a STI LINK project (2003-2006) by Brunel University (DEFRA, 2006a). The project focused on the development of continuous steam expansion processing of cereal straws and utilisation of straw fibre in pulp moulding and starch composites. It has been demonstrated that, with mild chemical pre-treatment, wheat straw can be finely fractionated and restructured into a feedstock containing finely dispersed straw fibre within the lignin-rich bonding phase using an extrusion process. The chemical treatment left a very low trace of residue and can be neutralised during the extrusion if necessary. The processed straw feedstock can be compounded with additional biopolymer resins to produce a diverse range of bi-composites for property enhancement in terms of mouldability, strength, rigidity/ductility and moisture resistance (Avella et al., 2000; Avella et al., 2009; Xia et al, 2007; Xia 2010). Additionally, in the research of Kang et al (2009), the processed feedstock (consisting 100% processed straw) also presents good thermoplastic characteristics and can be compression moulded, without any additional resin, into bio-composites with good surface finish and mechanical properties. These advances have laid a solid foundation for the proposed work here, which is to make the proven concept - biocomposites based on whole utilisation of wheat straw- to an industrial reality.

1.2 Overview of the project

This PhD work is part of the TSB project (project number: CAS 7531-LK0830 and HGCA project ref: RD-2007-3351) co-sponsored by DEFRA (Department of environment, food, and rural affairs, UK) under the Sustainable Arable LINK programme and HGCA (Home Grown Cereal Authority) to develop novel bio-composites based on the whole utilisation of wheat straw.

The potential applications of the wheat straw biocomposites are identified in the following high volume and relatively low-tech applications (detailed descriptions and performance requirements will be given in the literature review) to meet the demands of the industrial partners in finding renewable alternatives to oil-based products:

- Biodegradable alternative to pitch tar bonded ‘clay’ pigeons and cartridge wads used in shooting sports.
- Flowerpots and packaging containers in horticulture;
- Tree and vine shelters and mulch mat (i.e. tubular structures for protection of young trees);
- Traffic management products (e.g. barriers, supports and connection parts used for roadwork and construction);
- Binder-less straw boards for supporting component in the furniture industry for furniture and/or building/construction industry.

The newly developed products for specific applications are expected to bring benefits to the environment in the following aspects:

- The biocomposites are based on an abundant annually renewable raw material resource in the UK;
- The whole utilisation of straw eliminates the problems caused by the traditional fibre extraction processes (like pulping) in terms of high-energy consumption and effluent treatment;
- The biocomposites can be designed to facilitate environmentally efficient end-of-life management by controlling their degradability, which will reduce the wastes going to landfill;

- The reliance on oil-based material resources will be reduced by involving feedstock based on renewable materials.

Besides, as the applications do not end up on landfill sites but left on land (e.g. for the biodegradable “pigeons” and gun cartridge wads), in composts (e.g. plant pots), or in surface soil (e.g. for the tree shelters, mulch mats and road barriers to be fragmented and biodegraded on site), the impact to environment and cost of collection will also be reduced by employing the straw based biocomposites.

The consortium members from both academic and industry contribute their expertise in research and development, consultant, supply of materials, experimental tests and industrial trials. The research participants include:

- Wolfson Centre for Materials Processing, Brunel University, the leading research partner specialized in material formulation, processing and characterisations.
- BRE Centre for Innovative Construction Materials, specialized in renewable materials for building industry;
- Division of Biology, Imperial College London, specialised in plant biological science and LCA of renewable materials;
- Biocomposites Centre, Bangor University, specialised in plant cell biology, polymer chemistry and plant-based biocomposites;
- Royal Military College of Science, Cranfield University specialised in design and characterisation of ballistics systems.

The industry participants include:

- HGCA (Home Grown Cereal Authority), who co-sponsors Brunel University;
- Biopac UK Ltd , a manufacturer and developer of bio-based products for packaging and horticulture applications;
- Dixon Brothers Ltd, a specialist in processing and supply of straws;
- Parkes Group, a manufacturer of road/building utilities;
- Tubex Ltd., the world leading manufacturer of tree shelters;
- Primace Associate, consultant in new technologies/materials for agriculture, sports and construction industries;

- Clay Pigeon Company Ltd , a leading manufacturer of clay pigeons for shooting sport;
- Ecodek Vanplastic Ltd. a major manufacturer of wood plastic composites (WPC) for construction applications.
- Proman Coatings Ltd , specialist in wax and silicone coating technology.

1.3 Aims and objectives

Aim of the project

The proposed work aims to develop a commercially viable technology for the production of straw-based biocomposites for industrial applications.

Compared with the traditional approaches, the key novelty here is to achieve a “whole utilisation” of wheat straw without extraction of the cellulose. This will enable the reduction of the unit processing costs, maximise yield of saleable product and minimise any waste generation and environmental impact.

The industrial partners representing different sectors across the whole supply chain are seeking renewable alternative materials to replace non-renewable plastics in their products. To achieve widespread applications, bio-based materials have to be competitive in both price and performance, as well as demonstrated environmental benefits. The straw-based biocomposites are believed to have excellent potential for development into a new class of cost-effective and renewable materials tailored for a diverse range of applications in the packaging, horticulture, shooting sport, building and construction sectors.

Objectives:

The PhD work focuses on materials formulation, processing and characterization and contributes to most of the objectives of the project:

1. Develop a ‘close-loop’ extrusion technology for processing the straw-based feedstock with optimised process conditions and multi-feeding or venting ports for *in situ* modification treatments and compounding with biopolymer additives.

2. Assess the melt flow behaviour of the materials and the effects of material composition/modification so as to establish suitable moulding techniques for the range of composites.
3. Enhance the functionalities of the bio-composites to achieve a balanced combination of mouldability, performance stability and biodegradability by:
 - Inclusion of suitable biopolymers in the matrix;
 - *In situ* chemical modification of the constituents in straw.
4. Design and produce prototype composites and carry out a comprehensive assessment of the economic, technical performances in the required service environments including assessment of degradation behaviour of the composites designed for short service life and for ease of post-use management.
5. Promote commercial exploitation of the renewable materials for industrial applications.

1.4 The general approaches

This PhD work in development straw based biocomposites is particularly challenging and a systematic approach is necessary. The broad range of the target products requires careful considerations in materials formulation design to meet the needs in technical performance, manufacturing, application and disposal options, as well as cost efficiency. Processing of the materials and fabrication of prototypes also plays a vital role in controlling the material structure and commercial suitability.

The general approach in this work is to group the material types into three categories based on commonalities in the straw feedstock (degree of straw refinement), the required material properties and processing routes: These are:

- a) Clay-straw- biopolymer composites for bio-pigeon application
- b) Binder-less whole straw composites for board applications
- c) Straw-biopolymer composites for moulding/extrusion

In each category, considerations will be given to the necessary straw processing, taking account of processibility and costs into consideration, and the selection of biopolymer

systems, the processing routes and additives. Material properties (mechanical and rheological) will be characterised against bench references or technical requirements and microstructure will be analysed to understand the mechanisms of materials behaviour and to guide modifications of formulation and processing. Optimum material systems will be used for prototyping to assist assessment of product performance and commercial exploitation by collaborators.

1.5 Structure of the thesis

Chapter 2 gives a general overview of relevant areas associated with this work, including bioplastics, natural fibres, biodegradation, and natural fibre based composites. Potential applications derived from this PhD work are also presented in this chapter.

Chapter 3 describes experimental details including raw materials, pre-treatment on straw, formulation designs and processing details and characterisation of materials and properties.

In chapter 4, the experimental results on clay-flour-straw composites are presented and discussed in detail. Effects of formulation and adjustment on processing are analysed and examined. Formulations are compared and screened and then modifications are made by adjusting parameters such as straw concentration, fractionation level of straw, and glycerol content in flour. In conjunction with formulation study, three processing methods are involved assessed and optimum candidate formulations/processing route combination were selected.

Chapter 5 describes the physical properties and mechanical behaviour of straw-biopolymer composites. Effects of straw refinement, concentration on the mechanical performance of the biocomposites are analysed in details, in terms of tensile, tear and flexure properties. Besides, through examining the thermal properties and rheological behaviours, deeper understanding is achieved on the structure and processibility of straw filled biocomposites.

Chapter 6 describes the experimental results on wheat straw binder-less boards. Effects of straw size and boards processing condition on the properties of the boards are systematically studied. Attempts were made to understand the binding mechanisms by

microscopic and chemical analysis. The performance of the binder-less straw boards is also compared with commercially used chipboards and straw boards made in fractionated straw.

Chapter 7 outlines the key conclusion of the study and suggests further work this project was unable to address.

Chapter 2 Literature review

Background information and literatures associated with natural fibre & biopolymer composites are briefly reviewed in this chapter. It consists of five sections, covering the introduction of bioplastics, natural fibres, mechanisms of biodegradation, basic knowledge of natural fibre reinforced composites, and some latest research in straw based composites. The first section mainly talks about the definition of bioplastics and their classification based on origins with examples of some commonly used bioplastics derived from the four different origins. Then, section 2.2 summarises the mechanisms of biodegradation of typically used bioplastics, including the controlling factors which effect on biodegradability. Section 2.3 describes the nature of natural fibres and reviews the characteristics of several commercially used natural fibres with emphasis on cereal straw. Afterwards, section 2.4 describes the basic knowledge of natural fibre composites and summaries previous research results of straw based composites. Through the review of work in the associated areas, the research focus and directions of this PhD work together with the introduction of potential applications of straw composites are identified in 2.5.

2.1. Bioplastics

2.1.1 Classification of bioplastics

According to the European Bioplastics Association , bioplastic is a definition of two different kinds of plastics: plastics based on renewable resources, and biodegradable and compostable plastics according to EN13432 (2000) or similar standards. Following these definitions, bioplastics are a combination of plastics (as shown in Figure 2.1) which may be biodegradable and derived from renewable resources, non-biodegradable and derived from renewable resources as well, and biodegradable but derived from fossil resources (J. Song et al., 2011). American standards define that biodegradable polymers are “capable of undergoing decomposition into carbon dioxide, methane, water, inorganic compounds, or biomass in which the predominant mechanism is the enzymatic action of microorganisms, that can be measured by standardised tests, in a specified period of time, reflecting available disposal condition” (ASTM-D6400-99, 2002). According to definition, the biodegradable polymers are defined focusing on the mechanisms of degradation apart from the origins. Therefore, biodegradable polymers or biodegradable plastics are actually just a subset of bioplastics.

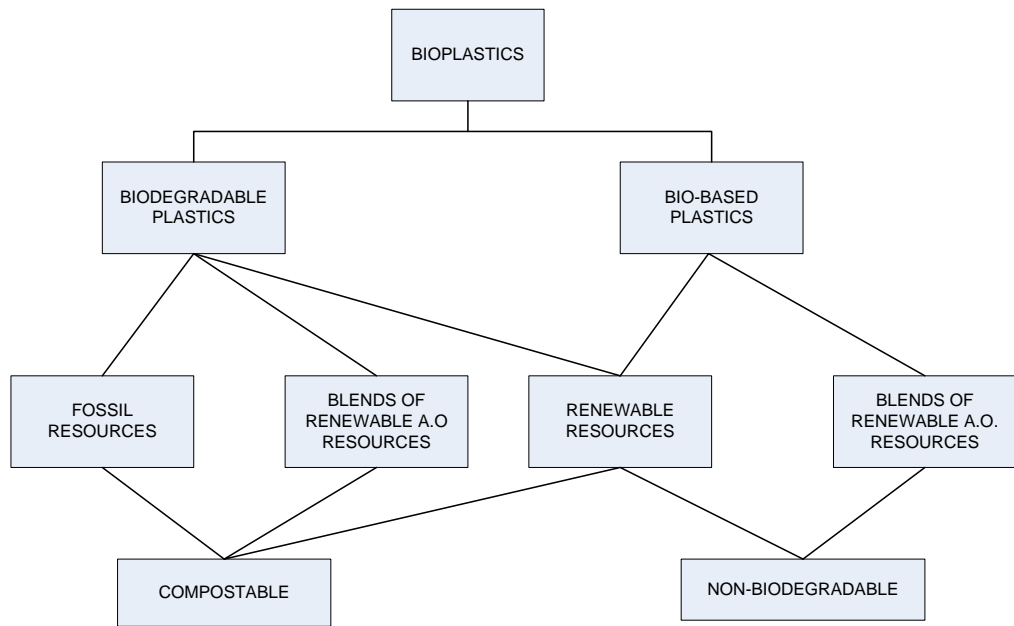


Figure 2.1: Types of bioplastics (Song et al., 2011)

Bioplastics are named in a variety of ways by different researchers or producers, such as biopolymers, biodegradable polymers and biodegradable plastics. Just as the bioplastics are variedly named, their classifications are also different from literature. Bioplastics can be classified in different ways based e.g. on their origins, chemical compositions, synthesis methods and applications. Typically used classification is based on the origins. A more particular classification by Song et al (2011) is illustrated in Figure 2.2. As to four groups by origins: directly derived from biomass, synthesised bio-derived monomers, synthesised from petrochemicals, and directly produced from natural/genetically modified organisms. It must be noted that most researchers do not take modified polyolefins as part of bioplastics as degradation mechanisms of such polyolefins are not biodegradation by nature.

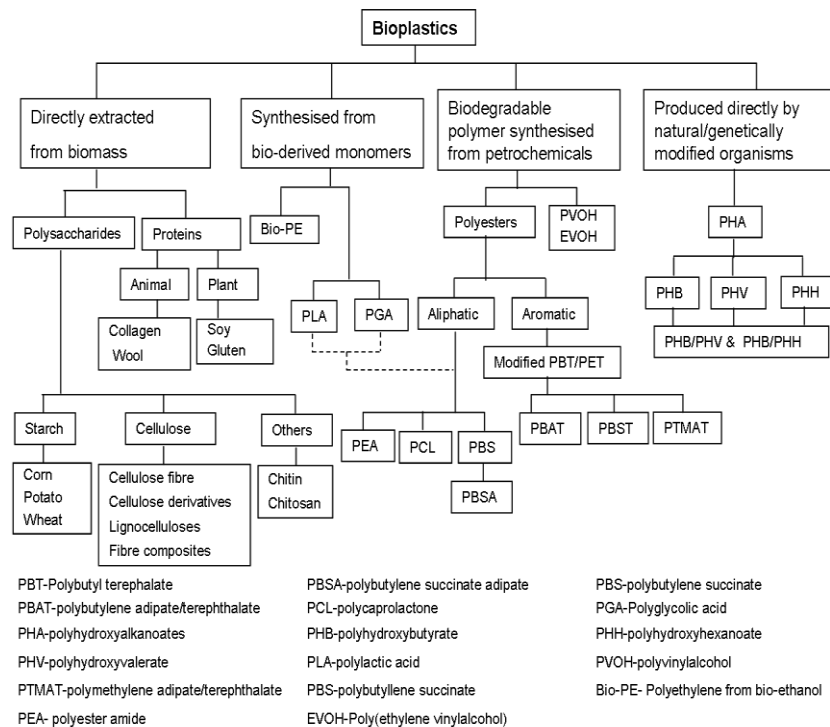


Figure 2.2: Classification of bioplastics by origins (Song et al., 2011)

In the four sub-groups of bioplastics based on different origins, most commonly used biopolymers in industry are polysaccharides, polylactic acid and its blends, synthesized biodegradable polymers from petrochemicals like Polycaprolactone, and PHAs. More details about these bioplastics will be presented in the following part. Commercially speaking, bioplastics are rarely applied in practice alone and they are normally modified or combined by other polymers or additive producing blends or composites which could match particular performance requirements.

2.1.2 Polysaccharide based bioplastics

Starch and cellulose (cellulose is reviewed separately in section 2.3) are the most popular used polysaccharides which attract most interests. Starch and its blends are normally made in various forms as film, foams and composites used typically in the packaging industry. Cellulose mainly deriving from wood and some other plant fibres is widely used for paper, membranes, dietary fibres, explosives and textiles.

2.1.2.1 Chemical structure and properties of starch

Starch granules are essentially composed of two main polysaccharides, amylose and

amylopectin with some minor components such as lipids and proteins.

The structure of amylose and amylopectin are represented in Figure 2.3 and Figure 2.4

(<http://www.rsc.org/education/teachers/learnnet/cfb/carbohydrates.htm>).

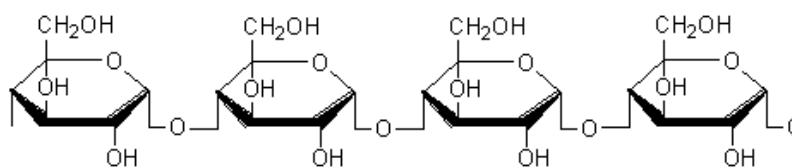


Figure 2.3: Molecular structure of amylose

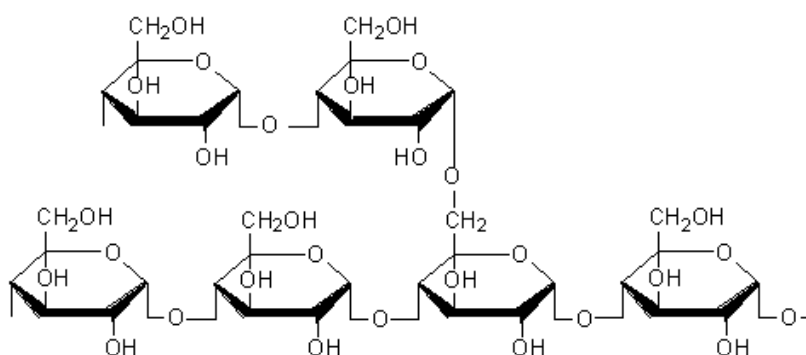


Figure 2.4: Molecular structure of amylopectin

Typically, molecular weight of amylose is about 10^5 to 10^6 g/mol, while amylopectin is a highly branched polymer, with molecular weight ranging from 10^6 to 10^8 g/mol.

Starch granules derive from numerous botanical origins, for example, wheat, oats, rice, barley, potato, and corn etc. Halley (2005) pointed out that not only the granule size distributions and granule structure, but also the starch composition, molecular weight, crystallinity and degree of branching of amylose and amylopectin are diverse between starches from different sources. That's so called starch genetics, which influenced on the ultimate processing and final properties of starch products (Halley, 2005).

2.1.2.2 Starch based bioplastics

Due to lack of required mechanical properties in its native structure, starches are used as bioplastics in the industry mainly in three types, plasticised starch, starch blends, and composite.

Plasticised starch is starch with the addition of plasticisers such as water through a gelatinisation process. At the beginning of the gelatinisation process, the addition of water cleaves the crystallinity and disrupts helices. Then heat and more water penetration lead to the swelling of the granules, with amylose (linear molecules) leached out. Finally, granules, containing mostly amylopectin (branched molecules), are collapsed and held in the matrix of amylose (Halley, 2005). The thermoplastic starch after such plasticising process, is still sensitive to moisture, and hence often modified using additives. Halley states that the modification of starch is mainly performed to involve more hydroxyl groups substituting on the starch, which will lower gelatinisation temperatures and improve the flexibility of the final products (Halley, 2005).

Addition of organic and inorganic esters, hydroxydiethers and irradiation will form cross linked starch which could increase water resistance (Jane et al., 1994). Therefore, blending thermoplastic starch with other polymers is typically used to enhance properties of starches. Commonly used starch blends are: starch/ PLA, Starch/ cellulose acetate (e.g. Bioflex or Bioplast); Starch/Polycaprolactone, which involves glycerol as plasticiser and formulated for injections or extrusion (Clarival and Halleux, 2005).

2.1.2.3 Cellulose derivatives

Although cellulose itself could not be used as thermoplastics, chemical reactions such as etherification and esterification are conducted on the free hydroxyl groups to improve thermoplastic behaviour. Numerous derivatives from cellulose are commercially used as bioplastics, such as cellulose acetate, ethyl cellulose, hydroxyl ethyl cellulose, hydroxyl propyl cellulose, carboxy methyl cellulose and fatty acid esters of cellulose (Chiellini et al., 2002). For example, Cellulose acetate is mainly used in the synthesis of membranes for reverse osmosis. Modified cellulose acetate can also be thermal-formed, which can be injected or film extruded for packaging applications.

2.1.3 Biodegradable Polyesters

Biodegradable polyesters could be divided into two groups which contain different

backbone structures in their chemical structures, aliphatic groups and aromatic groups. In the family of aliphatic polyesters, polymers are of natural origin like, polyhydroxyalkanoates (PHAs), mineral origin like, polycaprolactone (PCL) and those derived from both like polylactic acid (PLA) and polyglycolic acid (PGA). While in the family of aromatic polyesters, polymers like modified polyethylene terephthalate (PET) or polybutylene terephthalate (PBT) are mainly synthesised from mineral origin.

2.1.3.1 Polylactic acid (PLA) based bioplastics

1) Chemical structure and properties of PLA

Poly lactic acid, or Poly (lactic acid), is a kind of biodegradable thermoplastic polyester, manufactured by biotechnological processes (like fermentation) from renewable sugar-based materials such as starch or cellulose, like corn (Plackett, 2004). Figure 2.5 (Zhang and Sun, 2005) represents the chemical structure of Lactide monomer in PLA.

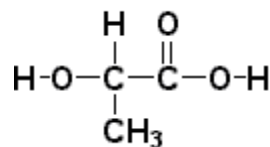


Figure 2.5: Lactide monomer

Generally, high molecular weight PLA is prepared by ring-opening polymerisation of lactide, a cyclic dimer prepared by the controlled depolymerisation of lactic acid as shown in Figure 2.6 (Zhang and Sun, 2005).

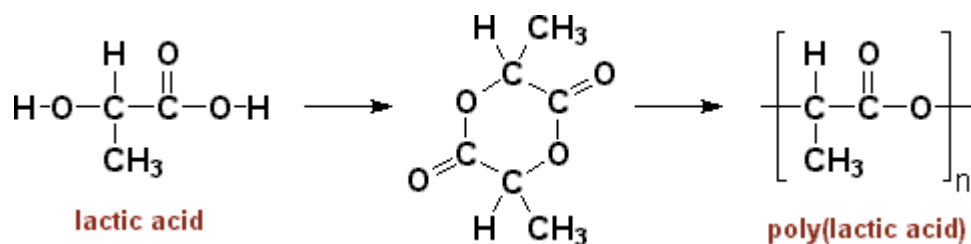


Figure 2.6: Polymerisation progress of PLA

PLA is readily commercialised by owing to its combination of renewability, biodegradability and good transparency and mechanical properties which are comparable to petroleum-based polyesters (Plackett, 2004). PLA is classified as a water-sensitive

polymer because it degrades slowly compared to water-soluble or water-swollen polymers (Gajria et al., 1996).

There are two stereo-isomeric forms of lactic acid: poly (levo-lactic acid or L-lactide) (PLLA) and poly (dextro-lactic acid, or D-lactide) (PDLA), and the stereo-isomeric L/D ratio (L/D ratio is the ratio between PLLA and PDLA in PLA system) of the lactate unit influences PLA properties. Several types of PLAs are classified:

Poly-L-lactide (PLLA) is the product resulting from polymerisation of L-lactide. PLLA has a crystallinity of around 37%, a glass transition temperature between 50-80 °C and a melting temperature between 173-178 °C (Hideto Tsuji and Ikada, 1992). By physically blending PLLA polymer with PDLA (poly-D-lactide), the melting temperature of PLLA can be increased by 40-50 °C and its heat deflection temperature can be increased from approximately 60 °C to up to 190 °C PDLA and PLLA form a highly regular stereocomplex with increased crystallinity (Tsuji and Ikada, 1992).

Poly (D, L-lactic acid), a racemic polymer obtained from an equimolar mixture of PDLA and PLLA, is amorphous with weak mechanical properties. Generally speaking, an increase of stereo-isomeric L/D ratio decreases crystallinity and melting temperature (Urayama et al., 2002). Thus, control of the ratio of L to D monomer content influences significantly the PLAs' properties.

2) Processing and Application of PLA

As a semi-crystalline thermoplastic, PLA can be processed by conventional techniques, such as injection moulding, extrusion, compression or blow moulding, fibre spinning or stretching. However it needs to be carefully controlled because mechanical and thermal degradations may take place during the process if the temperature exceeds 200 °C (Plackett, 2004). In practice, additives are frequently used, such as nucleation agents, plasticisers, lubricants, impact modifiers and pigments.

PLA is transparent, printable and heat sealable, with excellent barrier properties. Thus PLA is of interest as a packaging material for food products, replacing commonly used plastics such as polyethylene terephthalate (PET) (Plackett, 2004). Increasingly, PLAs and their blends are developed as matrix for bio-composites (more information is mentioned in section 2.5).

2.1.3.2 Polycaprolactone (PCL)

Polycaprolactone is a semi-crystalline linear aliphatic polyester synthesised by ring-opening polymerisation of epsilon-caprolactone. Figure 2.7 illustrates the polymerisation reaction of PCL and its repeat unit.

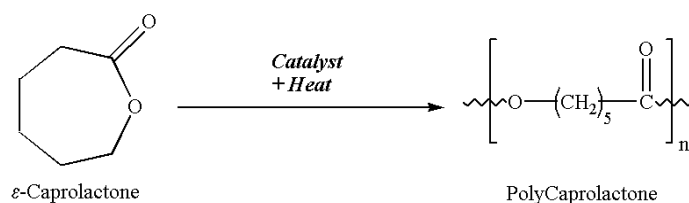


Figure 2.7: Synthesising reaction of PCL

As Song reviewed (Song et al., 2011), the initial commercial grades have been of comparatively low molecular weight (15,000-40,000) and the main lines of interest have been as precursors for polyurethanes and as additives in other polymers. PCL has low T_g of about $-60\text{ }^\circ\text{C}$ and T_m of $50\text{-}64\text{ }^\circ\text{C}$ (Song et al., 2011), and Tone® (Union carbide USA, www.ucarbide.com) and CaPA® (solvay Belgium, www.solvaypress.com) supply PCL polymers. Due to its high ductility and low processing temperature, it has to be blended with up to 45% starch etc, into a range of starch blends including some of the grades in commercial Bioplast® (Biotec, Germany) and Mater-Bi® (Novamont, Italy). The low melting point and poor mechanical properties limits the application of starch-PCL blends (Nolan-ITU Pty Ltd, 2002). The PCL/starch blends have been developed for biodegradable film application through the process of injection, flat extrusion, or blowing injection. Properties of the blends are comparable to LDPE films and better than pure PCL film (Clarival and Halleux, 2005).

2.1.3.3 PHAs

Polyhydroxyalkanoates (PHAs) are aliphatic polyesters synthesised by certain microbes (where they act as energy storage material in cells) and produced commercially using bioengineering methods to accumulate and extract the polymers. (J. Song, et al., 2011) As Chen (2005) reviewed, PHAs are synthesised by various bacteria (e.g. alcaligenes, eutrophus and cyanobacteria). By controlling the length of aliphatic chain, T_g , T_m and the

flexibility of the materials can be adjusted. Many grades of PHA exist with different degrees of crystallinity and they can be processed with conventional melt flow technologies. The PHAs family include polyhydroxybutyrate (PHB), polyhydroxyvalerate (PHV) polyhydroxyhexanoate (PHH) and their copolymers.

PHB has a T_g of 5°C and T_m of 180°C. The properties of PHB are similar to those of polystyrene but more rigid and brittle than polypropylene (Clarival and Halleux, 2005). Examples of commercially available PHB are some grades of Biomer® (Biomer, Germany, www.biomer.de). In practice, copolymers of PHB, PHV and PHH are more commonly produced to enhance biodegradability and processibility, such as PHBV (copolymer of PHB and PHV) and PHBH (copolymer of PHB and PHH). Commercialised example of such blends is Biopol® PHBV (Metabolix USA, www.metabolix.com) and PHBH from some grades of Nodax® (Kaneka, Japan, www.kaneka.com). Plackett reviewed (Plackett, 2004) that PHB has very narrow thermal processing window with degradation temperature at about 160 °C, quite near from its melting temperature. Thus care has to be taken to control the processing temperatures. In order to avoid the degradation during breaks in processing, LDPE are used to clean equipment. The mechanical properties of PHB and PHBV are similar to those of polypropylene (PP), but more rigid, brittle and denser than PP. PHB is insoluble in water and relatively resistant to hydrolysis (Plackett, 2004). Most of the materials are biocompatible and bioresorbable and hence have found medical applications (e.g. implants). Certain grades are for more general applications such as in packaging like film, container and bottles. (Hocking and Marchessault, 1994; J. Song, et al., 2011).

By controlling the crystallinity of PHAs, a profile of mechanical and barrier properties can be obtained, to match the performance of engineered thermoplastics. The polymers will biodegrade either aerobically or anaerobically. Bio-degradation can occur in septic systems, commercial waste water treatment systems, composting environments or even in cold ocean waters. There is a wide range of applications from highly flexible films and fibres to thermoformed rigid packaging, including many single-use food service and liquid packaging applications. Song states that a major factor in the competition between PHAs and petrochemical based polyesters is in production cost (J. Song, et al., 2011). Use of low-cost biomass raw materials (such as corn steeped liquor and molasses) has been suggested

(Nolan-ITU Pty Ltd, 2002). Clear versions of these materials are yet to be developed.

2.2 Degradation of Biodegradable polymers

Plastic contributes a large part of the waste from no matter industry or home-use. Take packaging industry in the UK as an example, it is 18% of the 10.4 million tonnes of packaging waste produced annually in the UK (Defra, 2006b). There are a large number of different types of polymers containing different processing additives such as fillers, pigments and plasticisers used for packaging applications. Therefore, Davis and Song state that “although there have been significant increases in recycling of packaging materials in recent years, recycling rates for most plastic packaging remains low” (Davis and Song, 2006). Thus, industrial utilisation of biodegradable polymers is rapidly increasing in recent years due in part to the opportunities they offer in biological treatment of waste (European-Bioplastics, 2010). Biodegradable polymers have different biodegradability, which depends on their chemical and physical structure. In order to match the requirements of various applications, many modification approaches have been involved, like chemical/enzymatic modification, polymer blends, or chemical structural modification, etc. Development of biopolymer products is closely associated with challenges to control their biodegradability or compostability and thus understanding of mechanism of degradation is important in biopolymer products.

2.2.1 Classification of typical degradation mechanisms

Typical mechanisms of environmental degradation of polymers are summarised by Matsumura (2005) into three groups, as illustrated in Figure 2.8.

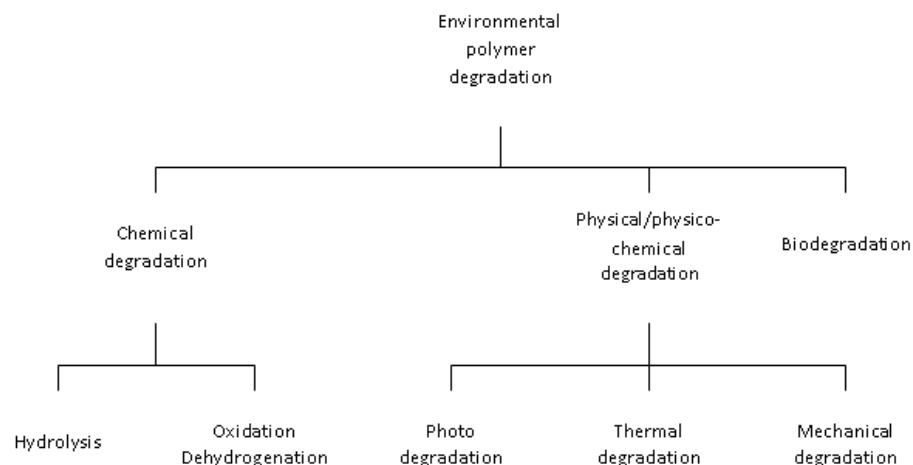


Figure 2.8: Classification of environmental polymer degradation

Compared with pure chemical and physical degradation, biodegradation is a complicated process, involving chemical reactions, such as hydrolysis, oxidation/reduction with/without the contribution of biological action in living organisms depending on the environmental conditions. Generally, biological action is represented by enzymatic reactions, which contain hydrolase enzymes relating to biological hydrolysis and oxidoreductase enzymes responsible for oxidation. The reaction rate of the biological hydrolysis is generally faster than the oxidation (Matsumura, 2005).

2.2.2 Biodegradation mechanisms

Generally speaking, the degradation process of biodegradable polymers consists of two steps, primary and ultimate biodegradation (Denchev, 2007) as represented schematically in Figure 2.9.

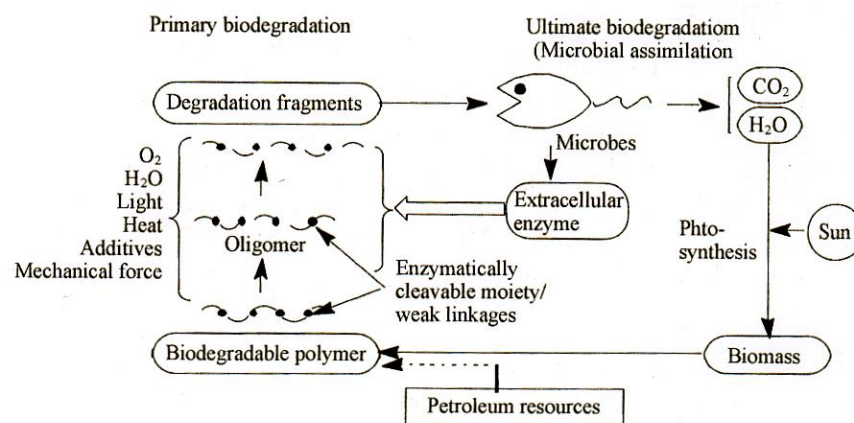


Figure 2.9: Degradation process of biodegradable polymers

The primary degradation is a stage where the main chain is cleaved by hydrolysis or oxidative chain scission, forming low-molecular weight fragments (oligomers). During this step, hydrolysis occurs using environmental water with the contribution of enzyme or under non-enzymatic conditions where autocatalysis, heat or catalytic metals/acids can all be responsible for the hydrolysis. Oxidative scission occurs mainly by oxygen, catalytic metals, UV light or enzymes.

In the ultimate degradation step, the low-molecular weight fragments produced by the polymer chain scission can be assimilated in to the microbial cells further, producing carbon dioxide, water and microbial cells or products.

2.2.3 Factors influent on biodegradation of biopolymers

Biodegradation of polymers is a complex process depending on various factors related to the sample or to the medium where degradation takes place (Chandra & Rustgi, 1998).

1. Chemical Structure

Many natural biodegradable polymers contain hydrophilicity-imparting functional groups. Under biotic conditions, they degrade by hydrolysis followed by oxidation. Most of synthetic biodegradable polymers also contain hydrolysable linkages, e.g. urethane groups. The introduction of functionalities, such as hydroxyl, carboxy and phenyl groups, also increase their biodegradability (Huang S et al., 1978). More flexible polymer chains are easier to fit in the active site of the enzyme and therefore will enhance the biodegradability

(Potts, 1984).

The other factor influencing on the flexibility of polymer chains is melting temperature (ASTM-D6400-99, 2002). The higher the T_m , the lower the biodegradation of the polymer (Tokiwa and Suzuki, 1978). In general, T_m is represented by the following formula: $T_m = \Delta H / \Delta S$, where ΔH was the change of enthalpy in melting and ΔS is the change of entropy in melting. It is well known that the interactions among polymer chains mainly affect the ΔH value and that the internal rotation energies corresponding to the rigidity (the flexibility) of the polymer molecule remarkably affect the ΔS value.

2. Molecular weight and crystallinity

The molecular weight is important for the biodegradability because it determines many physical properties of the polymer. Increasing the molecular weight of the polymer decreased its degradability. In Tokiwa and Suzuki's research, PCL with higher molecular weight ($M_n > 4,000$) was degraded slowly by *Rhizopus delemar* lipase (endo-cleavage type) than that with low M_n (Tokiwa and Suzuki, 1978).

Moreover, the morphology of polymers greatly affects their rates of biodegradation. Generally speaking, polyesters with side chains are less assimilated than those without side chains (Tokiwa et al., 1976). By controlling the size of side chains, adjustment of the crystallinity can be achieved. The degree of crystallinity is a crucial factor affecting biodegradability, since enzymes mainly attack the amorphous domains of a polymer. The molecules in the amorphous regions are loosely packed, and thus make it more susceptible to degradation. The crystalline portion of the polymers is more resistant than the amorphous region. The rate of degradation of PLA decreases with an increase in crystallinity of the polymer (Iwata and Doi, 1998; H Tsuji and Miyauchi, 2001).

3. Microorganisms

During the biodegradation progress, different microorganisms are involved. Microorganisms live in all parts of the biosphere where there is liquid water, including soil, hot springs, on the ocean floor, high in the atmosphere and deep inside rocks within the Earth's crust. They can be classified into two groups: prokaryotes without nucleus, including bacteria and archaea and eukaryotes with organelles such as nucleus, including

fungi, animals, protists and plants. Some bacteria existing in biosphere like, eubacteria, archeobacteria and eucaryotes, have the ability to degrade every kind of organic compound given an appropriate period (Denchev, 2007).

4. Biodegradation environment

The environment of biodegradation occurring is the main factors influent on the biodegradability of biopolymers. Typically, soil, compost and vermiculite are the three different substrates where biodegradation can be carried out. All the factors in the environments, like organic being content, PH value, temperature, moisture content and oxygen supply, all affect on the biodegradation rate and final products from biodegradation (Sawada, 1994).

5. Type of enzyme

Enzymes are by far more important than the other four factors mentioned above for the biodegradation process. As mentioned in 5.2, enzymes are all specialised proteins, which have different functions during the biodegradation process. Active sites of enzymes are conformed at certain regions on the surface. Reactions actually occur between enzymes and substrates at the region of active sites. Normally, enzymes are classified into six groups based on their activities: Hydrolases, esterases, isomerases, reductases, lyases and ligases (Denchev, 2007). They contribute different mechanisms of catalysis during the biodegradation.

2.2.4 Biodegradation of polysaccharides and polylactic acid (PLA)

As this PhD work focuses on materials based on polysaccharides (starch and cellulose based materials) and biopolymers containing polylactic acid, a review on degradation processes and mechanisms of starch, cellulose based materials and PLA is given in some details.

2.2.4.1 Degradation of starch-based materials

Starch granules vary from plant to plant, but are in general composed of a linear polymer, amylose (in most cases up to about 20% of the granule), and a branched polymer, amylopectin (Lawton, 1996). Both amylose and amylopectin are built up of α -form glucose

repeat units, but differ significantly in their physical properties. Amylose is semi-crystalline, and is soluble in hot water. Amylopectin is insoluble in hot water. During its biodegradation, starch undergoes enzyme-catalysed acetal hydrolysis (Madras, 2005). The progress is schematically represented in Figure 2.10.

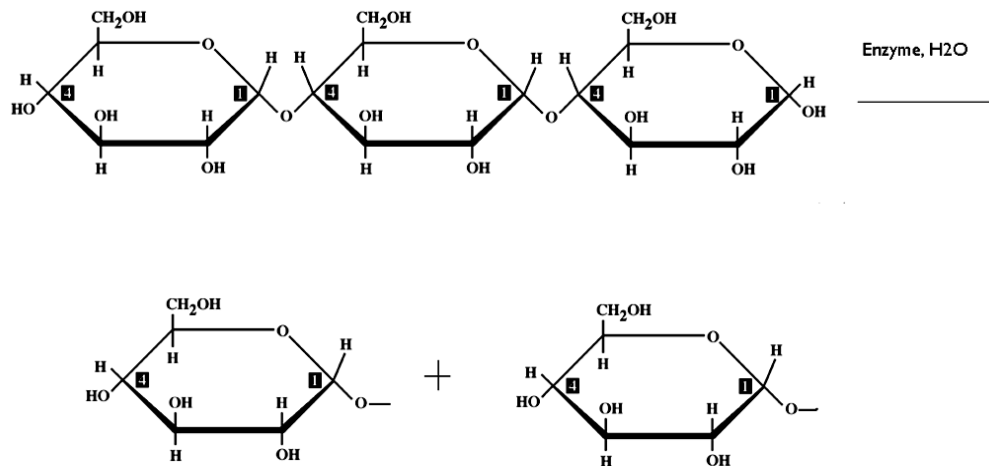


Figure 2.10: Biodegradation of Starch (Madras, 2005)

2.2.4.2 Degradation of cellulose-based materials

Because of the different bonding of the glucose monomeric units, the enzymes that catalyse acetal hydrolysis reactions during the biodegradation of starch and cellulose are different and not interchangeable (Madras, 2005). Enzymes secreted by some fungi can catalyse the oxidation reactions of either cellulose itself or the lower molecular weight oligomers produced from the enzymatic hydrolysis of cellulose (Aubert et al., 1988). As represented in the Figure 2.11, the peroxidases can provide hydrogen peroxide from free radical attack on the C2 –C3 positions of cellulose to form “aldehyde” cellulose, which is very reactive and can hydrolyse to form lower molecular weight fragments.

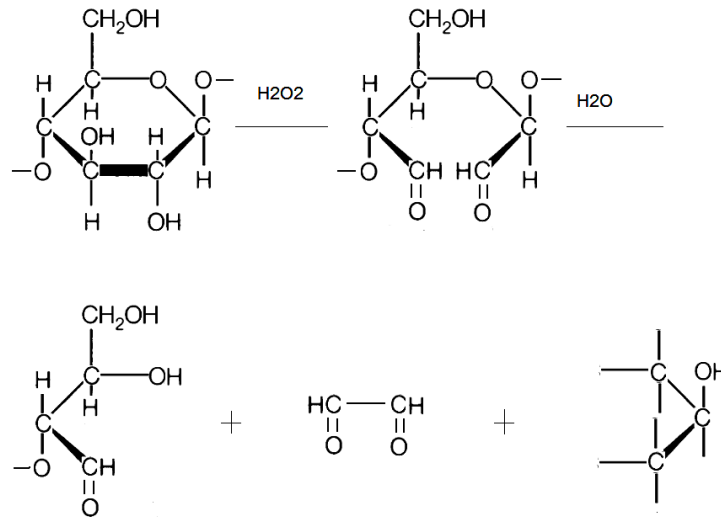


Figure 2.11: Biodegradation of Cellulose (Madras, 2005)

Hemicellulose and lignin are the main parts of cellulosic materials produced by photosynthesis, in addition to cellulose. Hemicelluloses are biodegraded into monomeric sugars and acetic acid. The biodegradation of lignin is influenced by its water insolubility, high molecular weight, and complex structure. Microorganisms like white-rot fungi, secrete exocellular peroxidises to degrade saccharides in order to produce sugars, which serve as nutrients for themselves. Brown-rot fungi, secrete enzymes for the degradation of cellulose and the hemicelluloses. Soft fungi also degrade these two types of polysaccharides.

2.2.4.3 Biodegradation of polylactic acid (PLA)

Ecological studies on the abundance of PLA-degrading microorganisms in different environments have confirmed that PLA-degraders have a limited distribution, and thus it is less susceptible to microbial attack compared to other microbial and synthetic aliphatic polymers like PHB and PCL (H Pranamuda et al., 1997; Suyama et al., 1998). Urayama (2002) states that the degradation of PLA in soil is slow and that it takes a long time for the degradation to start. There are two different mechanisms for the biodegradation of PLA: microbial degradation and enzymatic degradation. Microbial degradation of PLA using *Amycolatopsis* sp. was first reported by Pranamuda et al (1997). Since then, further studies on microbial and enzymatic degradation of PLA have been reported.

In the microbial degradation of PLA, the process is carrying out in a two step reaction. During the primary degradation step, PLA undergoes non-enzymatic hydrolysis, which is both temperature and humidity dependent. After that, Mn decrease to 10,000-20,000 in the following secondary degradation step. Microorganisms existing in the soil start to digest the low molecular weight oligomer and lactic acid, transferring to carbon dioxide and water (Pranamuda et al., 1997). During actual compost investigated by Kawashima et al. (2002), the 60% of PLA was converted into inorganic substances in 10 days, while over 90% was degraded in about 20 days.

Williams (1981) investigated the enzymatic degradation of PLA using proteinase K, bromelain and pronase. Among these enzymes, proteinase K from *Tritirachium album* is the most effective for PLA degradation. Proteinase K and other serine proteases are capable of degrading L-PLA and DL-PLA but not D-PLA. Furthermore, proteinase K preferentially hydrolyses the amorphous part of L-PLA and the rate of degradation decreases with an increase in the crystalline portion (MacDonald et al., 1996). Fukuzaki et al. (Fukuzaki et al., 1989) reported that the degradation of PLA oligomers was accelerated by several esterase-type enzymes, especially *Rhizopus delemar* lipase. The purified PLA depolymerase from *Amycolatopsis* sp. was also capable of degrading casein, silk fibroin but not PCL, PHB (Hardaning Pranamuda et al., 2001) Their studies showed that PLA depolymerise was a kind of protease and not a lipase.

2.2.5 Standards of bio-degradability and compostability

2.2.5.1 Biodegradable or compostable?

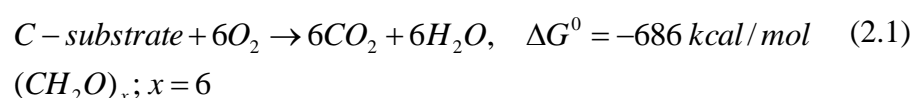
A material is said to be biodegradable if it is able to completely break down under the action of microorganisms into carbon dioxide, water and biomass, although the biodegradation may take a very long time depending on environmental conditions. Composting is the accelerated biodegradation process of heterogeneous organic matter by a mixed microbial population in a moist, warm, aerobic environment under controlled conditions. It is a purposeful biodegradation to transfer biodegradable waste, such as yard and food waste including biodegradable plastics, into useful soil amendment products. The decomposition is performed by micro-organisms, mostly bacteria, but also yeasts and fungi

(Cornell Composting, 2009). Therefore, compostable materials are a subset of biodegradable materials and not every biodegradable material is compostable.

2.2.5.2 Relevant standards defining biodegradability and compostability

1). Concept of Biodegradability Measurement

Microorganisms use the carbon substrates to extract chemical energy that drives their life processes by aerobic oxidation of glucose and other readily utilizable C-substrates, with the chemical reaction is as follow (Narayan, 1993):



From the reaction, glucose can be depolymerised into water and CO₂ in presence of oxygen. The energy released through the reaction is 686 kcal/mol. Therefore, the biodegradability can be obtained by measuring the rate and amount of CO₂ produced in the process, which is a direct method to quantify biodegradation of polymers. This forms the basis for various international standards for measuring biodegradability or microbial utilisation of the test polymer/plastics (J. H. Song et al., 2009). Thus, one can measure the rate and extent of biodegradation or microbial utilization of the test plastic material by using it as the sole added carbon source in a test system containing a microbially rich matrix, like compost in the presence of air and under optimal temperature conditions (preferably at 58 °C – representing the thermophilic phase).

2).Standards of Biodegradability

Based on the above concepts, ASTM committee D20.96 on biobased and environmentally degradable plastics (www.astm.org) developed a Specification Standard ASTM D6400 (2002) for products claiming to be biodegradable under composting conditions or compostable plastic. The above specification standard is in harmony with standards in Europe, Japan, Korea, China, and Taiwan. EN13432 (2000) states “Requirements for Packaging Recoverable through Composting and Biodegradation—Test Scheme and Evaluation Criteria for the Final Acceptance of Packaging” is the European standard (norm) and similar to ASTM D6400 (2002). The current UK standard BS EN 13432 (2000) covers

the requirements for packaging recoverable through composting and biodegradation and test scheme and evaluation criteria for the final acceptance of packaging.

The fundamental requirements of these world-wide standards discussed above for complete biodegradation under composting conditions are:

1. Conversion to CO₂, water & biomass via microbial assimilation of the test polymer material in powder, film, or granule form.
2. 90% conversion of the carbon in the test polymer to CO₂. The 90% level set for biodegradation in the test accounts for a +/- 10% statistical variability of the experimental measurement; in other words, there is an expectation for demonstration of virtually complete biodegradation in the composting environment of the test.
3. Same rate of biodegradation as natural materials -- leaves, paper, grass and food scraps.
4. Time - 180 days or less; ASTM D6400 also has the requirement that if radiolabeled polymer is used and the radiolabeled evolved CO₂ is measured, then the time can be extended to 365 days (ASTM D6400, 2002).

Two further requirements are also of importance:

Disintegration : <10% of test material on 2mm sieve, using the test polymer material in the shape and thickness identical to the product's final intended use.

Safety : The resulting compost should have no impacts on plants, using OECD Guide 208, Terrestrial Plants, Growth Test or similar such as PAS 100(BSI, 2002). Furthermore, regulated (heavy) metals content in the polymer material should be less than defined thresholds e.g. 50% of prescribed threshold by the Environmental Protection Agency (EPA) of USA and Canada.



