1 **The influence of additives on the interfacial bonding mechanisms between**
2 **natural fibre and biopolymer composites**

3 **Seyed Hamidreza Ghaffar[a]*, Omar Abo Madyan[a], Mizi Fan[a], Jorge Corker[b]**

4 [a] College of Engineering, Design and Physical Sciences, Brunel University London,
5 Uxbridge, Middlesex, UB8 3PH, United Kingdom

6 [b] Instituto Pedro Nunes, IPN Led&mat, Rua Pedro Nunes, 3030 199 Coimbra, Portugal

7 * Correspondence email: seyed.ghaffar@brunel.ac.uk; Tel: +44 1895 265770

8 **Abstract**
9 The subject of interfacial bonding quality and the interaction mechanisms of biopolymers and
10 natural fibres have not been extensively researched. In order to increase the functionality and
11 performance of biopolymers synthesised from natural sources/microbial systems, attempts
12 have been made to incorporate natural fibres/fillers (biofibres) to manufacture composites.
13 However, interfacial bonding quality and other substantial technical challenges yet need to be
14 addressed for their industrial realisation. The interfacial bonding quality ultimately dictates
15 the mechanical and physical performance of bio-composites. This review paper attempts to
16 collate the state-of-the-art about coupling agents/additives and their role in interaction
17 mechanisms with biofibres and biopolymers. Two potential pathways for narrowing the
18 performance gap between biopolymer-based bio-composites and their petroleum-based
19 counterparts are: i) the synthesis of a specific coupling agent to improve the interfacial
20 bonding quality and ii) two or more biopolymers blending for improved process-ability of
21 bio-composites.

22 **Key words:** Interfacial bonding; Biopolymers; Bio-composites; Coupling agents; Additives.

23 **1. Introduction**
24 Plastics are one of most extensively consumed materials on a daily basis; however
25 unfortunately, manufacturers do not adopt bioplastics because the price of oil is low, even
26 when the prospect of future economic conditions will possibly increase the cost of fossil
27 feedstock. However, the global production capacity of biopolymers has demonstrated a
28 dynamic growth, reflected by numerous research efforts, e.g. [1–9]. The main objective has
29 been to develop novel bio-based products with functionalities superior or, at least equivalent
30 to those of the existing petroleum-based options, such as lower weight, higher heat and water
31 resistance, increased durability, toughness and fire performance. Biopolymers often contain a
32 number of reactive groups offering excellent possibility for the reactive compatibilisation of
33 their blends. The addition of a compound miscible with one blend component and reactive
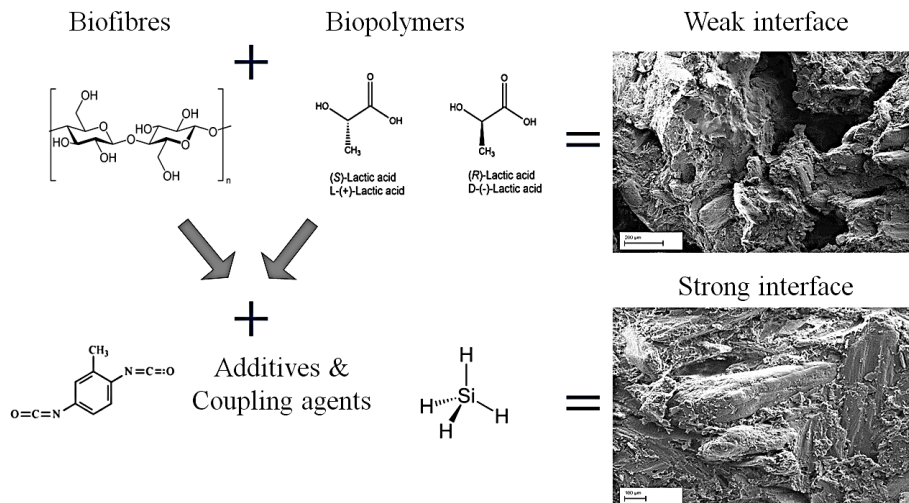
34 towards the functional groups of the other results in the *in-situ* formation of grafted or block-

35 copolymers acting as compatibilisers [10].