2.2.5.3 Standards of Compositing

Considering the potential toxicity upon ecology which is involved in the degradation products, suitable international standards for compostable polymer products have been formed and adopted. For example, EN 13432 (2000) requires that compostable polymer materials have to fulfil European, or where none exists, national requirements for compostability. In December 2003, the Composting Association in the UK launched a Certification Scheme for Compostable Packaging, in order to assist UK local authorities

with the selection of sacks for organic waste collections. As there is currently no European standard on compost quality, the UK adopted the BSI PAS 100 in November 2002 (BSI, 2002). Other standards in worldwide such as the ASTM D 6400 and ISO 17088 also define the product classification and requirements for composting.

In the UK, Murphy and Bartel (2004) reported that home composting has been identified by the strategy unit of the cabinet office as one of the key measures to reduce the growth rate of household waste. Comparing with industrial composting, the conditions of home composting are difficult to regulate and less optimised on temperature etc. Bioplastics certified for industrial composting may not be able to biodegrade sufficiently under the conditions of home composting. Thus, some bioplastic polymers are certified only “OK Compost” standard for industry composting and not applicable for home composting except the “OK HOME” scheme is clarified. Table 2.1 makes a comparison between industrial composting and home composting (EN13432, www.aib-vincotte.com).

Table 2.1: Comparison of standards of industrial and home composting (J. Song, et al., 2011).

	Industrial Composting (EN 13432)	Home Composting (Vincotte Certification)
Biodegradation	Test at 58°C in 180 days Biodegradation min. 90%	Test at 20-30 °C in 365 days Biodegradation min. 90%
Disintegration	Test at 58°C in 90 days Sieve 2mm mesh Disintegration > 90% Max 10% of dry weight allowed to be retained by 2mm sieve	Test at 20-30°C in 180 days Sieve 2mm mesh Disintegration > 90% Max 10% of dry weight allowed to be retained by 2mm sieve
Certification	Din Certco/OK Compost 	OK Home 

2.3. Natural Fibres

2.3.1 Natural Fibres – subset of biodegradable fibres

Based on the sources, biodegradable fibres are classified by Okada into three categories (Okada, 2005), as shown in Figure 2.12. Natural fibres clearly distinguish themselves with the other two by the fact that the fibres are synthesised by nature and can be obtained by extraction. They can be divided into four categories by sources as shown in Table 2.2 (Nishino, 2004).

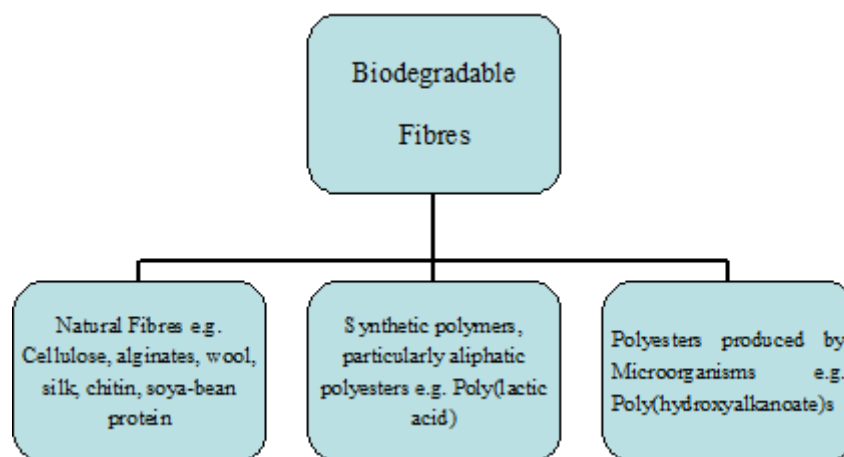


Figure 2.12: Classification of biodegradable fibres based on sources.

Table 2.2: Classifications of natural fibres.

Natural Fibres	Wood Fibres	Soft and hard woods
	Vegetable Fibres	Cotton, hemp, jute, ramie, kenaf, etc.
	Animal Fibres	Wool, silk, spider silk, feather, down, etc.
	Mineral Fibres	Asbestos, inorganic whiskers, etc.

In terms of chemical compositions, plant fibres (such like, wood and vegetable) are essentially celluloses based, while the animal fibres are largely based on proteins.

According to the research area of this PhD work, plant fibres will be the focus of in this section.

2.3.2 Plant fibres

2.3.2.1 Macrostructure of plant fibres

Figure 2.13 schematically presents the structure of a cell wall in a typical plant fibre, which is known as macrofibril. A macrofibril is a hollow tube with lumen, an open channel in the centre and covered outside by four layers of cell wall, one primary wall, and three secondary walls.

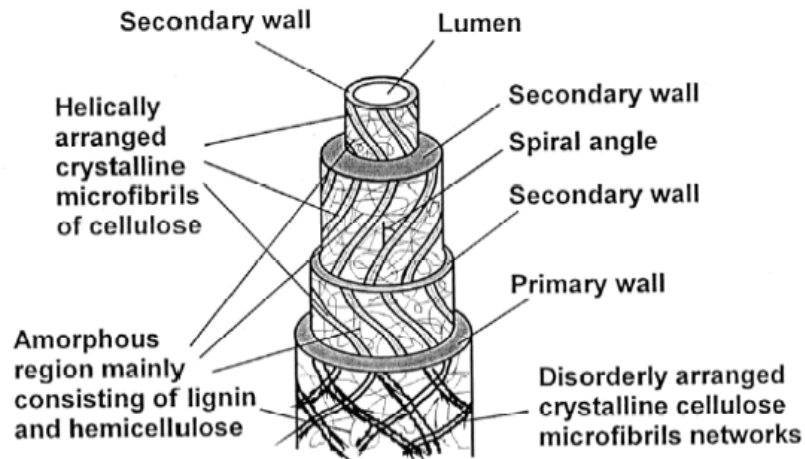


Figure 2.13: Macrofibril of Natural fibres (Rong et al., 2001).

The primary wall cell walls consists of disordered networks of crystalline cellulose known as microfibrils and amorphous region mainly consisting of lignin and hemicelluloses, while in the secondary wall , there are helically arranged crystalline microfibrils of cellulose, embedded in an amorphous region of lignin and hemicelluloses. Figure 2.14 (Ridge, 2009), illustrates finer details within and between microfibrils in the plant fibres. Cellulose molecules shown in Figure 2.14 are crystalline arrays in the cellulose microfibrils, which are bonded by polysaccharides in between them.

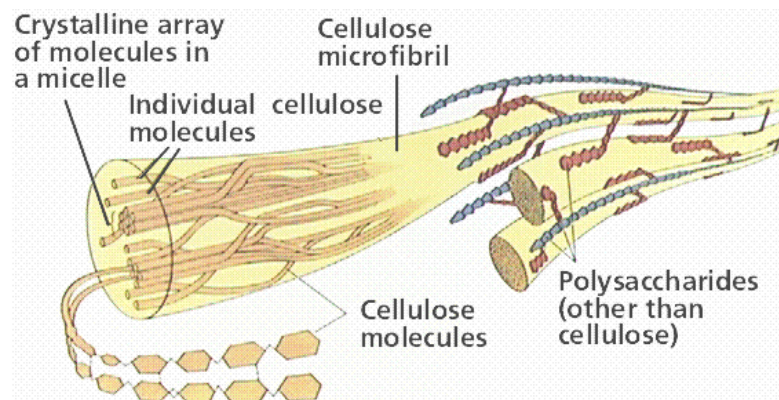


Figure 2.14: Cellulose microfibril arrangement in the plant fibres (Ridge, 2009).

2.3.2.2 Chemical components in plant fibres

Cellulose, lignin, and hemicellulose are the three main chemical components making up the plant fibres, which will be described below in detail. In addition, small amount of extractives and ashes also exist in natural fibres. The chemical composition varies in different natural fibres. Table 2.3 shows the comparison of chemical components in some typical natural plant fibres (Satyanarayana and Wypych, 2007) and characteristic of these components are briefly described below.

Table 2.3: Chemical content in typical natural plant fibres (I-Indian).

Fibre	Cellulose (wt. %)	Hemi-cellulose (wt. %)	Lignin (wt. %)	Ash (wt. %)	Extracts (wt. %)
Flax	62-71/70-72	16-18/14	2-2.5/4-5	1.5	6.0
Jute	59-71/61-63	12-13/13	11.8-12.9/5-13	0.7/0.14	0.5-2
Ramie	68-76/80-85	13-14/3-4	0.6-0.7/0.5	0.3	6.4
Hemp	67-75/57-77	16-18	2.8-3.3/9-13	0.7/3.0	0.8
Rice straw	51-70/28-48		12-16	15-20	9-14
Wheat straw	40/29-51	28	18/16-25	4.5-9	
Pineapple (I)	80		12	0.1-1	4
Sisal (I)	60-67	10-15	8-12	0.55	
Coir (I)	43.77		45		
Cotton	92-95/90	6	0.7-1.6	0.8-2	0.4

(EN 13432) Cellulose

Cellulose molecules in microfibrils, as shown in Figure 2.15, are highly crystalline and generally water insoluble. Chiaramonti (2007) states that “cellulose is a high-molecular weight linear polymer consisting of chains of bonded glucose monomers”. During growth of the plant, the cellulose molecules are arranged into larger structural elements comprising the cell wall of fibres.

Glucose monomers are a six sided ring combined together by one oxygen atom and five carbon atoms. Each of them have one primary and two secondary hydroxyl groups which are the functional groups used to form intermolecular bonding in crystalline regions as shown in Figure 2.15. But in non-crystalline regions, the hydroxyl groups play the role of

hydrophilic groups, which can form polar bonding with water.

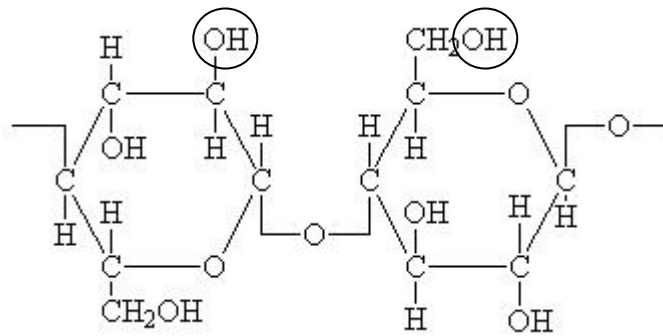


Figure 2.15: Chemical structure and polar groups of cellulose (Joanne and Stefanie's plastics website, 2009).

As highlighted by circles in Figure 2.15, cellulose contains many hydrophilic groups, which will help to absorb water vapour from the atmosphere. Water exists in plant in two types after being absorbed, bound water and free water. Water usually flows from one region to another after absorption. Normally, bound water exists in the non-crystalline region and forms interface with cell walls. This type of water normally moves little, while free water can flow around the porous structure. Normally, moisture content should be controlled when plant fibres are used. This is because most mechanical properties increase with the decreasing in moisture content. Chemical reactions such as etherification and esterification are conducted on the free hydroxyl groups to improve its thermoplastic behaviour and moisture resistance (Clarival and Halleux, 2005).

(EN 13432) Lignin and Hemicelluloses

Lignin, as a three dimensional non-sugar polymer, is made up of aliphatic and aromatic hydrocarbon polymers (Nishino, 2004). Lignin strengthens the cell structure of plant by filling the space between cellulose, hemicelluloses and pectin components. It forms the covalent bonding with hemicellulose and crosslinks with plant polysaccharides (Wikipedia, 2009). Hemicellulose is made up of highly branched polysaccharides, including glucose, mannose, galactose, xylose, etc. It is very stable, insoluble in water and resistant to a number of physical and chemical treatments (Okada, 2005). In the traditional pulping processing for paper industry, lignin and hemicellulose are removed as waste. While according to latest research, lignin is potentially served as the binding phase in biocomposites through the extraction from plants or biosynthesis. Figure 2.16 (Wikipedia,

2009) and Figure 2.17 (Savage Group, 2009) represent the chemical structures of lignin and main components of hemicellulose respectively.

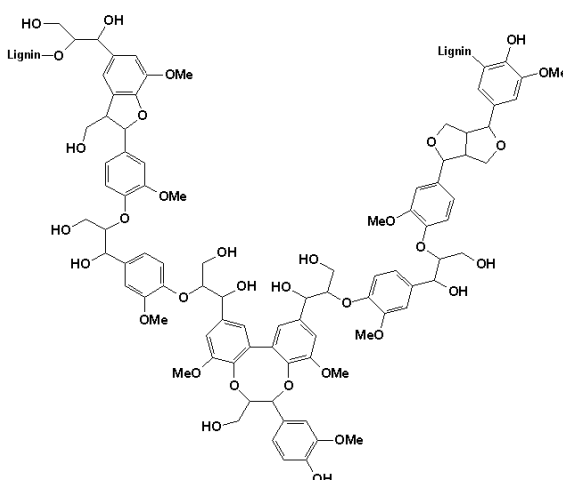


Figure 2.16: Chemical structure of lignin (Wikipedia, 2009).

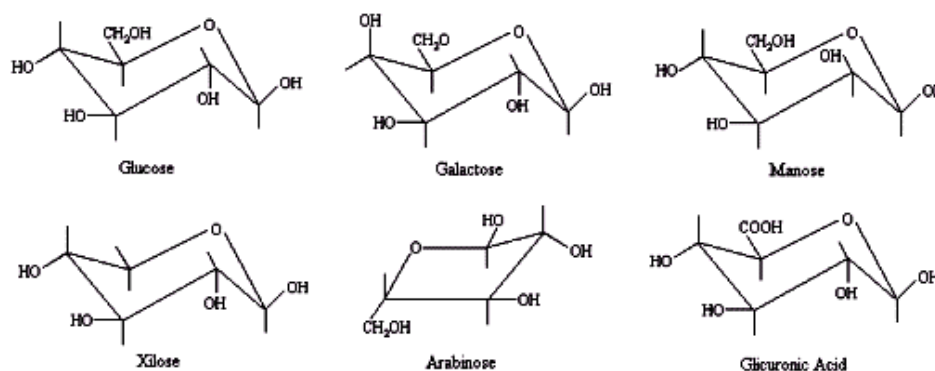


Figure 2.17: Chemical structure of the main components of hemicellulose (Savage Group, 2009).

(EN 13432) Extractives and ashes

As reviewed by Chiaramonti (2007), extractives in natural fibres are normally some non-structural components like fat waxes, and phenolics. They mainly contribute to a range of properties like colour, odour or taste to the biomass and can be extracted by solvents such as water, alcohol and benzene. Ashes normally represent the inorganic salts contained in natural fibres.

2.3.3 Sources of plant fibres

Wood and plants listed in Table 2.3 are the typical sources of plant fibres. The selection of

fibre source depends on the applications. In the composite industry, wood fibre is the major commercial material used as reinforcements in composites especially in structural applications. Details of wood and wood fibres are reviewed in section 2.3.3.1.

It has been proved that straw, hemp, and flex, etc are also being developed as reinforcements or fillers in the novel composite systems (Faruk et al., 2012). Straws as the by products of crops are potentially due to their substitute wood fibres as its relative cheap cost and comparable properties. Regarding to the topic of this thesis, straws are also described in detail in section 2.3.3.2.

2.3.3.1 Wood

Wood is normally divided into two broad classes, usually referred to as “hardwood” and “softwood”. Figure 2.18 illustrates the cell structure of hardwood and softwood.

The name of hard or soft wood is not defined by hardness but the density of structure. Some of the softwoods are actually harder than hardwoods.

Wood cells, which make up the structural elements of wood, are of various sizes and shapes and are quite firmly combined together. Most wood cells may be empty and some wood cells are partially filled with deposits, such as gums, resins, or tyloses. The majority of wood cells are considerably elongated and pointed at the ends, so they are normally called fibres or tracheids. The length of wood fibres is highly variable in the same tree and during different kinds of trees. Hardwood fibres average about 1 mm in length; softwood fibres range from 3 mm to 8 mm in length.

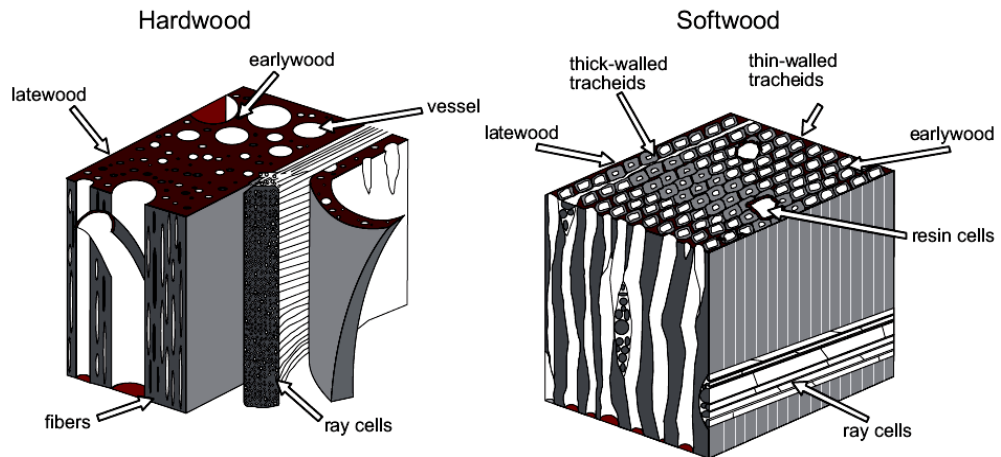


Figure 2.18: Comparison of 3-dimensional cell structure between hard and soft wood (Bond and Hamner, 2009).

In addition to their fibres, hardwoods have cells of relatively large diameter which can be called pores, while softwoods do not contain pores (as shown in Figure 2.18). Both hardwoods and soft woods have cells that are oriented horizontally in the direction from the pith toward the bark. Wood also has other cells, known as longitudinal or axial parenchyma cells, which function mainly for the storage of energy.

Wood has been used in varieties of fields such as paper productions, construction and building (Peltola, 2004). In recent years, wood fibres have been developed as the filler or reinforcement phase in composites, which will be described in detail in section 2.4. (Forest Products Laboratory, 2010)

2.3.3.2 Straw

As the cost of wood fibres rises year by year, straws are increasingly being considered as low-cost potential alternatives to wood fibres. Figure 2.19 shows that straw has the lowest cost compared with other commercial natural fibres (Thomas, 2007). If the price of cotton fibres is assumed as 100, straw costs less than 5, as shown in Figure 2.19. Apart from the paper industry, it has been utilised to produce straw based composites. In addition, researches have been carried out to produce bio-ethanol from wheat straw through pre-treatment, enzymatic hydrolysis and fermentation (Talebna et al., 2010).

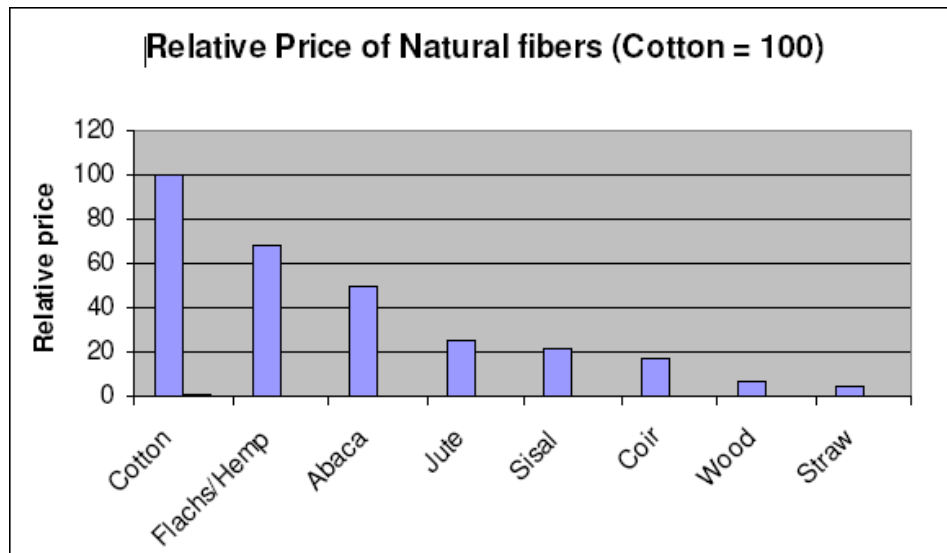


Figure 2.19: Price comparison between typical natural fibres (Thomas, 2007).

Straw fibres can be obtained from many resources such as wheat, rice, or barley. Straw from different resources varies in chemical composition and properties. In the research of Tavakoli et al (2008), the mechanical properties of internodes position of barley and wheat straw are compared in Figure 2.20. The IN1 IN2 and IN3 mean the different position in Figure 2.21. The mechanical properties of straw are highly dependent on the moisture content and internode position (O'Dogherty et al., 1995). Overall, the average shear strength, specific shearing energy, bending stress and young's modulus for wheat straw were around 1.5, 1.5, 2 and 2.5 times greater than those of barley straw.

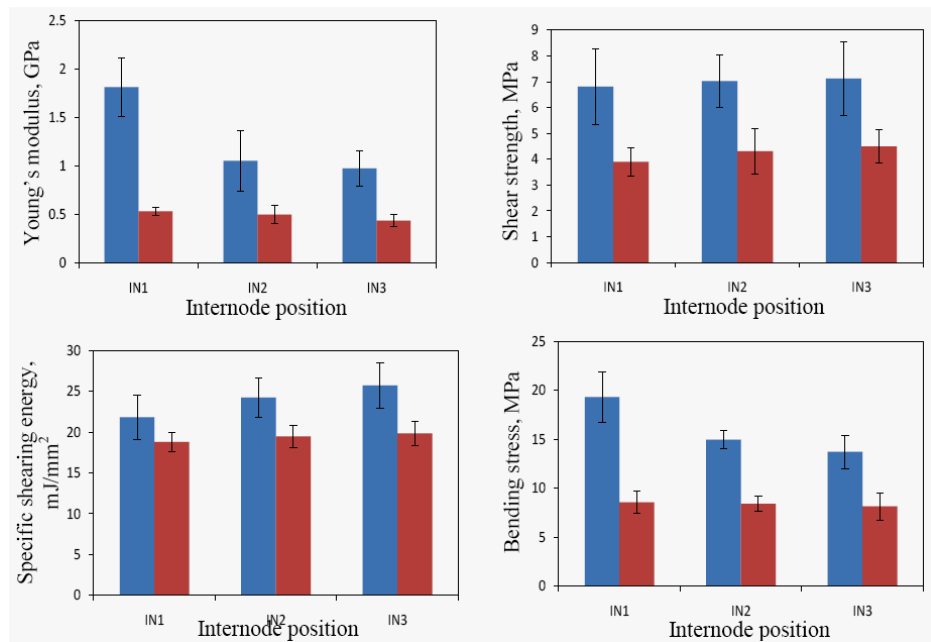


Figure 2.20: Mechanical properties of barley and wheat straw (barley: red and wheat: blue).

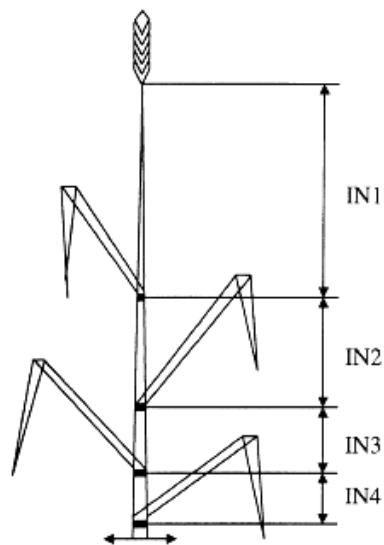


Figure 2.21: Internode position.

In the UK, wheat is the most widely grown arable crop covering around 2 million hectares and producing about 15.5 million tonnes each year (DEFRA, 2011). Therefore, wheat straw is one of the most popular renewable sources of lignocellulose feedstock for materials, chemicals and energy applications. Figure 2.22 (Malhotra, 2012) shows a SEM image of microstructure of a cross-sectioned wheat straw showing the the hollow cell wall structure of wheat straw. Although the microstructure of wheat straw makes little

difference compared with other typical natural fibres, the mechanical properties which are closely relevant to the chemical content are different. Typically, wheat straw contains 29-35 wt% cellulose, 16-21 wt% lignin and 26-32 wt% hemicelluloses (Han et al., 1998).

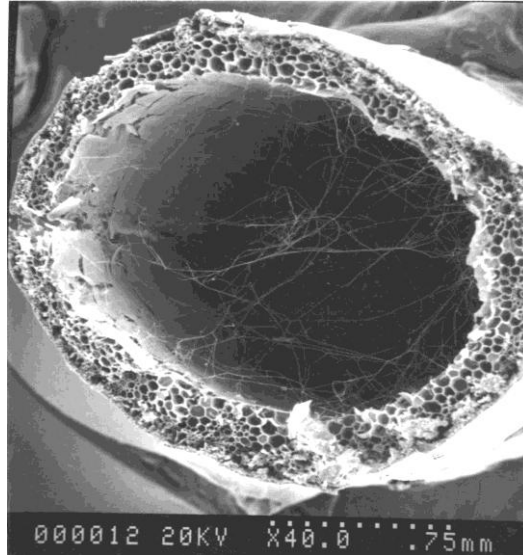


Figure 2.22: Microstructure of wheat Straw (Malhotra, 2012).

2.4. Natural fibre based composites

2.4.1 Introduction to Natural Fibre Based Composites

Fibre based polymeric composites can be divided into three groups based on whether they are made from renewable resources or not (Plackett, 2005).

- Totally petroleum-based composite such as most synthetic fibres (e.g. carbon or glass fibre) reinforced plastics
- Partially petroleum based composites or “Greener composites”; such as natural fibre reinforced plastics.
- Totally based on renewable resources or “Green composites” such as natural fibre reinforced bio-polymers.

Currently, plant fibres are the majority of natural fibres used in “greener” or “green” composite. Plant fibres like wood, flax, hemp, and straw fibres have many advantages in the composite production (Plackett, 2005):

- Environmentally benign

- Cost effective
- Abundantly available
- Non-abrasive during processing
- Acoustic and thermal insulators
- High specific properties
- Sustainable raw resource
- Under utilized
- Societal need

Biodegradable/compostable

Besides, plant fibres can also be incinerated after service life to close the carbon neutral circle, as it is only the CO₂ sequestered during growth of plants is released during incineration. (Netravali, 2007; Peijs, 2002).

However, the use of plant fibres also faces some challenges in comparison with carbon or glass fibres (Plackett, 2005):

- High moisture adsorption
- Poor microbial resistance
- Low thermal resistance
- Local and seasonal variation in quality
- Demand and supply cycles

Although plant fibres do not possess as good mechanical properties as glass fibres, they complete well on basis of properties in terms of material density and price and thus have been widely applied to replace glass fibre where mechanical properties are not critical.

Table 2.4 listed properties of some commonly used plant fibres compared with those of E-glass fibre (Bledzki and Gassan, 1999; Lilholt and Lawther, 2000; Wambua et al., 2003).

Table 2.4: Density and mechanical properties of commonly used fibres.

Fibre Type	Density (g/cm ³)	Tensile Strength (MPa)	Yong's Modulus (GPa)	Elongation (%)
E-glass	2.5	2000-3500	70	2.5-3.0
Hemp	1.5	550-900	30-70	1.6
Flax	1.5	345-1500	28-80	1.2-3.2
Jute	1.45	200-800	10-55	1.2-1.8
Sisal	1.33	100-850	9-38	2.0-3.7
Coir	1.25	130-220	4-6	15-40
Ramie	1.5	400-938	44-128	1.2-3.8

2.4.2 Greener Composites

Many researchers and companies have used plant fibres as reinforcement or fillers for petroleum-based polymers to make them “greener”. These kinds of composites have been well and widely developed because the plant-based fibres are renewable, sustainable and plentiful (Netravali, 2007). Wood fibre or wood flour is the typical plant fibre used in greener composites. Considering the cost reduction, straw fibres becomes more and more popular to replace wood fibre as reinforcement or filler in plastic composite systems, especially in some applications which do not require critical properties. Therefore, description focuses on the polymer composites with wood and straw fibres in section 2.5.2.1 and 2.5.2.2.

2.4.2.1 Wood Fibre Reinforced Polymer Composites (WPC)

Wood fibres have been commonly combined with thermoplastic or thermoset matrices to enhance mechanical properties such as stiffness and impact strength for many years (Oksman and Bengtsson, 2007). The mechanical properties of wood fibres are comparable with those of synthetic fibres such as glass fibre as shown in Table 2.5 (Peltola, 2004).

Table 2.5: Comparison of the properties of wood fibre and glass fibre.

Properties	Wood Fibre	Glass fibre (E-glass)
Density (g/cm ³)	0.6-1.1	2.6
Tensile Strength (GPa)	0.98-1.77	3.5
Specific Strength (GPa cm ³ /g)	1.63-2.95	1.35
Modulus of elasticity (GPa)	10-80	72
Specific modulus (GPa cm ³ /g)	17-133	28

Wood fibre conventionally comes from soft wood/ hard wood or from recycled paper. The non-purified form as wood flour has been widely used as a cost-cutting alternative in commodity plastics. Many common thermoplastics, not only polypropylene, polyethylene, and polyvinyl chloride, but also ABS and polystyrene, can be used as the matrix (or binder) of wood plastic composites. Netravali (2007) listed the advantages of using wood flour/fibres in WPC:

- Increase rigidity, stiffness or hardness
- Improve heat resistance
- Modify appearance
- Lower cost
- Increase strength and reduce creep
- Reduce abrasion to processing equipment
- Increase dielectric permittivity

The typical processing route to produce wood plastic composites is presented in Figure 2.23 below. This processing route is also applicable to biocomposites filled with other kinds of natural fibres. It is observed that processing temperature above 200° C for a long period of time will lead to the thermal degradation of wood fibre and thus the processing temperature is normally controlled below 205° C (Oksman and Bengtsson, 2007).

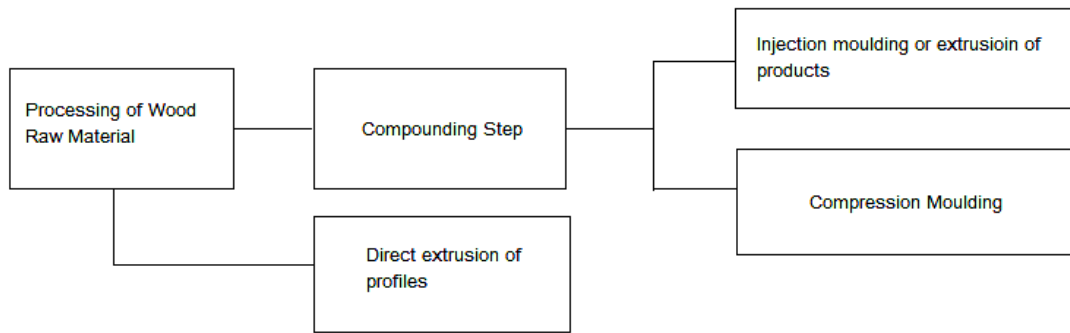


Figure 2.23: Flow chart of typical WPC processing.

Normally, larger wood fibre size will lead to an increase in modulus and strength of composites. Stark and Berger (1997) reported that the tensile modulus of PP/WF composites increases up to a wood content of 60-65 wt. % and decrease afterwards, while tensile strength of these composites increases from 10 to 40 wt. % and decrease beyond 40 wt. %. From the results above, it is suggested that there is a capacity of wood fibre content of the polymer matrix. If the fibre content increases over this capacity, too much interfaces are involved and lack of binding phase (polymer matrix) will definitely result in a drop of modulus and strength.

If the main requirement is to increase the composite stiffness, the interfacial adhesion is not so important, but if strength or long-term properties are specifically required, the modification of the interface between wood fibre and plastics is necessary to enhance the adhesion between fibre and matrix. The most commonly used method of modifying interfacial adhesion (or compatibility) in WPC is to add coupling agents. Take maleic anhydride (MA) modifier as an example (English et al., 1996; Felix and Gatenholm, 1991), by adding MA modified PP into the PP/WF composite, nearly all the mechanical properties have been enhanced, as shown in Table 2.6.

Table 2.6: Influence of MAPP on the mechanical properties of PP-WF composites.

Composite Type	Flexural Strength (MPa)	Bending Modulus (GPa)	Tensile Strength (MPa)	Tensile Modulus (GPa)	Impact Strength (KJ/m ²)
WF-PP	46	4.0	22	5	8
WF-PP-MAPP	59	4.2	30	5	10

2.4.2.2 Straw fibre filled polymer composites

In recent years, agricultural crop fibres have been also considered as an alternative fibre source to wood fibre for the production of a reconstituted lignocellulosic composite, due to the rising cost and demand of wood fibre (Erwin, 1997). These agricultural by-products can originate from different sources, such as sisal, flax, jute, coconut, and cereal straws and they have significant potential as a source of low-cost reinforcements in polymers, particularly polyolefins such as polyethylene (PE) or polypropylene (PP). Cereal straws such as wheat-straw are natural by-product of cereal production. Incorporation of hydrophilic straw a hydrophobic matrix such as a polypropylene–polyethylene copolymer often requires chemical modification, whereas into a more hydrophilic matrix such as biodegradable polyester are likely to present better interfacial compatibility. The examples below describe the use of wheat straw in thermoplastic and thermoset resins.

1) Wheat straw in thermoplastic resins

Mechanical and thermal properties of wheat straw in form of milled flour into polyolefin and the influence of interfacial interactions have been investigated by Le Digabel (2004). Figure 2.24 lists the mechanical properties of wheat straw flour (WF in the Figure 2.24 stands for wheat straw flour not wood flour) filled HDPE,PP and their blend, HDPE/PP thermoplastics (Mengeloglu and Karakus, 2008). Composites with MA coupling agents treated matrices (MAPP and MAPE), show a significant increase in tensile properties, flexural strength, modulus, and impact strength.

Specimen ID		Tensile Strength (MPa) ¹	Tensile Modulus (MPa)	Elongation at Break (%)	Flexural Strength (MPa)	Flexural Modulus (MPa)	Impact Strength (J/m)
HDPE-WF	None	8.11 ¹ (1.44) ²	202.6 (17.5)	5.63 (0.54)	13.16 (1.64)	802.9 (130.9)	47.37 (6.42)
	MAPP	11.49 (1.38)	249.8 (72.9)	5.42 (0.71)	21.20 (1.92)	1267.2 (133.1)	50.83 (2.86)
	MAPE	14.55 (0.71)	271.3 (42.0)	6.27 (0.38)	24.79 (2.18)	1311.1 (140.0)	46.04 (4.73)
PP- WF	None	6.42 (1.11)	252.4 (52.8)	3.70 (0.62)	17.76 (1.06)	703.2 (126.0)	11.06 (1.50)
	MAPP	11.15 (1.85)	260.3 (36.9)	4.19 (0.20)	22.41 (3.20)	1296.5 (291.6)	10.89 (1.71)
	MAPE	8.67 (1.61)	273.8 (91.54)	3.63 (0.36)	20.12 (3.75)	1320.9 (153.5)	9.74 (2.95)
HDPE/PP- WF	None	6.17 (1.93)	239.7 (39.5)	3.37 (0.70)	13.25 (3.94)	969.6 (323.2)	13.22 (1.26)
	MAPP	9.80 (1.12)	298.5 (49.8)	3.50 (0.28)	21.61 (2.42)	1378.1 (187.7)	13.66 (1.13)
	MAPE	9.07 (1.14)	252.9 (17.8)	3.54 (0.26)	20.50 (3.73)	1462.3 (313.1)	14.76 (1.29)

Figure 2.24 Mechanical properties of composites with wheat straw flour filled in HDPE, PP and their blend HDPE/PP with or without MA modification of the thermoplastic matrix (Mengeloglu and Karakus, 2008).

2) Wheat straw in thermosetting resins-straw boards

Straw board is one of the most commonly developed products to replace wood fibre composites. Han et al (Han et al., 2001; Han, et al., 1998) reported work on fibreboard from straw and reed residues bonded with urea formaldehyde. Silane was used as a coupling agent to increase the adhesion between the fibre and binder. Properties of medium-density fibreboards made from both reed and wheat straw were significantly higher than those of the conventional particleboards.

Karr and Sun (2000) and Karr et al (2000) found that straw boards with acetylated treatment were more dimensionally stable than the ones without, which is due to the straw being more hydrophobic after the treatment and the per-bulking effect caused by acetylation. They also reported that the resin content significantly affects on the dimensional stability, water resistance, and mechanical properties. The straw boards were found to be more dimensionally stable and had higher mechanical properties at higher resin binder contents.

2.4.3 Green Composites

As a result of difficulties associated with composite disposal, pollution and non-sustainability of oil, significant research efforts are currently being spent in developing fully bio-based or “green” composites by combining natural fibres with bioplastic resins bio-based or biodegradable polymers (Luo and Netravali, 1999).

2.4.3.1 None-straw fibre reinforced green composite

PHAs, PLA and plasticised starch are the commonly used bioplastics in “Green composites” as binders. For different applications, all lingo-cellulosic fibres like bast fibres can be chosen as reinforcement/fillers. The conventional processing methods are extrusion/hot pressing, film stacking or compression moulding. Table 2.7, 2.8, and 2.9 list a selection of studies in composites made from several combinations of natural fibres and bioplastics and their mechanical properties (Plackett, 2005). Fibres like jute, wood pineapple, and kenaf were located in the biopolymers in short fibre length. While for flax fibres, it exists in the biopolymers in a variety of ways like short fibre, continuous fibre or even woven fabrics. Compared to the conventional fibre reinforced composites, the mechanical properties of natural fibre-biopolymer composite were still much lower due to the lack of strength in the fibre. But it was sufficient for some applications.

Table 2.7: Mechanical properties of natural fibre-PHA Composites.

Fibre type and content	Polymer	Manufacturing method	Tensile strength (MPa)	Tensile modulus (GPa)
Jute(25%)	Biopol D 300G	Extrusion/ Hot pressing	33.6	–
Pineapple (30%)	PHBV	Film stacking/hot pressing	55.8	2.25
Jute (40%)	PHB	Film stacking/Heating under Vacuum	68	8.5
Wood (18%)	Biopol D400G	Hot pressing	23	2.9

Table 2.8: Mechanical properties of natural fibre-PLA Composites.

Fibre type and content	Polymer	Manufacturing method	Tensile strength (MPa)	Tensile modulus (GPa)
Flax (30%)	PLA	Extrusion	70	8.4
Flax (40%)	PLLA	Injection moulding	68	7.2
Flax (50%)	PLA	Compression moulding	99	6.0
Jute (40%)	PLLA	Compression moulding	100	9.4
Kenaf (20%)	PLA	–	–	7.6

Table 2.9: Mechanical properties of natural fibre-starch composites.

Fibre type and content	Polymer	Manufacturing method	Tensile strength (MPa)	Tensile modulus (GPa)
Flax (15%)	Wheat starch	Extrusion	37	–
Cellulose (7%)	Commercial Starch	Injection moulding	7	–

2.4.3.2 Straw based green composites

Cereal straws, such as those from wheat, rice and rapeseed are the most abundant and low cost lignocelluloses agricultural residues that can be potentially utilised in green composites. These residues can be used in various forms such as chopped straws, mechanically milled powders or fine fibrous feedstock pre-treated with some fractionation techniques and used as a reinforcement/filler in bioplastics (Faruk, et al., 2012).

A systematic study was carried out by Xia et al (2007), Kang et al (2009) and Xia et al (2010) in processing of wheat straw for green composites applications. Wheat straw was pre-treated with alkaline solutions (at 4-6 wt. % NaOH based on dry straw) and then fractionated with a twin screw extruder at a range of processing conditions, to produce

straw fibre with various degrees of fractionation. In addition to fractionation to finer straw bundles or single fibres, lignin and semi-cellulose were leached out and coated on the straw fibres. Without having to remove such non-cellulosic constituents, they may well act, or contribute at least partially as a bonding agent for the straw fibre/bundles when incorporated into composites. The straw feedstock was then utilised in different bio-based matrix systems at different straw contents and moulded samples were characterised for structural analysis and property assessment.

Kang et al (2009) reported that wheat straw feedstock from alkaline treatment and extrusion fractionation could be compression moulded without the addition of any resin. The non-cellulose constituent leached out from native straw structure acts as a binder in the composites to achieve a good combination of mechanical properties. This proved feasible to produce composites from 100% straw, known as self-bonded biocomposites

The fractionated straws were then compounded with bio-based resins to produce biodegradable composites with enhanced processibility, so more complex shaped components can be moulded. When incorporated into Solanyl, a bioplastic based on potato peels, the composite can be injection moulded at 30 wt. % straw loading (Xia et al, 2007). Good quality mouldings can also be made up to 80% straw loading by compression moulding. 6 folds increase in Young's modulus and 1.7 times in tensile strength were achieved at 30 wt. % straw loading when compared with unfilled resin.

The fractionated straw feedstock was also compared with mechanically chopped straw and extrusion compounded into plasticised wheat flour matrix for low-cost and high biodegradability applications. Xia et al (2010) reported that chopped straw and 4% NaOH were filled into wheat flour, which was plasticised by glycerol at 25 wt. %, at a variety of weight percents. The chopped straw and its wheat flour compounds present lower density than NaOH pre-treated straw and its flour compounds. All flour compounded composites demonstrate higher density than their un-compounded straws. Overall speaking, the wheat straw-wheat flour composites presented more ductile property than raw straw materials. Thus, their toughness and stiffness are reduced in terms of impact strength and Young's modulus. However, their elongation at break is remarkably improved as a ductile material does.

2.5 Summary and potential application of this research

2.5.1 Summary

This chapter has reviewed the areas related to this research, covering bioplastics, mechanisms of biodegradation, natural fibres and natural fibre composites. It has been found that bioplastics are being developed to substitute the petroleum based plastics and they have been increasingly used because of their biodegradability or even compostability. One restriction that limits the development of bioplastics is the cost, which is normally 2-3 times over that of petroleum polymers. At the same time, natural fibres, especially the plant fibres, as derived from the renewable resources, are also developed as the filler or reinforcement into the petroleum plastics to make the composite more eco-friendly. According to increasing requirements on environmental protection and sustainability, it is necessary to combine the bioplastics and natural fibres together making the whole system biodegradable or compostable as well as cost reduced. Following these considerations derived from the literature review, straw as a renewable material with extremely low cost was taken into consideration to be used as the filler or reinforcement in the biopolymer-natural fibre composites.

Many potential products listed in section 2.5.2 are the application of straw composites. In order to develop biocomposites with comparable properties to the existing products, the selection of biopolymer as the matrix/binder is a challenges to address by taking consideration of both cost and performance together. In addition, the formulation design and processing control in this study also effect on the energy consumption and final properties of the straw biocomposites, which is the other challenge to be addressed.

2.5.2 Potential applications derived from this research

2.5.2.1 Clay pigeons

Clay pigeons are used for in shooting sports and usually in the shape of an inverted saucer designed to be stable in flight as a Frisbee. Clay pigeons are made in various sizes and shapes between approximately 75 mm and 150 mm in diameter (see Figure 2.25). They are

launched at speeds up to 35 m/s from a spring-loaded device known as a trap.



Figure 2.25: Example of commercial clay pigeons based on petrol chemical binders (Hempstown Clay Pigeon Club, 2011).

Conventional clay pigeons are made from a mixture of pitch and chalk designed to withstand being launched from traps at high speeds, but at the same time being easily broken when hit by just a very few lead or steel pellets shot from a gun. This represents a unique combination of requirements in strength and brittleness. In addition, these traps have an automatic feed mechanism and the clay pigeons must be sufficiently strong to withstand passing through this. They are also required to be able to withstand being transported and handled while being manually loaded into the trap.

Clay pigeons are used in open-air ranges, usually in the countryside away from built up areas where the noise of firing may cause nuisance. The fragments from broken clay pigeons are spread over quite a large area of the countryside. Currently, UK consumes of clay pigeon approximately 3500 tonnes annually (source: The Clay Pigeon Company-Supplier of 35% of all clay pigeons in the UK). The pitch and chalk fragments take several years to break down and thus are potential hazard, especially if they get in any watercourse. There is an adverse impact on soil quality and a risk of contaminated ground water from run-off, particularly adjacent to the shooting grounds. The pitch tars in the clay pigeons (approximately 24 wt. %) have been classified as potential carcinogens and have health and safety implications for the manufacturing workers. The alternative clay pigeons made from a bio-based and biodegradable binder are potentially able to eliminate the problems mentioned above and be truly “environmental friendly”.

2.5.2.2 Gun cartridge wads

Gun cartridge wads (shown in Figure 2.26) are currently made of a plastic container used to accommodate the bullets used in shooting sports. A shotgun cartridge consists of a cartridge case that houses the propellant and the very small spheres of dense material known as “shot”. Between the propellant and the shot is a wad. This provides a gas tight seal and pushes the shot up the barrel. (HGCA, 2011). The wad is fired from the barrel and reaches a typical range of 40 meters before falling to the ground. Traditionally the wad is made of greased woollen felt and the material of the shot is lead. Several decades ago a plastic wad was developed that improved the performance of the cartridge by protecting the outer lead balls that would otherwise be in contact with the gun barrel when fired.



Figure 2.26: Plastic cartridge wads in shotgun (left) and their assembly position in a cartridge (right)

(Remington, 2011)

About 320 million/annum plastic shotgun cartridge wad are used in the UK (Data source from Hull Cartridges, a major UK cartridge manufacture). Although relatively low in terms of tonnage (~1000 tones/annum), the littering on farmland and the danger to live stock have raised serious concerns and most farmers have banned the use of cartridges on their land (HGCA, 2007). A safe biodegradable shotgun wad to substitute the plastic cup is urgently required.

2.5.2.3 Mulch mats and tree shelters

Tree shelters or tree guards, currently made in polypropylene or HDPE, are used to nurture trees in the early stages of their growth. A conventional mulch mat is a thin polyethylene

film used to control weeds in the early growth stage of a plant. Figure 2.27 shows an example of their utilisation.

Tubex Ltd is the world's largest plant shelter producer employing around 100 employees in Aberdare, Wales. It currently manufactures over 20 million tree and vine shelters made of polypropylene and exports to a large number of countries including France, Spain, Italy, Germany, Canada and the USA. Being non-degradable, the products left on forestland or vineyards have caused long-term environmental concerns. To deal with the products, it is highly desirable to develop a biocomposite not only biodegradable, but also a renewable alternative to plastics. It will lead to a new generation of products, which will return to nature after their intended service life by controlled fragmentation and biodegradation.

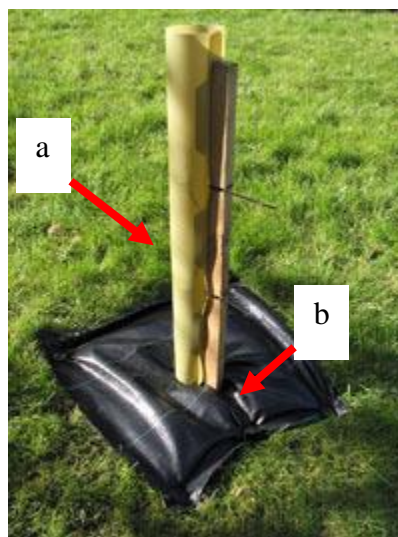


Figure 2.27: Commercially used tree shelter and black mulch mat (HGCA, 2011), There are numbers of sizes and colours of mulch mat available in the market. (a: tree shelter; b: mulch mat).

2.5.2.4 Road barriers

It is estimated that among plastic road barriers on road maintenance or building sites half of them are not collected for re-use at the end of a project due to damage or lack of infrastructure. Most are disposed of on-site or are land filled with other construction debris.

The straw biocomposite alternative is expected to solve this problem by on-site granulating and composting the used products in the surface soil at the end of a project.

2.5.2.5 Flower pot

A flowerpot is a container in which flowers or other plants are cultivated. Flower pots are often made from plastic, wood, stone, or sometimes biodegradable material. Bioplac[®] Ltd manufactures and supplies plant-based products for packaging and horticulture applications. Figure 2.28 illustrates the plant pots produced by Biopac Ltd. The new straw based biocomposite is expected to produce cost-effective moulded horticultural packaging containers/trays such as compostable flowerpots. When being transferred into soil, the cultivated plants are expected to be buried together with compostable pots. At the end of service life, pots made in straw biocomposites biodegrade and compost quickly with low impact to the environment.



Figure 2.28 Plant pots, image source: Biopac UK company (Biopac, 2011)

2.5.2.6 Binder-less straw boards

Chip boards, fibre boards and particle boards are normally made with wood fibre bonded with thermoset binders such as urea-formaldehyde and phenol-formaldehyde while WPC are wood fibre filled plastics such as PE, PVC or PP for application in constructions, or component in furniture (<http://en.wikipedia.org/wiki/Fiberboard>). According to the research of Kang et al (2009), the feasibility of producing straw boards with fractionated straw without addition of any binder (hence binder-less) has been proved. However, the extrusion fractionation process will add cost and can also lead to fibre damage. It is highly

desirable therefore to utilise the natural binder (lignin and hemicelulose) within straw itself and minimise processing of straw to produce cost effective straw board without having to use external binder in substitution of the commercially used chipboards or particle boards.

Chapter 3 Experimental details

In this chapter, the experimental details are described. The raw materials and pre-treatments of them are described in section 3.1; Details in preparation of material systems and prototyping are described in section 3.2 including formulation & processing of the material systems and prototyping of target products; Characterisations of the material systems using a range of methods are described in section 3.3 and section 3.4.

3.1 Raw materials & treatments

3.1.1 Wheat flour

A wheat flour (known as “Temple” grade) supplied by Heygates Limited (Northampton, UK) was selected for development of cost effective resin in the clay-straw-starch composite system for the bio-pigeon application based on two reasons: it is cheaper than purified wheat starch and it has been used successfully in previous work at Brunel University for extrusion of foams (Kang, 2006; Zhou et al., 2006) and thermoplastic sheet (QI et al., 2007) for packaging applications. The composition and other technical data of the flour are presented in Table 3.1 and Figure 3.1 illustrates the morphology of the flour granules.

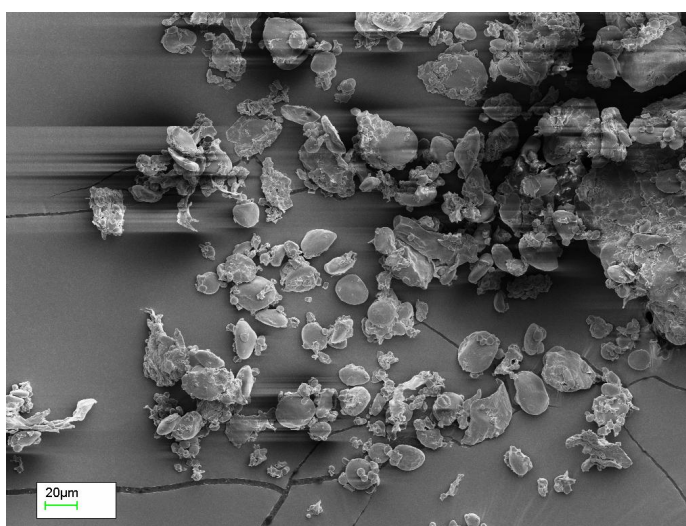


Figure 3.1: Morphology of the flour granules.

Table 3.1: Specifications of the “Temple” wheat flour (Data sheet, provided by Heygates Limited).

Contents	Target	Range	Method
Protein (%)	9.0	±0.8	FTWG 0014
Moisture (%)	13.7	15.0 Max	FTWG 0014
F.C.G (flour colour grade)	1.0	±1.0	FTWG 0007
Hagberg FN (s)	300.0	260 Min	FTWG 0006
Texture	35.0	±4.0	Particle size
GST	375.0	300 - 450	Gluten separation time
Bran content (%)	1.0	0.9-1.2	Bran Scan

3.1.2 Clay

The clay employed in the research as filler for the bio-pigeons is Minfil[®]L75-BT supplied by Omya UK Ltd. It is a finely ground carboniferous limestone. The composition and product data are listed in the Table 3.2 and the morphology particle size distribution of the clay are presented in the Figure 3.2 and 3.3. The mean particle size of the clay is 10 µm and 98% particles finer than 100 µm.

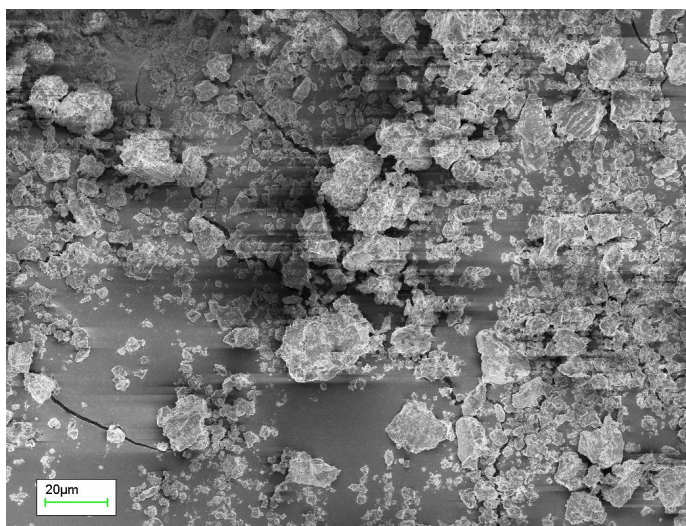


Figure 3.2: Morphology of the Minfil[®]L75-BT Clay.

Table 3.2: Product data and composition of the Minfil®L75-BT clay.

Contents		Whiteness	
CaCO ₃	99%	Brightness (RY, C/2x, DIN53163)	77%
SiO ₂	0.4%	Moisture content	
FeO ₃	0.02%	ex works(ISO 787/2)	0.1%
HCl insoluble content	0.5%	General product data	
Fineness (ISO 787/7)		Loose bulky density (ISO 787/11) g/ml	0.9
Residual on a 150 µm sieve	0.07%	Packed bulky density (g/ml)	1.5
Residual on a 75 µm sieve	5%	Specific gravity (ISO 787/10) g/ml	2.7
Residual on a 45 µm sieve	17%	Oil absorption (ISO 787/5) g/100g	480
Top cut (d98%)	100µm	Blain surface area (m ² /g)	16
Mean particle size (d50%)	10µm	pH value (ISO 787/9)	9

PARTICLE SIZE DISTRIBUTION (MasterSizer 2000)

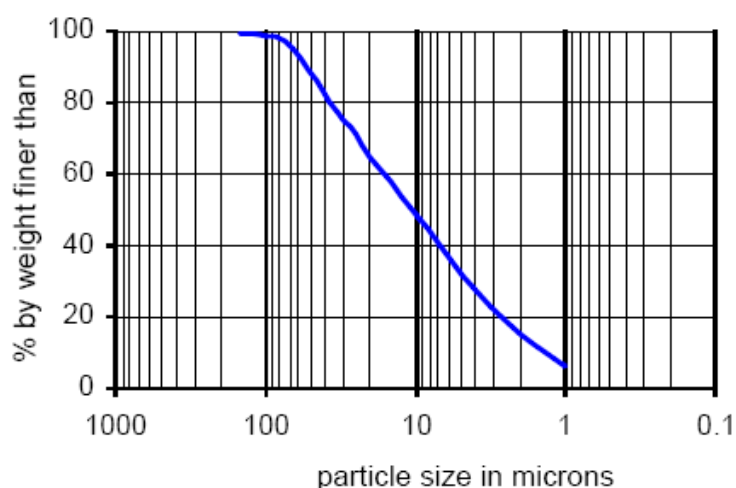


Figure 3.3: Particle size distribution of the Minfil®L75-BT Clay.

3.1.3 Biopolymers

Two biopolymers have been selected as matrix for straw-biopolymer composites required for different applications: Bio-Flex F6510 (prev. Bio-Flex 682 CF), and Biolice 50C.

BioFlex F6510 supplied by FKUR (Kunststoff GmbH, Germany) is a blend of PLA and co-polyester without any starch or starch derivatives. Bioflex series are designed to replace conventional used LDPE, HDPE or Polypropylene in packaging industry. Bioflex F6510 is a comparable rigid grade over other polymers in bioflex series. It is ideally used for

injection and blow moulding, and sheet extrusion and subsequent are also applicable to it. (<http://www.fkur.com/produkte/bio-flex.html>).

Biolice 50C, developed by Limagrain (France), is a flexible film grade of biopolymer based on corn starch and polyester. It was selected for its computability, largely due to its high starch content and flexibility. Biolice 50C mainly contains around 47 wt. % maize flour, 47 wt. % Ecoflex, as well as small amount of additives like, polylactide, glycerine and corn oil. Ecoflex in the biolice system is made from 36.4% 1,4-butanediol, 26.2% adipic acid and 37.3% terephthalic acid (Chang et al., 2010).

The processing characterisations and key mechanical properties of the biopolymers are presented in Table 3.3 and 3.4 respectively.

Table 3.3: Characterisation of the biopolymers (from technical data sheet).

Trade name	T _m (°C)	MFI	Density (g/cm ³)
Bio-Flex F6510	148.1	3.5 – 4.5 g/10mins (190 °C /2.16 kg)	1.295
Biolice 50C	110-115	8-16 g/10mins (160 °C /5 kg)	1.2-1.4

Table 3.4: Mechanical properties of biopolymer.

Trade name	Tensile modulus of elasticity (MPa)	Tensile strength (MPa)	Tensile strain at break (%)	Flexural modulus (MPa)
BioFlex F6510*	2600	47	19	2650
Biolice 50C**	28	7.5	No break	---

* The mechanical properties of Bioflex F6510 is from the data sheet of supplier.

** The mechanical properties of Biolice 50C are from the tensile test in this PhD study which will be mentioned in section 3.3.4.

3.1.4 Wheat straw & treatments

3.1.4.1 Straw as received (chopped straw, CS)

A winter wheat straw supplied by Dixon Brothers (Norfolk, UK) was used to produce cost-effective filler/reinforcement in straw-based biocomposites. Based on chemical analysis at Bangor University, (HGCA, 2011), it consists of 30 wt. % cellulose, 47 wt. % of hemicellulose, 22 wt. % of lignin, 9 wt. % of ash, and 4 wt. % of wax extracts. The straw as-received contains ~10 wt% moisture and was mechanically cut and supplied as a dust-free grade. The average length of the chopped straw is around 10 mm.

3.1.4.2 Treatments of wheat straw

In order to match the design of products and processing routes, some of the raw materials were treated before being processed. The treatment processes mainly referred to straw, as the target products require specific grades of straw. Treatment of the wheat straw was of two types for specific applications: mechanical size reduction & grading, and extrusion fractionation. Straw was employed as filler to produce cost-effective composites after the size reduction. Size grading following the size reduction was employed to produce straw particle boards made from differently sized straw. Wheat straw was applied as reinforcement in the biocomposites system. In order to improve the compatibility between reinforcement and matrix such as starch and biopolymers, wheat straw was fractionated through NaOH soaking treatment and extrusion.

a) Size reduction and grading of straw

The size of straw is considerably varied due to the nature of the chopping. In order to achieve an even range of sizes, the straw was subjected to either screening through different size of sieves or ground to obtain specific size ranges. In order to investigate the effect of straw size on the property of straw boards, three straw sizes were selected through different sieves. The group of short straw was also used as reinforcement or filler in biopolymer based composites and bio-pigeon products. The sieves employed were listed in the Table 3.5. A Zeiss Axioskop 2 MAT light microscope was used to measure the length of the straw bundles. Figure 3.4 shows the straw morphology of the three groups.

Table 3.5: Sieves used for size grading of straw.

Straw ID	Straw groups	Sieves	Average length (Akin et al.)
FCS	Short	$\leq 1.5\text{mm}$ (machine grinded*)	0.93
MCS	Medium	2mm – 3.35mm (screened)	10.9
LCS	Long	$\geq 4.5\text{mm}$ (screened)	29.8

*Note: Machine employed for grinding is SM2000 made from Retsch® (U.K.) Limited, UK with a 1.5mm sieve.



Figure 3.4: Morphology of graded straws prepared for straw boards (a) Short size straw; (b) Medium size straw; (c) Long size straw.

To investigate the effects of NaOH pre-treatment of straw on the properties of straw boards, both of the CS (mentioned in section 3.1.4.1) and the MCS (mentioned in Table 3.5) obtained from size selection progress were soaked by blended with 3 wt. % aqueous NaOH solution for 16 hours as detailed in Table 3.6 below. Moisture content after air drying at ambient temperature for two weeks was found by HR73 Halogan moisture analyzer, (made in METTLER TOLEDO, USA) to be around 10 wt. % and the NaOH

content was 6 wt. % based on the dry mass of straw.

Table 3.6: Straw with NaOH solution soaked only.

Straw Code	Straw code before treatment	Concentration of NaOH Solution	Soaking time
T6	CS	3 wt. %	16 hours
MT6	MCS	3 wt. %	16 hours

b) Refinement of straw by extrusion fractionation

To improve the straw compatibility and flow ability within the composite systems, the straw bundles needs to be further fractionated or refined. This can be achieved through chemical and mechanical treatments. Non-cellulose components (lignin and hemi-cellulose) in straw were retained as binder and plasticiser. The chopped straw was pre-treated into 6 grades to achieve different fractionation levels. The pre-treatment grades of straw are listed in table 3.7.

Table 3.7: Fractionation grades of straw.

Pre-treated straw code	Extrusion condition		NaOH treatment	
	Number of Barrels	Extrusion runs*	NaOH content	Soaking time
5B61R	5	1	6 wt. %	16 hours
5B61R/M	5	1	6 wt. %	16 hours
8B61R	8	1	6 wt. %	16 hours
8B61R/M	8	1	6 wt. %	16 hours
8B41R	8	1	4 wt. %	16 hours
8B43R	8	3	4 wt. %	16 hours

*Note: Extrusion runs: number of times that straw have been extruded, which is reflect to the residential time of fractionation.

The chopped straw as received was pre-treated with 4 or 6 wt. % NaOH (based on the dry mass of the straw) by soaking in a NaOH aqueous solution. Normally, 2kg of the chopped straw was manually mixed with 4 litres of 2 or 3 wt. % NaOH solution in each batch (i.e. the weight ratio between straw and water is 1:2). The straw was impregnated with the chemical in a sealed container for 16 hours at the room temperature before extrusion process.

The pre-treated straw was then extruded by using a five/eight-barrel 40mm Betol co-rotating intermeshing twin screw extruder to refine the pre-treated straw. The detail processing conditions and screw profiles of the extruder are listed in Table 3.8-3.11. Moisture content after air drying for two weeks was found, as described earlier, to be around 8-9 wt. %. 5B61R/M and 8B61R/M in Table 3.7 were grinded in the same way as FCS (mentioned in the note of Table 3.5).

Table 3.8: Screw profile of 8-barrel extrusion process.

Screw Length (Akin, et al.)	120	150	120	150	120	120	80	50r	80	120	80r	80	5	80
Pitch (Akin, et al.)	24	24	24	24	16	16	12	16	16	12	16	12	*	8
Flight width (Akin, et al.)	4	8	8	8	4	4	4	4	4	4	4	4		2

*- trilobal

r- reverse screws used in the positions

Table 3.9: Processing parameters of 8-barrel extrusion for straw fractionation.

Barrel number	1	2	3	4	5	6	7	8
Barrel temperature (°C)	60	70	90	120	140	140	140	140
Screw speed (rpm)	100							

Table 3.10: Screw profile for 5-barrel extrusion process.

Screw Length (Akin, et al.)	120	150	120	15*	120	80	160	25r	80
Pitch (Akin, et al.)	24	24	24		16	16	12	16	8
Flight width (Akin, et al.)	4	8	8		4	4	4	4	2

*-3 trilobals of 5mm each

r- 25 mm reverse screws with 3 slots of 8mm width were used in the position

Table 3.11: Processing parameters for straw fractionation in 5-barrel extrusion.

	Barrels				
	1	2	3	4	5
Temperature (°C)	90	90	150	150	130
Screw speed (rpm)	100-150				

3.1.5 Additives

- Glycerol

The glycerol employed in this work as a plasticiser for the wheat starch is a laboratory reagent grades supplied by Fisher Scientific UK.

- NaOH

A reagent grade sodium hydroxide (NaOH) was obtained from Fisher Scientific UK for treatment of straw prior to the extrusion to assist the straw fibre fractionation.

3.2 Materials formulation design and processing

The formulations and processing approaches designed for the three specific products are presented in details in this section. The Clay/flour/straw composite described in section 3.2.1 was designed to develop a candidate product to substitute the commercial pitch tar-bonded clay pigeons. Straw in this system was mainly used as filler to lower the cost and enhance stiffness. In section 3.2.2, fractionated wheat straw was incorporated into biopolymers as reinforcement or filler to develop 100% biodegradable composites specific for road barriers, mulch mats and tree shelter applications. Section 3.2.3 presents the processing details of straw boards. The concept of “binderless” straw boards is based on a hypothesis that the non-cellulosic resin (lignin and hemicelluloses) will be liberated and mobilised under temperature and pressure during hot pressing and acting as interfacial binder between the straw bundles and thus eliminate the need for addition of binder.

3.2.1 Clay-flour-straw composites

The purpose to develop a clay-starch-straw composite system is to use starch-straw to replace the pitch tar as binder in conventional clay pigeons. The target is to develop biocomposite material formulations and a commercially viable processing technology to produce bio-pigeons with the required combination of mechanical properties comparable to that of the conventional clay pigeon set as a bench mark. This section describes the details involved in the development of formulation of clay-flour-straw composites and three approaches to processing techniques:

- 1) Hot die compression moulding of granulated composites prepared by extrusion

compounding.

2) Cold die compressing of powders prepared by mechanical mixing.

3) Process integration combining cold-die compression moulding of powders prepared by extrusion compounding.

3.2.1.1 Hot die compression moulding of granulated composites prepared by extrusion compounding (EHP)

In this approach, formulations were designed to produce granulates by extrusion compounding and then hot compression moulding of specimens and/or prototype pigeons. The formulations are listed in Table 3.12 and Table 3.13. The mineral filler was maintained at 70 wt. % to give the required density to the composites, while the contents of the organic binder system, totalling 30 wt. % consisting of flour plasticised by glycerol and straw prepared with different treatment levels (CS, 8B41R and 8B43R), were varied systematically.

For the formulations in Table 3.12, the wheat flour was pre-blended with 25 wt. % glycerol as mentioned in 3.1.5. Then the flour/glycerol mixture was blended with clay and fed through one feeder into the extruder. A separate feeder was employed to feed straw to compound with the clay-flour/glycerol mixture. Water was injection fed at the second barrel with a water pump. The 5-barrel setup as mentioned in section 3.1.4.2 was used in the extrusion compounding of the composites under the extrusion conditions listed in Table 3.14.

Table 3.12: Extrusion formulations of clay-flour-straw.

Sample ID	Clay (wt.%)	Flour& Glycerol blend (wt.%)	Glycerol content (wt.% in the flour-glycerol blend)	Straw (wt.%)			Total of clay-flour-straw feeding rate (g/min)	Water Feeding rate (g/min)
				CS	8B41R	8B43R		
EHP-a	70	15	25	15	0	0	50	43
EHP-b	70	15	25	0	15	0	50	20
EHP-c	70	15	25	0	0	15	50	35
EHP-d	70	5	25	25	0	0	50	25
EHP-e	70	25	25	5	0	0	50	42

For formulations in Table 3.13, the concentration of glycerol in the flour/glycerol blends was varied in order to investigate the role of glycerol as a plasticising agent to assist flow during extrusion and moulding and modification of toughness of the composites. The extrusion compounding conditions were the same as for the above formulations in Table 3.12.

Table 3.13: Extrusion of clay-flour-straw at different level of glycerol.

Sample ID	Clay (wt.%)	Flour + glycerol (wt.%)	Glycerol content (wt.% in the flour-glycerol blend)			Straw (Joanne and Stefanie's plastics website) wt.%		Total of clay-flour-straw feeder rate (g/min)	Water Feed (g/min)
			15	8	0	CS	FCS		
EHP-f	70	30			√	---	---	50	20
EHP-g	70	15	-	-	√	15	---	50	40
EHP-h	70	15	-	√	-	15	---	50	40
EHP-i	70	15	√	-	-	15	---	50	50

Table 3.14: Processing condition of extrusion compounding.

	Barrels				
	1	2	3	4	5
Temperature (°C)	90	100	110	120	100
Screw speed (rpm)	90				

The extruded composites were air-dried and manually granulated with gardening scissors to about 5-15 mm diameter for compression moulding of the specimens. All samples with the formulations above were compression moulded at 140 °C without addition of water into planks of 100 x 60 x 4mm using a hot press (George E. Moore & Son Ltd, Birmingham, UK) at 48 MPa (kept for 5 minutes) for mechanical testing. Test Bars of dimension of 100 x 10 x 4mm were also produced using the same processing conditions. In order to clarify the criteria of formulation screen, a tar bonded commercial pigeon was made from compression moulding of granulated under the same condition into the dimension of 100 x 10 x 4mm.

3.2.1.2 Cold-die compression of powders prepared by mechanical mixing (MPC)

This approach is attempted to overcome some of the shortcomings in the method described earlier in 3.3.1.1. The concept of “powder compaction”, been widely used in metallurgy and ceramic industry, was involved. Powder compaction is a complex engineering process in which a material undergoes a transformation from a loose powder state to a dense compact. Formulations are designed for cold die moulding of a preheated and moistened powder blend prepared from mechanical mixing of clay, flour and straw in powder form for the following reasons:

- To lower down the energy consumption in extrusion. Extrusion compounding is simplified to prepare the feedstock for moulding, which only consists of the flour and straw. The powdered extrudates employed as binder phase in the composite were compounded with simple mechanical blending of constitute materials already in powder form.
- To shorten the moulding cycle time by separate preheating of the powder feedstock before moulding in a cold mould. The powder feedstock is also moistened so as to plasticise the organic particles to provide adhesion in subsequent moulding.

- To provide flexibility in control of the mechanical property (particularly brittleness) of the moulded composites, by controlling porosity and inter-particle bonding strength.

Formulations of the powder mixtures are given in Table 3.15 and 3.16.

Straw employed in the formulations in Table 3.15 is 8B41R, as mentioned in Table 3.6.

The total weight ratio of clay and binder are 70:30. The weight ratio of f/g: straw mentioned in Table 3.15 and 3.16 describes the ratio between flour plasticised by 25 wt. % glycerol and 8B41R straw.

The wheat flour (as mentioned in 3.1.1) was manually pre-blended with 25 wt. % glycerol (as mentioned in 3.1.5) as plasticiser based on dry matter of flour. Then the flour/glycerol (F/g) mixture and processed straw (8B41R as mentioned in section 3.1.4.2) were fed separately into the extruder at three different ratios. Water was injected by water pump through the second barrel of the extruder. The extrusion conditions are listed in Table 3.17. The extrudates were air-dried for two weeks to moisture content of 9.5 wt. % by the machine mentioned in section 3.1.4.2 and then ground in a mill (as mentioned in section 3.1.4.2) fitted with a sieve with 1.5 mm apertures.

Table 3.15: Formulations of clay-flour-straw powder mixtures.

Sample ID	Clay (wt. %)	Binder concentration (wt. %) and composition (weight ratio of F/g: straw)	Water* (wt. %)
MPC-a	70	30 (50/50)	20
MPC-b	70	30 (50/50)	25
MPC-c	70	30 (60/40)	20
MPC-d	70	30 (60/40)	25

*Note: based on total weight of clay-flour/straw

Table 3.16: Formulations of clay-flour powder mixtures.

Sample ID	Clay (wt. %)	Binder concentration (wt. %) and composition (weight ratio of F/g: straw)	Water* (wt. %)
MPC-e	70	30(100/0)	25
MPC-f	70	30(100/0)	20

*Note: based on total weight of clay-flour/straw

Table 3.17: Processing conditions of extrusion.

	Barrels				
	1	2	3	4	5
Temperature (°C)	90	100	110	120	100
Screw speed (rpm)	100				
Total F/g-Straw Feeding (g/min)	50				
Water feeding (g/min)	60-80				

The clay and flour/straw powders were firstly blended together with a high-speed food blender (made by Breville[®], UK). Then, water was added into the mixture at various concentrations to create a moistened yet free-flowing powder mixture. The mixture was then sealed in a metal container and heated in oven at 190°C to reach equilibrium for 3 mins. The reason to use 190°C is to achieve the softening temperature in a short time. The pre-heated materials were then transferred to a cold mould for compression moulding of the samples. The process is illustrated in Figure 3.5. Specimens of plates with dimensions of 100 x 60 x 4mm and bars with dimensions of 100 x 10 x 4mm and pigeon prototypes were made by compression in the cold mould at a pressure of 48 MPa.

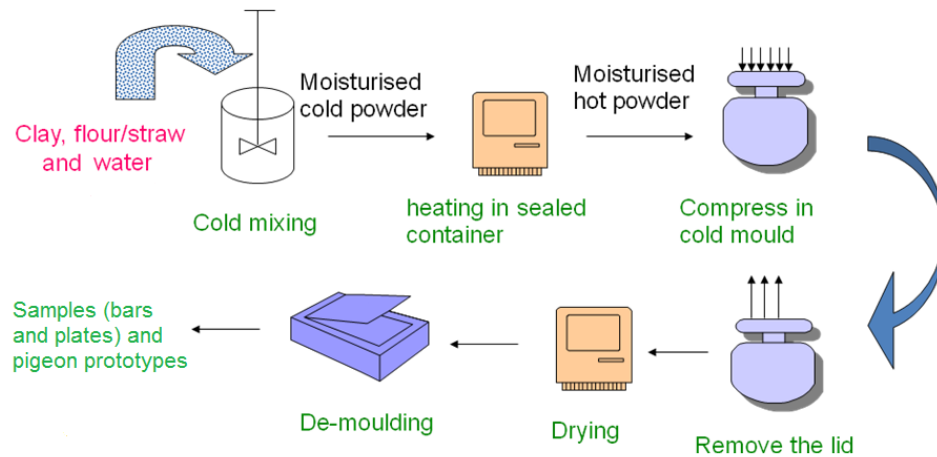


Figure 3.5: Illustration of specimens and prototypes made by powder compaction.

3.2.1.3. Process integration combining cold-die compression moulding of powders prepared by extrusion compounding (EPC)

This approach is evolved from the earlier approaches by combining the advantages in them. The method of preheating followed by cold die compression moulding proved to be practical to avoid prolonged heating cycles in the mould and facilitate fast demoulding. The mechanical mixing of powders, however, resulted in poor consistency of mouldings and premature fracture even during demoulding, due to lack of uniform distribution of the bonding phase, as discussed in details in chapter 4. Therefore extrusion compounding is necessary for uniform coverage of clay particles by a fully gelatinised layer of the bonding starch, to produce powder which can then be softened by heating and compression moulded in a cold die.

Table 3.18 lists the formulations selected through a screening process from the characterisation of properties as described later in Chapter 4. Figure 3.6 and 3.7 illustrate the process for preparation of the clay-flour-straw powder feedstock and the moulding process of test specimens and pigeon prototype, respectively. The machine employed for compounding was the same five barrel Betol co-rotating twin screw extruder as mentioned in 3.1.4.2, with the same screw profile mentioned in Table 3.10. Barrel temperatures are illustrated in Figure 3.6 and the screw speed is 30 rpm. Extrudates from extrusion compounding was air dried for two weeks with moisture content to be around 8 wt. % (tested by HR73 Halogan moisture analyzer). After that, the air dried extrudates were ground in the same way as the preparation of FCS (mentioned in section 3.1.4.2). The

average particle size of ground extrudates was lower than 1.5 mm.

Ground powder was manually blended in a stainless steel container with 10 wt. % extra water, sealed and oven-heated up to 120 °C in an oven for 3 mins, to reach the softening temperature. Testing Bars of 100 x 10 x 4mm dimension for 3-point bending and A Charpy impact tests as well as pigeon prototypes were produced with the hot press under pressure of 48MPa at mould temperature preheated to 60 °C to avoid rapid cooling of the feedstock and assist mould filling.

Table 3.18: Formulations of powder of clay-flour-straw feedstock.

Sample ID	Clay (g)	Flour (g)	Glycerol content (wt.% in the flour-glycerol blend)	Grinded straw (g)	Water (g)
				FCS	
EPC-a	70	30	0	0	40
EPC-b	70	15	0	15	60*

*Note: with straw added in the formulation, the volume of the material increase dramatically compared with the clay/flour blend, thus more water is necessary to assist material flow.

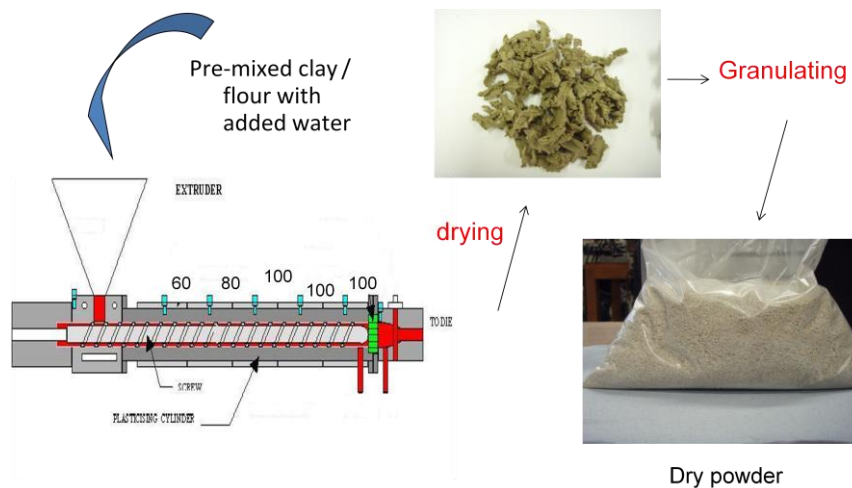


Figure 3.6: Preparation process for the Clay-flour-straw powder.

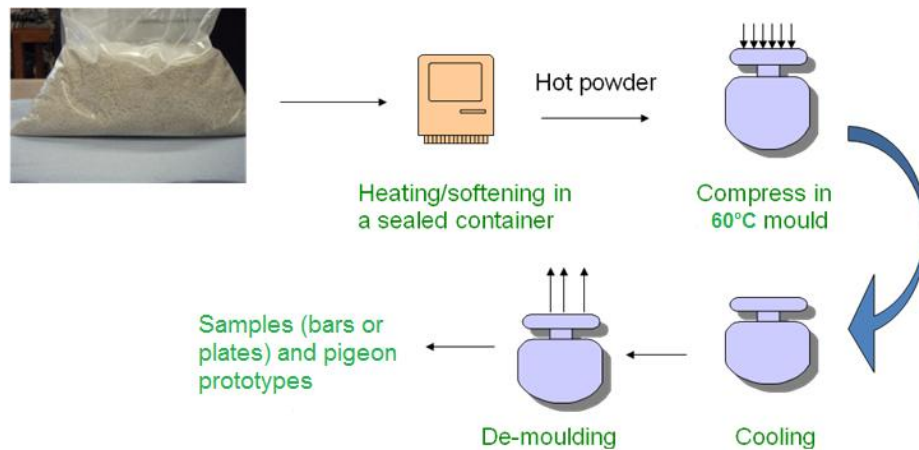


Figure 3.7: Process of sample moulding from the powders.

3.2.2 Biopolymer/straw composites

The straw feedstock was compounded with selected biopolymers to develop biocomposites for specific targeted applications including mulch mats, tree shelters, gun wads, flower pots and road barriers (as mentioned in section 2.6.2). The concept governing the design of these biopolymer/straw composites is based on a number of considerations:

- 100% post-use biodegradability of the biocomposites, to reduce the environmental impact. For the target applications mentioned above, the collection of waste after service is always a problem. Biodegradability of the biopolymer/straw composites facilitates the natural biodegradation in soil after service and hence eliminates the need for collection and waste management.
- The target products are all cost sensitive and the use of low-cost straw feedstock helps cost control by mitigating the relatively high cost of biopolymers;
- Mechanical properties to suit the performance requirements and processibility during manufacturing using current plastics in the applications as benchmarks.

Bioflex F6510 and Biolice 50C were the two major biopolymers blended with different concentrations of straw. The flexible Biolice/straw composites were designed for extrusion of mulch mats and injection moulding of gun wads, and flower pots while rigid Bioflex F6510/straw composites were designed as the potential materials for extrusion of tree shelters and road barriers. Fractionated straws were applied in order to increase their compatibility with the biopolymers and assist the material flow during extrusion or injection moulding, an attempt was also made to use chopped straw for further cost

reduction.

The biocomposites or biopolymer blends were prepared by extrusion compounding. Sheet and tubes were obtained directly by attaching a suitable die to the extruders. Gun wads and flower pots were made by injection moulding using masterbatches prepared by the extrusion compounding.

Biolice 50C and Bioflex F6510 were selected to blend with refined straw (8B61R) and short chopped straw (FCS) for the biopolymer/straw extrusion processing and the formulations are listed in Table 3.19. A Haake PolyLab OS (ThermoFisher Scientific, UK) 25 mm and 10-barrel twin screw extruder with a slit die of 150 mm width and 1 mm nip was employed to produce sheets of straw-biopolymer blends. The processing parameters are listed in Table 3.20.

Table 3.19: Formulations of biopolymer/straw composites.

Sample ID	Biolice 50C (wt. %)	Bioflex F6510 (wt. %)	Straw (wt. %)	Straw type *
BL-a	100	---	0	---
BL-CS-10-a	90	---	10	CS
BL-8-10-a	90	---	10	8B61R
BL-8-20-a	80	---	20	8B61R
BL-8-30-a	70	---	30	8B61R
BF-a	---	100	0	---
BF-8-10-a	---	90	10	8B61R
BF-8-20-a	---	80	20	8B61R
BF-8-30-a	---	70	30	8B61R

*See Table 3.5 and 3.7 for details

Table 3.20: Extrusion conditions for the biopolymer/straw composites.

Barrel No		1	2	3-10
Biolice 50C/straw compounds	Temperature (°C)	145	145	145
	Screw speed (rpm)	100		
Bioflex F6510/straw	Temperature (°C)	90	130	150
	Screw speed	150		

compounds	(rpm)	
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To study on the mechanical properties of composites at higher straw concentrations (for the traffic barrier application), biocomposites with formulations listed in Table 3.21 were also prepared. The 5-barrel Betol twin-screw extruder (described in section 3.1.4.2) was employed to extrude bars with rectangular cross-section of 4mm × 6mm. The processing parameters are listed in the Table 3.22.

Table 3.21: Formulations of Bioflex F6510/straw for extrusion of test bars.

Sample ID	Bioflex F6510 (wt. %)	Straw (8B61R/M)* (wt. %)	Straw (5B61R)* as (wt. %)	Straw (5B61R/M)* (wt. %)
BF-b	100	---	---	---
BF-8F-20-b	80	20	---	---
BF-5F-20-b	80	---	---	20
BF-5-20-b	80	---	20	20
BF-5F-40-b	60	---	---	40
BF-5-40-b	60	---	40	---

*Note: extruded straw described in Table 3.7

Table 3.22: Extrusion conditions for the bioflexF6510/straw test bars.

Screw speed	30 rpm					
Barrel	1	2	3	4	5	Die
Temperature (°C)	140	150	150	150	150	140

Sheet samples in Table 3.17 were cut by a CEAST-6054 pneumatic hollow die punch (Torino, Italy), which is used to prepare specimen from film or thin sheet, for tensile test and tear test with the shape illustrated in Figure 3.8. Bar samples in Table 3.21 were cut into lengths of 100 mm for 3-point bending test and they are 45° v-shape notched in the depth of 2 mm by a Blacks CMB8 manual notch machine for the Charpy impact test.

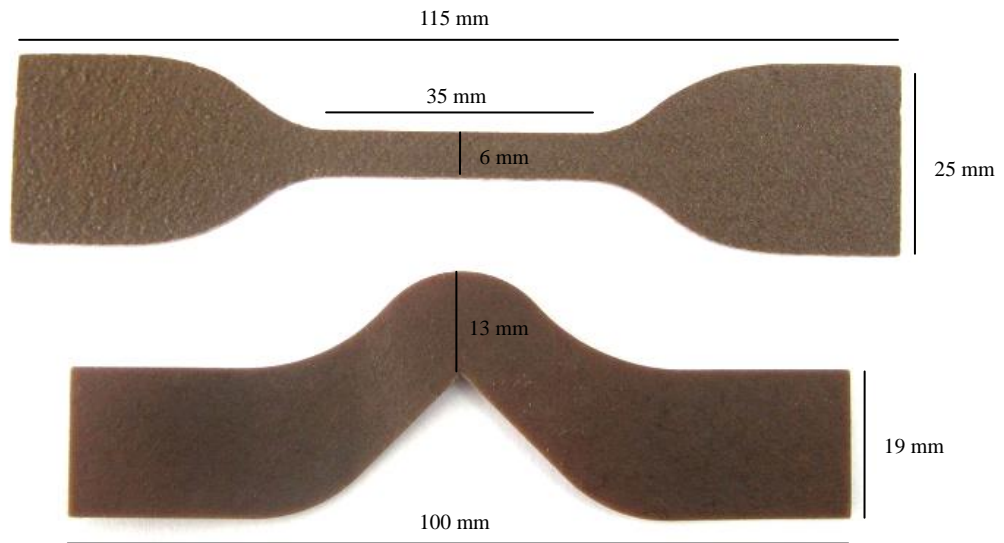


Figure 3.8: Morphology and geometry of the specimen for tensile and tear test (a: tensile specimen following BS EN ISO 2818:1996; b: tear specimen in BS ISO 34-1:2010).

Figure 3.9 illustrates some examples of the prototypes. Prototypes of mulch mats shown in Figure 3.9 (a) were extruded with the formulations (as mentioned in Table 3.19) of BL-a, BL-8F-10-a, BL-8F-20-a and BL-8F-30-a (from left to right). The gun wads in Figure 3.9 (b) were injection moulded by Primace Associates using biolice 50C and processed straw with the formulation of BL-8F-30-a.

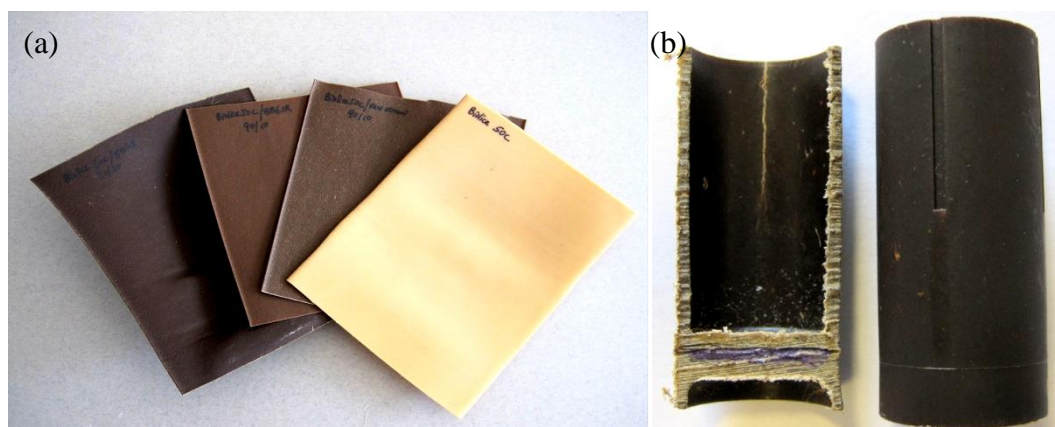


Figure 3.9: Prototypes of mulch mat (a, 150 mm in width) and gun wad (b, 55mm in height and 15mm in diameter).

3.2.3 Binder-less straw boards

Straw is an annually renewable source and a potential alternative to wood in the production of particle or fiber boards in applications such as furniture and construction. Almost all wood particle/fibre board products are bonded with added binders (e.g. formaldehyde resins) and this give rise to “probable human carcinogenic” risk in the living environment (Hodgson et al., 2002) and problems in recycling or incineration for energy recovery. The concept of binder-less straw boards has been proved by Kang et al (2009) where the natural binder within straw itself is utilised for bonding straw fibres in a simple process that combines heating and compression in board production. Straw employed to produce boards is fractionated straw, while whether the straw without refinement can be directly compressed into boards is going to be proved in this PhD work. This section gives details of a work using straws with minimum preparation, i.e. chopped straw without any fractionation refinement to evaluate the property of the straw board and their dependence upon straw preparation, the compression temperature and pressure. Experiments were designed so that a relationship between processing conditions and properties can be established. The selection of temperature and pressure were based on preliminary test and are listed in Table 3.23. Chopped and graded “medium” straw with average length of 10.9 mm (CS and MCS, mentioned in Table 3.5) were used for screening all combinations of processing conditions for samples MA1 to MC3, while the “short” (FCS, mentioned in Table 3.5) and “long” (LCS, mentioned in Table 3.5) straw with average lengths of 0.93 mm (for sample FB2) and 29.8 mm (for sample CB2), respectively, were used under selected combinations of processing conditions for comparison of straw size effects on the properties of the boards.

TMB2 refers to “medium” straw with 6% NaOH treatment (TM6, as mentioned in Table 3.6), followed by air drying down to about 8.9% moisture content but without extrusion fractionation. This was to examine the effects of surface chemical treatment of chopped straw on straw board properties.

Table 3.23: Parameters in experimental design for straw boards.

Sample ID	Temperature (°C)			Pressure (MPa)		
	120 (EN 13432)	140 (EN 13432)	160 (EN 13432)	16 (A)	32 (B)	48 (C)
MA1	√	-	-	√	-	-
MA2	-	√	-	√	-	-
MA3	-	-	√	√	-	-
MB1	√	-	-	-	√	-
MB2	-	√	-	-	√	-
MB3	-	-	√	-	√	-
MC1	√	-	-	-	-	√
MC2	-	√	-	-	-	√
MC3	-	-	√	-	-	√
FB2	-	√	-	-	√	-
CB2	-	√	-	-	√	-
TMB2	-	√	-	-	√	-
LLC3	-	-	√	-	-	√

30g of straw were filled into a steel mould for compression moulding of planks preheated to the predetermined temperature in a hot press (as mentioned in section 3.2.1.1) and held under a pressure of about 1.6MPa for 5 minutes. It was then pressed to the predetermined pressure and held for 5 minutes followed by cooling under the pressure to room temperature.

Examples of straw boards of different sizes made from this compression moulding are shown in Figure 3.10. Boards with dimensions of 100 x 60 x 4mm (sample A) were used in the evaluation of drop weight impact tests. The boards were also cut into 100 x 10 x 4mm bars with a band saw for flexure tests and for analysis of fracture surface morphology. The boards with dimensions of 100 x 100 x 12mm (sample B) and 200x200x16 mm (sample C) were used for industrial assessment (at West Bridge Furniture, UK) of processibilities (such as gluing with PVA adhesive, stapling and cutting), typically involved in furniture manufacturing of upholsteries.

In order to examine the mechanism and morphology of internal bonding in the binder-less straw boards, the LCS straw (mentioned in section 3.1.4.2) was aligned in the longitudinal

direction and compressed into a oriented straw bar at a size of 100 x 10 x 4mm under the pressure of 48MPa and plate temperature of 160 °C (The Sample ID is LLC3 as mentioned in Table 3.23).



Figure 3.10: Straw boards of different dimensions:
(A) 100x60x4mm; (B) 100x100x12mm; (C) 200x200x16mm

3.3 Mechanical test

The mechanical testing methods employed in the research are described in this part. All samples were pre-conditioned in an environmental conditioned room for two weeks at 23 °C, 55% R.H before testing.

3.3.1 Flexural test

A Zwick/Roell Instron ZMART.PRO universal mechanical test machine (Hertfordshire, UK) was employed to conduct the 3-point bending tests of the following bar samples:

- That prepared for bio-pigeon (as formulations described in Table 3.12, 3.13, 3.16 and 3.18. A comparison was also made with the control sample made from compression moulding of granulated commercial clay pigeons, which were named as CPC control)
- That prepared from extruded biopolymer-straw composites, as described in Table 3.21.
- That prepared from binder-less straw boards, as described in Table 3.23.

A 5 kN load cell was employed and a 64 mm span and 2 mm/min crosshead speed were used according to BS EN ISO 178:2003. Key flexure properties, such as strength, modulus, strain at maximum force and strain at break were obtained from the test of six specimens for each formulation.

3.3.2 Charpy impact test

Charpy impact tests were carried out to examine the impact strength of the straw based composites. Charpy impact strength indicates the required energy per unit area to break the samples under instant loading and it is related to the brittleness of the materials. A CEAST Analog Pendulum Charpy Tester (Type 6546, Torino, Italy) was used with a 2J striker. Six specimens were tested following the standard of BS EN ISO 179-1:2001) for each group of sample at 40mm span and the impact energy was averaged. Bar samples tested include:

- The 100x 10 x 4 mm bar specimens for bio-pigeon without notch (formulations were as mentioned in Table 3.12, 3.13, 3.16, and 3.18, as described in section 3.2.1. Comparison was also made to CPC control sample as mentioned in section 3.3.1).
- Extruded 100x 6 x 4 mm bar samples of Bioflex F6510 and Bioflex-straw composites with notch (as described in Table 3.21)

3.3.3 Instrumental impact test

A drop-weight impact tester (CEAST FRACTOVIS PLUS, Torino, Italy) was used for the testing of the binder-less straw boards (as listed in Table 3.23). A mass of 5kg fitted with a 10 mm diameter striker with hemispherical head was dropped over 1 meter upon the specimen supported with a hollow cylindrical ring of 20 mm internal diameter at a speed of 4.26 m/s. The total energy during the penetration and the maximum force were recorded from six specimens, which indicates the mechanical behaviour of straw boards under instant loading.

3.3.4 Tensile and Tear test

Tensile and tear tests were conducted mainly on the biopolymer-straw composite sheets prepared for gun wads and mulch mat applications (as described in section 3.2.2 with formulations in Table 3.19).

The tensile and tear tests were carried out on a Hounsfield mechanical tester (H10KT, Surrey, UK). For tensile tests, the crosshead speed was 2 mm/min and an extensometer with a gauge length of 25 mm was employed. For the tear test, the speed of crosshead displacement was 500 mm/min (ASTM D624). Key properties, such as tensile strength, E-modulus, strain at maximum force, strain at breakage and tear strength were obtained from the test of six specimens for each formulation. There were six specimens of each formulation for the tensile and tear tests with the average value recorded.

3.4 Characterisations of straw based composites

3.4.1 Thermal analysis of biopolymer blends by using TGA and DSC

The thermal degradation properties of the two biopolymers (as mentioned in 3.1.3) and specimens mentioned in Table 3.19 were investigated by using TGA (TA Q600, USA) to record the sample change with temperature over the course of the pyrolysis in the gas condition of nitrogen. Samples were weighted and heated from room temperature up to 950 °C at 10 °C/min.

The thermal properties of the two biopolymers (as mentioned in 3.1.3) and specimens mentioned in Table 3.19 were examined by using DSC (TA Q2000, USA). The sample was heated from -100 °C to 300 °C at 10 °C /min and cooled down to ambient temperature at 20 °C /min. From the DSC curves, influence of straw on the glass transition, melting and crystallisation of the two biopolymers was investigated.

3.4.2 Rheology test

A capillary rheometer (Rheograph 6000, Gottfert, Germany) was employed to assess melt viscosities of the biopolymer-straw composites (compositions as mentioned in Table 3.19) at their extrusion temperatures so as to understand the influence of straw on the rheological behaviour of the composites so as to reflect the adhesion property between matrix and straw in the composite system.

3.4.3 Microscopy and FTIR

Scanning electron microscopy (Mirbagheri)

A Zeiss Supra™ 35VP scanning electron microscope was used to assess the morphology of the cross-section of the fracture surface of bio-pigeon bars after flexure test as well as biopolymer-straw composites after the tensile test (specimens as mentioned in Table 3.12, 3.13, 3.16, 3.18, 3.19). The fracture mechanisms and the adhesion properties the specimens were investigated through SEM images. The cross section of LLC3 sample, as shown in Table 3.23, was polished and examined by SEM to check the morphology of interfacial bonding between straw bundles.

Optical microscope

A Zeiss Axioskop 2 MAT light microscope was used to observe the surface and length of size-graded straw as well as the surface morphology of the CS straw and binder-less straw boards.

Chemical mapping analysis by Fourier transform infrared spectroscopy (FTIR)

The chemical mapping of cross-section of straw board was conducted using a Perkin Elmer Spectrum Spotlight FT-IR Imaging System. The straw board made of 100% of raw straw without any additives presents excellent mechanical properties. It was expected that lignin can be released from straw bundles during compression and redistribute within the board to act as a binder needs to be clarified. A 100x60x4mm straw bar compressed with oriented straw bundles (with the sample ID of LLC3) was made in order to obtain an absolute cross-section without any disoriented bundles. This cross-section surface was polished and analysed through FTIR. Function groups of lignin were tracked in the scanned area and the distribution of lignin in the mapping area was obtained.

Chapter 4 Clay/Flour/Straw Composites

The mechanical properties and characterisations of bio-composites containing clay (CaCO_3), wheat flour and/or wheat straw are discussed in this chapter. Section 4.1 describes firstly the requirements of clay pigeon application, which are used as the criteria for formulation selection. While the concentration of the clay was fixed at about 70 wt. % to satisfy the required density of the composites, the organic compositions (the wheat flour, plasticiser and straw) are varied in terms of glycerol concentration in the wheat flour, the straw concentration with different pre-treatments to study their influence to the mechanical properties. Formulations are screened and the ones with properties close to the criteria are selected as candidates for further investigation in processing.