36 Biopolymers are either bio-based synthesised from biomass and renewable sources, for

37 instance poly(lactic acid) (PLA) and polyhydroxyalkanoate (PHA) or, biodegradable,

38 produced from petroleum including aliphatic plastics such as polybutylene succinate (PBS)

39 [11]. The evaluation and description of the bio-based content of polymeric materials is

40 defined in the European standard CEN/TS 16295:2012 [2]. This method is based on the

41 amount of bio-based carbon as a fraction of the total organic carbon content. Fully

42 biodegradable polymers, i.e. PLA, starch blends and PHAs, have the highest worth amongst

43 bio-based polymers. Alternatively, the productions of conventional polymers such as bio-

44 polyethylene (Bio-PE) or polyethylene terephthalate (PET) based on renewable resources are

45 also gaining attention [2].
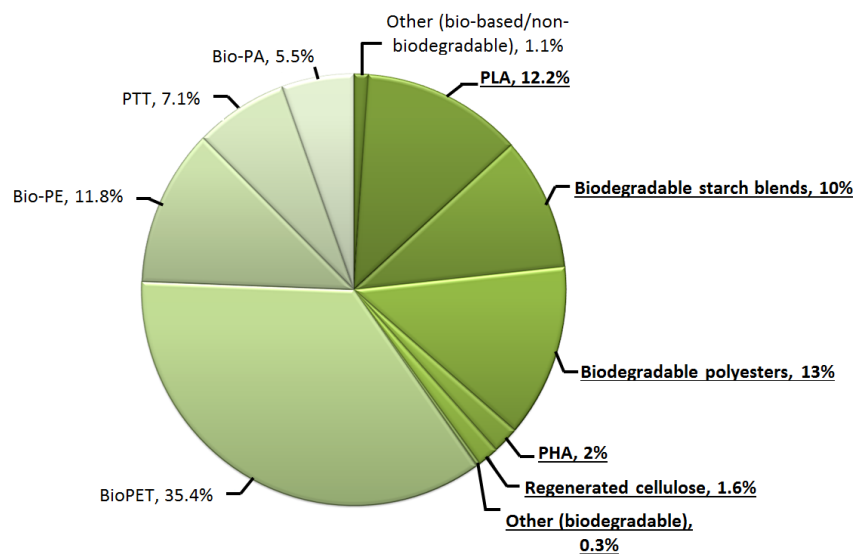
46
47 **Fig. 1 Worldwide biopolymer production capacities in 2014**

48 It is reported that in 2014, biopolymers overall production capacities amounted to 1.7 million

49 tonnes (Fig. 1). The biopolymers written in bold and underlined in Fig. 1 are fully

50 biodegradable and account for 39% of the total global production while non-biodegradable

51 biopolymers amount to 61%. This paper attempts to deliver a sensible overview of recent

52 scientific trends and achievements in the field of biopolymer-based bio-composites, where

53 the interfacial bonding mechanisms is discussed with the role of coupling agents/additives

54 and their impact on performance of biopolymer-based bio-composites. Fig. 2 represents the

55 schematic illustration of the topic reviewed and the importance of interfacial bonding quality.
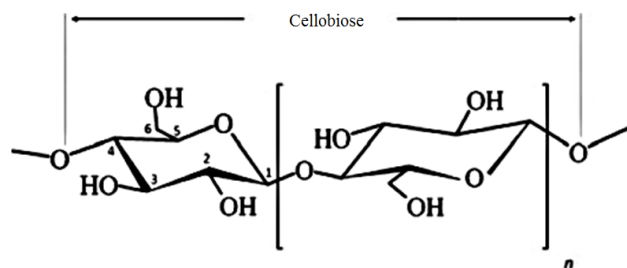
2. Biopolymers

2.1. Cellulose-based polymers

Cellulose is the most abundant natural biopolymer, a linear homo-polysaccharide composed of β-D-glucopyranose units connected by β-1-4-linkages with a repeating unit of cellobiose [12] (see Fig. 3).


Fig. 3 Molecular structure of a cellobiose unit [13]

Cellulose can also be produced by green algae and some bacteria, primarily of the types: *Acetobacter*, *Sarcina* and *Agrobacterium* [14]. In terms of chemical structure, bacterial cellulose (BC) is the same as that produced by plants. However, it exhibits higher crystallinity, water-holding capacity, degree of polymerisation, and mechanical strength [15]. BC has proved to be effective in producing hierarchical composites, which can offer a way for long micrometre sized fibres to be more successfully utilised in composites by improving coupling between the biofibre surface and the biopolymer matrix [16].

Cellulose is an extremely crystalline polymer, with a high molecular weight, that can be infused in all but the most aggressive hydrogen bond breaking solvents, i.e. N-methylmorpholine-N-oxide. As a result of its infusibility, cellulose is usually converted into derivatives to permit easier processing. Such derivatives include cellulose ethers, for example methylcellulose (MC), carboxymethyl cellulose (CMC), hydroxypropyl cellulose (HPC),

78 hydroxypropyl methylcellulose (HPMC), and cellulose esters, such as cellulose acetate (CA),

79 cellulose acetate propionate (CAP), and cellulose acetate butyrate (CAB). Among the

80 cellulose ethers, HPC is a true thermoplastic resin and is, therefore, able of being extruded

81 into films from the molten state [17]. Huber et al. [13], in their review paper propose the all-

82 cellulose composites as a strategy and approach to formulating green composites that

83 eliminate the chemical incompatibilities between reinforcement and matrix phases by

84 utilising cellulose for both components although there is a need for further investigation to

85 find appropriate and/or successful industrial applications for all-cellulose composites. The

86 hydrophilicity of cellulose will require further processing to avoid swelling and degradation

87 in long-term applications.

2.2.   Starch-based polymers

89 Starch is generally constituted of two homo-polymers of D-glucose: i) amylase, a linear α-

90 D(1, 4')-glucan and ii) branched amylopectin, which has the same backbone structure as

91 amylose however with many α-1, 6'-linked branch points [18] (see Fig. 4).
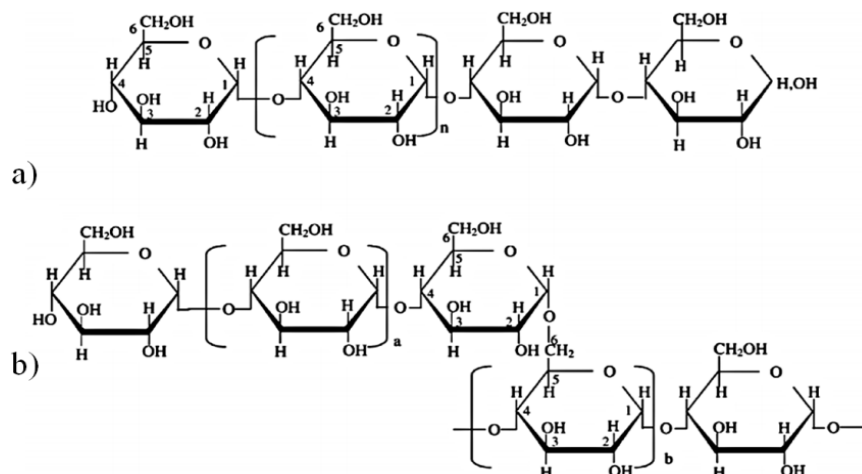
92
93 **Fig. 4 Chemical structure of (a) amylose and (b) amylopectin** [19]

94 Starch degrades into sugars and organic acids that serve as feedstocks for producing

95 bioplastics (i.e. thermoplastics). Starch could be changed into a continuous polymeric

96 entangled phase by mixing with adequate aqueous or non-aqueous plasticisers, i.e. polyols

97 such as glycerol [20]. Blending starch and PLA could dramatically reduce the cost and

98 enhance the biodegradability of biopolymers [7,21,22]. Starch blends with aliphatic

99 polyesters, from microbial sources present good potential in the future [23,24]. Starch

100 rheology may not always be appropriate for the use as matrix in composites, i.e. their high

101 sensitivity to creep and scattering of properties [25]. Blending with nano-metric form of clay

102 could be a strategy to overcome this issue. Results suggested that during gelatinisation, the

103 structural part of starch (i.e. amylose), interacted with a nano-clay interlayer and so enhanced

104 the reinforcement and modulus values. This was mainly effective with wheat and corn starch,

105 but not so much with potato and waxy corn, as their modulus values decreased rapidly at

106 higher temperatures [26]. The multiphase transitions of starch, results in the mechanical and

107 microstructure characteristics of starch-based polymers to be dependent on the processing

108 methods and conditions [27].