Based on the candidate formulations, section 4.2 deals with how processing routes influence the mechanical properties and microstructure of the composites. The candidate formulations produced by different processes are compared in this section. The most appropriate processing method is selected which is able to match the process-ability of the candidate formulations with lower energy consumption and shorter circle time for production. Section 4.3 describes the bio-pigeon prototyping to demonstrate the feasibility to manufacture such product with comparable mechanical properties to those of conventional clay pigeons. Finally, the main academic outcomes of this study are summarised in section 4.4.

4.1 Formulation screening

Formulation design of the clay-flour-straw system is guided by the benchmark requirements of current clay pigeons. Section 4.1.1 describes such benchmark targets. As 70 wt. % clay was pre-determined in the system (around 50 % in volume fraction) to match the requirement of material density, section 4.1.2 to 4.1.5 focus on variation of formulations within the 30 wt. % organic composition and their effects on the mechanical properties of the composites. The flour was used as the thermal plastic binder which is modified by plasticiser and the low-cost straw filler to achieve the required balance of strength, stiffness and brittleness.

However, native starch granules in flour need to be transformed to thermal plastic starch by

gelatinisation process. As Lai and Kokini (1991) illustrated in Figure 4.1, with the addition of heat and water, the crystalline and helix structure of native starch granule is broken up and amylose diffuses out of the starch granule. As a result of gelatinisation, the starch granules transform into a dominant amorphous structure giving rise to thermoplastic behaviour. Shearing in extrusion compounding also enhances gelatinisation by destructuring the native crystalline structure and mixes of the gelatinised starch with the filler particles uniformly.

These studies on the influence of straw content, straw type and glycerol content in the formulations on the physical and mechanical properties of the composites led to Section 4.1.6 which summarises the result of formulation selection.

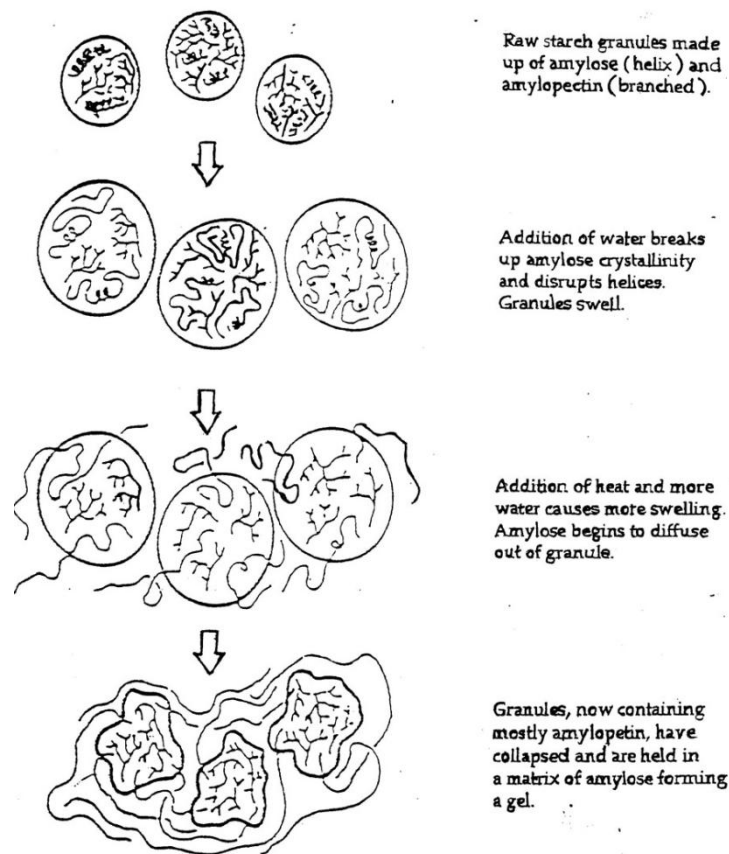


Figure 4.1: Schematic illustration of Starch gelatinisation (Lai and Kokini, 1991).

4.1.1 Benchmark properties

According to the shape requirement of Clay Pigeon Shooting Association (2011) and International Shooting Sport Federation (2008), clay pigeons are made to very exact specifications with regard to their weight and dimensions. There are several types of clay pigeons that are used in shooting sports, but only the standard 110mm clay pigeon is the most commonly used one in all traps and skeet disciplines. They must weight 105 grams (± 5 g) and be of 110 mm (± 1 mm) overall diameter and 25-26 mm in height. These impose a tight constraint on the material density.

With regards to material mechanical properties, there are no details of the data available in the rules and regulations of international shooting sport (2008). However, clay pigeons need to have sufficient strength and stiffness to withstand the launching force and at the same time be sufficiently brittle to shatter into fine debris when hit by bullets. In order to assess the mechanical properties of clay-flour-straw composites in comparison with existing clay-tar pigeons, the mechanical properties of commercial pigeons made by Clay Pigeon Company (CPC, UK) were selected and tested for mechanical properties and used as control samples (as mentioned in section 3.3.1 and 3.3.2). The results provide benchmark properties to be targeted by the designed formulation. In addition, clay pigeons are used in the open-air, so the product should be able to withstand all weather conditions, particularly high humidity.

4.1.2 Effect of straw content

As the total amount of the organic portion - straw and flour (with or without plasticiser) is fixed at 30 wt. % in the composite system, the adjustment of straw content will lead to proportional changes in the flour content. Figure 4.2- 4.5 presents flexural strength, flexural modulus, strain at maximum force and impact strength, respectively for formulations with chopped straw (CS, as mentioned in 3.1.4.1) at straw contents of 5 wt. % (EHP-e), 15 wt. % (EHP-a) and 25 wt. % (EHP-d) prepared by extrusion, as mentioned in Table 3.12. In these formulations, weight percentage of glycerol in flour is fixed at 25% (based on flour alone).

In Figure 4.2, flexural strength decreases with the increase of straw content. The strength

rises up by around 11.7% when straw content reduced from 25 wt. % (EHP-d) to 15 wt. % (EHP-a) and approximately 30% while straw content at 5 wt. % (EHP-e) reaching a level that only 10% lower compared with the CPC control sample.

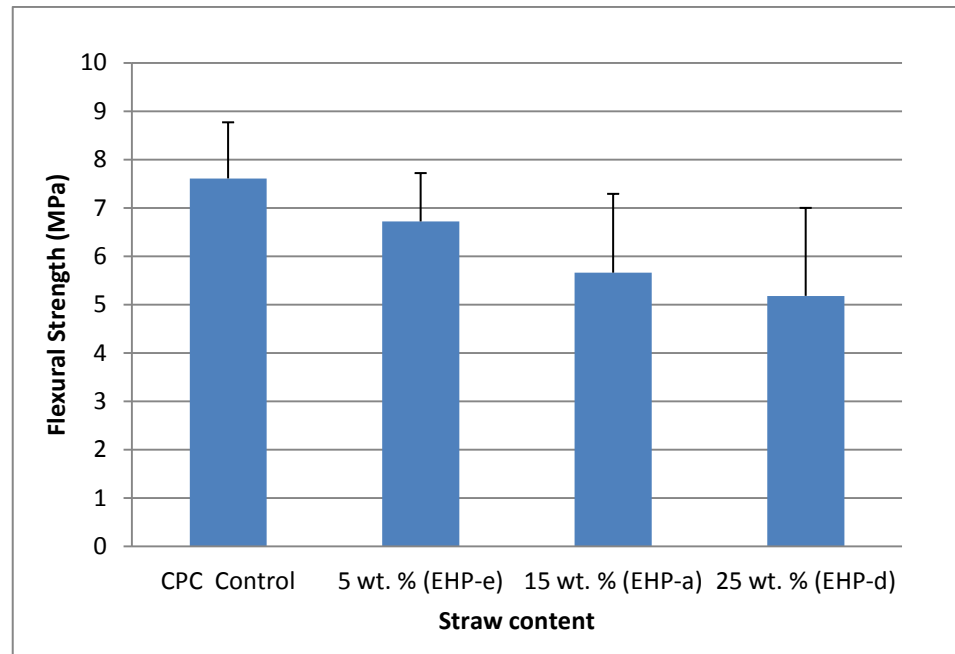


Figure 4.2: Effect of straw content on the flexural strength of the composites

Figure 4.3 illustrates that formulation containing 15 wt. % straw (EHP-a) presents the highest modulus in the three formulations, which is 35% lower compared to the CPC control, indicating the need for further enhancement in stiffness. According to the law of mixture, straw with higher modulus than plasticised flour will functionally contribute to the whole composite system (modulus is expected to go up with straw content). At higher straw content, the lack of binder (plasticised flour) in the organic system may have limited the compatibility in the composite system and resulted in a reduction of modulus.

Strain at maximum force presents the flexibility of materials and for this particular application. Clay pigeons are required to be rigid and thus low values are preferred. All the composites are more flexible than the control samples. EHP-a (15 wt. % straw) with lowest strain at maximum force is around twice the value as the CPC control. Considering the Figure 4.3 and 4.4 together, the formulation of EHP-a with the highest modulus and lowest strain at maximum force, is the most closest to the CPC control under low strain rate 3 – point bending tests.

Under high strain rate impact strength test, the three formulations present a similar trend to strain at maximum force, as demonstrated in Figure 4.5. EHP-a (15 wt. % straw) has the lowest impact strength, which means it is the most brittle formulation among the three. But even so, it is still tougher than the CPC control.

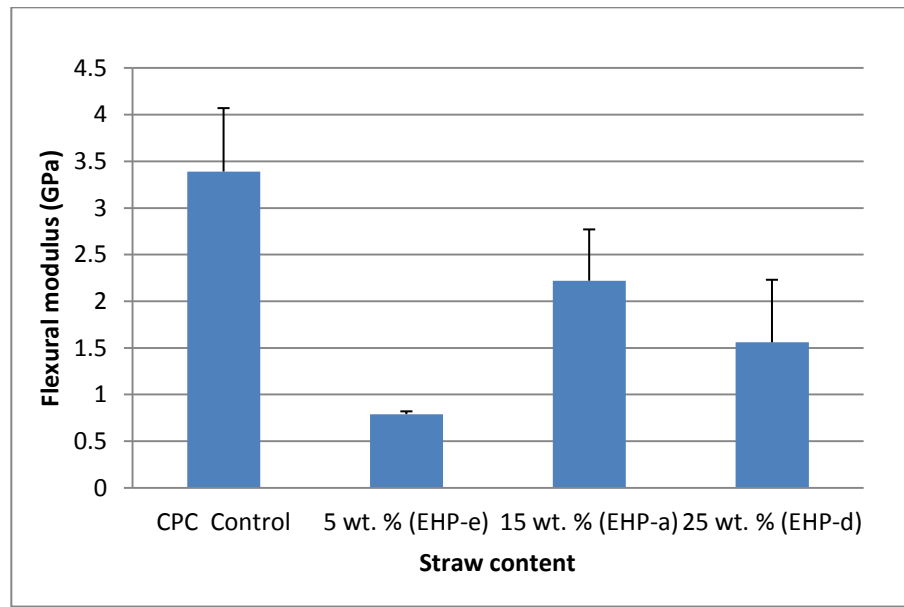


Figure 4.3: Effect of straw content on the flexural modulus of the composites.

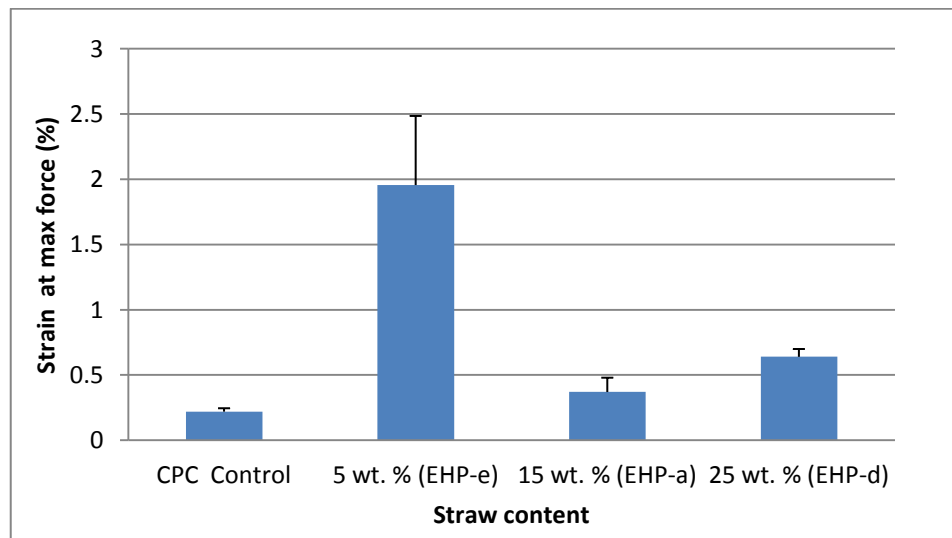


Figure 4.4: Effect of straw content on the flexural strain at maximum force of the composites.

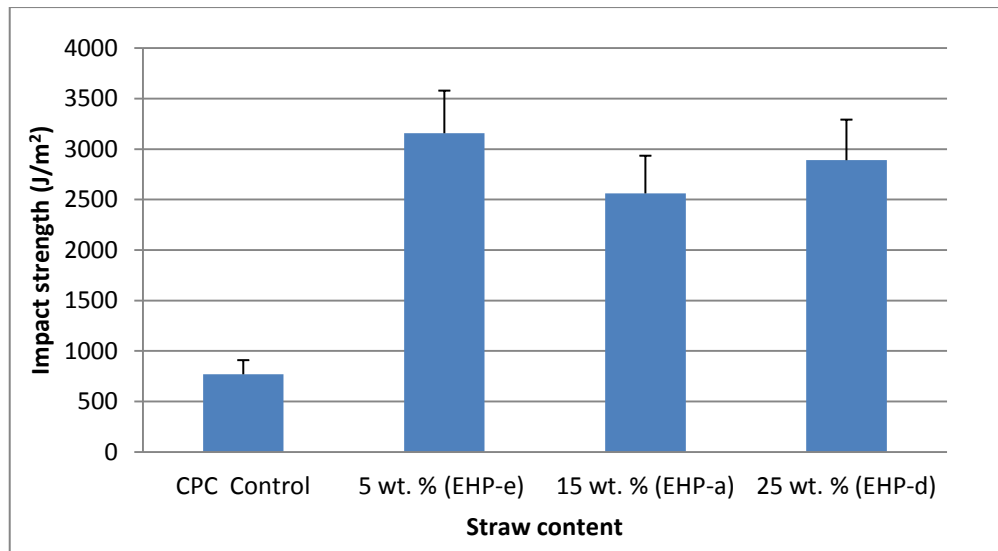


Figure 4.5: Effect of straw content on the impact strength of composites.

It can be concluded that increasing straw content in the organic composition increases the stiffness of the composites and reduce strength and ductility. Therefore a balance needs to be found. This may be attributable to the fact that an increase in straw content leads to a reduction of the starchy binding phase in the composites, which results in lack of compatibility or adhesion.

Although there are still some gaps in comparison to the benchmark, the intermediate level of straw content at 15 wt. % resulted in a good balance of stiffness, strength and low ductility and provided a base for further formulation refinements.

4.1.3 Effect of straw type

Following the study on the effects of straw content in the above section which yields promising formulation with intermediate straw content of 15 wt. % and closest properties to the benchmark, this section investigates the influence of different straw preparation at the same level of straw content (15 wt. %) in the composite.

8B41R and 8B43R (as mentioned in section 3.1.4.2) are fractionated straw through extrusion in different levels where 3R means that the residential time in extrusion is three times as 1R. Figure 4.6- 4.9 compare flexural strength, modulus, strain at maximum force and impact strength in each formulation with 15 wt. % of CS (EHP-a), 8B41R (EHP-b),

and 8B43R (EHP-c) respectively, as mentioned in Table 3.12.

In Figure 4.6, flexural strength of EHP-a and EHP-b does not differ much, although that of EHP-b presents a slight reduction of 6% compared to EHP-a. The strength of EHP-c rises dramatically and outperformed the CPC control by around 60%.

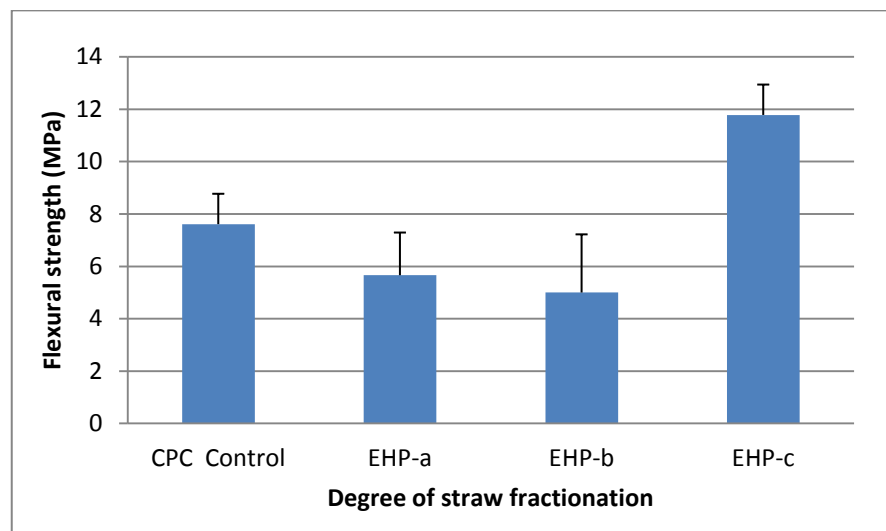


Figure 4.6: Flexural strength of the composites incorporating 15 wt. % straw with different degree of fractionation:

- a) chopped straw without extrusion pre-treatment;
- b) straw through one run of extrusion pre-treatment (8B41R);
- c) straw through three runs of extrusion pre-treatments (8B43R)

The same trend is observed for modulus. Figure 4.7 illustrates that EHP-c presents the highest modulus of the three formulations, although still around 24% lower than the CPC control.

Kang et al (2009) showed that, with increasing intensity of extrusion straw fractionation, finer fibres are exposed and non-cellulose binding agent (lignin and hemicelluloses) within the straw is leached out contributing to the matrix binder. This is also accompanied by damage of straw fibre and average fibre length shortens as a result. The reduction in strength from the formulation containing straw without extrusion pre-treatment (EHP-a) to that containing straw 8B41R (EHP-b) seems to indicate the effect of straw fibre damage, while the strength increase in EHP-c containing straw 8B43R may well be attributable to the release of much finer fibres, which provide more effective fibre reinforcement by the

lignin/hemicelluloses which act as the additional binding phases in the composite system.

Figure 4.8 shows that all the three composites, EHP-a, EHP-b, and EHP-c have high ductility and by around 40%, 120% and 270% higher strain at maximum force than the CPC control sample, respectively. This increase in ductility as the level of fractionation increase, especially for EHP-c containing the most refined 8B43R straw, indicates the contribution from the additional binding phase from the leach-out of lignin and hemicelluloses assisted by the alkaline treatment. Under high strain rate impact test condition, a similar trend as Figure 4.9 is observed. Higher level of fractionation of straw gives rise to higher impact strength, as illustrated in Figure 4.9. EHP-b, being the most brittle sample out of the three, is 200% higher in impact strength than the CPC control.

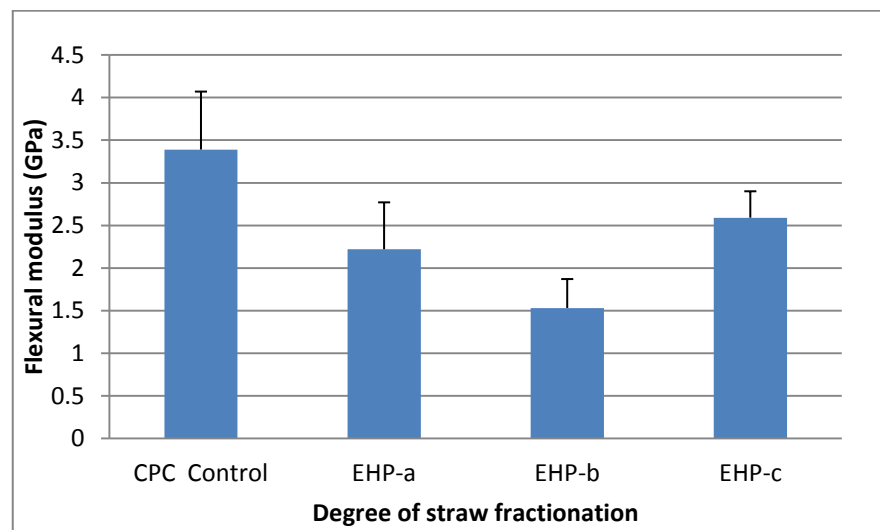


Figure 4.7: Flexural modulus of the composites incorporating 15 wt. % straw with different degree of fractionation:

- a) chopped straw without extrusion pre-treatment;
- b) straw through one run of extrusion pre-treatment (8B41R);
- c) straw through three runs of extrusion pre-treatments (8B43R)

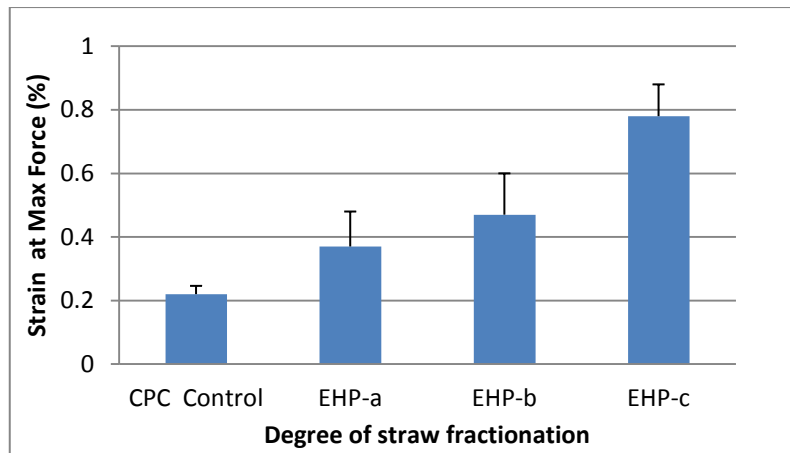


Figure 4.8: Flexural strain at maximum force of the composites incorporating 15 wt. % straw with different degree of fractionation:

- a) chopped straw without extrusion pre-treatment;
- b) straw through one run of extrusion pre-treatment (8B41R);
- c) straw through three runs of extrusion pre-treatments (8B43R)

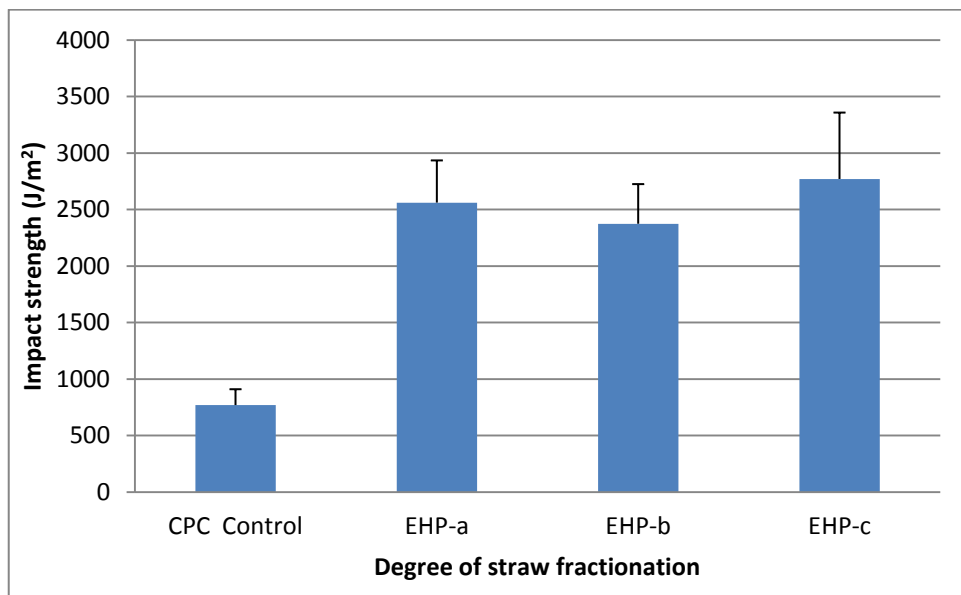


Figure 4.9: Impact strength of composites incorporating 15 wt.% straw with different degree of fractionation

- a) chopped straw without extrusion pre-treatment;
- b) straw through one run of extrusion pre-treatment (8B41R);
- c) straw through three runs of extrusion pre-treatments (8B43R)

In agreement with the observations in Kang et al (2009), extrusion straw fractionation can

adversely affect strength and stiffness at low intensity due to straw damage but the release of finer fibres and lignin/hemicelluloses leach-out lead to increase in strength, stiffness and ductility at higher level of fractionation owing to increased interfacial area and available additional bonding agents from the leach out. The high straw fractionation level clearly benefits strength and stiffness but it is undesirable for achieving low toughness which is essential for the application. On balance, and taking account of the cost of intensive straw refinement, low level of refinement, such as for EHP-a and EHP-b are therefore preferred overall with further measures to be considered for reduction of toughness to a level comparable to the benchmark.

4.1.4 Effect of glycerol content in the wheat flour

As mentioned in Chapter 3, glycerol is mainly used as a plasticiser in the wheat flour to assist extrusion compounding and moulding of the composites. The formulations discussed in section 4.1.2 and 4.1.3, which contain 25 wt. % glycerol (based on flour alone), are still much too ductile compared to the benchmark, reduction of glycerol content in flour is thus sensible to adjust ductility of the flour matrix. This section examines the effect of reducing the glycerol content in flour from 25 wt. % to 0 wt. % on the properties. Following the findings in section 4.1.2 and 4.1.3, the study focused on straw content 15 wt. % using chopped straws. Details of samples containing different concentrations of glycerol are described in Table 4.1 and listed below for clarity:

Table 4.1: Change of glycerol content in flour in the clay/flour/straw composites

Sample ID	Glycerol content in flour
EHP-g	0 wt. %
EHP-h	8 wt. %
EHP-i	15 wt. %
EHP-a	25 wt. %

As shown in Figure 4.10 to 4.11, a reduction in glycerol content from 25 wt. % has resulted in a significant increase in flexure strength and modulus. Compared with the CPC control, the formulation without glycerol in flour (EHP-g) has the closest match of modulus and strength (around 23.5% and 6.7% higher than the CPC control, respectively). In addition, EHP-g gave rise to the lowest strain at maximum force (Figure 4.12), which is only about

13% higher than the CPC control and lowest impact strength (Figure 4.13).

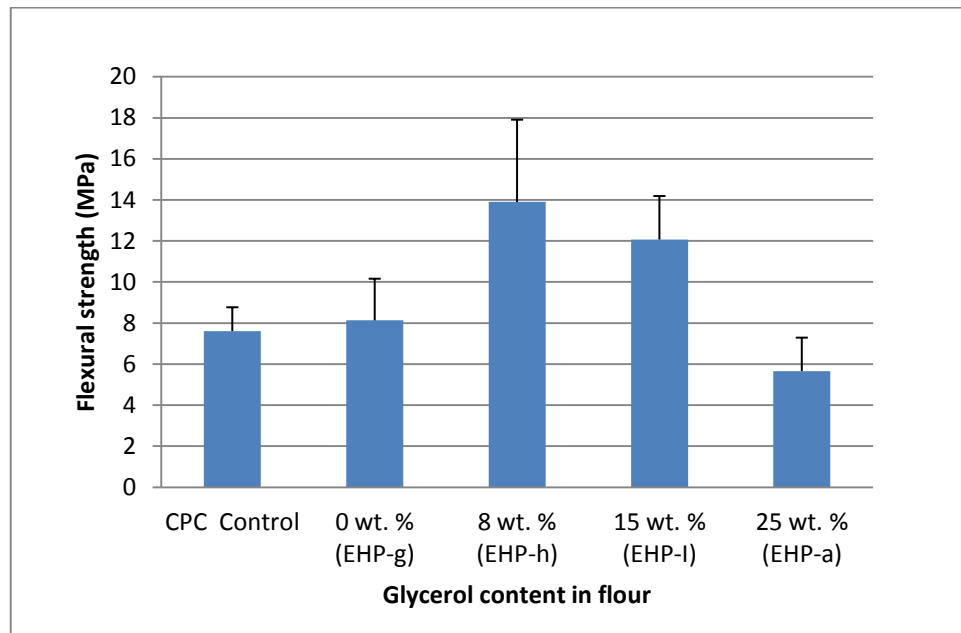


Figure 4.10: Effect of glycerol content in flour on the flexural strength of composites through the extrusion.

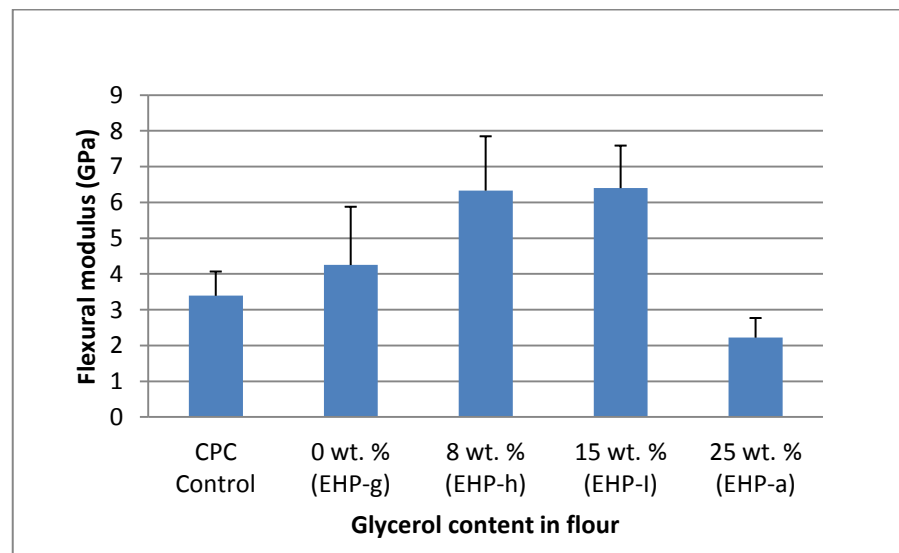


Figure 4.11: Effect of glycerol content in flour on the flexural modulus of the composites.

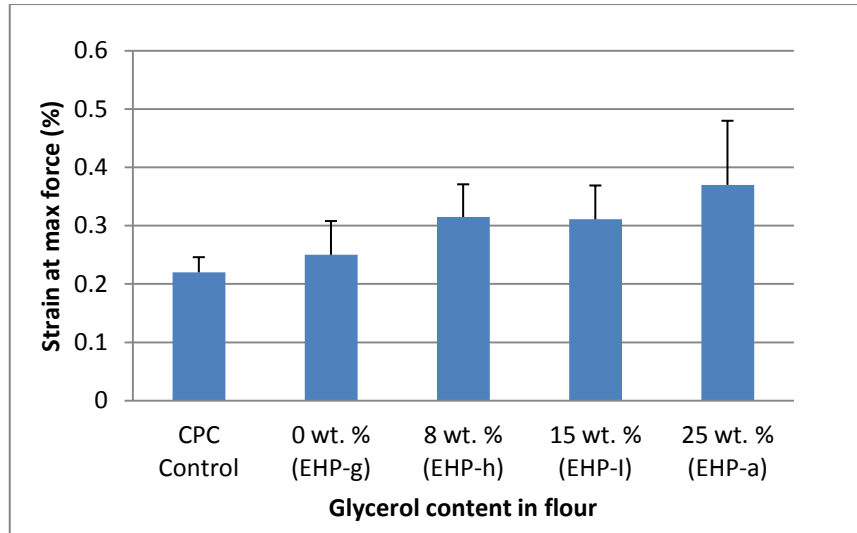


Figure 4.12: Effect of glycerol content in flour on the flexural strain at maximum force of the composites.

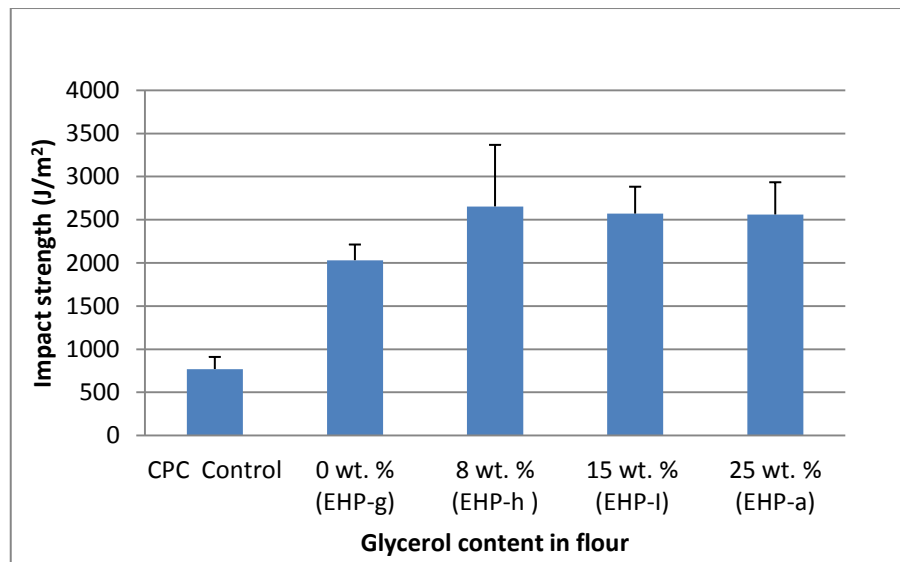


Figure 4.13: Effect of glycerol content in flour on the impact strength of composites.

Compared to the formulation with 25 wt. % glycerol content in flour (EHP-a), removing glycerol completely in EHP-g has resulted in the closest match to the CPC control. Not only strength and modulus have increased, it also resulted in lower toughness or brittleness required. In terms of enhancement to strength and stiffness, glycerol content seems to reach an optimum level at around 8 wt. % (EHP-h) in flour (as shown by Figure 4.10 and 4.11), while impact strength reaches a plateau as the glycerol content in flour (increased beyond 8 wt. %). Although the addition of glycerol has enhanced the flow ability and packing

efficiency of materials, it has increased the ductility of the composites at the same time. At the glycerol content in flour over 8%, the softening function becomes more significant than the increase in packing efficiency, this is called over plasticisation. This explains why there is a drop in strength and modulus above 8% in Figure 4.10 and 4.11. It is also proved in Figure 4.12 that ductility increases with the glycerol content in flour. This is also supported by the loss of tensile strength to that observed by Torres et al (2007). The study showed that the decreasing value in tensile strength which occurred at higher glycerol contents might be associated with the presence of free volume in the sample (Torres et al., 2007). These free volumes affected the tensile strength in the composites. Munthoub et al (2011) also states that although addition of glycerol as plasticiser to the biodegradable composites helps to promote the mobility and increase mechanical properties, excessive amount of glycerol results in poor mechanical properties and water absorption due to the properties of glycerol itself.

From the discussion above, the impact strength of clay-flour-straw composite is concluded to be sensitive to glycerol content in flour. Regarding the primary requirement on the brittleness of clay shooting targets, removal of glycerol reduces impact strength dramatically and the addition of glycerol should not be considered for this application.

4.1.5 Influence of formulations on material density

The averaged density of the six compression-moulded plate samples in each formulation are illustrated in Figure 4.14 (Sample ID as shown in Table 3.12 and 3.13, together with the CPC control for comparison). It is shown that when moulded under the same moulding condition, material density, which is determined by packing efficiency of the constitute compositions, is closely related to formulations and thus fractionation level of straw, straw content and glycerol content in flour all have some influence on the mobility of the clay particles and flow behaviour of the organic phases.

The increase in the level of straw fractionation, the reduction in straw content (which means increase of flour content, because the weight percentage of flour and straw together is fixed as 30 wt. %), together with more glycerol content in flour has enhanced the compressibility of the processed straw and resulting in higher density. Three incremental trends can be observed from Figure 4.14:

a) With improvement of straw fractionation;

According to the research of Kang et al (2009), fractionation results in refined straw fibres coated with the natural resins that leached out. This enhanced flow and lubrication of clay particles and increased the packing efficiency of the composite system. Therefore, formulations involved higher fractionation level will contribute more to the compressibility of the composites.

b) With the decrease of straw content (EHP-d to EHP-f ranging from 25 to 5 wt. %);

Firstly, because of the lower particle density of straw fibre is around 0.4-1 g/cm³ depending on the position as examined by Lam et al (2008) which is lower than flour at around 1.3 g/cm³ (Dengate et al., 1978). Reduction in straw content reduced the density of the composite system. In addition, decrease of straw content means more flour (as binding phase) in the composite, which enhances the flow of straw, thus improving the packing efficiency of the composites.

c) With the increase of glycerol content in flour (EHP-g to EHP-a ranging from 0 to 25 wt. % in the flour). Glycerol (as the plasticiser) will also enhance the packing efficiency of the composites owing to enhanced flow of the matrix and enable the mobility of clay particles.

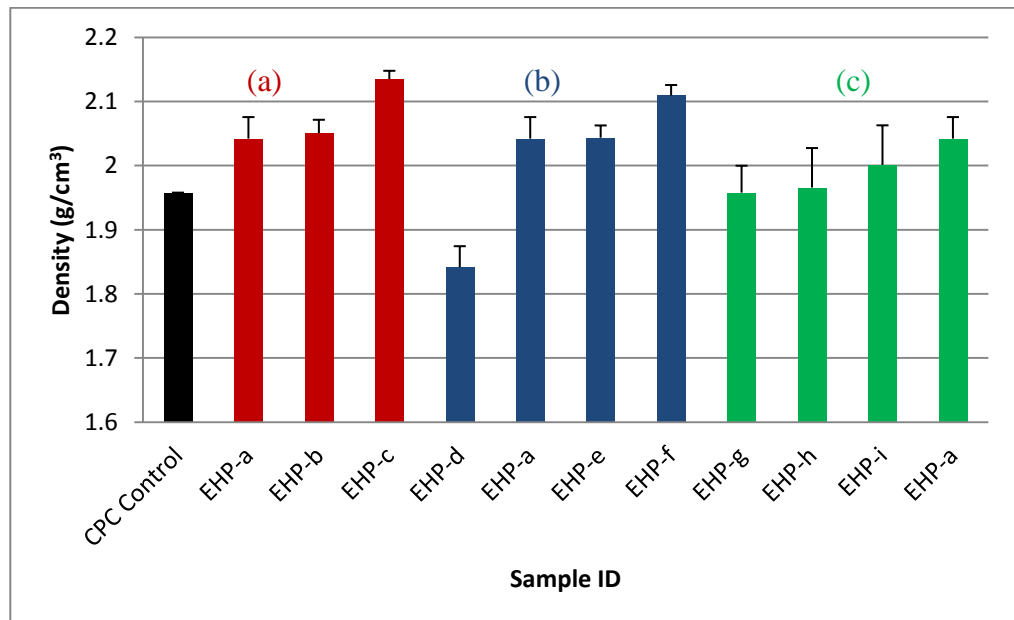


Figure 4.14: Density of compression moulded composites with formulation variations:

- a) Degree of fractionation (red)
- b) Straw content (blue)
- c) Glycerol content in the flour (green)

From all the formulations listed in the Figure 4.14, EHP-g containing 70 wt. % clay, 15 wt. % flour (none plasticised by glycerol), and 15 wt. % CS straw presents the closest density to the CPC control sample. However, density does not have to be identical to the control. Sufficient density will give the clay pigeons sufficient kinetic energy and flight stability. Clay Pigeon Company has suggested 2 g/cm^3 as a target. Apart from EHP-d with 25 wt. % of straw, most of the densities are within 1.9 and 2.1 g/cm^3 , which are close enough to the requirements.

4.1.6 Morphology the composites made from extrusion compounding followed by hot press moulding

Figure 4.15 illustrates the distribution of straw in composite EHP-g with 15 wt. % of raw straw without fractionation, as single fibre or straw bundles. It is evident that there is good adhesion between straw and the clay-filled matrix, in agreement with the work of Xia et al (2010). There are also pull-out fibres from the fracture surface (as the red arrows pointed in Figure 4.15) and this may have contributed to the high impact strength and ductile fracture behaviour of the EHP-g show in Figure 4.17.

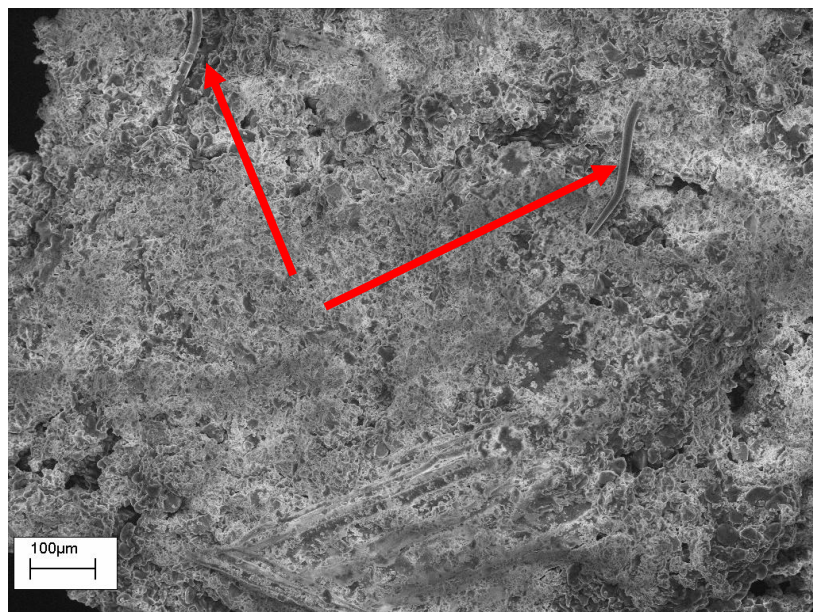


Figure 4.15: Morphology of EHP-g showing the arrangement of straw fibre or fibre bundles in clay-starch-straw composites.

In Figure 4.16, it is apparent that the clay and flour composites (EHP-f, as shown in Table

3.13) involved extrusion compounding are more closely blended, and the clay particles are embedded within flour matrix. As shown in Figure 4.16, flour in EHP-f is well destructured and gelatinised to form a continuous phase acting as a binding phase, just like Figure 4.1 shows. This indicates flour in EHP-f is well gelatinised, with the clay particles homogeneously surrounded by gelatinised flour. This has resulted in much higher flexural stiffness, strength, and impact strength compared with the control. Comparing with those formulations containing straw, EHP-f with continuous microstructure results in higher ductility, as shown in Figure 4.17.

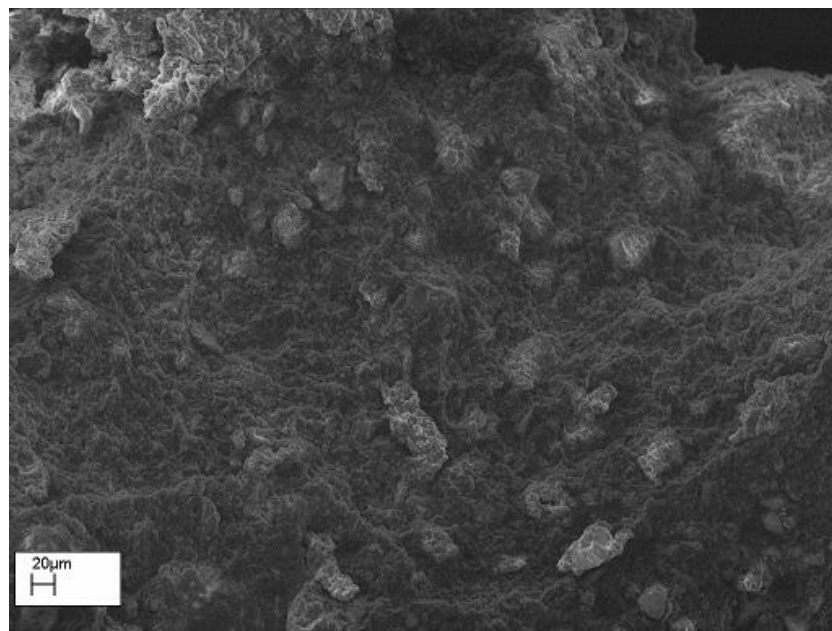


Figure 4.16: Morphology of EHP-f showing the continuous microstructure of clay-starch composites with clay particle embedded in well gelatinised starch.

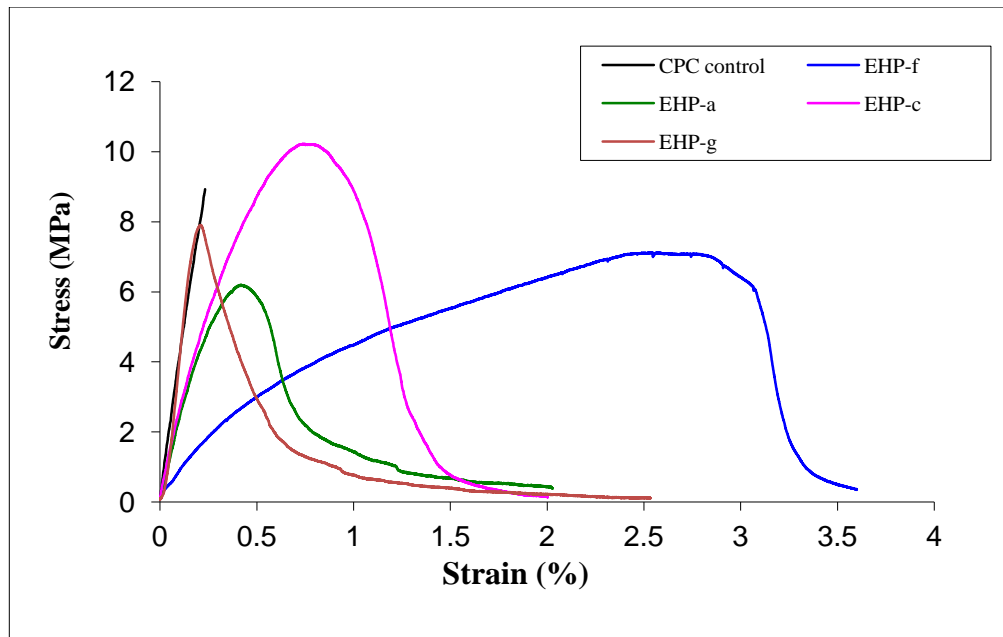


Figure 4.17: Comparison of flexural curves of samples from selected formulations.

4.1.7 Summary of formulation screening

The addition of straw in the clay-flour-straw composites will have two functions working at the same time: increase the stiffness of the composites and lower the system compatibility. A balance has been found at composites with 15 wt. % straws, which presenting the lowest impact strength without losing stiffness and strength. From the influence of straw fractionation level on the properties, it is also found that high fractionation level of straw will involve a double side function to the system. It leads to reduction of the mechanical properties of the composites due to the self-damage involved to straw bundle. On the other hand, it also have positive influence on mechanical properties of composite because more plastics leached out as binding phases. Glycerol content in flour does increase most of the mechanical properties of the composites but it seems to reach the maximum at around EHP-i (8 wt. % glycerol in flour). After that, an increase of glycerol content in flour influences the composites in a reverse way (for modulus and strength) or keeps it to a constant level (impact strength).

Based on the above assessments of the mechanical properties and density, EHP-g stands out as the most promising candidate among the formulations. It has the closest match in density and mechanical properties to the CPC control. As shown in Figure 4.17, its elastic deformation region is almost identical to that of the CPC control. In addition, its flexural

curve also indicates more desired brittle fracture than other formulations. The formulation of EHP-g is featured in the absence of glycerol in the flour and the chopped straw was used without extrusion fractionation, which is more cost-effective in materials. Two problems remain to be addressed are:

- The impact strengths of the preferred candidate formulations are still too high compared to the target;
- Long circle time of the processing route cause by the drying of materials

4.2 Selection of processing routes

Due to the high impact strength of the formulations presented in section 4.1, powder compaction, as a standard technique in food, ceramic or pharmaceutical industry (Sinka, 2007) was involved as the moulding process to create a composite structure with high brittleness. Besides, Extrusion compounding of the clay-flour-straw feedstock followed directly by hot compression moulding, used for the formulation screening in section 4.1, is hindered by the long cycle time associated with drying of the moisture within the feedstock. According to the commercially used melting compression process, short moulding cycle time is required for the mass production.

There are two possible solutions based on the requirements mentioned above:

1) Produce a dry feedstock in powder followed by powder compression moulding. In order to allow the fusion of powder particles, the starchy binding phase must be in a molten state. This can be achieved by either cold powder compressed in hot mould or hot powder compressed in cold mould. The first option is undesirable as heating materials in mould needs a long cycle time. So pre-heated powder compression in cold mould is potentially the most suitable option. There are many advantages to this process:

- Rapid process that can adopt many existing technologies, for example, heating of feedstock powder can adopt existing technologies e.g. conveyer with heating band;
- Degree of binding between clay particles can be utilised to control impact strength—the remaining challenge to be addressed, by varying pressure and temperature.