109 ### 2.3.   Lignin-based polymers

110 Lignin is a complex three-dimensional polymer created by radical coupling polymerisation of

111 *p*-hydroxycinnamyl, sinapyl and coniferyl alcohols which lead to *p*-hydroxyphenyl (H),

112 syringyl (S) and guaiacyl (G) phenylpropanoid units [28] (see Fig. 5).

113
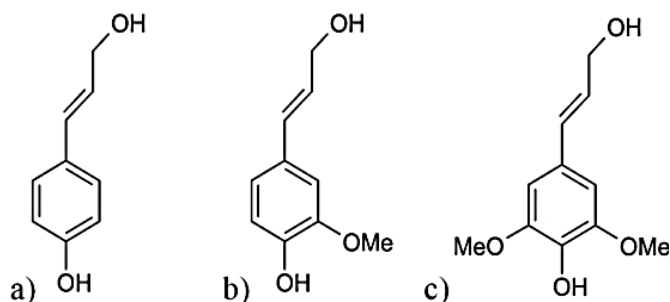
114 **Fig. 5 Three primary lignin monomers: (a) monolignols p-coumaryl alcohol MH, (b) coniferyl**
115 **alcohol MG and (c) sinapyl alcohols MS**
116

117 The bio-refinery projects for developing of biofuels, bio-based materials and chemicals from

118 carbohydrates (i.e. cellulose and hemicellulose) generate huge quantities of lignin. Hence,

119 lignin and its potential use in biopolymer-based bio-composites have been reviewed

120 extensively [29,30]. Lignin can also be implemented as an additive in the production of

121 biopolymer-based bio-composites for added functionalities. The evolution of lignin-based

122 polymers needs better processing technologies along with tailored bioenergy crops having

123 lignin with the desired chemical and physical characteristics [31]. Lignin chemical

124 modification and plasticisation is employed to improve its dispersion in polymers [32]. The

125 distinctive phenolic chemistry of lignin enables its utilisation for the high value polymer

126 industries, such as replacement of phenolic by lignin in resins systems [33,34]. Chung et al.

127 [35] developed a catalytic and solvent free method for synthesis of a lignin–PLA copolymer

128 in order to increase the miscibility of lignin with other bioplastics. Graft polymerisation of

129 lactide onto lignin catalysed by triazabicyclodecene led to a lignin-g-PLA copolymer which

130 showed a glass transition temperature range from 45 to 85°C and a multiphase melting

131 behaviour. The lignin-g-PLA copolymers can be utilised as dispersion modifiers in PLA-

132 based composites to improve UV absorption and reduce brittleness without impeding the

133 modulus of elasticity [35].

2.4. Vegetable oil-based polymers

Vegetable oils are esters formed by glycerin and different fatty acids containing from 8 to 24 carbon atoms and between 0 and 7 carbon-carbon double bonds, subject to the type of plant and environment conditions of growing (see Fig. 6) [36]. Vegetable oils derived fatty acids can be a good source for different polymers and polymer precursors. They count as a valuable renewable feedstock processed in the chemical industry and in the preparation of bio-based functional polymeric materials [37–39]. They have been applied for the production of biopolymer composites incorporating organic or inorganic fibres, with micro- and/or nano-size [40,41]. Vegetable oils have reactive functional groups in their fatty acid chains, such as hydroxyls (castor oil and lesquerralla oil) or epoxies (vernonia oil), that can be utilised directly for polymerisation [37]. This can be attained via chemical modification of the naturally occurring reactive sites found in triglycerides (e.g., ester groups and carbon-carbon double bonds), thus opening synthesis routes similar to those established for petrochemical polymers [42]. Vegetable oils with aliphatic chains have been implemented in the production of polyols as soft amorphous segments, adding flexibility to the resulting polyurethane (PU), whereas cyclic isocyanates function as hard segments, adding mechanical strength. These segmented structures bring a stable combination of characteristics to the PUs, including elasticity, mechanical strength, toughness and degradation [43]. Condensation polymers, like polyesters and polyamides, have also been derived from vegetable oils, long-chain polyamides and polyesters derived from plant oils through olefin metathesis and isomerizing alkoxy carbonylation methods are rather interesting as polymeric materials [44,45]. These materials have been put forward as potential renewable replacements for polyethylene [46].
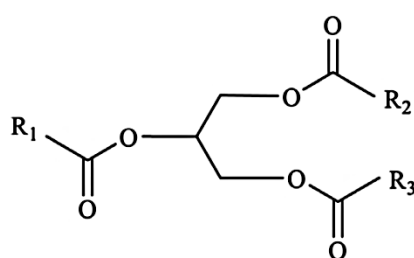
Fig. 6 Tryglyceride structure, R_1, R_2, R_3 represent fatty acid chains

2.5. Polyhydroxyalkanoates

Polyhydroxyalkanoates (PHA), have a range of side chains and fatty acids with hydroxyl groups. They consist of (R)-3-hydroxy fatty acids [47] and can be produced by many different types of microorganisms from renewable sources. PHAs are composed of 3-hydroxy fatty acid monomers, which form linear, head-to-tail polyester shown in Fig. 7 [48].
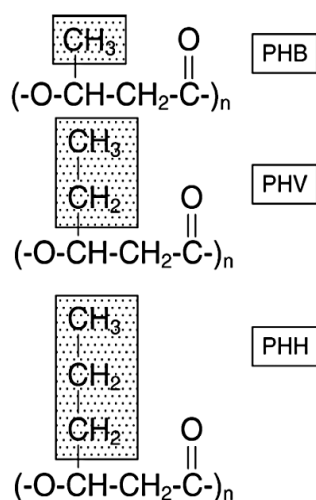
Fig. 7 Chemical structure of PHAs; Structures shown here are polyhydroxybutyrate (PHB), polyhydroxyvalerate (PHV), and polyhydroxyhexanoate (PHH)

The monomer of this bio-polyester differs in composition, macromolecular structure and physicochemical properties, depending on the producer organism and on the carbon source used for the growth [49]. The statistics illustrates that starch and whey-based materials are easily utilised by microorganisms, as shown by their much higher production levels (Table 1).

Table 1 Some of PHA production from various sources and media types

Microorganism	Carbon source	Production level (g/L)	Ref.
Azotobacter vinelandii	Molasses	23	[50]
Pseudomonas fluorescens	Molasses	22	[51]
Ralstonia eutropha	Potato starch	94	[52]
Cupriavidus necator	Glycerol	38	[53]
Cupriavidus necator	Glycerol	16	[54]
Escherichia coli	Whey	96.2	[55]
Bacillus megaterium	Sugarcane molasses	1.27	[56]

The realisation of high yields of PHA with acceptable economic feasibilities for scaling up is a bottleneck for researchers to tackle. Parameters such as efficient bacterial strains, cheap carbon sources, optimised fermentation and recovery processes are vital for the successful industrial commercialisation of PHA. It has been stated in a study that the carbon source, e.g.

177   glucose, contributes almost to 30% of the total cost of PHA from *Escherichia coli* [57].

178   Moreover, it was proved that the cost of producing PHA via syngas fermentation is more

179   economic than producing PHA by sugar fermentation, which ranged from 4 to 6 US$/kg

180   [58]. PHA synthesis using renewable organic wastes as a carbon source and mixed cultures

181   [59] similarly presents a potential route to successful industrialisation of PHA, as it is

182   important to develop strains that could extent high final cell density in a relatively short

183   period of time and produce high PHA content [60]. Polyhydroxybutyrate (PHB)

184   homopolymers, polyhydroxybutyrate-co-hydroxyvalerate copolymers (PHBV) and other

185   associated linear polyesters, can present substantial opportunities for successful

186   commercialisation. Natural isolates, recombinant bacteria, biomass with different

187   methodologies are being investigated to apply more control over the quality, quantity and

188   economics of poly(3-hydroxybutyrate) (PHB) commercialisation [61]. PHB is brittle,

189   therefore, co-polymerisation of -hydroxybutyrate with hydroxyvalerate is a strategy used to

190   synthesising a polymer called poly(hydroxybutyrate-co-hydroxyvalerate) (PHBV) [62] this is

191   also in line with optimising the performance which leads to wider applications and therefore

192   commercialisation. Additionally, the blending of PHAs can provide robust grounds for

193   expanding their variety of applications. The P(3HB)/PLA blend is one of the most studied

194   blends, which exhibits mechanical properties that are intermediate between the individual

195   components [61,62].