There are two possible ways to prepare of the feedstock powder for moulding:

- a) Mechanical mixing of the clay (already in powder form) and the organic composites in powder form which can be

- Flour alone without any straw
- Flour-straw composites, extrusion compounded and pulverised to powder.

The advantage of this powder preparation process is that clay and flour are already in powder form and may skip extrusion compounding and can be directly used in mechanical blending of powders. This process creates a less intensive structure and weaker binding between clay particles and the organic particles, which may give rise to the required low impact strength.

- b) Extrusion compounding of clay-flour-straw followed by drying and pulverisation to obtain the powder feedstock. The potential advantage of this process is a homogenous coating of the clay particles can be obtained by the organic phase, leading to ease of moulding, good uniformity and surface finish. But some drawbacks also exist: 1) high energy and processing cost in extrusion compounding (incorporation of 70 wt. % clay already in powder form); 2) wear of tooling due to hardness of the clay particles.

4.2.1 Cold-die compression moulding of powders prepared by mechanical mixing (MPC: mechanical mixing + powder compaction)

In this process, clay and flour/straw compounds are prepared by mechanical mixing of the clay powder and powders of either the as-received flour granules or the flour/straw compound pulverised from dried extrudates. The formulations are summarised in Table 4.2 below. The feed stock powder mixtures were then preheated and moulded in a cold die as described in section 3.2.1.2. Water was sprayed prior to the powder preheating (in a sealed container) for softening of the flour/straw powder and surface gelatinisation of the flour granules binders for it to act as a binder.

Table 4.2: Explanation of formulations made from the processing of MPC (details refer to section 3.2.1.2).

Sample ID	Straw content (wt. %)	Water added (%)
MPC-a	15	20
MPC-b	15	25
MPC-c	12	20
MPC-d	12	25
MPC-e	0	25
MPC-f	0	20

Figures 4.18 and 4.19 show that the flexural property of mixed powder compacts are much weaker in terms of flexural modulus and strength than the control and the formulations in serie EHP (as shown in Figure 4.2, 4.3, 4.6, 4.7, 4.10 and 4.11). Even the best sample (MPC-e) is still lower than the control sample by 76% in modulus and 57% in strength. This had led to some problems experienced during demoulding of prototype “clay pigeons”, and the breakage lead to a high scrap ratio of over 50%. Clearly the strength is not sufficient to withstand the launching force. Careful microscopic assessments of the fracture surface of the samples (Figure 4.20) revealed that the distribution of organic powders among the clay particles was very inhomogeneous. Not only at particle level, where there is a lack of organic particles around clay particles, but there are also regions where hardly any binder phase can be found. This led to both micro and macro scale defects, weak strength and low modulus.

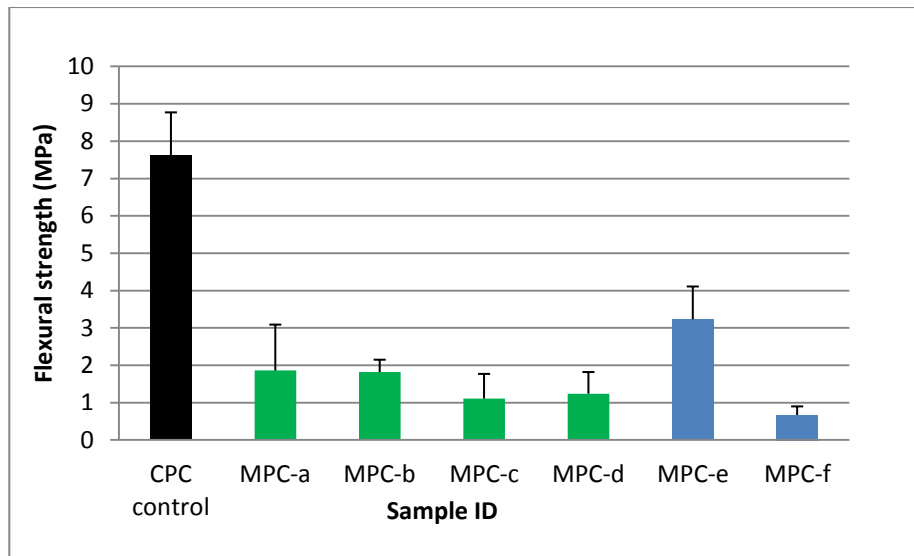


Figure 4.18: Flexural strength of samples prepared by compaction of mechanically mixed powders (Green bars stand for the formulations with straw and blue bars stand for the formulations without straw).

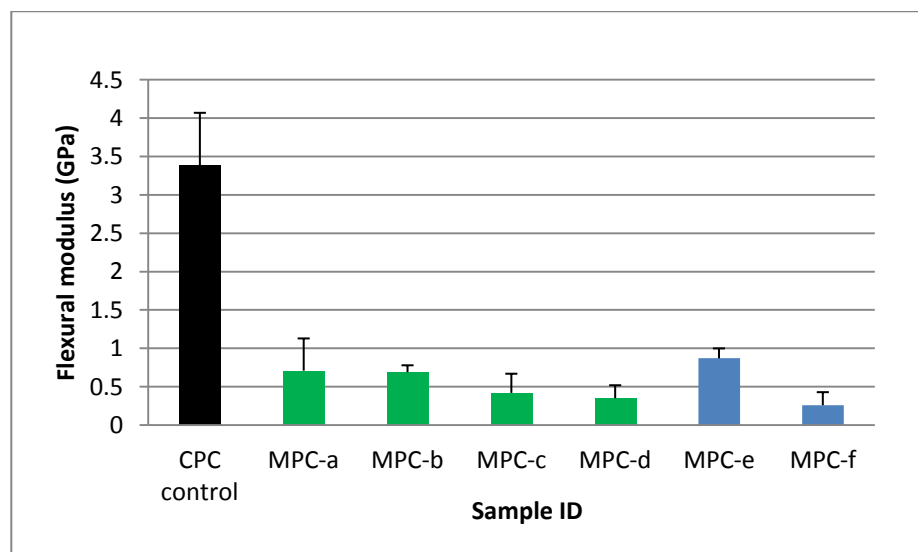


Figure 4.19: Flexural modulus of samples prepared by compaction of mechanically mixed powders (Green bars stand for the formulations with straw and blue bars stand for the formulations without straw).

Figure 4.20, illustrates the morphology of MPC-e formulation. The starch retained its granular form (as shown in Figure 4.20) and was surrounded and loosely attached by the clay particles. Therefore, the binding force between flour and clay is much weaker comparing with an extruded composite (EHP-f) followed by hot press (shown in Figure

4.16 and 4.17). This explains why formulations made from MPC is lower than EHP in terms of strength and modulus. Figure 4.20 also shows that the distribution of starch granules is not uniform and there are regions with low bonding phase where the clay particles are not bonded at all. This makes MPC formulations are difficult to be demoulded without damage after compression moulding.

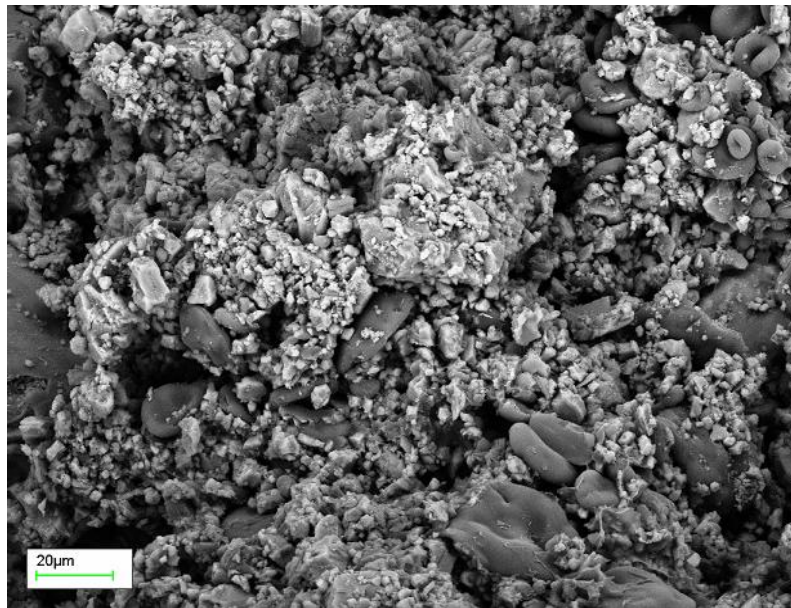


Figure 4.20: Morphology of MPC-e showing in-homogenous and loose compacted microstructure of clay-starch composites.

According to Figure 4.18 and 4.19, 5% difference on water addition has limited influence on the formulations containing straw (MPC-a, b,c, and d) for flexural modulus and strength. But for the formulations excluding straw, there is a significant increase in modulus and strength by adding 5% more moisture (from MPC-f to MPC-e). Strength and stiffness of formulations without straw are mainly contributed by the binding force provided by gelatinised flour. Therefore, it is suggested that the high flour content of formulations without straw blended makes the composite system more moisture sensitive than the formulations containing straw. In Figure 4.21, the trend of strain at maximum force is different. For the formulations with straw, the 5% increase in water addition results in a rise of 16% (BP-02-a to BP-02-b) and 20% (BP-02-c to BP-02-d) in strain at maximum force respectively. But for the formulation without straw, 5% difference in water addition makes little change from BP-02-f to BP-02-e. This indicates that water addition improved the mobilisation of clay particles and straws, which led to an increase in ductility.

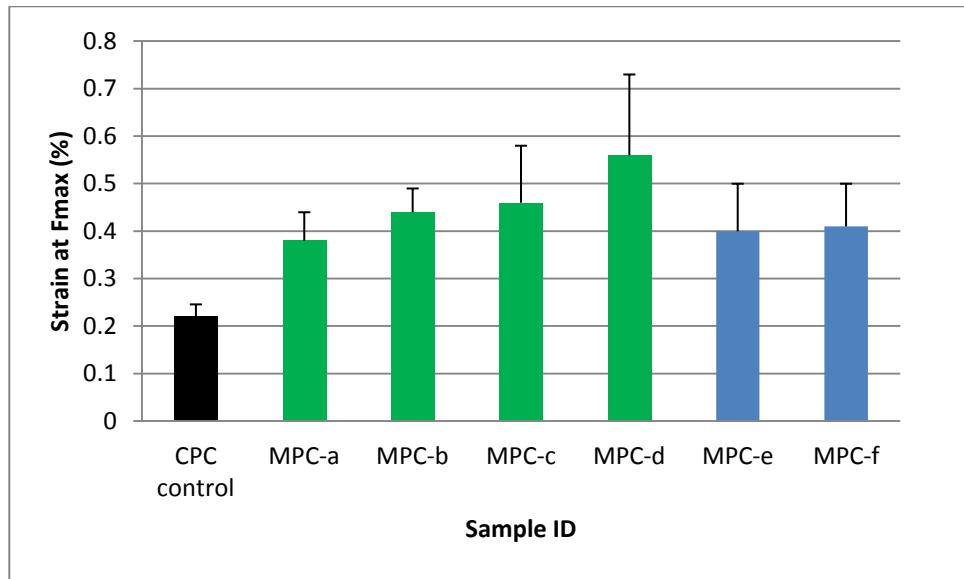


Figure 4.21: Flexural strain at maximum force of samples made through MPC processing (Green bars stand for the formulations with straw and blue bars stand for the formulations without straw).

However, there have been improvements in the desired brittleness. As shown in Figure 4.22 except for MPC-a, all other formulations present lower Charpy impact strength than EHP-g (Figure 4.13), which have the lowest Charpy impact strength in EHP series at around 2000 J/mm^2 , resulting in much closer match to the CPC control. Generally speaking, the impact strength of MPC series decrease gradually with the reduction in straw content, from 15 wt. % (MPC-a and b) to 0 wt. % (MPC-e and f). Although the flour content increases with the reduction in straw content, the impact strength still drops down. This is also an indication of the poor bonding between starch granules and clay particles. The formulations in Figure 4.5 with more stable interfacial bonding present a different trend, where impact strength increases when straw content decreases from 15 to 5 wt. %.

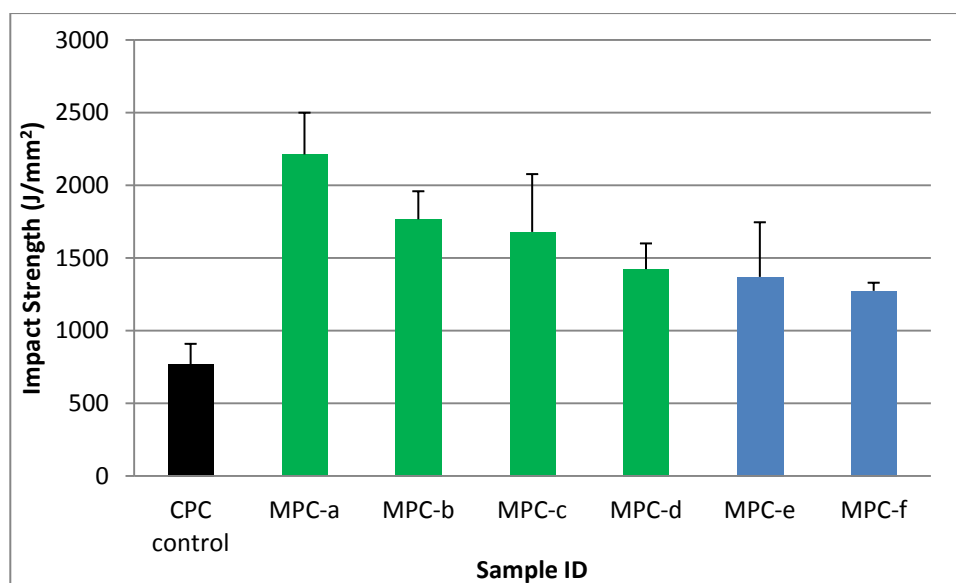


Figure 4.22: Charpy impact strength through of samples prepared by compaction of mechanically mixed powders(Green bars stand for the formulations with straw and blue bars stand for the formualtions without straw).

The processing route does offer potential in controlling the mechanical properties by processing parameters (uniformity of mixing, presure and hold time, temperature and the processing aid such as water content). It is also demonstrated that the key to obtain edequate combination of mechanical properties is improvement in powder mixing at particle level. Mechanical mixing will need systematic study in terms of particle size and discription and optimisation of mixing techniques and processing condition and this is beyond the the scope of the project. Powder compaction route is thus continued but focus is given to the enhancement of uniform binder discription within feedstock by preparing the powder feedstock using extrusion compounding of clay and the binder systems followed by pulverisation.

4.2.2 Compression moulding of powders prepared by extrusion compounding (EPC: extrusion compounding + powder compaction)

The formulations involved in this section are EPC-a containing 70 wt. % clay and 30 wt. % flour (none glycerol plasticised) and EPC-b, made from 70 wt. % clay, 15 wt. % none glycerol plasticised flour and 15 wt. % raw straw without fractionation. The two formulations were pre-blended and extrusion compounded with addition of water to destructure and gelatinise the flour so that the individual clay particles are coated with

binder and achieve homogeneous distribution of binder. The extrudates were then dried, pulverised and compression moulded as described in section 3.2.1.3.

Figure 4.23 to 4.26 summarise the mechanical properties of the two formulations. With only a few exceptions, most formulations present close match of properties to the CPC control sample, as shown in Figure 4.23 to 4.26 in terms of flexural strength, modulus, strain at maximum force and impact strength, respectively. In comparison with samples prepared by MPC (mechanical mixing followed by powder compaction) in Figure 4.18 to 4.19, the significant improvement in flexural strength and modulus is clearly attributable to the improved uniformity of bonding phase as within each powder granule of the feedstock (shown in Figure 4.27).

Figure 4.27 illustrates the morphology of the formulation of EPC-a containing 70 wt. % clay and 30 wt. % flour without glycerol. It shows that, like in Figure 4.16, the starch has formed a continuous phase and coated all clay particles. The clay particles in each powder granule are coated by the binder which allows plastic deformation and adequate bonding of the granules when brought into contact to form sufficient bonding during the compression moulding process. Porosity (pointed out by arrow in Figure 4.27) in this compact is from voids between granulated powder particles, not within the particles. The voids and porosity result in closer brittleness to the target.

Figure 4.27 shows good fusion of granulated powder particles. This enhanced bonding force between clay particles and the fusion between granulated powder particles resulted in higher stiffness and strength than those compacted from mechanically mixed powders. Using conditions of compression moulding (temperature and pressure in particular) the powder compaction method can control porosity between the granulated powder particles. These defects can act as crack initiator and reduce toughness of the composites as required.

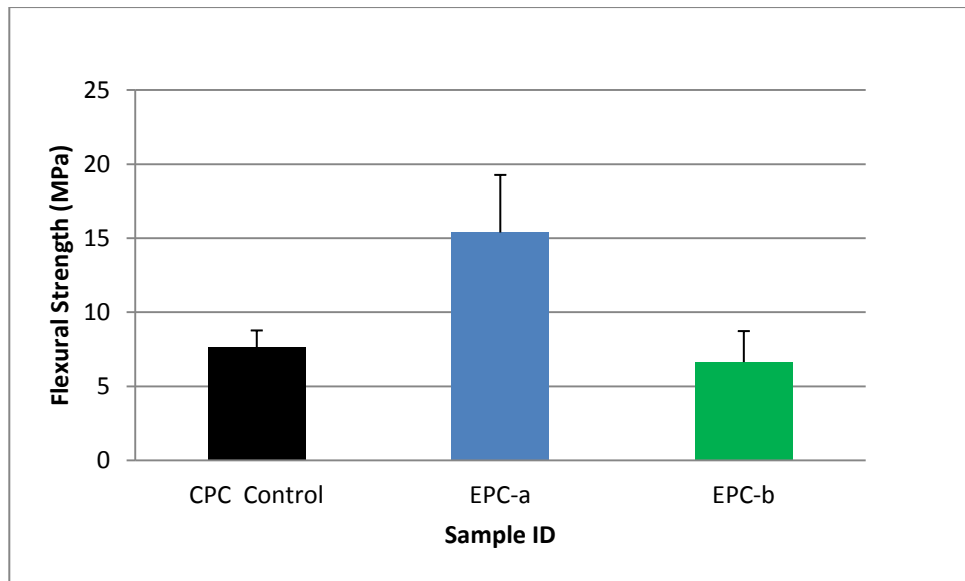


Figure 4.23: Flexural strength of clay-flour-straw composites compression moulded from powder prepared by extrusion compounding and pulverisation.

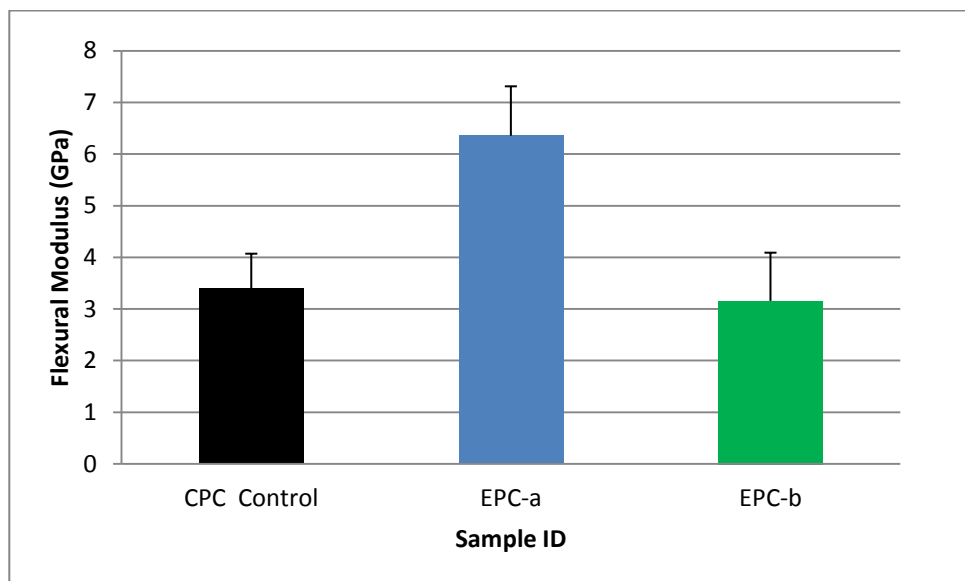


Figure 4.24: Flexural modulus of clay-flour-straw composites compression moulded from powder prepared by extrusion compounding and pulverisation.

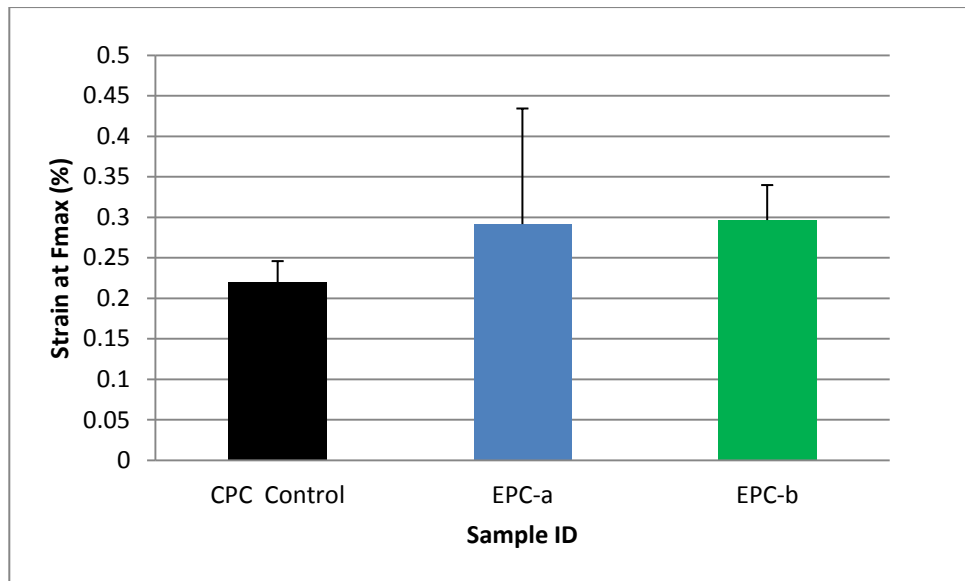


Figure 4.25: Flexural strain at maximum force showing ductility of the clay-flour-straw composites compression moulded from powder prepared by extrusion compounding and pulverisation.

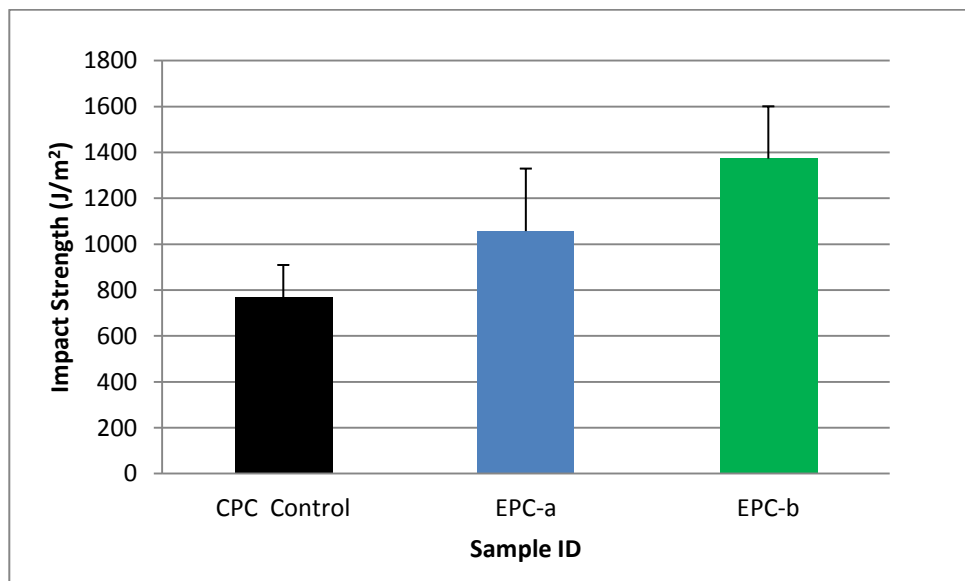


Figure 4.26: Charpy impact strength showing comparable close toughness (to the CPC control) of the clay-flour-straw composites compression moulded from powder prepared by extrusion compounding and pulverization.

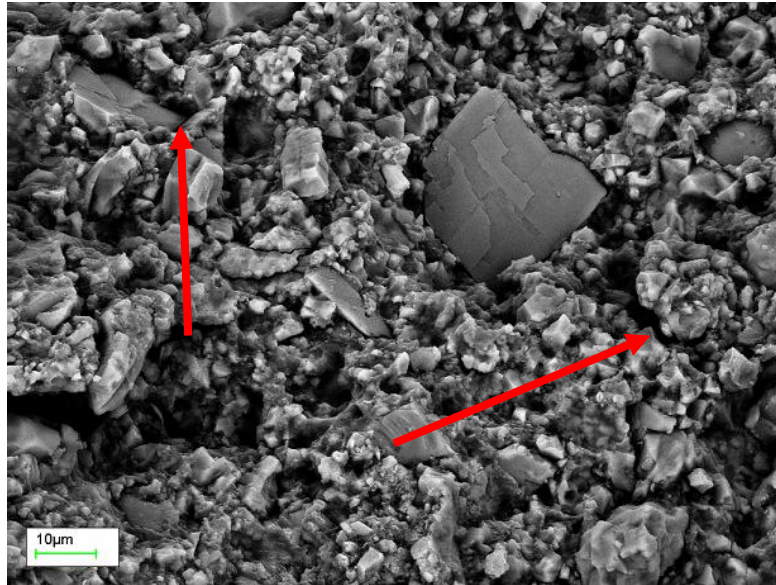


Figure 4.27: Morphology of EPC-a showing the microstructure of clay-starch composites with boundaries and voids between granulated powder.

On balance, EPC-a presented the closest match to the CPC control. Not only it has a comparable combination of properties in strength, modulus and impact strength, but also desired brittle failure behaviour similar to the CPC control sample (as shown in Figure 4.28). Therefore, apart from other consideration, EPC-a emerges as the most suitable candidate for further development.

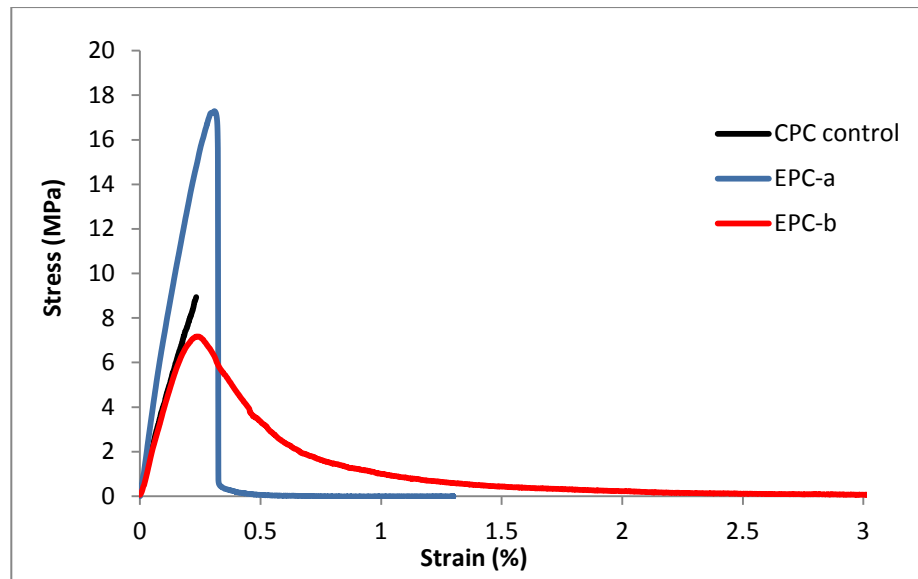


Figure 4.28: Stress-strain relationship during 3-point bending tests of the clay-flour-straw composites compression moulded from powder prepared by extrusion compounding and pulverisation.

4.2.3 Summary of processing route selection

The process of extrusion compounding followed by hot mould compression has the disadvantage of long cycle time and high impact strength. After changing the element in formulations, gap to the target is still exist. Changing the elements in formulation does not make impact strength drop significantly. So, adjustment in processing is the most reasonable option to solve the problem. It has been proved that the employment of powder compaction does enhance brittleness.

The MPC and EPC are the two processing routes with similar moulding process but different from the powder preparation method. Powders are prepared by mechanical mixing in MPC method, while EPC prepares powder through extrusion compounding and pulverisation. Through the investigation on the mechanical properties and morphology detection, MPC is found to have in-homogenous structure and loose interfacial bonding together with poor strength and stiffness, which results in challenges in demoulding. Therefore, extrusion compounding in EPC was adopted to enhance the homogeneity and interfacial bonding between starch and clay particles. Finally, the composites (EPC-a and EPC-b) made from extrusion compounding, followed by powder compaction are found to be the best choice to satisfy the requirements of processing cycle time and closest

mechanical properties to the target.

4.3 Prototyping of bio-pigeons

Compression moulding described in section 3.2.1 has proved sufficient to form the bio-pigeons. Figure 4.29 illustrates the appearance of the prototypes at different stage of formulation development. It is shown that the prototypes from the candidate formulations can create the shape and intricate details (e.g. the sharp steps and flow lines on the top surface (in Figure 4.2 b c d), trade mark on the top (in Figure 4. b), and teeth on side for friction enhancement during launching (in Figure 4. b). The prototypes of bio-pigeon weighing from 98g to 104g are all within weight range of the commercial requirement.



Figure 4.29: Examples of bio-pigeon prototypes:

- a) The CPC control; b) Prototypes made from formulation EHP-g;
- c) Prototype made from formulation of EPC-b; d) Prototype made from formulation EPC-a

A primary flying test was carried out at the Defense Academy of Cranfield University for some of the prototype bio-pigeons. The test concluded that:

- The density, shape and dimensions of the Bio-pigeon prototypes are satisfactory.
- Launch: All the formulations were launched as normal.
- Fly distance: The fly distance of the bio-pigeons ranges 75 to 78 meters, which makes

them suitable for the 50m rifle shooting in outdoor range.

- Fly stability: All the bio-pigeons fly in stable condition after launching.
- Deviation during flying:

For the formulation of EHP-g, EHP-h and EHP-I, the flying tracks of bio-pigeons were 3-5 degree to right to the required direction. The bio-pigeon made in the formulation of EHP-a flew 12-15 degree to right to the required direction. The deviation during flying is expected due to the shape distortion caused by manually demoulding. In the bio-pigeons produced in practice, automatical demoulding with uniformly distributed force is required to limit the deformation and damage.

4.4 Conclusion remarks

This chapter mainly deals with the development of an alternative material for the shooting target by using clay-flour-straw composites. The formulation has been screened to find a proper composition which presents similar properties to the target. Through the formulation screening, the key influences from each factor such as, straw content, fractionation level of straw and binder glycerol content, in the composite have been analysed.

The addition of straw in the clay-flour-straw composites has two functions working at the same time: increase the stiffness of the composites and decrease of system compatibility. In the existing formulations, 15 wt. % of straw content presents the closest brittleness to the target without reducing of strength and stiffness. Glycerol in flour increases the impact strength significantly, thus it is not desirable for applications which require high brittleness. It was also found that high fractionation level of straw will also involve a two reverse function to the system, which reduce the mechanical properties of the composites, owing to the self-damage involved to straw bundle and enhance the compatibility of elements in the composites as more plastic leached out as binding phase. Compare to EHP-g filled with 15 wt. % of raw straw without fractionation, formulations with fractionated straw presents higher impact strength, so the fractionated straw may not be adopted.

It is proved that the employment of powder compaction does enhance brittleness. The

powder preparation process leads to many differences in both mechanical properties and microstructure. Compared to the mechanical mixing process in MPC, extrusion compounding followed by pulverisation can produce a composite with more homogeneous structure and closer properties to the target. The formulations made by MPC process have achieved brittleness on expense of dramatic reduction in strength and stiffness, which make demoulding of samples difficult. Therefore, EPC using extrusion compounding and pulverisation to prepare powders has been finally adopted. Two formulations made from EPC process do have the closest impact strength, without reducing tensile strength and stiffness.

Chapter 5 Biopolymer-straw composites

This chapter mainly deals with biopolymer composites with wheat straw as reinforcement or filler. Many publications have covered investigations on composites made from petroleum thermoplastics and plant fibres. The composites investigated in this chapter, however, are designed to substitute petroleum plastics matrix with biopolymers for applications where full biodegradability of composites is desired. The straw biocomposites are in two biopolymer matrices: Bioflex and Biolice, and the formulations and processing are described in Chapter 3.2.2. Their effects on structure and mechanical properties are discussed Section 5.1.1 and 5.1.2. Characterisations of thermal and rheological behaviour of the biocomposites are represented and discussed in section 5.2 and 5.3, respectively. Section 5.4 summarises the key outcomes of research on the newly developed biocomposites.

5.1 Mechanical properties of biopolymer-straw composites

Depending on target applications (film, sheet or mouldings, as mentioned in section 2.5.2), tensile and tear properties of the biocomposites were investigated to check their behaviour under stretch force and tear force during delivery and service life. According to the properties of the two biopolymers represented in Table 3.4, Bioflex F6510 is rigid and strong while Biolice 50C is soft and weak. The two biopolymers were blended with wheat straw for different applications. Biolice-straw composites were designed for flexible sheets and injection mouldable parts, which do not require critical mechanical properties. Bioflex-straw composites were designed to produce extruded profiles and rigid sheet for structural applications, thus the flexural properties and impact properties are also investigated in addition to the tensile and tear properties. Straw in the composite system is expected to keep stiffness and reduce costs by replacing wood fibres.

5.1.1 Mechanical properties of Bioflex-straw composites

5.1.1.1 Tensile properties of Bioflex-straw composites

A comparison between the mechanical properties of wheat straw and Bioflex F6510 is made in Table 5.1. It lists the modulus and strength of raw wheat straw without

fractionation, measured via tensile and 3-point bending test. The elastic modulus, no matter if tested in tensile or bending test, is normally expected to be the same, but there is a significant difference between tensile modulus and bending modulus of straw in Table 5.1. This is because straw is not a material with continuous structure, so the theory of the elastic modulus is not applicable here.

Table 5.1: Comparison on the mechanical properties of wheat straw and Bioflex F6510.

	Tensile modulus (GPa)	Tensile strength (MPa)	Flexural modulus (GPa)	Flexural strength (MPa)
Raw wheat straw	2.8-3.6*	37-49*	0.98-1.82**	15-20**
Bioflex (from this study)	1.08	36.33	1.43	44.88

Note: *Data from research of Hornsby et al (1997); **Data from the research of Tavakoli et al (2008).

Figure 5.1 to 5.3 illustrates the E-modulus, tensile strength and elongation at break, of the Bioflex-straw composites respectively. Details of the formulations are shown in Table 3.19 in chapter 3, and their straw content ranges at 0 (BF-a), 10 (BF-8-10-a), 20 (BF-8-20-a) and 30 wt. % (BF-8-30-a) respectively. Generally speaking, compared with the neat Bioflex F6510 matrix, all the composite formulations have achieved significant improvement in the E-modulus (Figure 5.1) but a decrease in tensile strength (Figure 5.2) and elongation at break (Figure 5.3) with increase in the straw content.

The tensile modulus tested by hornsby et al, (1997) in Table 5.1 is much higher than that of Bioflex F6510. Although the fractionated straws used in this study have been proved by Kang et al (2009) results in a reduction of mechanical properties, the tensile modulus of Bioflex-straw composites still increases with straw content. As illustrated in Figure 5.1, the E-modulus increases from that of the neat matrix by approximately 108%, 160% and 192% at straw contents of 10, 20 and 30 wt. %, respectively. However, in Figure 5.2, tensile strength of Bioflex-straw composites reduces with the increase of straw content. It decreases from that of the neat matrix by approximately 30%, 49% and 59% at straw contents of 10, 20 and 30 wt. %, respectively. Similarly in Figure 5.3, elongation at break reduced dramatically from 87% for the neat Bioflex F6510 (BF-a) to around 0.3-1.4% at the straw concentrations.

Avella et al (2000) and Buzarovska et al (2008) observed the same effect of both rice and wheat straw in PHBV matrix in their researches. They demonstrated that the composites with straw exhibited higher E-modulus and lower values of both the strength and strain at break than the neat matrix. Similar results are also reported in a paper on rice straw-polypropylene composites (Grozdanov et al., 2006).

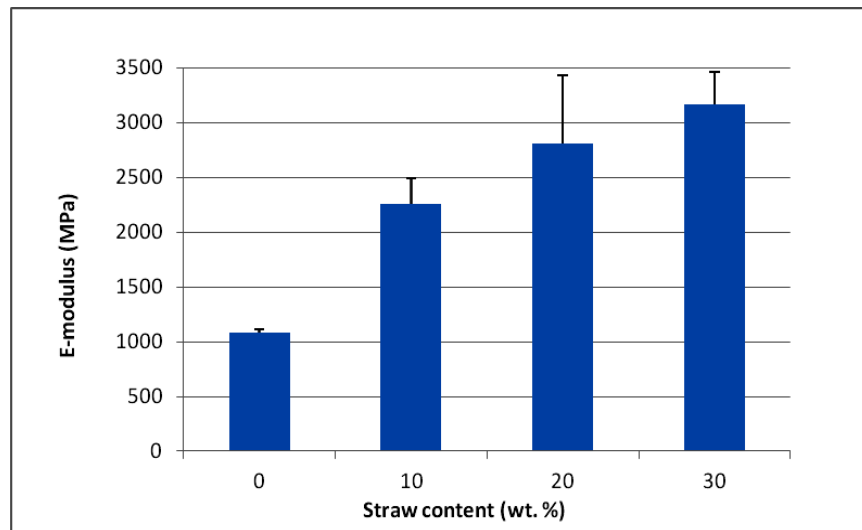


Figure 5.1: E-modulus of the Bioflex-straw composites at different straw contents.

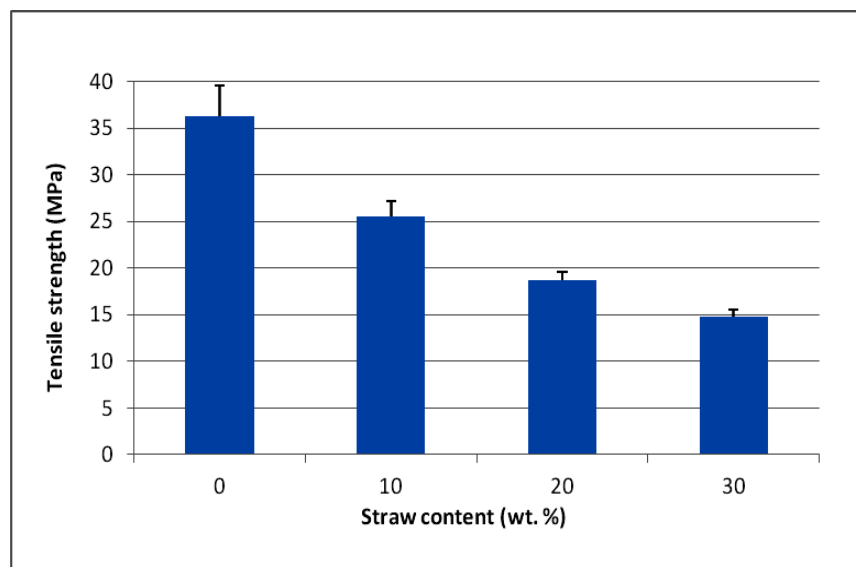


Figure 5.2: Tensile strength of the Bioflex-straw composites at different straw contents.

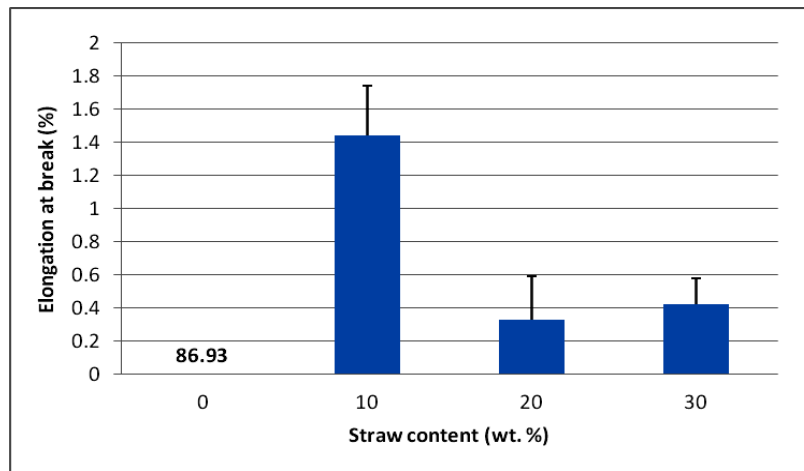


Figure 5.3: Elongation at break of the Bioflex-straw composites at different straw contents.

The reduction of strength with addition of straw in Bioflex is mainly due to two reasons:

- 1) Firstly, straw fibres are not reinforcing the Bioflex matrix in terms of strength. As Table 5.1 presented, the raw straw without fractionation has close tensile strength to the Bioflex matrix. Fractionated straw involved in this study should have even lower strength than the raw straw (Kang et al, 2009). Thus, fractionated straw can't reinforce the matrix without significant advantages in tensile strength.

- 2) Secondly, poor adhesion between fibre and matrix. Poor adhesion between the Bioflex matrix and straw fibres can be observed from the SEM images (as shown in Figure 5.4) of the tensile fracture surface of the composites containing 20 wt. % straw. They present the fracture occurs mainly in the matrix and straw fibres or bundles are mostly pulled out from the matrix (as red arrows pointed out in Figure 5.4a). The voids left by the pulled-out fibres during tensile are clearly seen as indicated selectively by the yellow arrows. Besides, the surface of relaxed straw bundles was also found, at higher magnifications, to be clear and smooth with little attached polymer matrix (as the red arrows pointed in Figure 5.4b). This indicates poor adhesion between the Bioflex F6510 matrix and straw. It could be supported by observations that composites filled with irregularly shaped fillers often result in a decrease in strength due to inability of the filler to support stresses transferred from the polymer matrix due to poor interfacial adhesion (Ismail et al., 2002; Ismail and Jaffri, 1999). Ke et al (2000) also state that as loading of the dispersed phase

increases, the effective cross-sectional area of continuous phase is reduced, and subsequently results in a decrease of tensile strength.

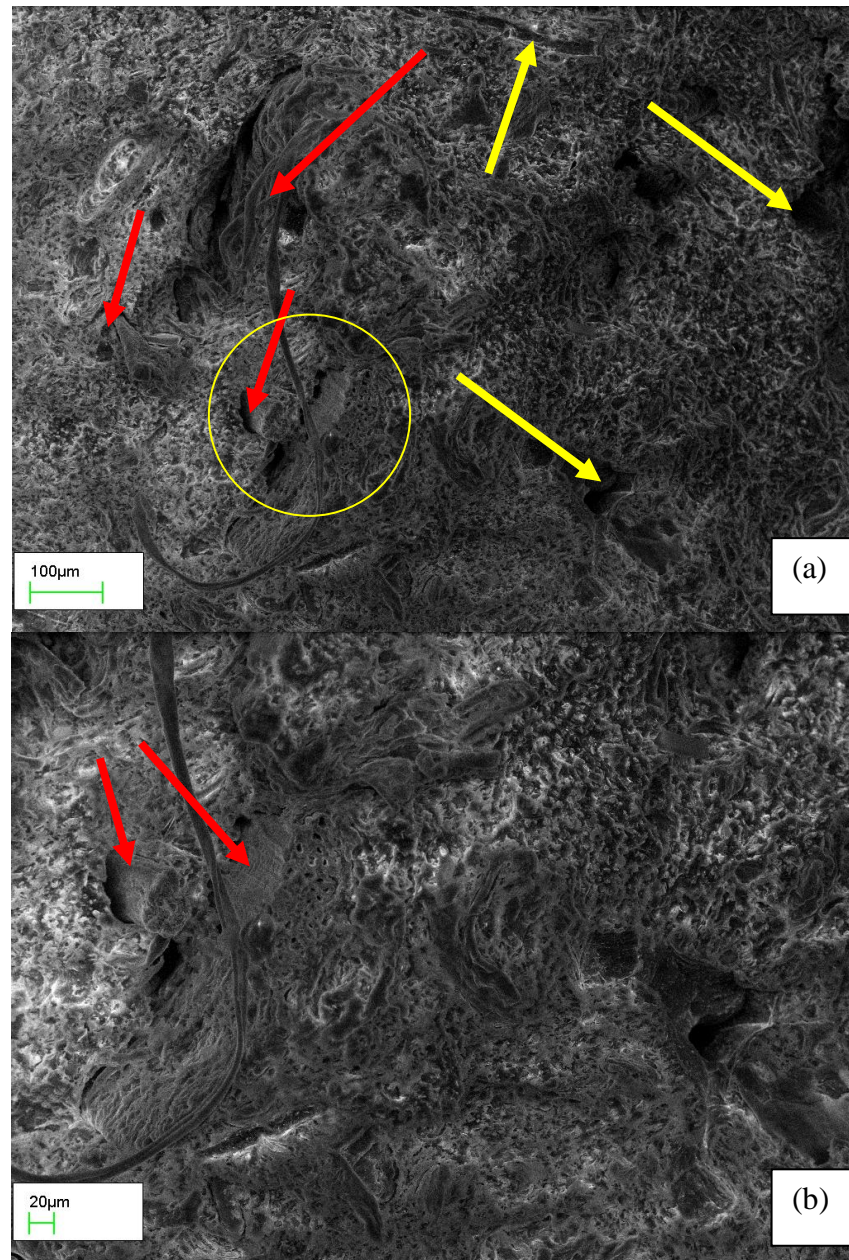


Figure 5.4: SEM image of tensile fracture surface of BF-8-20-a showing pull-out fibre or straw bundles (red arrows) and voids left behind (yellow arrows) the microstructure of Bioflex-straw composites (Figure 5.4b is the magnified image of the area in the yellow circle in Fig 5.4a).

Figure 5.5 compares behaviours of the materials in tensile tests. Bioflex is featured by ductile failure with clear yielding followed by a plastic plateau before the breaking point.

Despite of the enhancement in modulus, the failure mode changed significantly with addition of straw to typical brittle failure with cracks occurring immediately after yielding at an extremely low strain level. The breaking change of failure mode under tensile stress also indicates the poor adhesion between matrix and fibres. Straw is not able to take loading from matrix to sustain the plastic deformation, that's why the Bioflex-straw composites all crack in the elastic zone.

Therefore, it can be summarised that tensile strength rely on good adhesion to transfer load from the matrix to straw, while E-modulus is less sensitive to the interfacial bonding, as it is measured in the elastic period without any plastic deformation occurred. As long as adequate adhesion is sufficient to transfer stress to the straw, the reinforcement of straw on the matrix can be observed in terms of modulus.

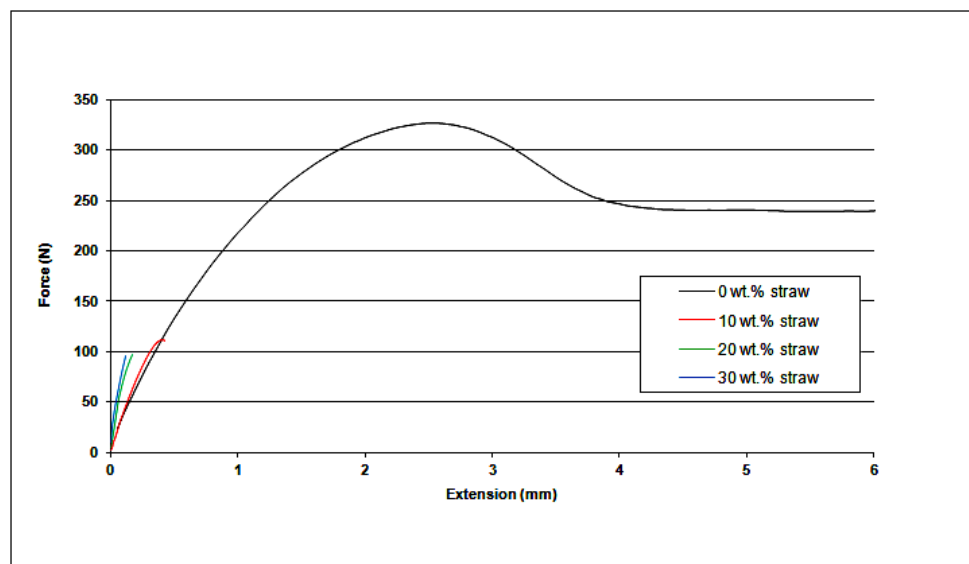


Figure 5.5: Comparison of the tensile test curves of the neat Bioflex F6510 and the bio composites.