196   **2.6.   Polylactic acid**

197 Polylactic acid (PLA) is biodegradable by hydrolysis to lactic acid, and eventually to water

198 and carbon monoxide. Its biodegradability hugely depends on the molecular weight. This

199 aliphatic polyester is a thermoplastic derived from renewable plant sources. Corn, is the most

200 effective source for providing high-purity PLA [65]. The first full-scale industrial plant

201 capable to produce 140,000 metric tons per year of PLA was started in Blair, Nebraska, USA

202 in 2002 [6]. Lactic acid, (i.e. 2-hydroxy propionic acid), is the basic monomer of PLA. The

203 monomer occurs in two stereo isomers, L-LA and D-LA. Fig. 8 illustrates chemical structures

204 of these two isomers [66].

(*S*)-Lactic acid
L-(+)-Lactic acid

(*R*)-Lactic acid
D-(-)-Lactic acid
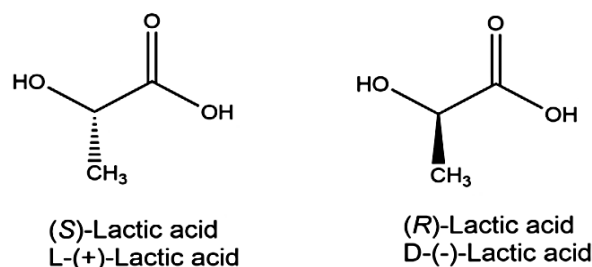
205
206 **Fig. 8 Chemical structure of L(+) and D (-) lactic acid**

PLA is composed of lactic acid (2-hydroxy propionic acid) building blocks and has high
tensile strength and modulus properties. The addition of reinforcing fibres, micro- and/or
nano-fillers, and selected additives within PLA matrix is considered as an effective method
for obtaining bio-based composites with specific end-use characteristics and improvements of
properties. PLA was grafted to glycidyl methacrylate (GMA) as a possible compatibiliser for
PLA and bamboo flour [67]. The mechanical performance, phase morphology and thermal
decomposition temperature of the PLA-g-GMA composites were improved compared to
those composites without this compatibiliser. Amongst PLA blends, poly(butylene adipate)-
co-terephthalate (PBAT) and poly(butylene succinate)-co-adipate (PBSA) have hugely
helped to combat some of the PLA's disadvantages [68].

2.7.   Chitin

Chitin and chitosan come from the linear polysaccharides family distributed randomly and
not blocked together, the residues are linked completely in the β-1, 4-configuration (see Fig.
9). Chitosan is a linear polysaccharide formed by deacetylation of chitin, and is used in
agriculture, biomedicine and filtration technologies.
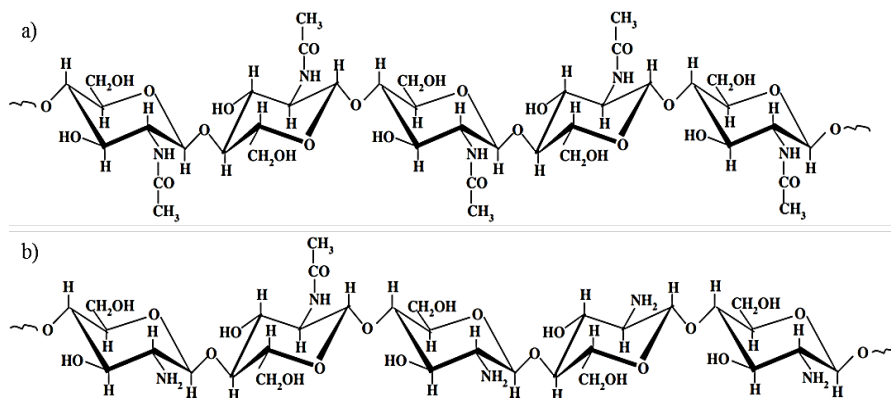
Fig. 9 Structure of a) chitin and b) chitosan [69]

After cellulose chitin is one of the most abundant biopolymer. Both chitin and chitosan are
linear copolymers of D-GlcN and D-GlcNAc residues
Regardless of its enormous availability, the utilisation of chitin has been restricted by its
intractability of molecular structure and insolubility [70]. The insolubility of chitin in
virtually all common solvents has been a main bottleneck in its appropriate utilisation [69].
Moreover, the corrosive and degradative nature of solvents is problematic and the
environmental tolerability of these solvents has to be measured. The high value of viscosities
of chitin solutions in certain solvents lead to complications in processing and therefore it
needs to be investigated.