5.1.1.2 Tear properties of the Bioflex-straw composites

Figure 5.6 presents the tear strength of the neat Bioflex 6510 and the Bioflex-straw composites with formulations described in Table 3.19, as described in section 5.1.1.1. The data of BF-8-30-a (30 wt. % straw content) is missing, because it was difficult to produce the tear sample due to its high brittleness. Compare with the neat Bioflex matrix (BF-a), the tear strength of composite formulation decreases dramatically by up to 46.2% at straw

content of 10 wt. % (BF-8-10-a) and to 58.5 % at 20 wt. % straw content (BF-8-20-a). Therefore, similar to tensile strength, tear strength of Bioflex-straw composites is reduced by increasing the straw content. This can be attributed to the low interfacial strength as discussed in section 5.1.1.1.

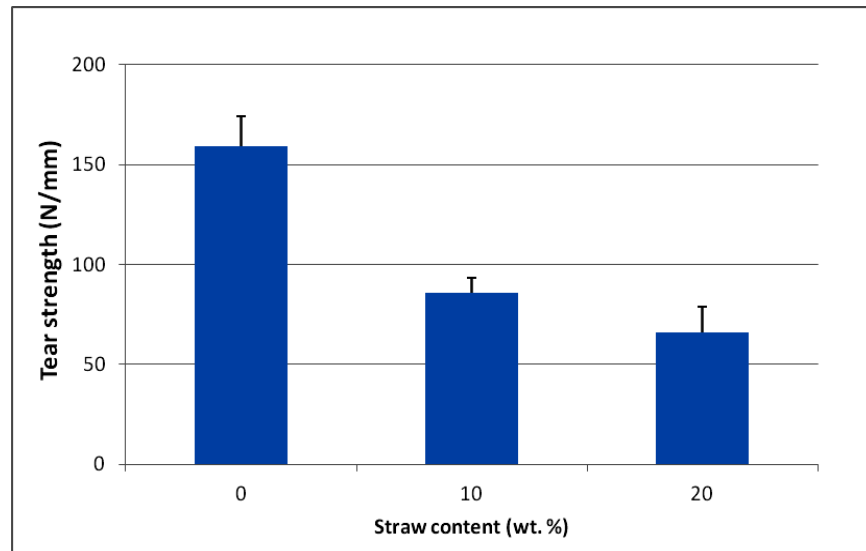


Figure 5.6: Tear strength of the neat Bioflex and the bio-composites containing 10 and 20 wt. % straw.

Figure 5.7 shows the force and displacement during tear tests. It indicates that the Bioflex-straw composites fail under shear in less ductile manner than the neat polymer. The more the straw content is in the composite system, the shorter the displacement at fracture failure. Therefore, the Bioflex-straw composites are easier to fail in tear mode than the biopolymer matrix itself. In addition, the Bioflex matrix presents higher tear modulus than the composites indicated by the slope of curves in Figure 5.7. More interfaces between matrix and straw fibres will not carry the shear loading with increased straw content as thus such reduction in tear resistance, which indicates a poor adhesion between the Bioflex matrix and straw fibres.

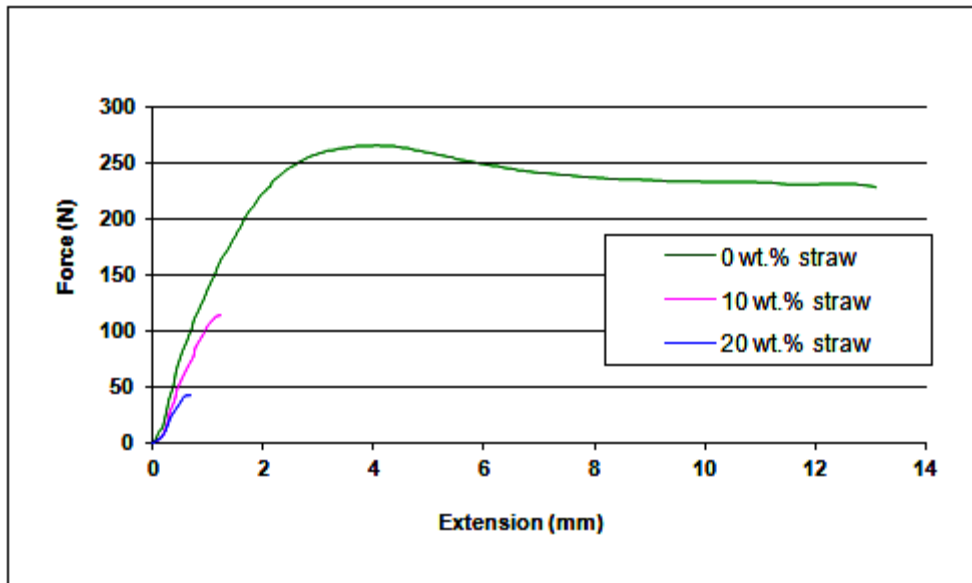


Figure 5.7: Tear test curves of the neat Bioflex and Bioflex-straw composites showing transition from ductile to more brittle tear with addition of straw.

5.1.1.3 Flexural and impact properties of the Bioflex-straw composites

As the neat Bioflex has comparable properties to the conventional used high density polyethylene and polypropylene in terms of strength and stiffness, it was selected as the matrix for to combine with straw for structural applications (e.g. extruded profiles) as a alternative to wood plastic composite for shorter service life (so that the used materials can be treated by biodegradation on sites of construction). The formulations used for preparation of the bar samples (as mentioned in section 3.2.2) are listed in Table 5.2.

Table 5.2: Description of formulations of Bioflex-straw composites for flexural and impact test.

	Bioflex F6510 (wt. %)	5B61R (wt. %)	5B61R in fine size (wt. %)	8B61R in fine size (wt. %)
BF-b	100			
BF-5-20-b	80	20		
BF-5F-20-b	80		20	
BF-8F-20-b	80			20
BF-5-40-b	60		40	
BF-5F-40-b	60			40

Straws involved in this section are prepared in different ways and their contents range from

20 to 40 wt. %. The main difference between the two fractionated straws (8B61R and 5B61R) is that the former used 8-barrel extruder and achieved finer fractionation of straw than the latter using 5-barrel extruder (Kang et al., 2009). 8B61R straw experienced longer residential time in the extrusion during the fractionation process than 5B61R. In order to investigate the influence of straw size on the mechanical properties of biocomposites, two sizes of 5B61R straw were blended into Bioflex F6510. Figure 5.8 to 5.10 illustrate the flexural properties and impact strength of the Bioflex-straw composites and the effects from straw content and different straw preparations are discussed below.

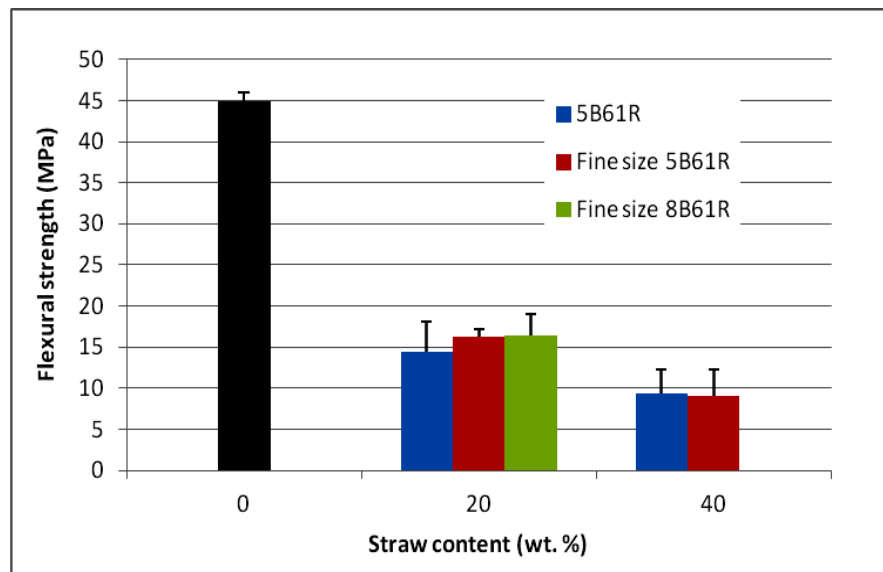


Figure 5.8: Flexural strength of Bioflex-straw composites (the black bar in the figure is the neat Bioflex matrix, blue, red and green bars stand for the composites containing 5B61R, fine 5B61R and fine 8B61R straw respectively).

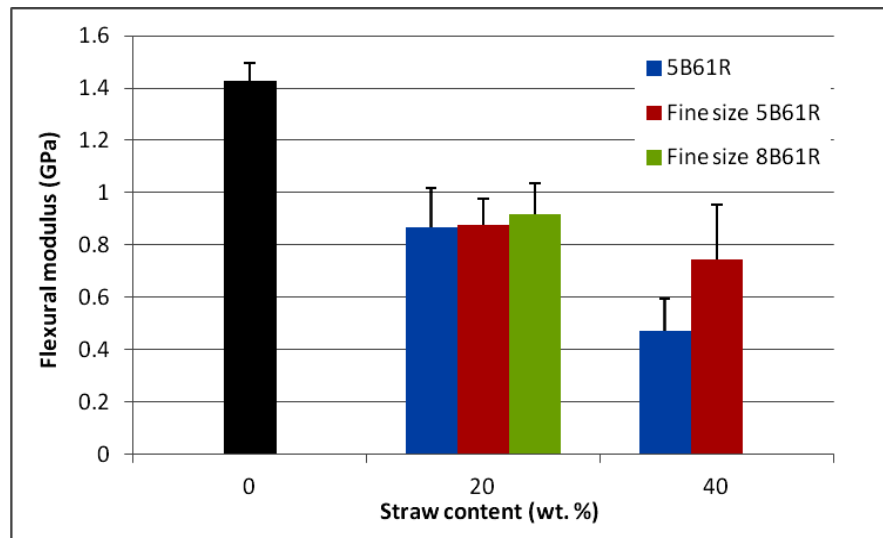


Figure 5.9: Flexural modulus of Bioflex-straw composites (the black bar in the figure is the neat Bioflex matrix, blue, red and green bars stand for the composites containing 5B61R, fine 5B61R and fine 8B61R straw respectively).

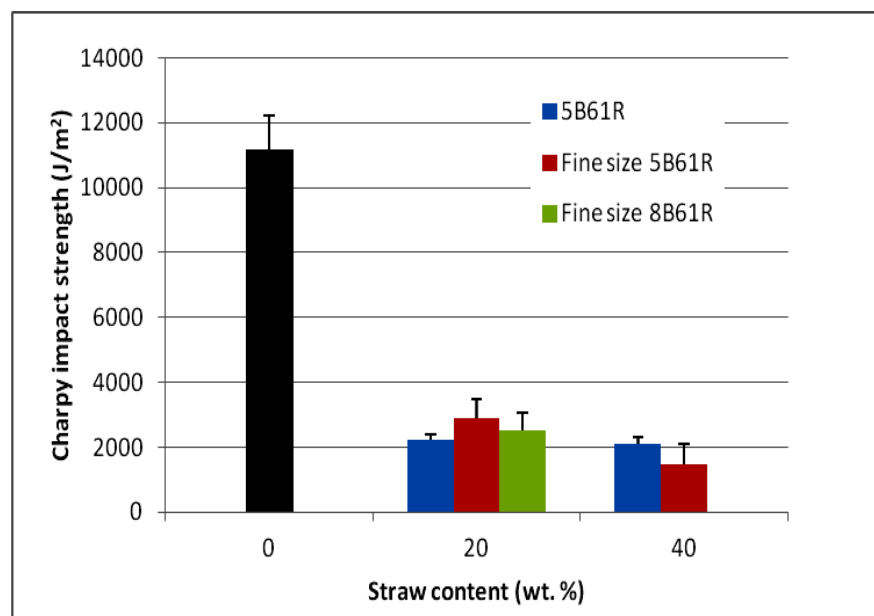


Figure 5.10: Charpy impact strength of Bioflex-straw composites (the black bar in the figure is the neat Bioflex matrix, blue, red and green bars stand for the composites containing 5B61R, fine 5B61R and fine 8B61R straw respectively).

a) Effects of straw content

In general, the Bioflex-straw composites showed lower flexural strength and modulus than the neat Bioflex polymer (Fig 5.8 and 5.9). As shown in Fig.5.8, adding straws at straw

content of 20 wt. % (BF-5-20-b, BF-5F-20-b and BF-8F-20-b) resulted in a reduction in flexural strength by about 65% (on average of the 3 formulations) while by around 80% at the straw content of 40 wt. % (BF-5-40-b and BF-5F-40-b).

From the Figure 5.9, the flexural modulus of the Bioflex-straw composites also decreased with the increase of straw content, which is different from trend in tensile modulus (Figure 5.1). At straw content of 20 wt. % (BF-5F-20-b, BF-5-20-b and BF-8F-20-b), the flexural modulus reduced by up to 30% from that of the neat Bioflex matrix (on average of the 3 formulations), while at the straw content of 40 wt. % (BF-5F-40-b and BF-5-40-b), the modulus reduces by around 48 or 67%, depending on the fibre treatment. Same as Figure 5.5 and 5.7 shown, the addition of straw increases the brittleness of composites, which can be proved in Figure 5.10. The impact strength of Bioflex dramatically drops down by adding straw and it decreases with the increase of straw content.

Straw in the extruded bars was supposed to align along the extrusion direction. Afterwards, the loading force applied to the testing bars is perpendicular to the direction of straw aligned. Therefore, the bending strength and modulus of straw presented in Table 5.1 can be used to predicate the property of the composites. It is shown that the flexural strength of fibre is even lower than the Bioflex matrix, which results in a reduction of flexural strength with straw added in. Meanwhile, the flexural modulus of straw is quite close or even lower than the flexural modulus of Bioflex matrix. Considering together with the poor interfacial adhesion between straw and Bioflex matrix, the flexural strength and modulus will definitely go down with the addition of straw.

b) Effects of straw preparation

Compare with the two composites using refined 8B61R and 5B61R straw at the same content of 20 wt. %, there is little difference in the flexural and impact properties, as shown in Figure 5.8, 5.9 and 5.10. As the Figures shown, straw size also presents limited influence on most of the mechanical properties of composites except the flexural modulus at high straw content. For instance in Figure 5.9, at straw content of 40 wt. %, the composites with refined 5B61R straw (BF-5F-40-b) showed a 30% improvement in flexural modulus over that with 5B61R straw (BF-5-40-b). This improvement can be attributed to the increase in refinement (Kang et al 2009), which results in a higher specific

surface area of the straw to increase interfacial interaction with the matrix. However, in comparison with the effect of straw content, the enhancement by straw refinement is limited.

5.1.1.4 Summary

Over all speaking, the addition of straw in Bioflex matrix does not make a dramatically enhancement in most of the mechanical properties, except tensile modulus. Compare to the strength and stiffness of the matrix and estimated data of wheat straw in the Table 5.1, straw is not acting as reinforcement but weaker filler mainly used to reduce the cost and retain the biodegradability at the expense of reduction of properties of the matrix. In addition, poor interfacial adhesion is also attributable to such reduction and may be improvement by straw surface treatment and adding external bonding agent.

5.1.2 Mechanical properties of Biolice-straw composites

The formulations used for preparation of the sheet samples of Biolice-straw composites (as mentioned in section 3.2.2) are listed in Table 5.3. Details of the formulations are shown in Table 3.19 in chapter 3, and their straw content ranges at 0 (BL-a), 10 (BL-8-10-a), 20 (BL-8-20-a) and 30 wt. % (BL-8-30-a) respectively. In order to investigate the effect of fractionation level on the properties of composites, raw straw without fractionation (Joanne and Stefanie's plastics website) was blended in Biolice matrix at 10 wt. %.

Table 5.3: Description of formulations of Biolice-straw composites for flexural and tear test

	Biolice 50C (wt. %)	CS (wt. %)	8B61R (wt. %)
BL-a	100		
BL-CS-10-a	90	10	
BF-8-10-a	90		10
BF-8-20-a	80		20
BF-8-30-a	70		30

5.1.2.1 Tensile properties of Biolice-straw composites

Figure 5.11, 5.12 and 5.14 illustrate the tensile strength, E-modulus and elongation at break of the Biolice-straw composites respectively. In comparison with the neat matrix Biolice50C (BL-a), the Biolice-straw composites showed improvement in E-modulus and decrease in tensile strength and elongation at break.

Figure 5.11 illustrates that the addition of straw into the Biolice matrix has resulted in significant improvement in E-modulus of the Biolice-straw composites which also increases with the straw content. In comparison with the neat Biolice, E-modulus of Biolice-straw composites increased by approximately 88%, 157% and 337% at straw contents (the 8-barrel refined) of 10, 20 and 30%, respectively. Straw with much higher E-modulus than neat Biolice matrix (27.19 MPa) is working as the reinforcement phase in Biolice-straw composite.

Fig 5.12 showed that addition of straw at all levels from 10-30 wt. % resulted in an overall decrease in tensile strength from the neat Biolice. However, the tensile strength of Biolice-straw composites increased with straw content. With the straw content increased from 10% to 30wt. % tensile strength was increased by 30%. In contrast with the Bioflex-straw system (section 5.1), the improvement of Biolice-straw composites in stiffness and strength with straw contents indicate much better interfacial adhesion between the straw and the matrix in the Biolice-straw system. Biolice 50C contains nearly 50 wt. % starch and as observed by Xia et al (2010), gelatinised starch in extrusion compounding with fractionated wheat straw form good interfacial adhesion. This is also supported by the intimate matrix-straw contact and layer of the matrix adhered to the straw fibre (giving rise to the surface roughness as indicate by the arrow in Figure. 5.13).

Mechanical properties of wheat straw cut from stems were tested by Hornsby et al (1997) and it was shown that the wheat had typical values of 3.6 GPa in elastic modulus and 49 MPa in tensile strength. Tensile strength and modulus of straw is higher than Biolice 50C polymer (Fig 5.11 and 5.12) and thus based on the normalised law of mixture for randomly dispersed short fibre composites, the strength of the system should be improved with the increase of fibre content (Mirbagheri, 2007) provided that good interfacial adhesion is

achieved. However, due to fibre damage during the refinement treatments, straw might have significant reduction in its properties than that without fractionation treatment (Kang et al., 2009).

The neat Biolice is a grade developed for film application and exhibits good ductility. It has an elongation at break of about 443%. As shown in Figure 5.14, addition of 10 wt. % of straw (BL-CS-10-a and BL-8-10-a) has dramatically reduced the ductility to around 30-35%. While at straw contents of 20 wt. % (BL-8-20-a) and 30 wt. % (BL-8-30-a), the elongation at break drop to 22% and 11%, respectively. Based on the law of mixture, straw as a relatively rigid and heterogeneous phase will definitely reduce the ductility of the neat Biolice matrix which is soft and ductile. In addition, straw located in the police matrix will be the initiation of defects, where the fracture starts from.

It is also interesting to note that at the same level of straw content of 10 wt. %, composites containing the chopped straw (BL-CS-10-a) exhibit higher modulus and strength but a slightly lower strain at break than that containing the refined straw (BL-8-10-a), as shown in Figure 5.12 and 5.13 and Fig 5.14. This may be attributable to straw damages in the fractionated straw (Kang et al., 2009). In addition, it should be noted that lignocelluloses leached out from straw during the fractionation process (Le Digabel and Av érous, 2006) may act as a modifier of the matrix thus the behaviour of the composites such as flow behaviour during moulding (Kang et al 2009).

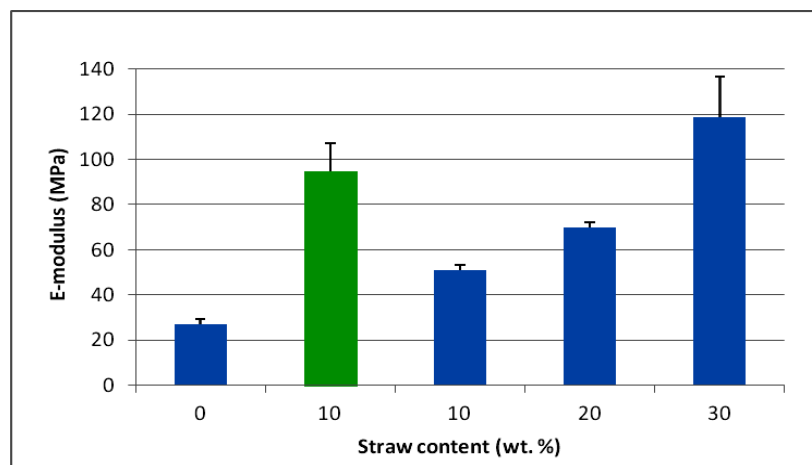


Figure 5.11: E-modulus of the Biolice-straw composites showing the increase of stiffness with increase of straw content (Green bar is composite filled with CS straw and the blue bars are composite filled with 8B61R straw).

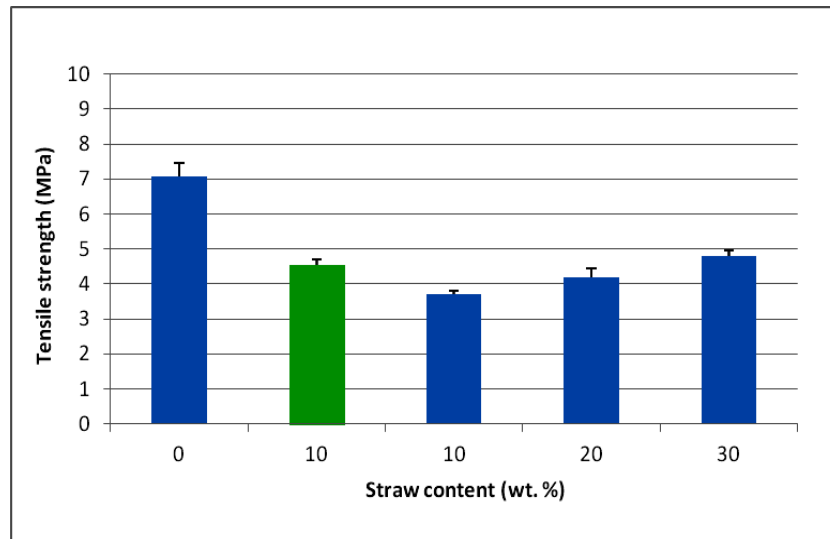


Figure 5.12: Tensile strength of the Biolice-straw composites showing a drop down of strength with the addition of straw (Green bar is composite filled with CS straw and the blue bars are composite filled with 8B61R straw).

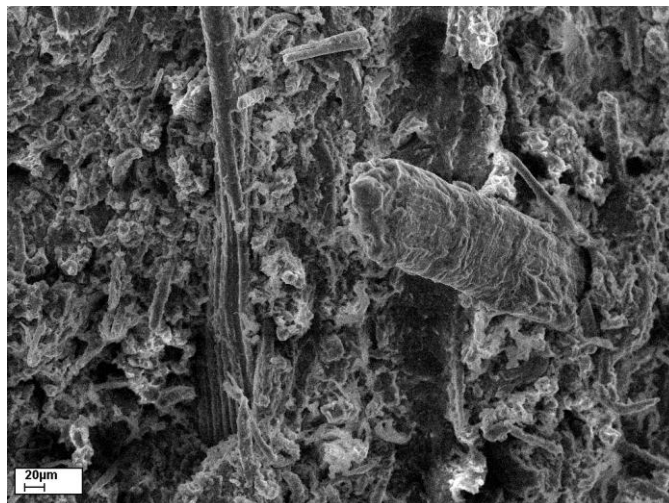


Figure 5.13: SEM image of tensile fracture surface of Biolice-straw composites containing 20 wt. % fractionated straw showing coating of matrix to the straw surface.

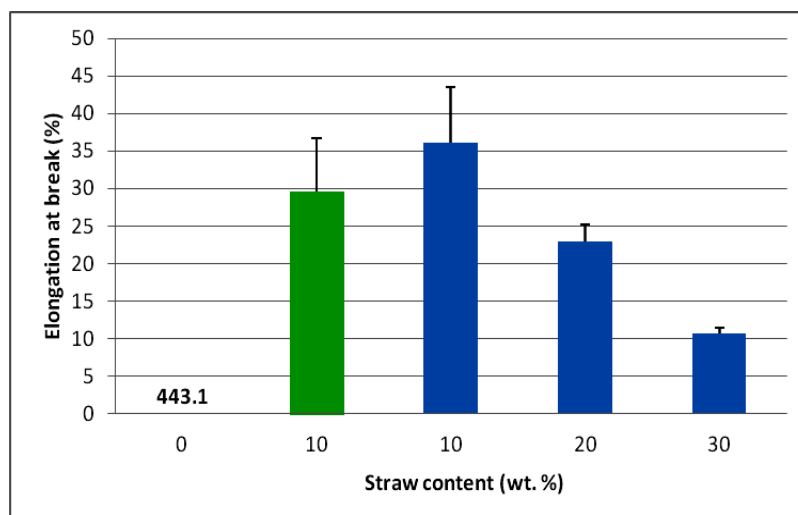


Figure 5.14: Elongation at break of the Bioice-straw composites showing the decrease trend in ductility with increase of straw content (Green bar is composite filled with CS straw and the blue bars are composite filled with 8B61R straw).

From the Figure 5.15, the tensile strength of Biolice (BL-a) constantly increases in a slow rate as it is elongated (up to an extension more than 120 mm). High ductility of Biolice gives it enough time to allow the polymer chains in the amorphous region oriented along the tension direction. The well aligned zones will form new crystal regions which are able sustain more energy. In this case, the enhancement of strength of Biolice 50C (BL-a) is carrying on during the long tension period. Straw fibres blended in reduce the ductility of Biolice 50C dramatically, so there is no longer enough time for the alignment of polymer chains occurring under the tension stress. So formulations with straw in are not able to obtain the extra improvement of strength during tensile test. This explains why the tensile strength has a significant drop from neat Biolice matrix while straw blended in.

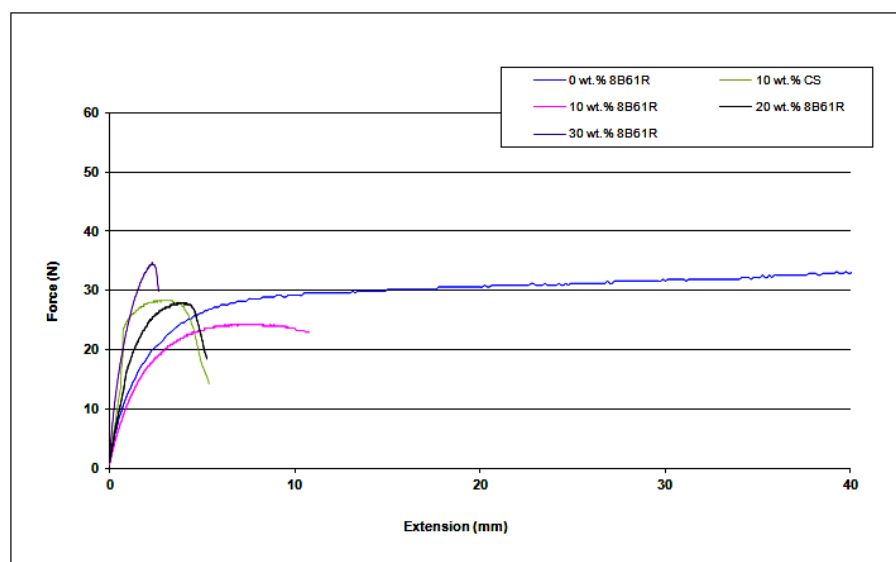


Figure 5.15: Comparison of tensile curves of the neat Biolic 50C (BL-a) and its composites.

5.1.2.2 Tear properties of the Biolice-straw composites

Figure 5.16 presents the tear strength of neat Biolice and the Biolice-straw composites. Compare with the neat Biolice matrix (BL-a), tear strength of the composites formulation decreases dramatically by up to 37, 63% and 56% at straw contents of 10 wt. % (BL-8-10-a), 20 wt. % (BL-8-20-a) and 30 wt. % (BL-8-30-a), respectively. Similar to tensile strength, at 10 wt. % straw content, composites containing the chopped straw (BL-CS-10-a) has a slightly higher tear strength than that containing the fractionated straw (BL-8-10-a), due to the fibre damage caused by fractionation in 8B61R

Figure 5.17 shows that the Biolice-straw composites have a much shorter extension at break compare with the matrix polymer and the more straw in the composite system, the shorter the extension at break is. Figure 5.17 also shows that the tear modulus of Biolice-straw composites increases with straw content, as indicated by the slope of the curves in the elastic region. This trend of modulus change of the Biolice-straw composites with straw content is rather different to that of the Bioflex-straw composites (see Figure 5.7). This can be seen as evidence of improved adhesion between in the Biolice-straw system under shear stress.

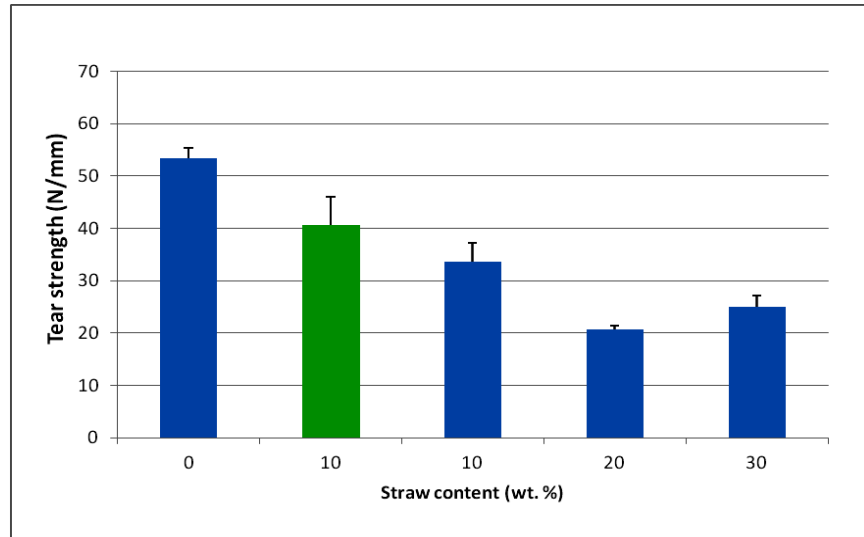


Figure 5.16: Tear strength of neat Biolice and the Biolice-straw composites, with green bar filled with CS straw without fractionation, and all others bars filled with 8B61R straw.

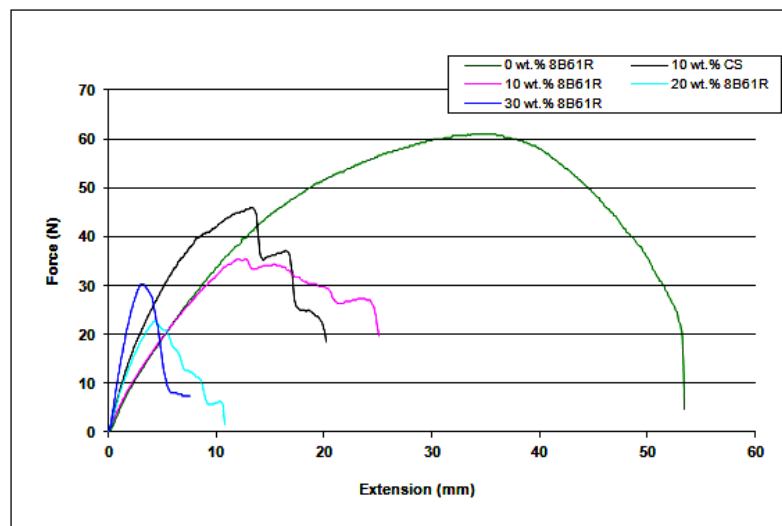


Figure 5.17: Tear curve of neat Biolice and the Biolice-straw composites showing the change of ductility and modulus with different straw content.

5.1.2.3 Summary

Generally, the addition of straw in Biolice matrix increases the stiffness of the composite significantly. Although there is a reduction of tensile strength from the neat Biolice matrix to the Biolice-straw composites, straw still works as reinforcement phase in the composite system because of the increase of tensile strength with the straw content. At the same time, inclusion of straw reduces the ductility and tear strength of Biolice matrix significantly. For

the Biolice-straw composite with high straw content, high stiffness and low ductility and tear strength is just the feature properties injection mouldable gun wads require, which make the gun wads easy to fracture into pieces.

5.2 Thermal properties of biocomposites

The thermal properties of biopolymer-straw composites are analysed in this section. The variations of chemico-physical behaviour of the composite structure caused by the inclusion of straw fibres can be investigated by TGA and DSC which yield useful information such as thermal degradation, glass transition, melting and crystallisation, which can be used to get a better understanding on the processing conditions and performances of the final products. Figure 5.18 and 5.19 present TGA curves of the two biocomposites systems while Figure 5.20 and 5.21 present that of the DSC analysis. Information summarised from the TGA and DSC analysis is given in Table 5.4.

From the TGA curves, Bioflex F6510 (Figure 5.18) presents single dip as it contains nearly 99 wt. % of PLA, while the double dips of Biolice 50C (Figure 5.19) due to its chemical composition containing Maize flour and Ecoflex in equal amount of 47 wt. %. From the two Figures, it is also found that the onset temperature of neat Bioflex and Biolice are around 350 and 250 °C respectively. As Mengeloglu and Karakus (2008) suggested, the onset degradation temperature of wheat straw is around 178 °C. This means the temperatures applied for the extrusion compounding have not degraded the composites. In addition, inclusion of straw reduces the onset degradation temperature of the biopolymers, as shown in Figure 5.18 and 5.19. Therefore, the first and second dips in the TGA curves of the two biopolymer-straw composites are due to lignocelluloses and cellulose respectively. Besides, for the Bioflex-straw composites, the onset degradation temperature was lower down by the increase of straw content, while the influence on Biolice-straw composites is not that significant. From the two figures, it is also found that most weight loss of the composites terminates at around 800 °C, so 900 °C is selected to calculate the percentage of the residue. As expected, the inorganic residue increases with the straw content as a result of the increase of ash content in straw.

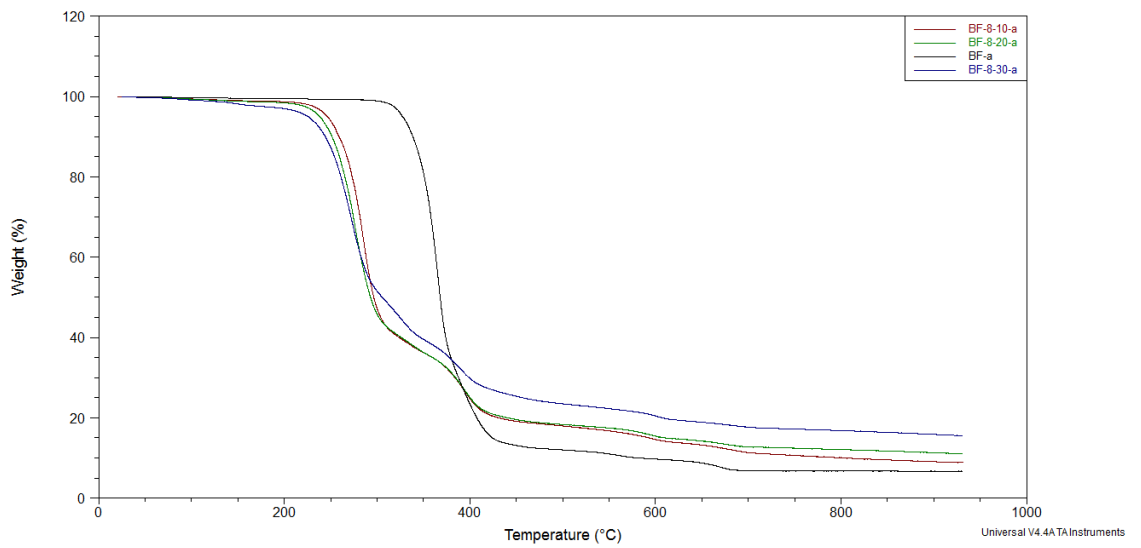


Figure 5.18: TGA curves of neat Bioflex F6510 and Bioflex-straw composites showing mass loss at given heating rate of 10 °C/min in Nitrogen.

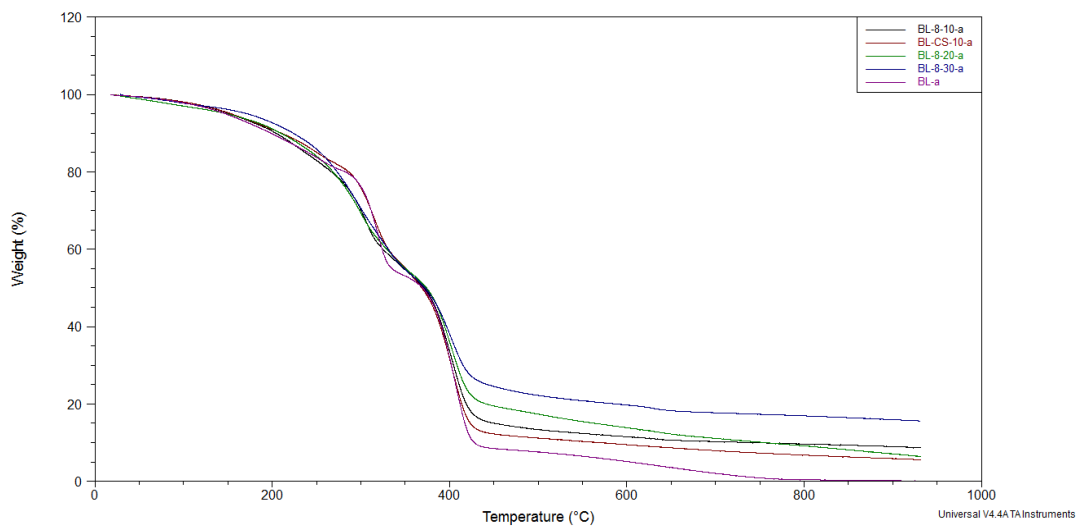


Figure 5.19: TGA curves of neat Biolice and the Biolice-straw composites showing mass loss at given heating rate of 10 °C/min in Nitrogen.

In Figure 5.20 and 5.21, DSC curves illustrate the thermal history of the two biopolymer-straw composites under one circle of heating and cooling. The typical features related to

glass transition (T_g), melting temperature (ASTM-D6400-99), melting endothermal (ΔH_m) and crystalline temperature (T_c) together with exothermal (ΔH_c) during crystallisation are presented in the figures and the parameters are derived from the software.

According to Figure 5.20, there is a presence of double peak in the curve of Biolice 50C (BL-a), which can be explained as a presence of two populations of crystals which melt at different temperatures (Bassett et al., 1988; Bell and Murayama, 1969). As mentioned in section 3.1.3, Biolice 50C is mainly made up of around 47 wt. % maize flour and 47 wt. % Ecoflex. This explains the double peak in the curves. But with the increase of straw content, the double peak feature of is diluted and becomes hardly recognisable at 30 wt. % straw (BL-8-30-a).

Biolice 50C has a glass transition temperature at $-31.40\text{ }^\circ\text{C}$, which results in its flexible behaviour at the ambient temperature. By adding straw fibres, the composites show a remarkable increase of the glass transition temperature up to around $40\text{-}41\text{ }^\circ\text{C}$ (as shown in Table 5.4). This explains the increase of rigidity and low ductility of the Biolice-straw composites tested at ambient temperature. But in the Bioflex-straw system, the glass transition temperature of the neat Bioflex is reduced by the presence of straw. This results in a reduction of shear stiffness with the increase in straw content, as observed in section 5.1.2.

Figure 5.20 shows an endothermic melt peak for Biolice 50C (BL-a) at $114.95\text{ }^\circ\text{C}$. Adding straw fibres resulted in remarkable shift to higher melt temperature together with the melting endotherm, which means higher temperature and energy is required to melt the composites when they are used as the feedstock of injection mouldable parts. While for Bioflex-straw system, the impact of straw fibres on melting temperature is not as significant.

Crystallinity (X_c) of the Biolice and Bioflex based composites is calculated using the Equation 5.1 and the results are presented in Table 5.4.

$$X_c = \frac{\Delta H_c}{\Delta H_m} \times 100 \quad (5.1)$$

It is found that with the addition of straw, the crystallinity is actually reduced in both Biolice-straw and Bioflex-straw systems. This has been observed by Avella et al (2000) and Tajvidi et al (2006) in their works where straw fibres were considered as a nucleating agent whom consequently increased the crystallisation rate during cooling from a molten state. They stated that straw fibres in biopolymers (like PLA and PHBV), increase the rate of crystallisation but not necessarily result in high crystallinity because straw restricts the molecular mobility of polymer chains. For both the Biolice and Bioflex composite systems, the decrease of crystallinity of the matrix with straw content results in a reduction in the mechanical properties of the matrices. This must also contribute to the reduction in strength, modulus and ductility as has been discussed in section 5.1 and 5.2 but difficult to quantify.

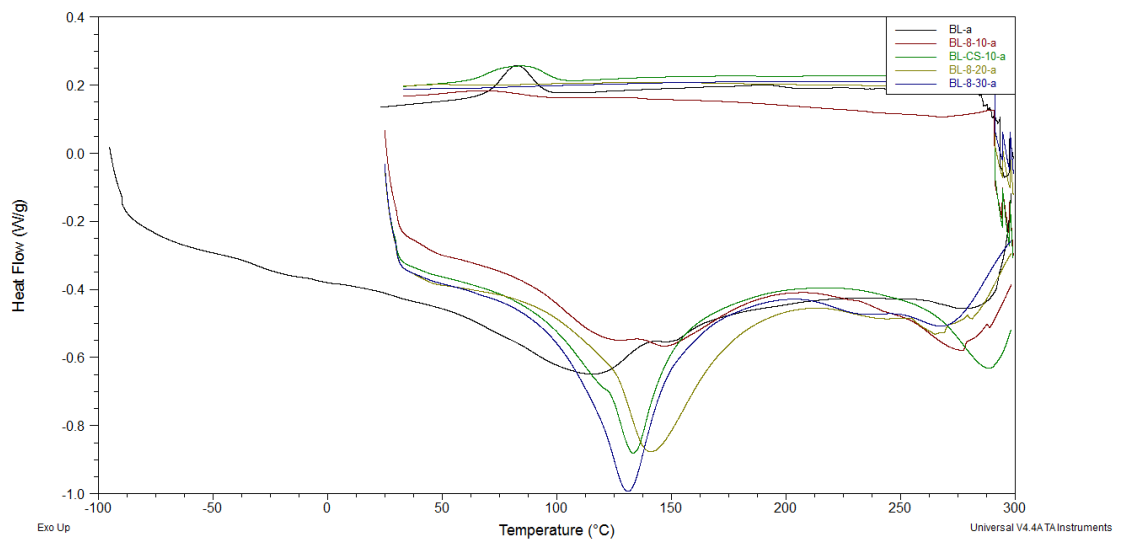


Figure 5.20: DSC curves of the neat Biolice 50C and the Biolice-straw composites.

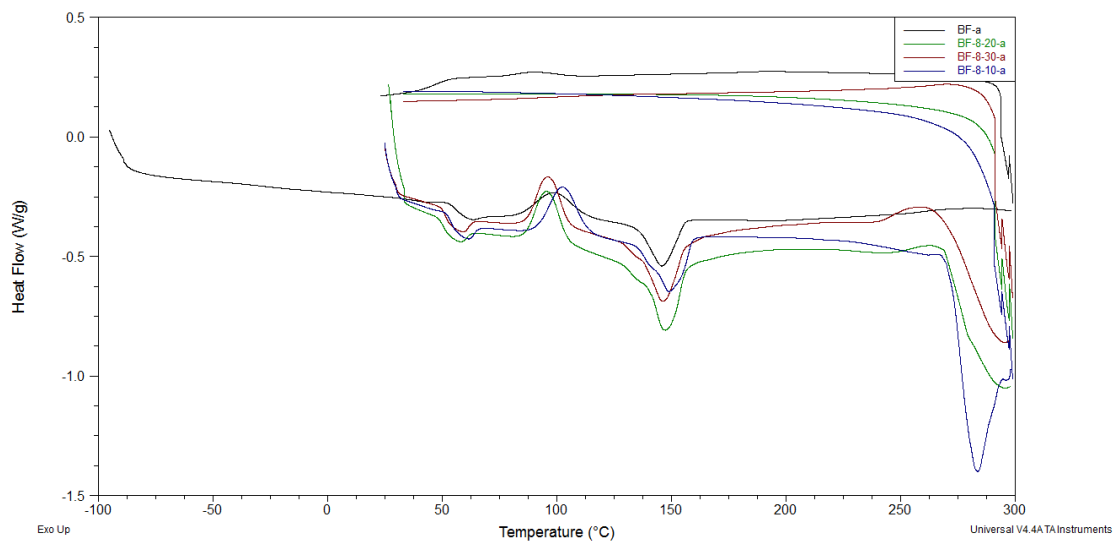


Figure 5.21: DSC curves of the neat Bioflex F6510 and Bioflex-straw composites.

Table 5.4: Thermal parameters of the neat matrix polymers and their biocomposites.

Sample ID	T_g (°C)	T_m (°C)/ T_m onset (°C)	ΔH_m (J/g)	Weight residue from TGA at 900 °C (%)	T_c (°C)	ΔH_c (J/g)	Crystallinity X_c
BL-a	-31.40	114.95/58.78	73.00	0.153	82.59	7.310	10.01
BL-CS-10-a	30.03	133.14/113.12	85.95	5.85	84.65	6.834	5.71
BL-8-10-a	41.96	146.22/90.61	55.66	8.95	68.61	3.180	7.95
BL-8-20-a	40.13	140.96/118.50	96.00	7.08	--*	--*	--*
BL-8-30-a	43.14	131.45/113.67	101.9	15.93	--*	--*	--*
BF-a	58.47	148.51/138.40	15.95	6.67	99.30	12.12	75.99
BF-8-10-a	53.93	149.26/138.77	17.54	9.07	102.48	14.66	83.58
BF-8-20-a	50.59	147.50/138.39	23.31	11.32	95.78	13.98	59.97
BF-8-30-a	51.79	146.66/135.33	22.27	15.86	96.32	14.06	63.13

*Note: there is no significant crystalline peak present in the DSC curves of BL-8-20 –a and BL-8-30-a.

5.3 Rheological behaviours of biocomposites

Figure 5.22 and 5.23 illustrates the rheological behaviours of the Biolice-straw and Bioflex-straw composites under their working temperature showing the influence of straw content and shear rate on the viscosity of the composites. Generally speaking, viscosity of

the biocomposites reduces as the shearing rate increase showing typical shear thinning behaviour.

By adding 10 wt. % straw, Viscosity of neat Bioflex matrix increases, while the straw content increases, the viscosity of the Bioflex-straw system continued to decrease, as shown in Figure 5.22. In the Biolice-straw system, as shown in Figure 5.23, the neat Biolice 50C matrix (BL-a) presents higher shearing melt viscosity and this desirable for film blowing as it is designed for. With addition of straw from 10 to 30 wt. %, there was firstly a decrease in shear viscosity, and then followed by an increase over that of the neat Biolice at the straw content of 30 wt. %. In addition, the Biolice composites containing straw without fractionation (Joanne and Stefanie's plastics website) appear very close viscosity to that containing 30 wt. % of fractionated straw (8B61R). Table 5.5 clearly shows the viscosity of the two biocomposites at the shear rate of 10 s^{-1} .

Table 5.5: Viscosity of BioFlex-straw and Biolice-straw composites at the shear rate of 10 s^{-1} .

Sample ID	Shear viscosity at the shear rate of 10 s^{-1} (pa.s)
BL-a	3837.24
BL-CS-10-a	4334.72
BL-8-10-a	2947.61
BL-8-20-a	3641.17
BL-8-30-a	4854.89
BF-a	455.67
BF-8-10-a	520.17
BF-8-20-a	259.93
BF-8-30-a	173.39

Two competing factors may effect on the viscosity of biocomposites:

- a) Viscosity normally increases with straw content as in most fibre filled systems, because straw absorbs polymer molecules on their surface which lower the effective volume loading of matrix and restrict molecule mobility (Barnes, 2003). The increase of the viscosity of Biolice-straw composites with the increase of straw

content is mainly caused by the polymer absorption, due to the good adhesion between straw and Biolice. While with poor adhesion between straw and Bioflex, the viscosity of Bioflex-straw composites reduces with the increase of straw content.

- b) Leach-out from the straw by the fractionation can plasticise the matrix and assisting the flow of fibres (Kang et al., 2009), which result in a decrease in viscosity. This explains why composite containing chopped straw (BL-CS-10-a) has higher viscosity than that with fractionated straw (BL-8-10-a) at 10 wt. % straw content, as shown in Table 5.5. In addition, as proposed by Nair et al (2000) and Pan et al (2009) formulations with chopped straw presents higher stiffness which will increase the friction between straw and tooling wall.
- c) Factor a may dominate factor be at a high straw concentration.

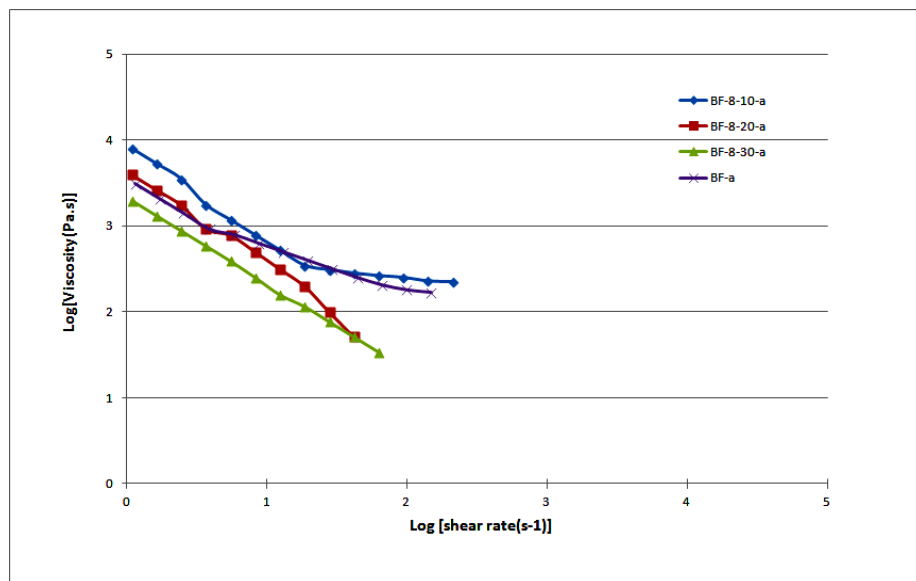


Figure 5.22: Shear viscosity as function of shear rate for the neat Bioflex and the Bioflex-straw composites at different straw content.

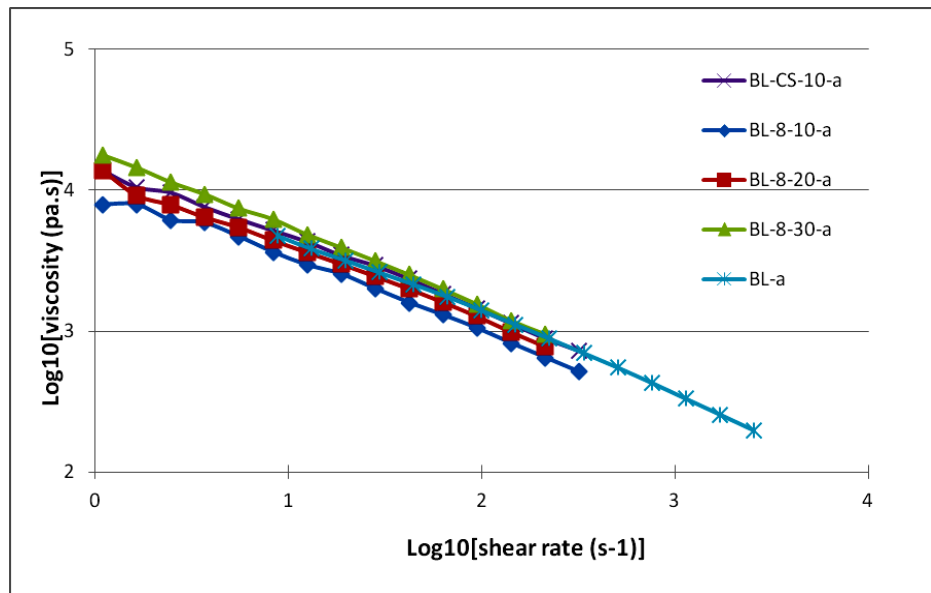


Figure 5.23: Shear viscosity as function of shear rate for the neat Biolice and the Biolice-straw composites at different straw content.

5.4 Summary

This chapter has analysed the newly developed biopolymer-straw composites on the required properties of the target applications. The study is mainly to investigate whether straw works as reinforcement phase in the biopolymer-straw composites apart from the function of cost reduction.

Overall, the addition of straw in Bioflex matrix has dramatically enhanced the stiffness, but reduced the tensile and tear strength at the meantime, which can be estimated data of wheat straw in the Table 5.1 by comparing to the strength and modulus of the matrix.

Straw, as a hollow cell structural material, performs better under tensile loading than the bending load. Its flexural properties can't reinforce the Bioflex matrix under the bending load.

Therefore, straw is not acting as reinforcement but weaker filler mainly used to reduce the cost and retain the biodegradability at the expense of reduction of properties of the matrix. In addition, poor interfacial adhesion between straw and Bioflex matrix proved in this study, is also attributable to such reduction and may be improvement by straw surface treatment and adding external bonding agent.

In Biolice-straw composites, the addition of straw increases the stiffness of the composite significantly. Although there is a decrease of tensile strength from the neat Biolice matrix to the Biolice-straw composites, straw still works as reinforcement phase in the composite system because of the increase of tensile strength with the straw content has been proven in Figure 5.12. The reduction of strength by adding straw into the neat Biolice is due to straw is an inhibitor which prevents the molecular movement and alignment of polymer chains under the tensile loading. At the same time, inclusion of straw reduces the ductility and tear strength of Biolice matrix significantly. For the Biolice-straw composite at high straw content, the high stiffness, low ductility and low tear strength are just the feature properties required by injection mouldable parts.

Through the investigation on the thermal behaviour of the biocomposites, a relationship between property and processing parameters are established. The thermal behaviour of the biocomposites has proved that the onset temperatures of degradation of the two biopolymers are reduced by the inclusion of straw. But it is observed in DSC that the melting temperature and melting endothermal increase with the addition of straw. So, the processing window (temperature range) is narrowed down with the inclusion of straw in the biopolymer-straw composites. In addition, the strength of biocomposites is also dependant on the crystallinity change with the addition of straw. It has represented that crystallinity decreases with the addition of straw, which indicates the reduction in strength.

The rheological behaviour of the biocomposites also reflects the relationship between structure and mechanical properties. With the increase of straw content, the increase of viscosity in Biolice-straw composites indicates the good interfacial adhesion between straw and Biolice matrix; while the decrease of viscosity in Bioflex-straw composites proves the poor adhesion between straw and Bioflex matrix.

Chapter 6 Binder-less straw boards

This chapter focuses on the analysis of binder-less straw boards. The effects of processing conditions, straw length and straw pre-treatment on structure and properties of the boards are discussed respectively. These include density and mechanical properties such as bending stiffness and strength and impact properties. The influences of processing conditions and straw treatment on the density of the binder-less straw boards are discussed in section 6.1. Section 6.2 deals with assessment of mechanical properties of binder-less straw boards and describe how flexural and impact properties of binder-less straw boards may be manipulated by controlling processing parameters, straw length and straw pre-treatment, respectively. The microstructure and the mechanisms of internal bonding of binder-less straw board are investigated in Section 6.3. Section 6.4 preliminarily evaluates the performances of binder-less straw boards in industrial practice and the main academic outcomes are summarised in section 6.5.

6.1 Density

The binder-less straw boards are potentially applicable as supporting components in furniture, as mentioned in section 3.2.3. Therefore, density is a factor that effects on the weight of the product and the cost of transportation. Figure 6.1 shows the density of the straw boards from the untreated straw with an average length of 10.9 mm under different processing conditions (details of the samples are shown in Table 6.1). The average values range from 1.05 to 1.28 g/cm³ and are dependent on the compression temperature and pressure. Generally speaking, an increase on either compression temperature or pressure will result in an increase in density of the straw boards.

Table 6.1: Binder-less straw boards produced under different processing conditions.

	120 °C (EN 13432)	140 °C (EN 13432)	160 °C (EN 13432)
16 MPa (A)	MA1	MA2	MA3
32 MPa (B)	MB1	MB2	MB3
48 MPa (C)	MC1	MC2	MC3

Note: M means the medium straw length of 10.9 mm; A, B, and C stand for the applied pressure of 16, 32, and 48 MPa respectively; 1, 2, and 3 represent the temperature of 120, 140 and 160 °C.

It also shows that under pressure of 16MPa, the density increases gradually by approximately 12.3% from 120 °C to 160 °C (MA1 to MA3), while under 48MPa, increases up to 16% (MC1 to MC3) under the same temperature increase. When the temperature is fixed at 120 °C, the density slightly increases up to 6% when the pressure goes up from 16 to 48 MPa (MA1 to MC1), but at 160 °C, density increases up to 13% from 16 to 48 MPa (MA3 to MC3). It suggests that an increase of temperature and pressure improves the compressibility of straw. Comparing the percentage change in density above, the density increases more significantly by increasing temperature than pressure.

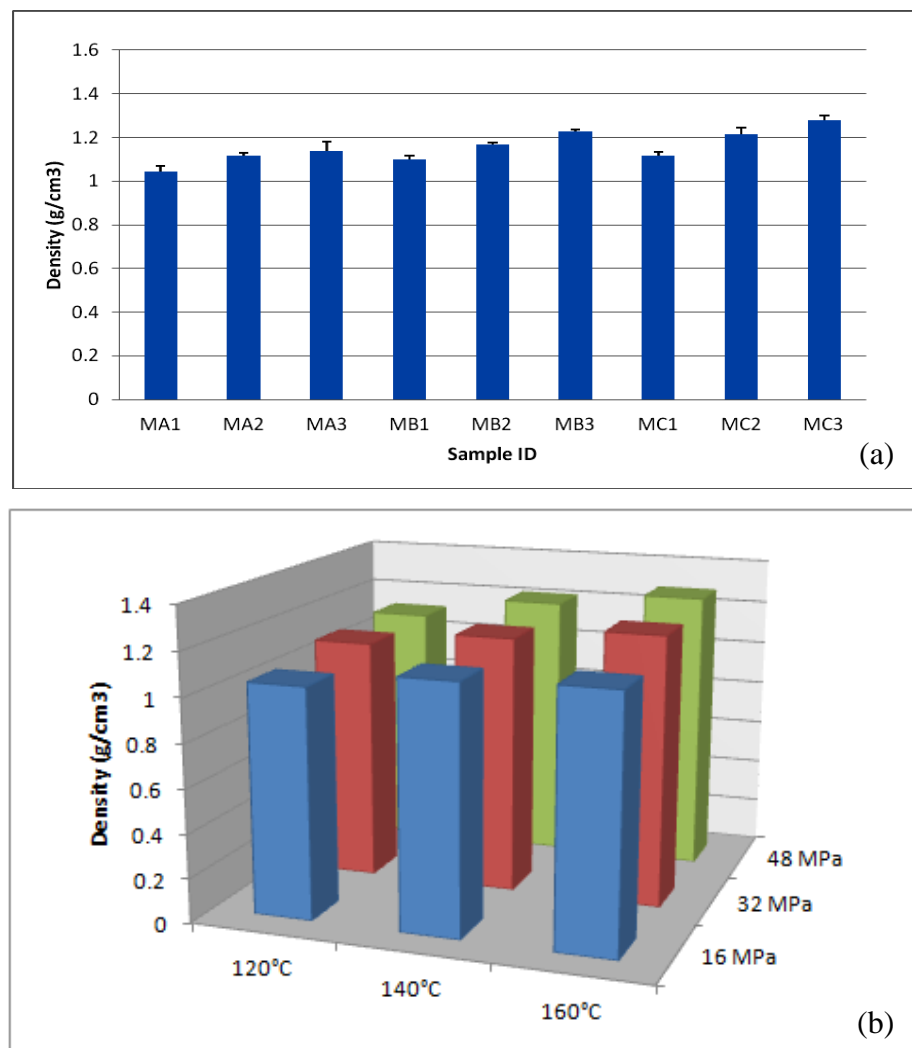


Figure 6.1: Density of straw boards made from untreated straw in the length of 10.9 mm under different compression conditions. (a: version in 2-D and b: version in 3-D)

The effect of straw length and straw pre-treatment (details of samples as shown in Table

6.2) on density is also investigated under pressure of 32MPa and at 140 °C, as illustrated in Figure 6.2. Without any chemical pre-treatment, when the average straw length increased from 0.93mm (FB2) to 10.9mm (MB2), the density reduced by 5.6%. If the straw length further increased to 29.8mm (CB2), it reduced by 12% compared to FB2 board. Under the same condition, the straw boards made with 6% NaOH pre-treated straw (TMB2) is compared with the same average length but untreated straw (MB2). There is a significant increase by approximately 13.6% presenting the highest density (1.33 g/cm³) over the other ones (as shown in Figure 6.2).

Table 6.2: Binder-less straw boards produced with different types of straw.

	FB2	MB2	CB2	TMB2
Average fibre length (mm)	0.93	10.9	29.8	10.9
6% NaOH Treatment	None	None	None	Pre-treated

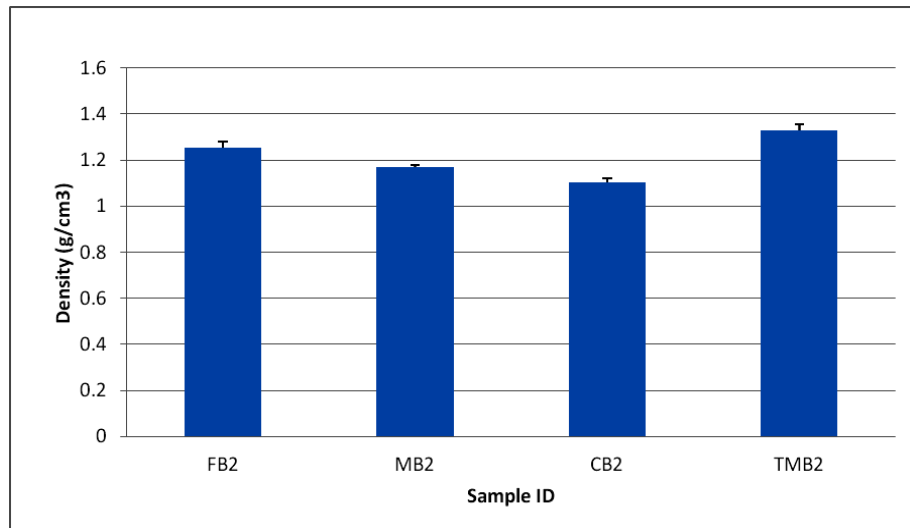


Figure 6.2: Density of straw boards compressed under 32 MPa at 140 °C using different types of straw, as shown in Table 6.2.

Density reflects packing efficiency of straw under the combined temperature and pressure. The factors influencing the packing efficiency are the geometric aspects and compressibility of straws. In the processing theory of ceramic, geometric aspects of a particle include particle shape, particle size distribution, particle arrangement, particle

surface roughness and degree of agglomeration (Mutsuddy and Ford, 1995).

Compressibility of straw means its ability to deform under pressure and heat. Initially, the cell structure of straw makes it compressible under pressure, which results in a density increase with pressure.

The aspect ratio of a particle is one way to represent its particle shape, which defined by Mutsuddy and Ford (1995) as the quotient of the larger dimension (fibre length or platelet diameter) and the smaller dimension (fibre diameter or platelet thickness).

Binder-less straw board is actually a fibre composite system and aspect ratio effects on the mechanical properties and packing efficiency significantly (T.-Y. Liu et al., 2004). Long straws with high aspect ratio restrict initial packing of straw and give rise to lower bulk density before pressure is applied. When pressurised, interlocking of long straws restricts their mobility and give rise to lower packing efficiency and density. This explains why board density decreases with the increase of the straw length.

In Kang et al., (2009), boards made from NaOH solution pre-treated and extrusion fractionated straw were compression moulded at 160 °C and 48MPa. The results are summarised in Figure 6.3. Compared with MC3 (in Figure 6.1 - without NaOH pre-treatment and extrusion fractionation but compression moulded at the same conditions), all boards have significantly higher densities which increase with number of extrusion runs the straw experienced (or residence time) and thus the degree of fractionation.

Kang et al., (2009) analysed the degree of straw fractionation via measuring their change in diameter and length. Fractionation of straw leads to better packing efficiency and flexibility of the straw fibre and together with more uniform distribution of the NaOH soluble constituents (the natural resin leached out) enhanced compressibility of the straw and hence able to produce higher density. In addition, fractionation has also resulted in the refinement and the liberation of straw fibres from the native straw structure, so it makes the length distribution of straw fibres wider. Following the discussion of geometrical aspect above, wider length distribution results in high packaging efficiency when short straws fill gaps between long ones

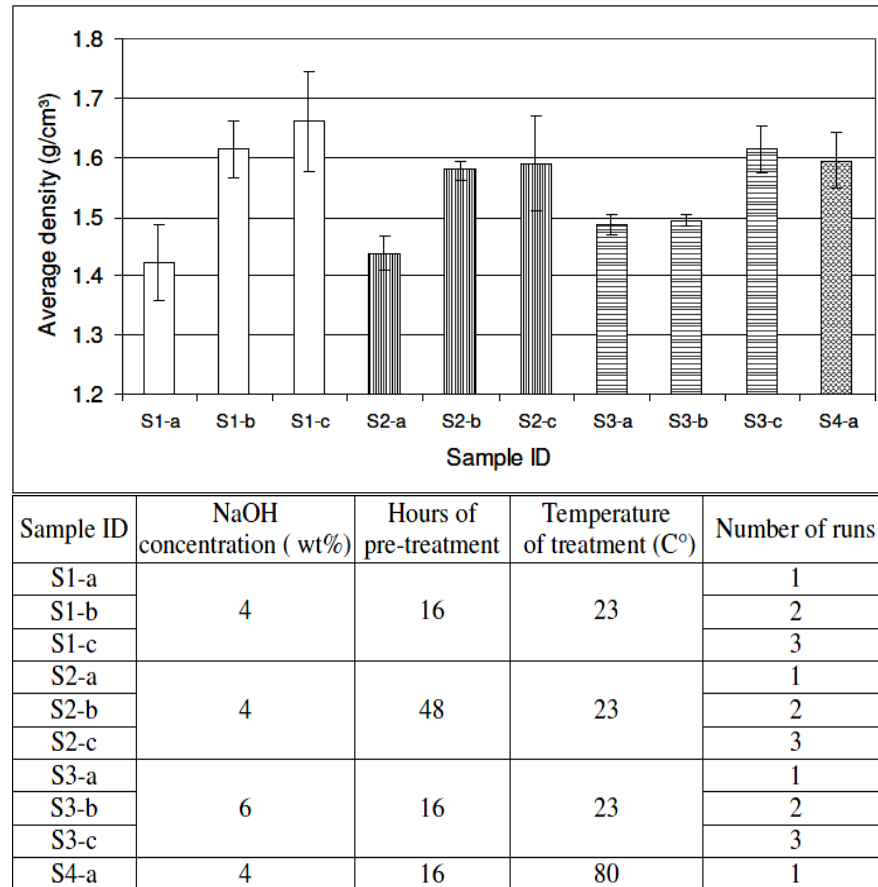


Figure 6.3: The averaged density of compression-moulded straw boards at 160 °C and 48MPa from extrusion fractionated straws with the treatment conditions shown in the table (Kang et al., 2009). Numer of runs represents number of repeated extrusion and thus residence time.

Straw used to produce TMB2 boards in Table 6.2 were chemically pre-treated only by using 6% NaOH solution. Aqueous NaOH solution pre-treatment of straw is derived from the soda pulping process in traditional paper industry. It is suggested that the cell wall structure of straw is weakened by the treatment when lignin and hemicelluloses are leached out from the native straw structure (Hornsby, et al., 1997; Kristensen et al., 2008; Ramalho Ribeiro, 1991). The lignin and hemicelluloses complex has thermoplastic characteristic which facilitates flow of straw bundles and leads to the improved compressibility (Biocomp, 2008). This is indicated, as shown in Figure 6.4, by thin flashes of materials squeezed from the die during compression moulding of TMB2 boards (from NaOH pre-treated straw) in comparison with absence of such flash in MB2 (from straw without NaOH pre-treatment). Furthermore, unlike the MB2 boards, straw bundles are well

embedded in the dark brown leach-out phase, giving rise to a shining surface finish.



Figure 6.4: Comparison of the appearance of compression moulded straw boards showing the effect of leach-out phase in improved flow (by the flash in 6.4b) and inter-straw bonding. a) MB2 from straw without NaOH pre-treatment; b) TMB2 from straw with 6% NaOH pre-treatment.

6.2 Mechanical properties of binder-less straw boards

6.2.1 Flexural property

6.2.1.1 Effect of processing conditions

The flexural properties of straw boards under different processing conditions are presented in Figure 6.5 and 6.6. According to the figures, flexural properties of straw board are found very sensitive to the compression parameters. The results of flexural modulus are shown in Figure 6.5. The values range from 0.6 to 2.5 GPa and are heavily dependent upon the pressure and temperature.

When temperature increases from 120 °C to 160 °C, flexural modulus increases by 23%, 98%, and 246% under pressure of 16MPa (MA1 to MA3), 32MPa (MB1 to MB3), and

48MPa (MC1 to MC3), respectively. At lower temperature of 120 °C (MA1 to MC1), there is a slight decrease in the modulus by 28% with increase of pressure from 16 to 48 MPa. While at 140 °C (MA2 to MC2) and 160 °C (MA3 to MC3), the flexural modulus has increased by 54% and 101% respectively, when a pressure increase in the same range. This represents that the effect of temperature on flexural modulus is more efficient than increasing the loading pressure.

Stelte et al (2011) addressed the softening temperature of lignin and hemicelluloses were at 53 °C and 2 °C respectively for moist wheat straw. The softening temperatures of the two natural resins in straw are actually the onset temperature and lower temperature like 120 °C is suggested not be able to provide enough mobility to the natural resins. At 120 °C, deformation of the boards is more elastic under pressure, and the higher pressure applied, the more elastic recovery involved in the board structure, which results in the detachment of straws. This explains why there is a decrease of flexural modulus at 120 °C with the increase of pressure.

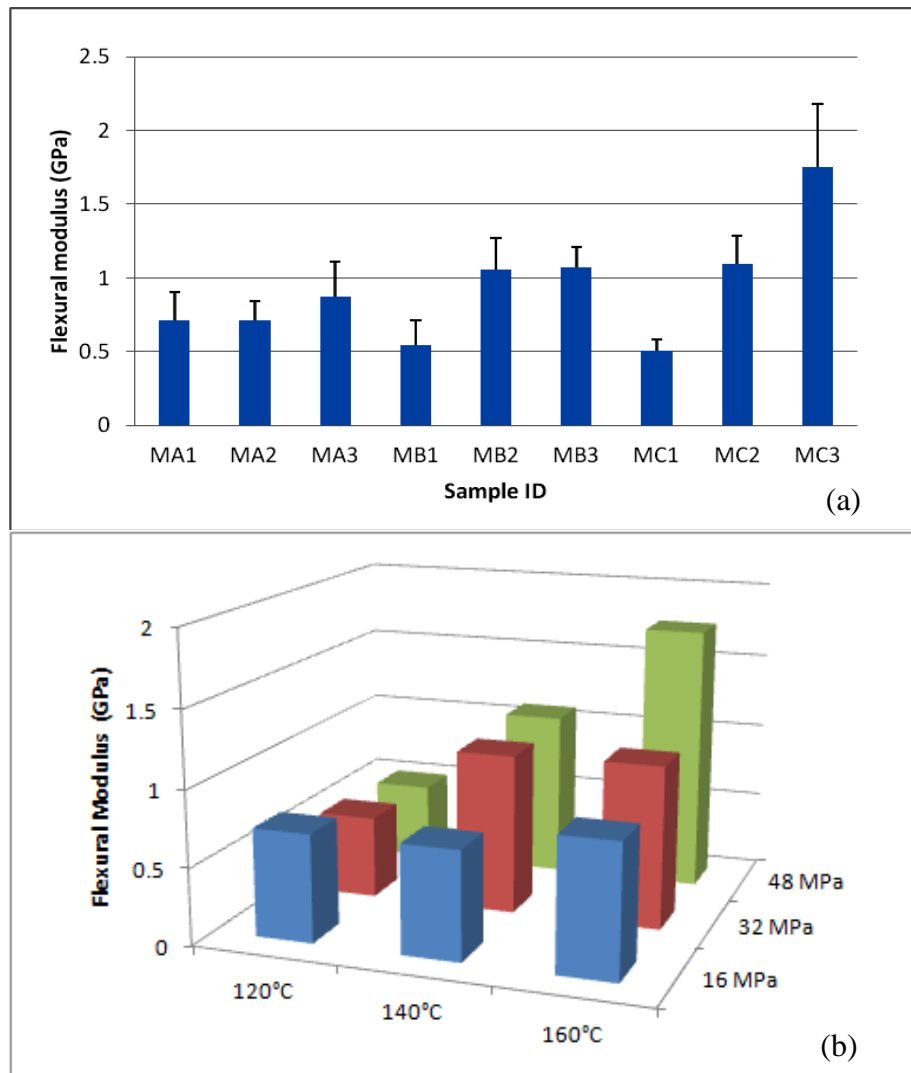


Figure 6.5: Flexural modulus of straw boards (made from untreated straw with the length of 10.9 mm) as function of compression moulding temperature and pressure. (a: version in 2-D and b: version in 3-D)

Figure 6.6 presents the flexural strength of the straw boards under different processing conditions. The average strength values range from 5MPa to 15MPa. When temperature increases from 120 °C to 160 °C, the strength increases by 63%, 118% and 181% under pressure of 16MPa (MA1 to MA3), 32MPa (MA1 to MA3) and 48MPa (MA1 to MA3), respectively. However, at temperature of 120 °C, there is little change of strength with pressure, while at 140 °C and 160 °C, the strength has increased by 43% and 72% respectively, when pressure increases from 16 to 48MPa. This indicates that temperature has a more significant effect on the strength than pressure, which is similar to the trend as modulus in Figure 6.5. Following the discussion on flexural modulus above, the effect of

pressure on strength is not active until the temperature is sufficient to mobilise the leach out.

According to Figure 6.5 and 6.6, the trends of dependence of strength and modulus on the processing parameters are similar. Comparing the changing rates, it is also found that temperature has a more significant influence than pressure on the value of modulus and strength.

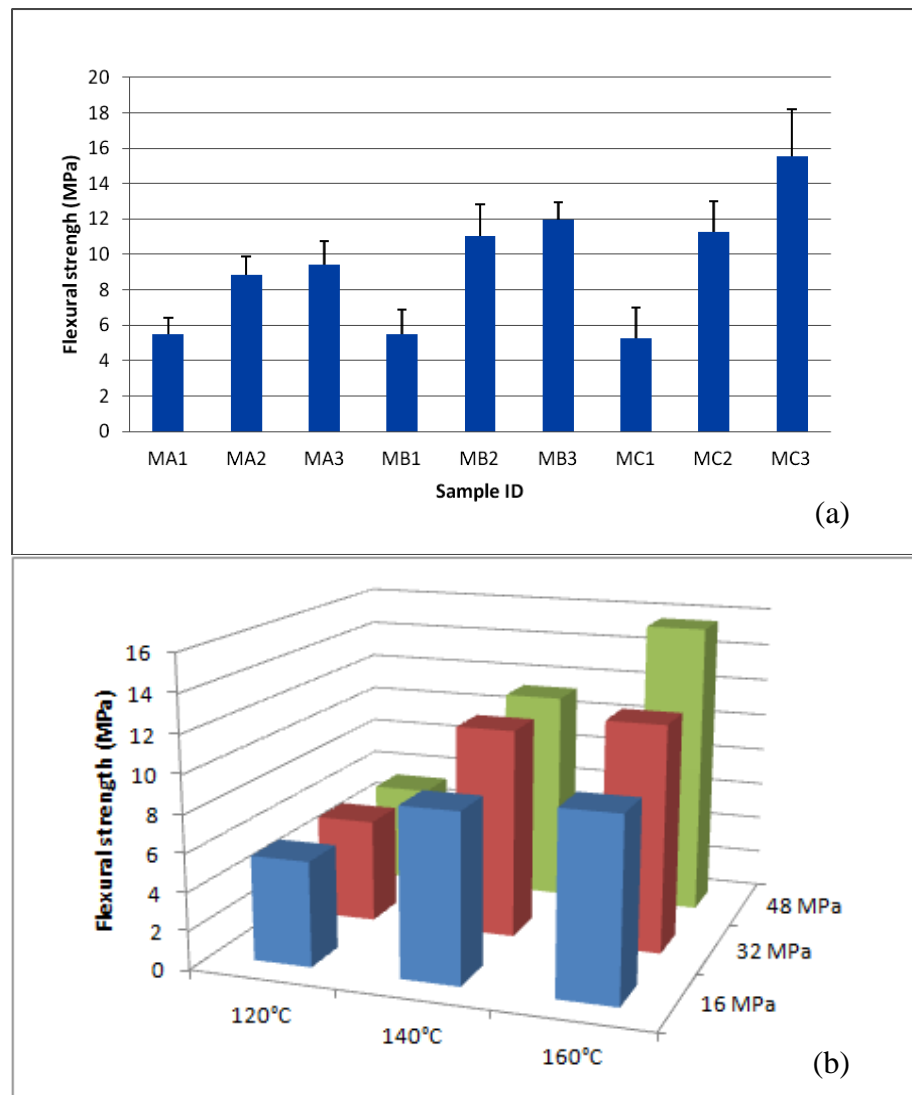


Figure 6.6: Flexural strength of straw boards (made from untreated straw with an average length of 10.9 mm) as a function of compression moulding pressure and temperature. (a: version in 2-D and b: version in 3-D)

6.2.1.2 Influence of straw size and pre-treatment

Figure 6.7 and 6.8 present flexural properties of straw boards made with straw various in size and treatment. Figure 6.7 shows that among the different straw sizes, the FB2 board made from finest straw (0.93 mm) has the highest average modulus of about 1.75GPa, while MB2 and CB2 boards made from the medium straw (10.9 mm) and long straw (29.8 mm) have lower average value of 1.05 and 1.15GPa, respectively. It suggests that under a given combination of pressure and temperature, shorter straw enables higher packing efficiency (reflected by higher density) which in turn lead to more effective load transfer between straws and thus higher modulus. In comparison with the modulus of MB2 boards (1.05 GPa), the TMB2 boards made from NaOH pre-treated straw are more than doubled the modulus to 2.4 GPa! This can be attributed to the enhanced packing efficiency reflected by high density achieved as discussed earlier in section 6.1.

Figure 6.8, in comparison with Figure 6.7, illustrates similar but much less dramatic trend of influence from the straw length and treatment on modulus. The long straw (CB2) resulted in lowest flexural strength as in modulus. But NaOH pre-treatment (TMB2) did not seem to improve flexural strength (compared with MB2 boards). This indicates that although the straw length and the NaOH pre-treatment of straw have significant influence on flexural modulus, their effects on the strength of straw boards is rather limited.

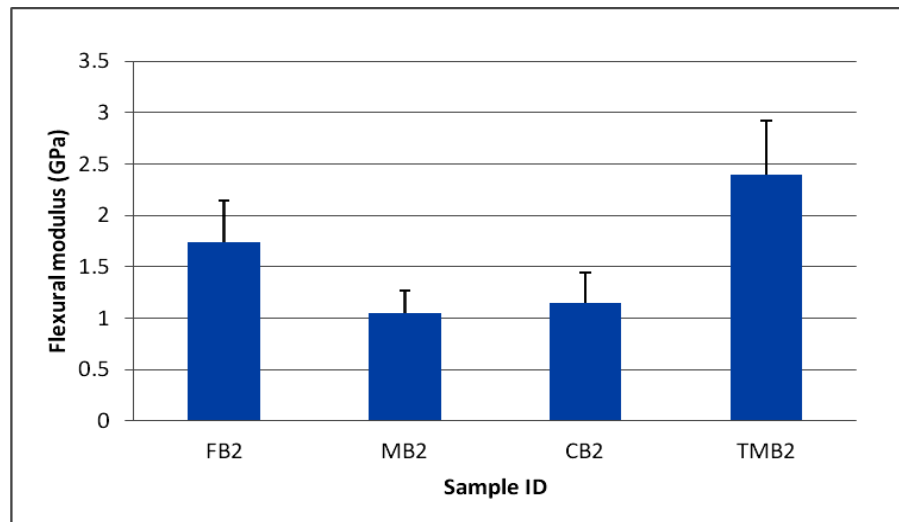


Figure 6.7: Flexural modulus of straw boards compression moulded (at 140 °C and 32 MPa) from straw with different average length and pre-treatment: FB2, MB2 and CB2-Boards made from untreated straw with 0.93, 10.9 and 29.8 mm average length; TMB2-Boards made from 6% NaOH treated straw with an average length of 10.9 mm.

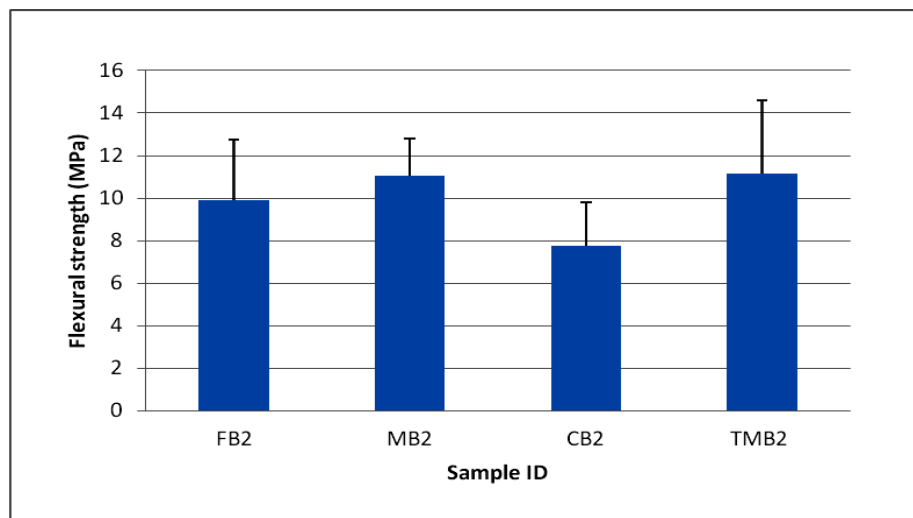


Figure 6.8: Flexural strength of straw boards compression moulded (at 140 °C and 32 MPa) from straw with different average length and pre-treatment: FB2, MB2 and CB2-Boards made from untreated straw with 0.93, 10.9 and 29.8 mm average length; TMB2-Boards made from 6% NaOH treated straw with an average length of 10.9 mm.

Kang et al (2009) stated that the NaOH pre-treatment was to soften the lignocelluloses and break the internal bonding between cellulose and lignocelluloses, which assists releasing straw fibres in the subsequent mechanical fractionation in the extruder. However,

high level of fractionation of NaOH pre-treated straw generally lead to reduce of the strength of straw boards because of the shortening and damage to the fibres during fractionation. In this research, straw was only NaOH pre-treated without any mechanical fractionation, thus there should be no fibre shortening and damage. This is supported by observation that strength of TMB2 boards remained at a similar level as the MB2 boards.

Indeed, as shown in Figure 6.9, in comparison with straw as-received (Figure 6.9a), morphology of straw with just NaOH pre-treatment (Figure 6.9b) remain almost unchanged, unlike the extrusion fractionated straw (5B61R, see Table 3.6 for details) in Figure 6.9c which has largely lost the original shape and straw bundles have been ruptured to expose finer fibres as pointed by the red arrow.

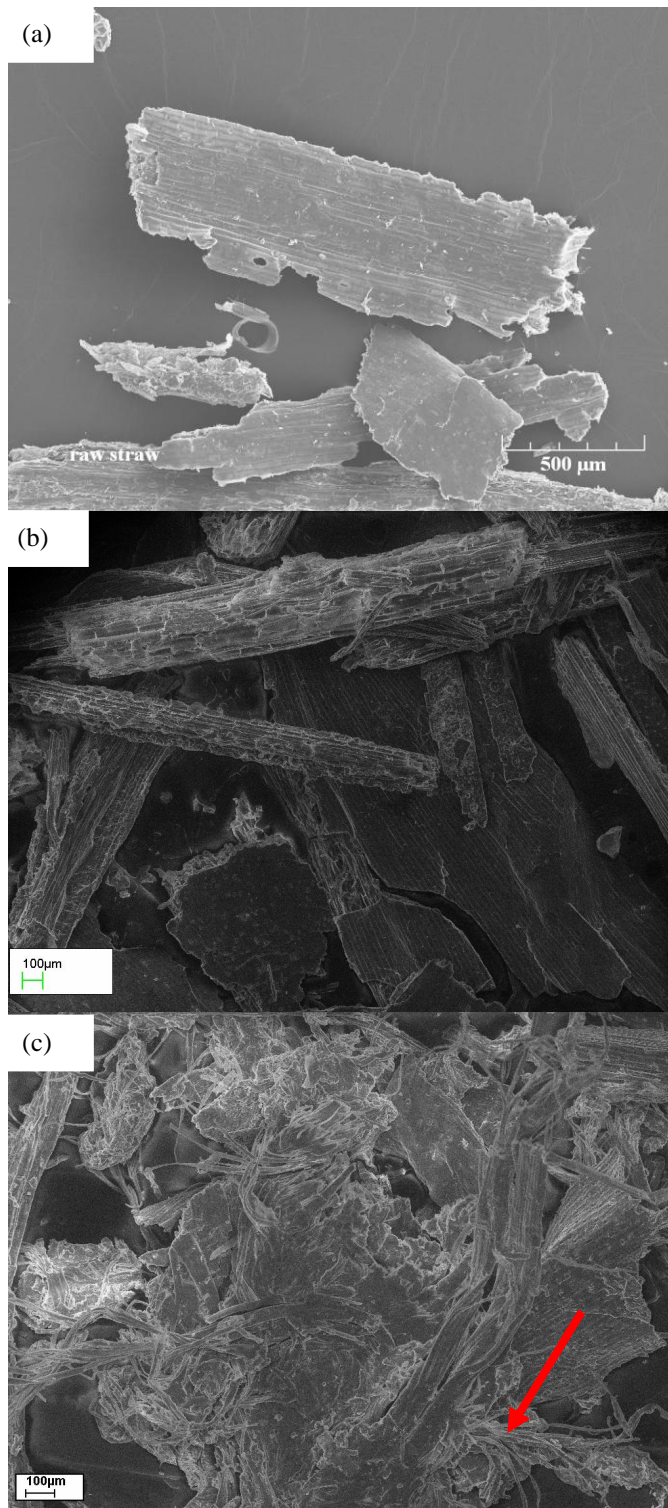


Figure 6.9: Comparison of the morphology of straws with different treatment

- a) As received raw straw
- b) NaOH solution pre-treated straw
- c) Extrusion fractionated straw pre-treated with NaOH solution (5B61R)

6.2.1.3 Flexural failure behaviour of the straw boards

All straw boards made from straw without any NaOH treatment share a common characteristic in their flexural curves. As shown in Figure 6.10-6.12 there exists two distinctive sections in the stress-strain curves separated by a “stress plateau” between them. It is just named “stress plateau” in the research because the area appears much lower slope compare with the two stress increase sessions before and after it. The retain of elastic modulus after the “stress plateau” proves the sample has not reached the yielding point, thus it is definitely not represent the failure of the sample. The curves in the three figures have some common features:

- In the first section before “stress plateau”, an elastic deformation is presented with relatively lower flexural modulus;
- When reach the plateau there is a considerable plastic deformation at a nearly constant stress;
- After the “stress plateau”, in the second section, elastic deformation resumes at a higher modulus than the first session;
- When peak stress is reached and boards fail progressively accompanied by delimitation and pull out of straws.

In compression moulded straw boards, strength and stiffness are determined by that of straw and more important the bonding between them which are dependent on the mechanical locking of straws and bonding provided by natural resins in the straw. The fact that the boards resume higher stiffness and continue to carry much higher load indicates that the “stress plateau” may have resulted from the relaxation of weak mechanical interlocking between the straw bundles or fibers. This is supported by observations that the stress plateau raises with compression pressure (Figure 6.10), the use of shorter straw (Figure 6.12) and to a less degree, with an increase in compression temperature (Figure 6.11). After the relaxation, the boards become stiffer as indicated by the increase in modulus in the second section of the flexural curves summarised in Figure 6.13. The modulus before relaxation is employed as the nominal flexural modulus of the sample (as in Figure 6.5 and 6.7). Generally speaking, the modulus after the relaxation is higher than the nominal modulus. Thus, the relaxation of mechanical interlocking can be seen as a re-arrangement of straws to eliminate the initial interlocking weakness. It is also found in

Figure 6.13 that there is less change in modulus before and after the stress plateau at 120 °C (MA1, MB1, and MC1), while the biggest change in modulus at 160 °C (MA3, MB3 and MC3). As discussed in section 6.1 and 6.2.1.1, lower temperature (120 °C) is not sufficient to mobilise the natural resins, which limited the packing efficiency of straw boards. Therefore, increasing temperature from 120 °C leads to a higher degree of interlocking, which results in more increase of modulus after the fibre relaxation.

Figure 6.14 illustrates the common feature in fracture mode shared by all samples listed Figure 6.13. Failure of the samples is mainly due to initiation and progressive delamination by the shear stress which is reflected by the fluctuation in stress shown in Figure 6.10-12. The final failure ended with a tensile fracture at the bottom centre. Without NaOH pre-treatment, only a limited amount of lignin and hemicelluloses is likely to be released under heat and pressure to bond the straw interface (see Figure 6.4) and hence mechanical interlocking is considered the main bonding mechanism in these boards.

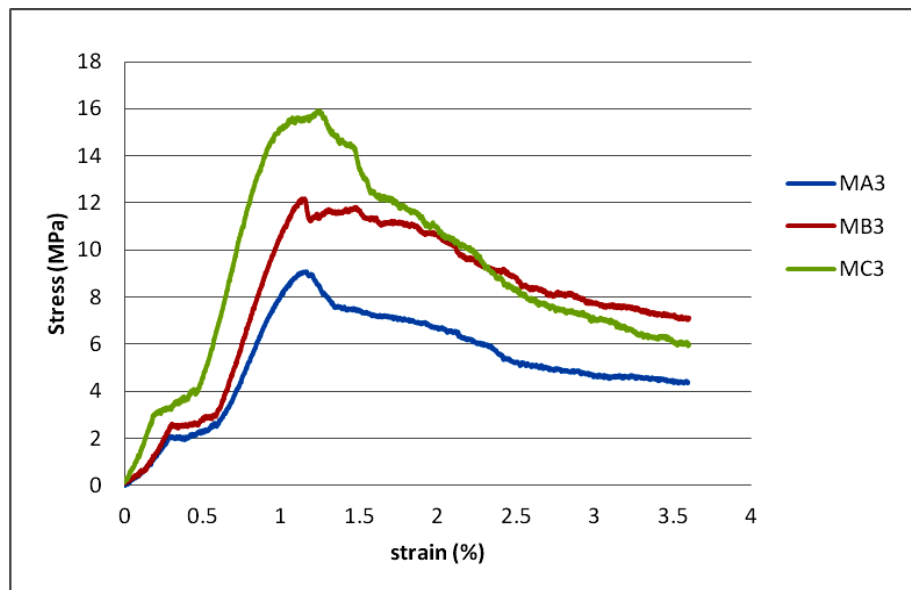


Figure 6.10: Flexural curves of straw boards compression moulded from untreated straw with an average length of 10.9 mm at 160 °C under pressures: 16, 32 and 48 MPa for MA, MB3 and MC3, respectively.

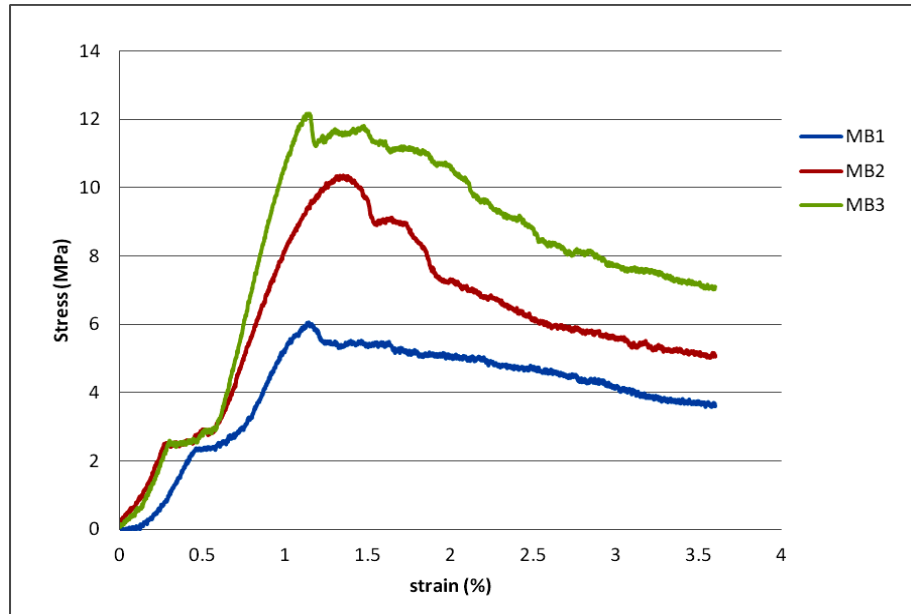


Figure 6.11: Flexural curves of straw boards compression moulded from as-received straw (straw average length of 10.9 mm) under 32 MPa at different temperature: 120, 140 and 160 °C for MB1, MB2 and MB3, respectively.

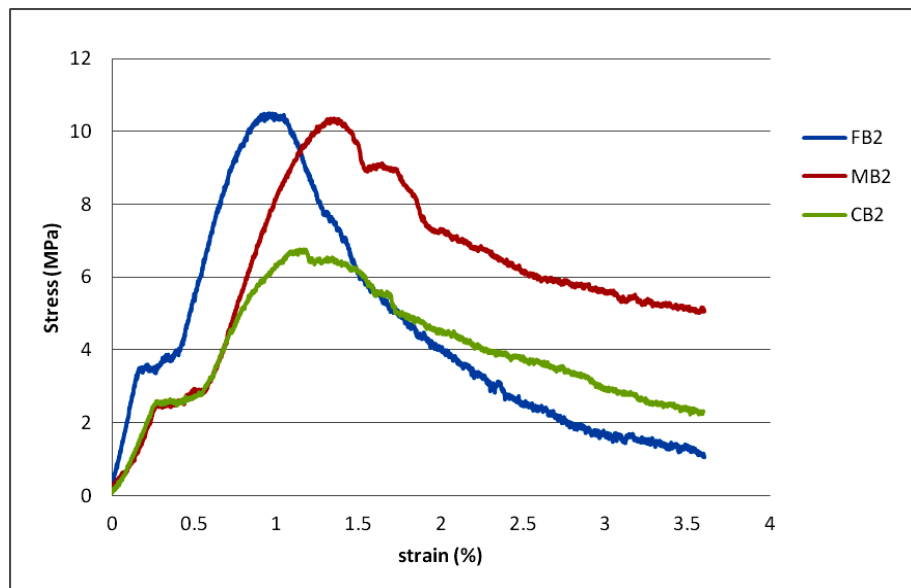


Figure 6.12: Flexural curves of straw boards compression moulded under 32 MPa and 140 °C from straw of different average length: 0.93, 10.9 and 29.8mm for FB2, MB2 and CB2, respectively

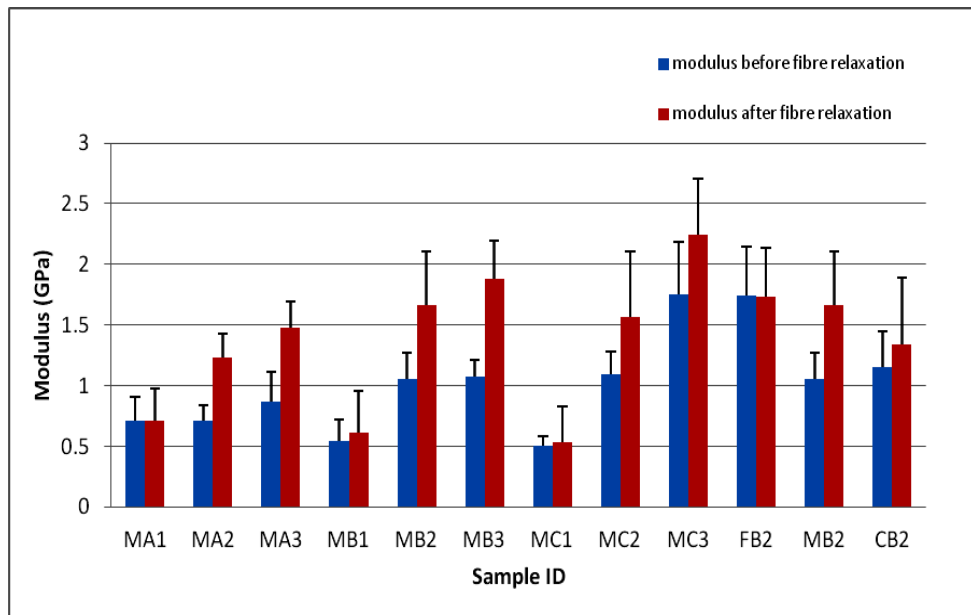


Figure 6.13: Comparison of modulus before and after the “stress plateau” derived from Figure 6.10-12.