Chitin and chitosan are utilised as biopolymer matrix and nano-filler for the manufacture of bio and nano-composites due to their renewability, biodegradability, distinctive biological and physicochemical characteristics. They also have huge structural possibilities for chemical and mechanical alterations which enable novel properties, functions and applications. The essential aspects of chitin and chitosan such as their preparation, crystallography, extent of N-acetylation, and some other properties are presented in a review paper [71], with discussion on their chemistry and elemental modification reactions, e.g. acylation, alkylation. On the other hand, Julkapli et al. [72] review the applications of chitosan based composites in the area of drug delivery, tissues engineering, and food packaging.

2.8. Silk proteins

Silks could represent a good potential as sustainable, environmentally friendly and commercial biopolymers source [73]. Silk fibres are composites made of silk protein and other accompanying molecules such as glycoproteins and lipids. Several animals produce silk-based composite materials which can be utilised for a variation of task specific applications. Out of all the natural silk-producing animals, mulberry silkworms (*Bombyx mori*) have the highest economic value, as it is possible to rear them in captivity [74]. Silkworms produce polyamino acid-based (silk protein) cocoons to protect themselves during their metamorphosis into moths. Humans have been harvesting silk fibres from these cocoons for centuries to yield textiles due to their characteristic luster, moisture absorbance and good strength [74]. A number of reviews have concentrated on the structure and properties of spider silks, with the main focus on dragline silks and also their applications for composite materials [73,75–78]. Spider silks have been a focus of research due to their outstanding mechanical and biophysical properties. Moreover, recent breakthroughs in genetic engineering have led to the synthesis of recombinant spider silks, leading to unravel of fundamental knowledge of structure to function to property relationships. Comprehensive understanding of the silk's primary structural elements and their contributions to the physical and biological properties of this biopolymer are important in order to maximise its potential.

3. Biopolymer-based bio-composites

Many parameters must thoroughly be investigated for a better understanding of performance mechanisms of biopolymer-based bio-composites, such as the volume fraction, characteristics, orientations and pre-treatments of natural fibres, and processing parameters of composite, all of which contribute to the interfacial quality and hence the overall performance of composites. The chemical incompatibility between a hydrophobic biopolymer matrix and hydrophilic biofibre results in a poor interfacial bonding quality. This then translates into an

267 inefficient stress transfer under load and therefore low mechanical strength/stiffness and
268 physical properties.

3.1. Addressing the limitations of biopolymer-based bio-composites

270 Most biopolymers are water sensitive, in that they absorb water and may even be water
271 soluble, causing their properties to deteriorate. This is normally overcome by blending them
272 with polymers or plasticisers to enhance their performance. The inherent biodegradability of
273 biopolymer means that it is essential to control the environment in which the biopolymers are
274 used, in order to prevent their premature degradation. This could be accomplished via the
275 control of moisture, nutrients or microorganisms. Moreover, some biopolymers are not
276 thermally stable, which limits their application. Some of drawbacks with the biofibres are the
277 tendency to form aggregates during processing and their poor resistance to moisture which
278 could lead to dimensional instability and hence deterioration of composites. The moisture in
279 biofibres can lead to poor process-ability. The most common way to reduce the moisture
280 absorption of biofibres is through the process of alkalisation [79]. Alkalisation partially
281 dissolves the hemicellulose, the most hydrophilic part of biofibre structures, which
282 subsequently leads to the reduction of the biofibres to absorb moisture. Alternatively,
283 polymer coatings can also reduce the moisture absorption. Doherty et al. [80] enhanced
284 moisture absorption properties of biofibres by applying a natural, lignin-based coating. This,
285 however, might only be effective for short term protection against moisture. Exposed
286 biofibres could also undergo photochemical degradation caused by ultraviolet light, although
287 this can be overcome by bonding chemicals to the cell wall or by adding a polymer to the cell
288 matrix. The production of thermoplastic composites with biofibres and/or fillers is limited by
289 the temperatures and processing times that they can be exposed to, before experiencing
290 significant degradation. This limits the biopolymer matrices to lower melt temperature ones
291 such as: PLA (i.e. [81,82]), poly(butylene adipate-co-terephtha-late) (PBAT) (i.e. [83,84])
292 and PHAs (i.e. [85–87]). In order to increase the thermal stability of biofibres, attempts have
293 been made to coat and/or to graft them with monomers. Grafting is possible as the lignin of
294 biofibres can react with the monomers. Mohanty et al. [88] showed that grafting of
295 acrylonitrile on jute improved the thermal stability as the degradation temperature increased
296 from 170 to 280˚C. Most importantly for construction sector, the fire performance of
297 biopolymer-based bio-composites is additional technical bottleneck for its commercialisation.
298 Although, substantial work has been done with the intumescent systems (coatings or
299 additives) which have potentials fire barrier treatments. When intumescent materials are

heated beyond a specific temperature, they begin to foam and expand, forming a cellular, charred surface that protects the underlying material from the heat flux or flame.