In comparison, straw boards made from the NaOH pre-treated straw behave rather differently. Figure 6.15 compares the flexural curves of MB2 and TMB2. There is no “stress plateau” in the curve of TMB2 board and little sign delamination (Figure 6.16). Fracture is initiated from the interface between straw and resin by the maximum tensile stress at the bottom centre surface. As many literatures suggested, the NaOH pre-treatment of straw can liberate the lignocelluloses from the native straw and partially removes the waxy layers and fatty substances by the mercerisation function of NaOH (Bismarck et al., 2001; X. Y. Liu and Dai, 2007). This contributes to the coating of lignicellulose on straw surface and redistribution of such binding phase in between straws under pressure and heat. With sufficient released lignocelluloses, the interfacial bonding between fibre bundles and lignocelluloses becomes a major contributor to strength and stiffness in addition to the mechanical interlocking of compressed straw. The changes in flexural behaviour shown in Figure 6.15 seem to suggest that the interfacial bonding between straw may be dominated by bonding from the lignicellulose phase (over that of mechanical interlocking) and hence the disappearance of the stress plateau (relaxation) and delamination.



Figure 6.14: Fracture mode of MB2 at different stage post the peak stress showing typical initial delamination.

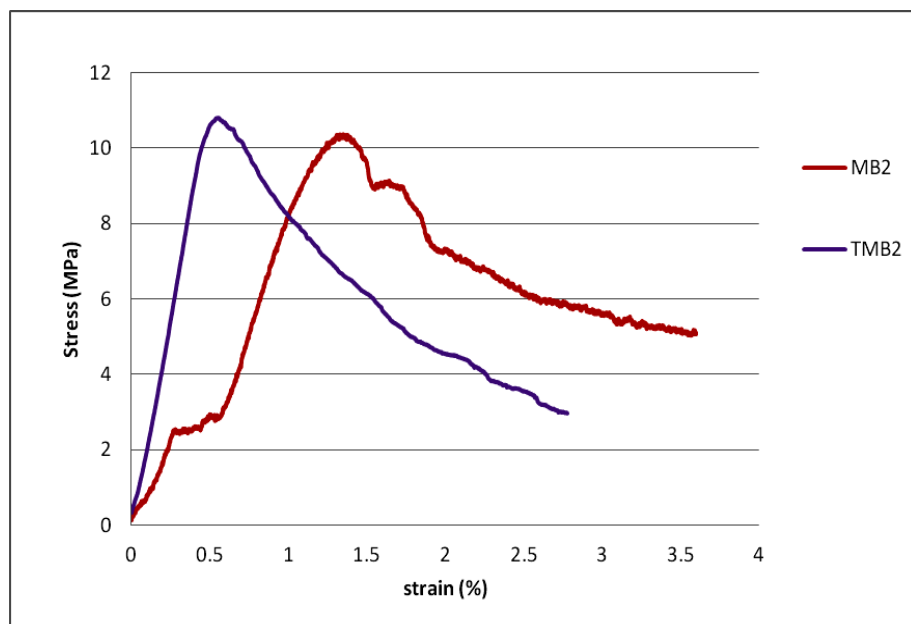


Figure 6.15 Comparison of flexure curves between boards compression moulded at 32 MPa and 140 °C from 6% NaOH pre-treated straw (TMB2) and the untreated straw (MB2) showing absence of the “stress plateau”.



Figure 6.16: Fracture mode of TMB2 board showing absence of delamination.

6.2.2 Impact property

6.2.2.1 Effect of processing parameters

The instrumental impact test as described in section 3.3.3 was conducted for the straw boards. All the boards were punctuated through by a punch with a dropping weight of 5 kg. The total energy during the impact and maximum force were recorded to reflect the energy required to break through the specimens.

The total kinetic energy of the drop weight absorbed by the samples, E , is calculated based on Equation 6.1:

$$E = \frac{1}{2} m(v_0^2 - v_1^2) \quad (6.1)$$

Where m is the mass of the drop weight, v_0 is the velocity touching the top surface and v_1 is the velocity after penetration.

It is assumed that this energy is dissipated by creating a new cylindrical surface of the punctured hole. E'' , the specific energy defined in Equation 6.2 therefore has taken account the variation of thickness of the boards and used in Figure 6.20 and 6.22 to

compare the impact energy of the boards.

$$E'' = \text{Total energy} / \text{penetration area} = E / 2\pi \cdot t \quad (6.2)$$

Where E'' is the specific energy (J/cm^2), t is the thickness of straw board and r is radius of the punch.

The specific energy of impact is illustrated in Figure 6.17. The average values range from $1.07 \text{ J}/\text{cm}^2$ to $2.45 \text{ J}/\text{cm}^2$. Under a chosen pressure, the specific energy increases with the increase of temperature. For instance, under pressure of 16 MPa, the specific energy increases gradually by about 48% from board MA1 to MA3, at 32 MPa, by 37% from MB1 to MB3, at 48 MPa, by 57% from MC1 to MC3 when temperature increases from $120 \text{ }^\circ\text{C}$ to $160 \text{ }^\circ\text{C}$. It is also shown that the specific energy required breaking through the boards reduces with the increases of compression pressure at a given temperature. For instance, at temperature of $120 \text{ }^\circ\text{C}$, the specific energy reduces by 35% from board MA1 to MC1, at $140 \text{ }^\circ\text{C}$, by approximately 28.7% from MA2 to MC2 and at $160 \text{ }^\circ\text{C}$, by 31% from MA3 to MC3 when pressure increases from 16 MPa to 48 MPa.

The specific energy is a measure of the energy needed to resist high-speed impact fracture.

It in fact reflects the ability of the materials to dissipate the energy in a number of ways:

- Energy to create new surface: plastic deformation, fibre movement, pullout, and deformation etc;
- Other associated plastic deformation adjacent to the puncture.

It therefore reflects the toughness of the material under the specific impact conditions.

The fact that board moulded under lower pressure can resist higher energy means that it can dissipate and observe more energy comparing with the board moulded with higher pressure. The specific energy has covered energy consumed by plastic deformation in the disc punched out and around the hole left after punching. Straw boards produced under low pressure have been proved to have weaker interfacial bonding than those made under high pressure. Therefore, delamination and detachment of straw from the mechanical interlocking and surface bonding dissipate energy, which results in higher specific energy

under low pressure.

Besides, it is also observed that temperature enhanced the specific energy (E'') at given pressure, this due to the improvement of packing efficiency and rigidity. As discussed in section 6.1, the packing efficiency of straw boards is more sensitive to pressing temperature. The dense structure with higher rigidity requires more energy to punch through, and fibre fraction or pull out may be also involved by the punching force, which also dissipates energy.

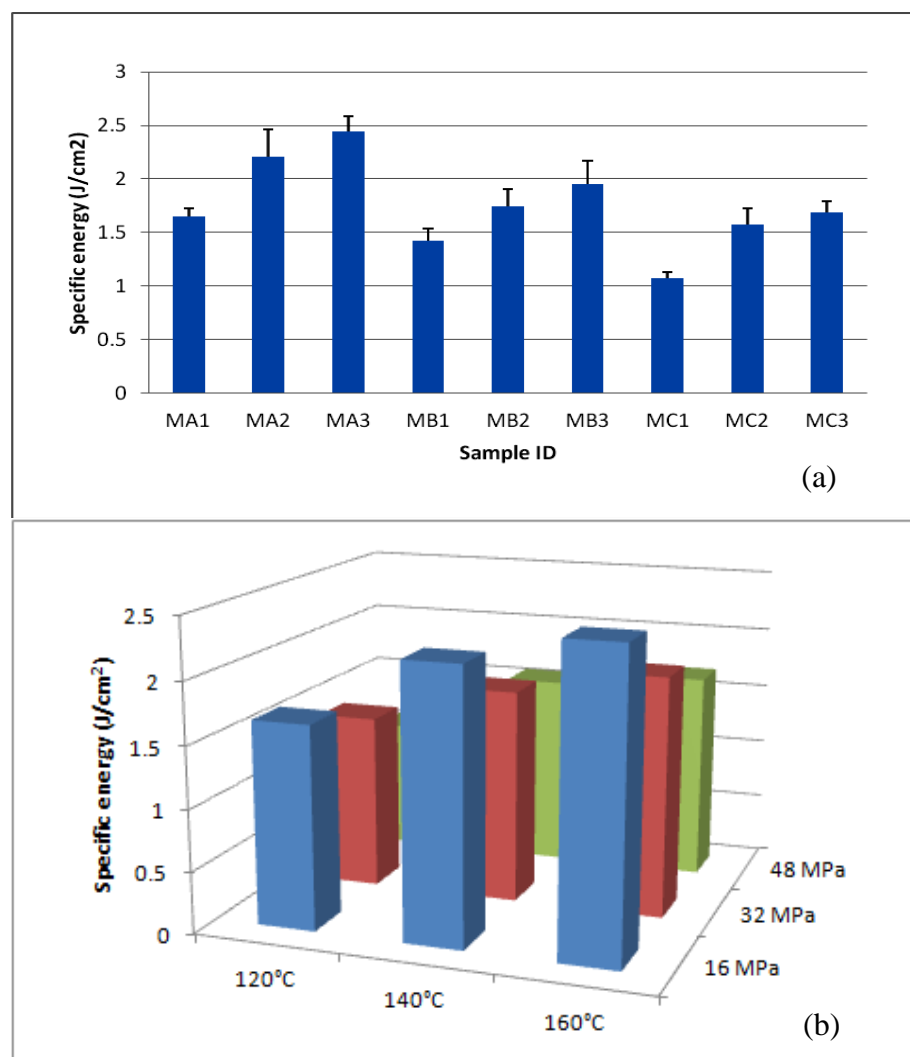


Figure 6.17: Specific energy as function of processing conditions (a: version in 2-D and b: version in 3-D).

6.2.2.2 Effects of straw length and pre-treatment

Figure 6.18 illustrates the specific energy of boards produced with different types of straw varying in average length and pre-treatment. Among the different straw length, the board made from medium-sized straw (MB2) has the highest specific energy of 1.74 J/cm^2 , while all other sized straws are relatively low and range from $1.32\text{-}1.41 \text{ J/cm}^2$. The possible reason suggested here is:

-If the fibre is too short, mechanical interlocking is weak with limited entanglement between straw fibres. So boards made from short straw dissipate lower energy during an impact test.

-If the fibre is too long, the specific surface for bonding and interlocking between fibres is also reduced, which also result in a loose structure, dissipating low energy during an impact test too.

The board made from NaOH pre-treated straw (TMB2) has clearly lower the specific energy and than that from the un-treated straw (MB2) at around 1.58 J/cm^2 . Pre-treatment enhanced interfacial bonding by the released lignocelluloses with straw tightly embedded in the released resins. So the energy dissipation is mainly used to break the matrix to failure with less energy consumed to create new surfaces by delamination or fibre pull out. It can be proved by the morphology of the punctured hole of TMB2 with a more clear surface finish and less fiber pull out than that of MB2 board. A disc has been punched out completely from the straw board. But for the MB2 board, impact process only leaves the punched hole without disc punched out. The punctured surface surrounding the hole is rough with more fibre pull out and delamination. So more energy was dissipated to make the plastic deformation and the creation of new surfaces.

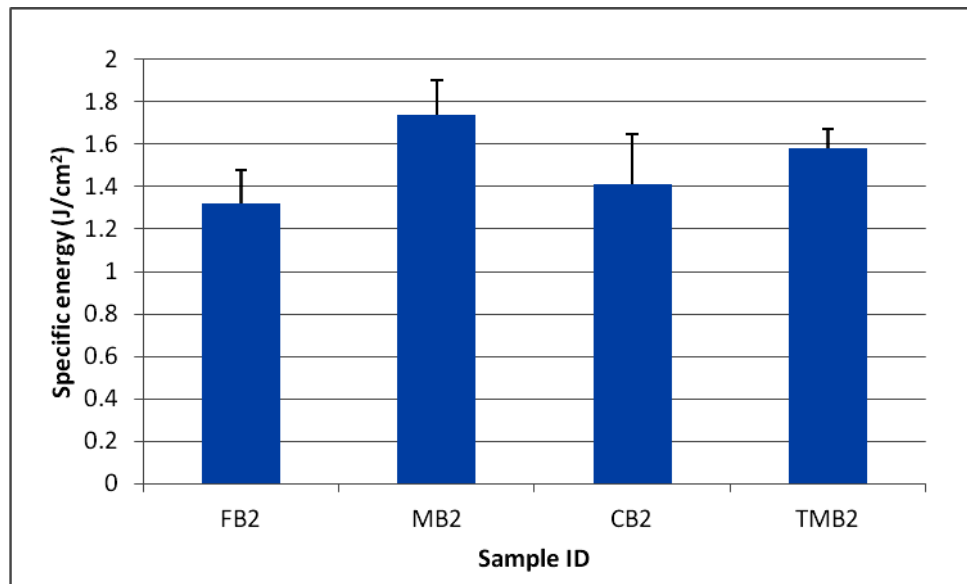


Figure 6.18: Specific energy of boards made from different types of straw.

6.2.3 Summary

The following conclusion remarks can be made based on the above investigation that:

- a) In general, an increase in pressure and temperature result in higher density, flexural modulus and strength of the boards, due to the increase of packing efficiency. Higher temperatures can also improve impact specific energy, while the increase of pressure at a given temperature reduces specific impact energy. This is because packing efficiency and rigidity of straw board is more sensitive to processing temperature than pressure. Therefore, dense structures obtained by increasing temperature can dissipate more energy. Increase of pressure can not increase rigidity of board dramatically but obtain a dense structure, which dissipate lower energy due to less delamination and fibre pull out during punching.
- b) At given temperature and pressure, there is an optimum straw length that results in a combination of good flexure modulus, strength and impact properties and hence a clear benefit in optimise straw length in the straw feedstock.
- c) NaOH pre-treatment of straw increase compressibility and interfacial bonding by the leach out of lignocelluloses and lead to higher density, modulus and strength but some reduction in impact specific energy.

6.3 Mechanisms of inter-straw bonding

The purpose of this part of work is to understand the nature of binding within compressed straw boards. Since there is no added resin in the straw boards to act as a binder, the binding must be generated inherently within the straw. It is proposed that in addition to the mechanical interlocking between compressed straws, natural resins like lignocelluloses may also be liberated or mobilised to different degrees, depending on processing conditions and pre-treatment and contributed to the interfacial binding. To investigate this hypothesis, a board made with uni-axially oriented straw bundles (LLC3 as described in section 3.2.3) was made to examine the cross-section. The surfaces of raw straw and straw boards were also examined. In a straw board structure, the strength and stiffness should mainly come from two aspects: mechanical interlocking between compressed straws and bonding provided by adhesion of lignocelluloses. Under pressure and heat, mechanical interlocking is considered a universal mechanism of bonding within compressed straw boards. This comes from the intimate contact from deformation and entanglement of straws similar to that pressed paper or non-woven fabrics. Adhesion from molecular force across the interface may also contribute to the bonding. The possible mechanisms of bonding caused by the natural resin within straw are the focus of this section by analysing the inter-straw interfaces and discussing how the processing conditions and pre-treatment of straw may facilitate mobilisation and deposition of such resin so as to contribute to inter-straw bonding in section 6.3.1 and 6.3.2, respectively.

6.3.1 Effect of processing conditions on re-distribution of natural resin and interfacial adhesion

Cereal straw consists primarily of cellular cell walls. A cross-section image of wheat straw was illustrated in Figure 6.19a and magnified image of cellular cell wall structure is shown in Figure 6.19b. A sketch of straw cell walls in Figure 6.20 illustrates the composition of cell walls and the location of the “natural resin” -lignin and hemicelluloses bonding cellulose to form a complex structure within the cell wall. Lignin with a clear function group are selected the tracer to detect the extract, mobilisation by pressure and temperature and redeposit at straw structure.

It is believed that lignin mainly located in primary wall and some are in secondary wall and

in the middle lamella (Yan et al., 2004). The macromolecules of lignin are composed of phenylpropanoid units of three basic types: guaiacyl (G), syringyl (S) and p-coumaryl (H) linked to one another by various types of inter-monomer bonds. Akin (1977) reported that syringyl lignin is tightly embedded within the ordered, close-packed structure of the secondary walls of sclerenchyma cells, whereas the guaiacyl lignin is preferentially located in the less ordered middle lamella and primary walls. Love et al (1998) found that syringyl-rich areas of lignin network were more rigid than the guaiacyl-rich areas. On the cellular scale, the guaiacyl-rich lignin of the middle lamella, which is not reinforced by cellulose, is probably the weakest point in the whole structure of the tissue and can be liberated mechanically to separate the cells during pulping (Westermarck, 1985).

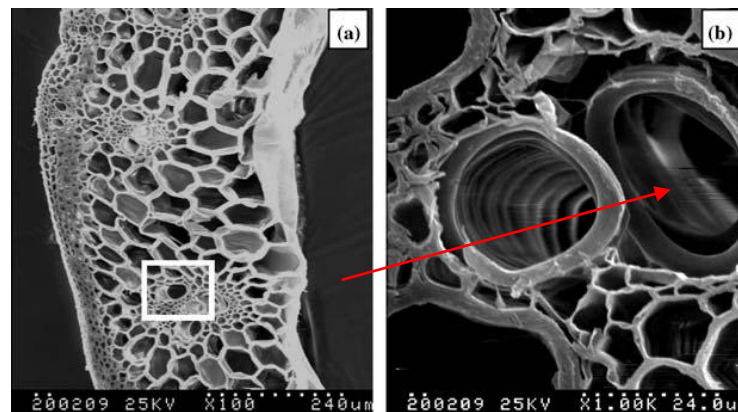


Figure 6.19: SEM image of wheat straw cell wall structure (R. Liu et al., 2005)

a) cross section image of wheat straw

b) magnified image of cellular cell wall structure

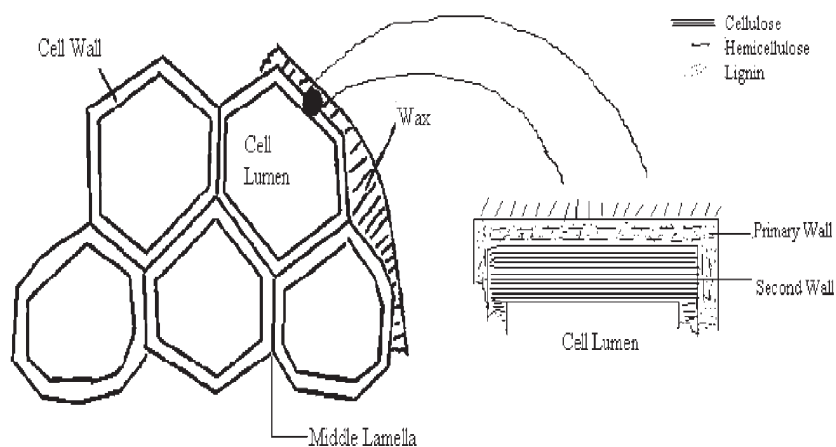


Figure 6.20: Sketch of straw cell wall structure showing the key composition within cell walls (Yan et al., 2004)

The morphology of cell walls changes dramatically when straws are compressed under heat and pressure as shown in Figure 6.21 and 6.22. Compressed cell cavity or cell lumen of the interior walls is clearly identifiable as the lightest areas (as red arrows pointed in Figure 6.21), while the brownish layers indicate the straw exterior wall and the straw interface are shown by the darkest regions (as yellow arrows pointed in Figure 6.21 and Figure 6.22).

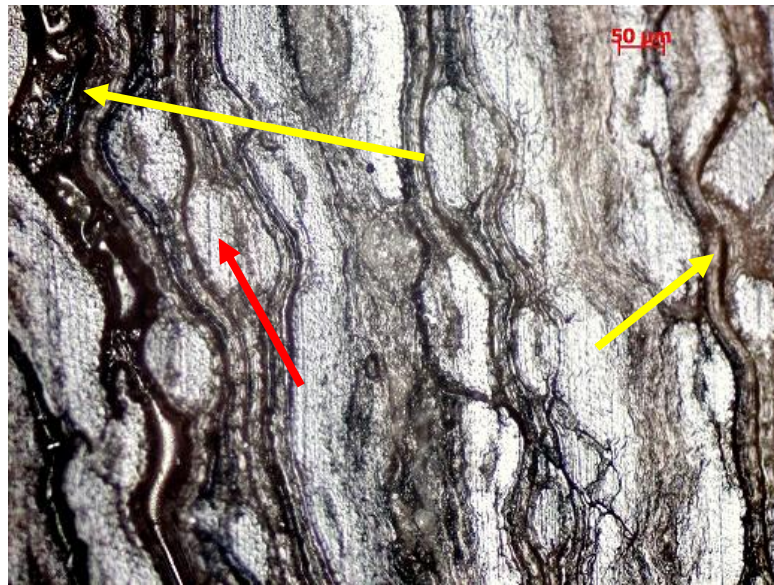


Figure 6.21: Optical micrograph of cross-section of a uni-axially oriented straw (LLC3) board showing morphology of the compressed cell structure of straw boards under pressure and temperature.

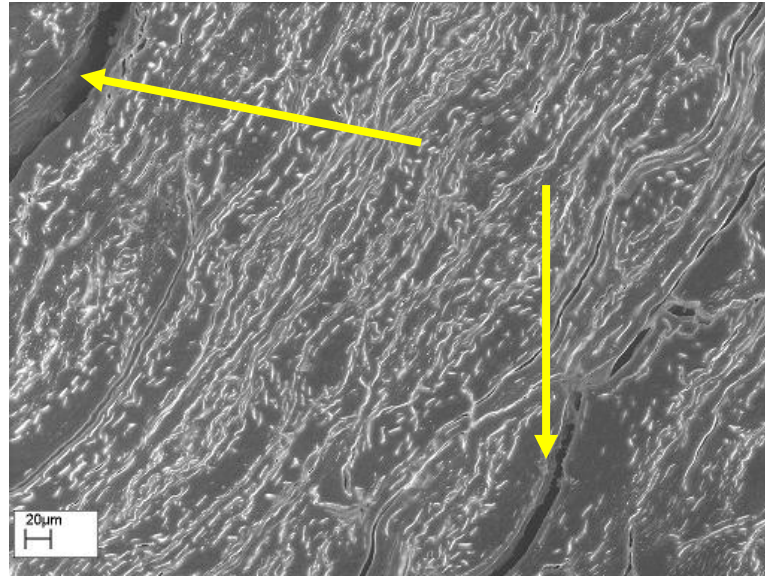


Figure 6.22: SEM micrograph of cross-section of a uni-axially oriented straw (LLC3) board showing morphology of the compressed cell structure of straw boards under pressure and temperature.

Both lignin and hemicelluloses act as a bonding agent between cellulose. Lignin form complex with hemicelluloses and it is assumed that they cannot be separated by simple pressure gradient. So tracking of lignin is considered to be sufficient to identify the distribution of the lignin-hemicellulose complex. FTIR chemical mapping was used to identify the location of the lignin within straw boards.

An area of interest was scanned on cross section of the LLC3 straw board (as shown in Table 3. 23). The bands of 1600cm^{-1} and 1510cm^{-1} from lignin (Moore and Owen, 2001) are selected as show in Figure 6.23 a as fingerprint of lignin. The presence of lignin and locations can be indicated quantitatively from the representative colour scale (red–yellow–green– blue from as highest to lowest).

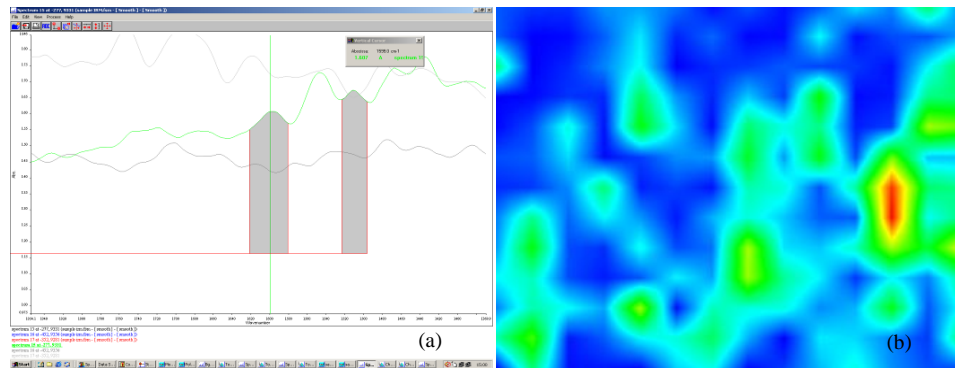


Figure 6.23: a) FTIR fingerprints of lignin aromatic ring vibrations (1600cm⁻¹ and 1510cm⁻¹) and b) an example of FTIR mapping on the cross section of the LLC3 straw board showing the lignin distribution.

Furthermore, by selecting 1340cm⁻¹ as syringyl ring and 1270cm⁻¹ as guaiacyl ring, the FTIR mapping of more specific lignin can be obtained, as shown in Figure 6.23. The SEM image in Figure 6.24 shows an area of 300 x300 μm, the same area was scanned with FTIR mapping as shown in Figure 6.24 a-b. The contour (shown by the dotted line) for higher lignin concentration seem to match that of the straw boundary in the SEM.

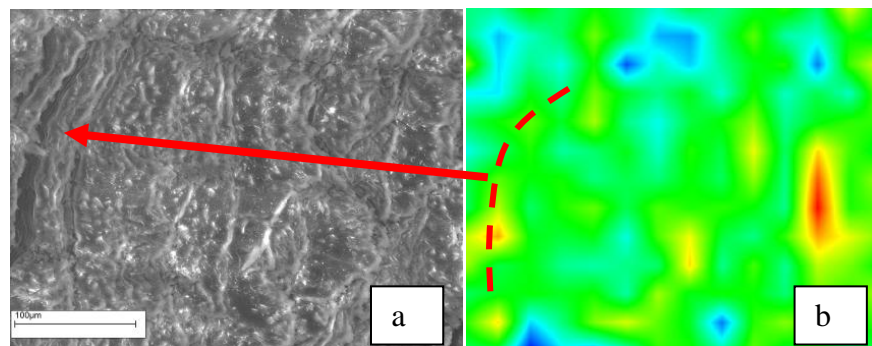


Figure 6.24: SEM of cross-section of the LLC3 straw board (a) and FTIR mapping (b) of guaiacyl rings showing lignin-rich zones along at the straw boundary (the dotted lines).

Further evidence of redistribution of lignin and hemicelluloses can be found in the changes of straw surface before and after the hot compression. The exterior of raw straw bundle is shown in Figure 6.25 a and extracted straw bundle from the fracture surface of straw board compression moulded at 160 °C, 48MPa was shown in Figure 6.25 b. In comparison with straw before hot pressing (Figure 6.25a), many dark-colour stains can be identified. The dark stains in Figure 6.25b appear to emerge from the orifices of stoma on the exterior

surface of straw are believed to be mobilised lignin/hemicelluloses.

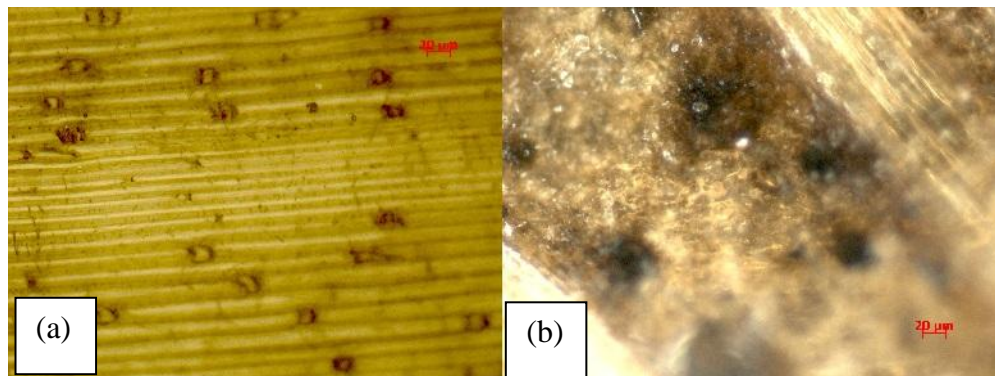


Figure 6.25: Optical micrographs of exterior surfaces of raw straw (a) and fracture surface of straw board (LLC3) moulded at 160 °C and 48MPa (b) showing stains from mobilised lignin/hemicelluloses.

It is possible that under heat and pressure lignin in the cell wall structure has been released from the native straw and redistributed under the pressure gradient toward the gap/voids between straws where pressure is relatively lower. One may argue that wax, existing on the surface of the outside wall of straw may block the migration of lignin. But as Bennett (1975) summarised, plant and mineral waxes possessed a wide variety of melting temperatures, ranging between 41 and 87 °C. Athukorala and Mazza (2010) stated that the wax extracted from the straw of triticale, which consists of fatty acids, sterols, fatty alcohols, alkanes, beta-diketones, and hydroxyl-beta-diketones, started to melt at 47 °C and reached its peak at 53 °C. It was found that linear and quadratic effects of temperature and interaction effects of temperature and pressure had a significant effect on the total wax yield and on the content of fatty acids, fatty alcohols, and sterols in the wax (Athukorala and Mazza, 2010). This supports that the wax can also yield and be removed under pressure and temperature only,

Redistribution of lignocelluloses relies on softening of lignin and hemicelluloses and thus the compression temperature relative to their glass transition temperature (T_g). Stelte et al (2011) measured T_g of lignin and hemicelluloses in wheat straw via DMTA (dynamic mechanical thermal analysis) and DSC (differential scanning calorimetry). Their study included both natural and solvent extracted wheat straw, in moist (8-9 % water content) and dry conditions, and was compared with spruce samples. The moisture content is an

important factor affecting the viscoelastic properties of lignin and hemicelluloses, because water acts as a plasticizer, resulting in a reduction of the energy required to initiate chain mobility (Kelley et al., 1987). Straw in the moist condition has the similar moisture content as that employed in this research, which make the result more reliable. It was found that the key transitions attributed to the softening of lignin and hemicelluloses were at 53 °C and 2 °C respectively for moist wheat straw (Stelte et al, 2011). Therefore, the temperature range employed in this work by far exceeded the temperatures to soften and activate motion of lignin and hemicelluloses under pressure. Overall speaking, the mobility of lignin and hemicelluloses are all closely related to the processing temperatures. This can explain why the density and mechanical properties are temperature sensitive.

6.3.2 Effect of NaOH pre-treatment on internal bonding

Alkali treatment of wheat straw disrupts the cell wall through dissolving hemicellulose, lignin, silica, and hydrolyzing uronic and acetic acid esters. Alkaline swells cellulose, decreasing the crystallinity of cellulose (Lawther et al., 1996; R. Sun et al., 1995). All of the ester-linked substituents of the hemicellulose and other cell wall components can be cleaved by alkali (Buranov and Mazza, 2008). Aqueous NaOH solution treatment is one of the typical methods used in pulping. For agricultural straws the reaction proceeds at lower temperatures, and can dissolve as much as 80% of the total lignin, and 80% of the hemicelluloses (Xiao et al., 2001).

Alkali treatment of lignocellulosics such as wheat straw dissolves the hemicelluloses from the reducing end of the chain, and breaks many of the bonds within lignin, it also cleaves α -ether linkages between lignin and hemicellulose, and ester bonds between lignin, hemicellulose and hydroxycinnamic acids. This process can easily fractionate the straw into soluble lignin and hemicellulose suitable for various applications as detected by the cold water extraction method. Extensive studies of straw lignins and hemicelluloses by Sun and coworkers revealed much about the nature of the alkali soluble material, the straw lignins cleaved at low temperature alkali hydrolysis for example are strongly associated with hydroxycinnamic acids such as p-coumaric and ferulic acid, and with glucuronic acid or 4-O-methylglucuronic acid (R. C. Sun et al., 1998). The p-coumaric acid and ferulic acid units form cross links between the lignin and the hemicellulose components of the straw. The ester linkage of the hydroxycinnamic acids to hemicellulose is relatively easily

cleaved in cold alkali, as observed by Sun et al. (1997) on detection of p-coumaric acid and ferulic acid in the lignin fraction rather than the hemicellulose fraction of their analyses. Wheat straw lignin contains a high proportion of beta-O-4' structures and small amounts of condensed units (beta-5, 5-5 and beta-1') guaiacyl units. p-coumaric acid is linked by a gamma-ester bond, and a few ether bonds, whereas ferulic acid is linked to lignin by ether bonds. The dehydrodimers of ferulic acid (5-5', 8-O-4') are also incorporated into the lignin polymer (R. Sun et al., 2002).

Bangor University, as the academic partner in this research, did the composition check on straw after the pre-treatment (HGCA, 2011). The straw which had been treated with a 6% solution of sodium hydroxide without any extrusion fractionation was subjected to the 48 hours stirring process to generate a cold extract for analysis. The composition of mass lost into the cold water extract, and proportions of the components in the fibre residues are shown in Table 6.1 and Table 6.2 respectively.

Table 6.3 shows that there is a dramatic increase of hemicellulose in the extracted cold water caused by the NaOH pre-treatment, while the lignin just increased from 1.97 to 2.31%. The total cold water solubles (including hemicelluloses and lignins) released from the cell structure of wheat straw will deposit, when the pre-treated straw are dried, as a complex resin on the straws and act as a bonding agent in the board structure. Such bonding may have become dominant over the contribution of mechanical locking in comparison with that without the NaOH pre-treatment (the MB2 boards). This leads to absence of stress relaxation and delamination during the flexural tests of the TMB2 boards.

Table 6.3: Fibre residue and composition of cold water solubles in straw treated with 6% NaOH solutions in comparison with untreated straw (HGCA, 2011).

Wt. %	CS	T6
Fibre residue	87.69	53.97
Hemicellulose	4.56	16.89
Lignins	1.97	2.31
Apparent other solubles	5.78	26.83

6.4. Preliminary industrial evaluations

The process designed for binder-less straw board production is schematically shown in Figure 6.26. The process proved to have the following distinctive features:

- a) Novelty -the process utilise straw's inherent bonding agent instead of added bonding agents which are often based on non-renewable resources and toxic, add cost and gave rise to problems in post-service waste management.
- b) Simplicity - the feedstock processing and pre-treatments are of low cost, none to low emission of water during manufacturing, and easily adaptable in commercial production lines for fibre boards.
- c) The products are 100% based on renewable resource and can be more easily recycled or biologically treated after the intended service life.

A range of prototypes of binder-less straw board were produced (e.g. Figure 6.27) and evaluated.

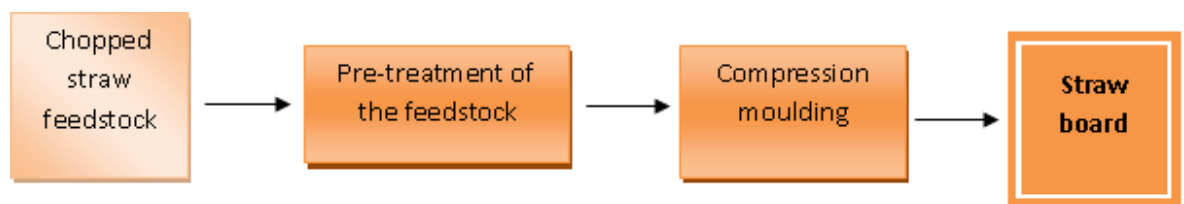


Figure 6.26: Flow diagram of the straw board production.



Figure 6.27: Samples of binder-less straw boards produced in this work.

Comparison of properties with some commercial wheat straw boards is made in Table 6.4. The commercial wheat straw-based and fibre board was produced with added bonding agents. It is demonstrated that in comparison with the commercial products, boards in this research have higher density but comparable mechanical properties have been achieved. High density is not desirable both in handling and transportation of products. In order to reduce the density of the binder-less straw boards without losing the mechanical properties, NaOH pre-treated straw is suggested, which need lower pressure and temperature to achieve required properties.

Table 6.4: comparison of mechanical property of the binder-less straw board samples (without any straw pre-treatment) with some commercial wheat straw based boards

	Binder-less wheat straw board in this research (100x10x4) mm	Wheat straw board (MDI binding) (Hefei, China)*		Compak boards** (12.7mm thickness)		
		4-6 mm	6-13 mm	wheat straw board	bagasse board	wood waste board
Density (kg/m ³)	1050-1300	650-880	650-880	650	710	750
Modulus of Rupture (MPa)	9 -16	≥15	≥14	19	23	17
Modulus of Elasticity (MPa)	1400 -- 2400	---	---	2850	2500	2750
Impact strength (charpy) J/m ²	4312	---	---	---	---	---
Tensile strength (MPa)	6	---	---	---	---	---
Tensile modulus (MPa)	6000	---	---	---	---	---
Internal Bond (MPa)	---	≥0.45	≥0.40	0.7	0.9	1.1

Note: *Data source: <http://www.17tree.com/product-8352-1-fibreboard.html>

**Data Source: <http://www.compaksystems.com>

In collaboration with Westbridge Furniture and M&S, the binder-less straw boards also underwent technical trials to evaluate the processing properties during manufacturing of upholsteries including stapling, drilling, sawing, and adhesive bonding using PVA, shown in Figure 6.28. The feedback shows that the binder-less straw boards are promising replacement for wood fibre based boards currently used. It also identified areas for further improvements:

- a) Reduction of density
- b) An enhancement to debonding of straw fibre during stapling, drilling in relation to insufficient bonding between the straws.
- c) Enhancement of water resistance during adhesive bonding using PVA glue.



Figure 6.28: Evaluation of manufacturing properties of binder-less straw boards showing that they are able to withstand the process of stapling, drilling and sawing without failure of board structure.

6.5 Summary

In conclusion, the properties of binder-less straw boards increase with pressure and temperature in terms of density, stiffness and strength. Meanwhile, pre-treatment and fractionation on straw also enhance the properties but reduce the impact strength, because of increase of packing efficacy.

The bonding mechanisms in the straw board have been investigated in this chapter, showing that there are two main components which contribute to the inherent bonding: mechanical locking of straws and interfacial bonding provided by the natural resin inside the straw. For the straw boards made from straw without pre-treatment, mechanical locking is suggested as the dominate bonding mechanisms whilst internal bonding by the natural resins may also make the contribution. Limited evidence of have proved the redistribution of natural resins (lignin and hemicellulose). Images from microscopy and distribution of lignin in FTIR mapping also found some disperse of natural resin at the straw boundary, which indicate the mobilisation of natural resins. For the straw boards made from straw with pre-treatment, inherent bonding also contributes a lot apart from mechanical locking,. Lignin and hemicellulose can be realised by the NaOH solution, especially hemicelluloses, making them freely migrated in the system.

Through this study, feasibility of production of boards from 100% wheat straw without any addition of adhesives and fractionation was proved. The redistribution of the lignin phase under combined heating and pressure is attributable for the adhesion between the straw bundles. Potentially, this could lead to the great saving in reducing costs of straw extrusion processing. The use of surface treatment such as dewaxing, interface modification and additional resins are expected to enhance the properties further. The materials are of particular interest for short service-life and non-structural applications such as profiles or boards in building/construction applications.

Chapter 7 Conclusions and suggested future works

This work started with the preparation of wheat straw and it has been processed into varieties of forms depending on applications. It was extensively fractionated through combined chemical and thermo-mechanical treatment using extrusion technology for feedstock in extrusion or injection moulding. On the other hand, simple chopping or chemical treatment was sufficient for compression moulding or moulding of relatively large sections. Then, the prepared wheat straw was kept completely for further compounding or moulding without extraction process, according to the concept of “whole utilisation”. The applications of wheat straw have been proved to be versatile. Three systems of wheat straw based composites have been developed in this study:

- 1) Straw-starch-clay system for the target in shooting sports.
- 2) Straw-biopolymer system for extrusion profiles or feedstock for injection moulding.
- 3) Binder-less strawboards without addition of external bonding agent.

Through mechanical tests and characterisation on the straw based products, relationship of formulation, processing and property has been established for each system. Modification of formulation leads to adjustment on processing parameters and then reflects on the properties of the end product. While for the same formulation, adjustment of processing parameters also results in a property change. At the end of this study, close match of mechanical properties of the three systems to the commercial products has been achieved and prototypes were demonstrated and evaluated.

This work has made significant contributions to the development of a novel technology for processing of wheat straw based composites in terms of processing, formulation and properties of the materials. The work has paved the way for the whole utilisation of wheat straw without separation of cellulose, lignocelluloses and other compositions, which dramatically reduced the waste and energy consumption as well as the environmental impacts in the conventional attraction process of cellulose. Besides, as a comparable advantages over petroleum based materials, most of the materials involved in this project are renewable resources (like straw and flour) or derived from renewable resources (clay

and biopolymers). According to the biodegradability and biocompostability, end products from this study facilitate the reduction of landfill and environmental impacts at the end of their intended service life. The key outcomes are summarised below.

7.1 Straw-starch-clay composites

7.1.1 Effect of formulation on the properties of bio-pigeon

The mechanical properties of bio-pigeon composites are affected by the straw content in the quadratic way. Although the addition of straw involves stiffness and strength into the bio-pigeon composites, the increase of straw content means a reduction of binding phase in the composites accordingly. In this case, the negative influence of mechanical properties is also applied to the system caused by decrease of binder.

The influences of straw fractionation on the mechanical property of bio-pigeon are also in a quadratic way. This is also because the with the fractionation level of wheat straw increased, there are two functions on the composites in reverse way. Firstly, high fractionation level of straw will reduce the mechanical properties of the composites, because of the self-damage involved to straw bundle. Then, high fractionation level of straw will enhance the compatibility of elements in the composites, because of more lignocelluloses leached out as binding phase and plasticiser. The two key influences will work at the same time, and the second one becomes more effective than the first one at a high fractionation level straw.

By changing straw content and fractionation level, there are limit effects on the impact strength of the composites, compared to the target. While changing the glycerol content in flour, the influence is different from the above two elements. Although the reduction of glycerol content results in a property drop in modulus and strength, it enhances the brittleness at the mean time dramatically. Therefore, addition of glycerol will not be considered based on the requirement on brittleness of a shooting target.

It can also be concluded that the increase in the level of fractionation, the reduction in straw content together with more glycerol content in flour has enhanced the compressibility of the processed straw and hence able to produce higher density.

7.1.2 Effect of processing on the properties of bio-pigeon

The process of extrusion compounding followed by hot mould compression has the disadvantage of long cycle time and high impact strength. After changing the element in formulations, gap to the target is still exist especially on impact property. Adjustment on processing is more efficient on increasing brittleness of bio-pigeon composites than changing the elements in the formulation. Two alternative processing routes have been developed to overcome the disadvantages. This first one is mechanical mixing followed by cold mould powder compaction. It has been proved that the employment of powder compaction does enhance the brittleness, but the strength and modulus of composites made through mechanical mixing is extremely low as poor internal bonding. In the second alternative processing route, extrusion compounding followed by the cold mould powder compaction, extrusion was involved again to create a homogenous distribution of binding phase, which enhanced the adhesion between particles. It has been found as the best choice to satisfy the requirements on processing cycle time and mechanical properties.

Therefore, it is proved that the employment of powder compaction does enhance the brittleness. Extrusion compounding is also a proper process which can uniform the microstructure of the composite system. Meanwhile, extrusion compounding can also enhance the gelatinisation level of flour by shearing force and temperature provided.

7.2 Biopolymer-straw composites

7.2.1 Effects of straw on the mechanical properties composites

Bioflex F6510 and Biolice 50C were selected to compound with straw for different applications. Overall speaking, Bioflex-straw composites have far better property than the Biolice-straw composites no matter in stiffness or strength. Bioflex-straw composites are suitable for structural applications; while for the applications need ductility or not critical on mechanical performance, Biolice-straw composites are more applicable.

By analysing the tensile properties of biocomposites, straw has been proved to have a significant enhancement on stiffness compared to both of the matrix biopolymers. But for

Bioflex-straw composites, the addition of straw results in a decrease of flexural modulus. This is due to Bioflex presents close bending modulus as wheat straw and straw does not perform as the reinforcement in the matrix. In addition, bad adhesion between wheat straw and Bioflex results in a discontinuous polymer structure, which also explains the decrease of flexural modulus.

Besides, a decrease of tensile, tear or flexural strength was obtained by blending straw in the biopolymers. The mechanisms of the strength decrease are dependent on the interfacial adhesion between straw fibre and matrix. In the Bioflex-straw composites, the closing strength and the proved poor interfacial adhesion between straw and Bioflex makes straw as filler in the system without function of reinforcement in strength. While for the Biolice-straw composites, the mechanism is different. A good adhesion between straw fibres and matrix is also confirmed. Therefore, the reduction of strength by adding straw in is due to the termination of alignment of polymer chains under the tension force.

7.2.2 Effects of straw on the rheological and thermal properties

Through the investigation on the thermal behaviour of the biocomposites, a relationship between property and processing parameters are established. It has been proved that the onset degradation temperature is reduced while the melting temperature is increased by the addition of straw, summarised from the TGA and DSC results. So, the processing window of biopolymer-straw composites is narrowed down with the inclusion of straw. It has also represented that crystallinity decreases with the addition of straw, which indicates the reduction in strength. The rheological behaviour of the biocomposites reflects the relationship between structure and mechanical properties. With the increase of straw content, the increase of viscosity in Biolice-straw composites indicates the good interfacial adhesion between straw and Biolice matrix; while the decrease of viscosity in Bioflex-straw composites proves the poor adhesion between straw and Bioflex matrix.

7.3 Binder-less straw boards

7.3.1 Innovated formulation and process

This PhD work has proved the feasibility of production of boards from 100% wheat straw

without any addition of adhesives. The redistribution of the lignin and hemicellulose phase under combined heating and pressure is attributable for the adhesion between the straw bundles.

The formulation used for binder-less straw boards utilise straw's inherent bonding agent instead of added bonding agents which are often based on non-renewable resources and toxic, add cost and gave rise to problems in post-service waste management. Meanwhile, the feedstock processing and pre-treatments are of low cost, none to low emission of water during manufacturing, and easily adaptable in commercial production lines for fibre boards.

7.3.2 Effect of processing parameters on board properties

An increase in pressure and temperature result in higher density, flexural modulus and strength of the boards, because pressure and temperature helps to form the mechanical interlocking in the straw boards, which is the dominant source of strength. However, the trend of the impact property is different. A higher temperature can improve the flexibility and toughness, while toughness decreases with increase of pressure. The dense structure with higher rigidity obtained by increasing temperature requires more energy to punch through. Generally speaking, the properties of straw boards are more sensitive to temperature than applied pressure. Therefore, with less increase of rigidity by increase of pressure, more energy dissipated by the detachment of straw fibre and creating of new surface around the punching hole. With only pressure and temperature applied, mechanical locking is the dominate bonding in the board structure. Through the investigation on the morphology and appearance of lignin at the interfacial area tracked by FTIR mapping, mobilisation of lignin-hemicellulose complex is suggested to occur under pressure and temperature, which also contribute to the bonding between straw fibres.

7.3.3 Effects of straw types on board properties

At fixed temperature and pressure, there is an optimum straw length that results in high density and a combination of good flexure modulus, strength and impact properties and hence a clear benefit in optimise straw length in the straw feedstock. Pre-treatment on straw does increase the density, bending properties in terms of modulus and strength, and brittleness of the straw boards. It has been proved that pre-treatment of wheat straw can

accelerate the leach out of lignocelluloses under temperature and pressure. Therefore, interfacial bonding between straw fibres and lignin-hemicelluloses complex becomes the other main contributor to the board strength apart from mechanical locking.

7.4 Suggestion for the further work

This work opened many avenues for further investigation in this exciting new class of biocomposites. Some further research subjects are suggested for future studies:

- 1) Investigation on water proof bio-pigeons. There are two directions to achieve the purpose: water proof emulsions blended into the bio-pigeon composites during the compounding process and simply spraying the water proof painting to form a surface coating.
- 2) Biopolymer blends for the matrix of straw based composites. There is a dramatic drop of mechanical properties from Bioflex F6510 to Biolice 50C. So it is suggested to compound the two biopolymers together in varieties of ratios. In that case, a profile of biopolymer blends with intermediate properties will be developed for the matrix of straw composites.
- 3) Investigation on the effect of straw on the crystallisation of biopolymers. X-ray diffraction can be employed to detect the crystal structure of biopolymers.
- 4) The performances of biocomposite samples are tested under a constant load. Dynamic mechanical analysis (DMA) is suggested to examine the viscoelastic behaviour of biopolymer-straw composites.
- 5) Detection on internal-bonding binder-less straw board. As the research suggested, strength of straw boards came from bonding and interlocking. In order to check the bonding behaviour of board prototypes, a bonding test is suggested following the standard of BS 5669, which is designed for particle boards.
- 6) The use of surface treatment such as dewaxing, interface modification and additional resins are expected to enhance the properties of straw boards further. As required by the manufacturer, binder-less straw boards are potentially used in supporting components in furniture, and PVA is a conventionally selection of glue in the furniture industry. PVA glue is water based; therefore the enhancement of water resistance during adhesive bonding is also suggested in the future work.

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