4. Enhancing the interfacial bonding quality of biopolymer-based bio-composites

It has been argued that the micro porosity could be the most influential factor for the formation of robust interfacial bonds. Similarly, it can be argued that the correct functional chemistry can have the same level of importance. Performance of biopolymer-based bio-composites strongly depends on the interface quality between the biofibres and the biopolymer [89,90]. There are various theories of adhesion proposed that could be both complementary and contradictory, i.e. mechanical interlocking, electrostatic theory, theory of weak boundary layer, thermodynamic (wettability), diffusion theory and chemical bonding theory [91]. The wettability of biofibres can be regarded as an essential precursor to bonding, where biofibre and biopolymer establish an intimate contact for the superior quality interface. Insufficient biofibre wetting translates into interfacial defects, which then acts as stress concentrators. Biofibre wettability can influence the toughness, tensile and flexural strength of composites. Physical and chemical pre-treatments can improve the wettability of the biofibre, and hence the interfacial quality (i.e. strength). This can be attained for example by bleaching, grafting of monomers, acetylation, corona or plasma pre-treatments. Some pre-treatments of biofibres focus on the removal of non-cellulosic constituents from the surface to provide an intimate contact, i.e. removal of impurities and waxes, which can increase the roughness and the chances of mechanical entanglement as predominant bonding mechanisms. Others focus on separating the large biofibre bundles into smaller bundles to provide greater surface area for biopolymer matrix interaction [92]. Biopolymer (PHB) composite, reinforced with sugarcane bagasse biofibres subjected to steam explosion pre-treatment showed a significant increase in the maximum stress compared to untreated biofibres. The surface morphology of untreated biofibres impeded the bonding with PHB, whereas the pre-treated biofibres were much more compatible with PHB and led to a homogeneous composite [93]. Interfacial tailoring/optimisation may also be considered from the biopolymer matrix side. The focus would be on interfacial effects caused by bulk modification of the biopolymer matrices through nano-fillers dispersion, and possible nano-structuring within the biopolymer matrix [94]. Interfacial bonding quality would also increase by using nano-sized forms of cellulose, i.e. bacterial cellulose, micro fibrillated cellulose and cellulose whiskers [13]. Improvements in mechanical performance can be achieved by the aforementioned approaches, though, additional cost and complexity to the mix formulation of biopolymer-biofibre composites would inevitably be encountered.

334 Graupner [95], showed that the addition of lignin has a promoting influence on the adhesion

335 between biofibre and matrix. Tensile strength and Young's modulus were improved (by 9%

336 and 19% respectively compare to samples without lignin), although the impact properties

337 were decreased [95]. The presence of lignin causes embrittlement of the composites. Oksman

338 et al. [96] reported similar results in their work. By adding lignin to biopolymer-based bio-

339 composites, an improved connection between biofibre and matrix and between the single

340 biofibre layers of the multilayer web could be achieved, resulting in reduced delamination.

341 Xiong et al. [97] reported template-guided assembly of silk fibroin on cellulose nanofibers

342 which can result in well-ordered and stable periodic silk fibroin-cellulose nanofiber

343 nanostructures that allows for the fabrication of ultrathin nanocomposite membranes with

344 enhanced mechanical robustness and added functionalities.

4.1. Coupling agents

346 Coupling agent acts as a bridge between the biofibre and biopolymer matrix to create the

347 chemical bond and promote interfacial bonding in composites. They facilitate the hydroxyl

348 groups at one end to react with the fibre surface and another functional group at the other end

349 to bond with the polymer matrix [98]. The mechanism of coupling agent may be illustrated in

350 Fig. 10. The coupling agent is chemically bonded with the hydrophilic fibres and blended by

351 wetting in the polymer chain [99].
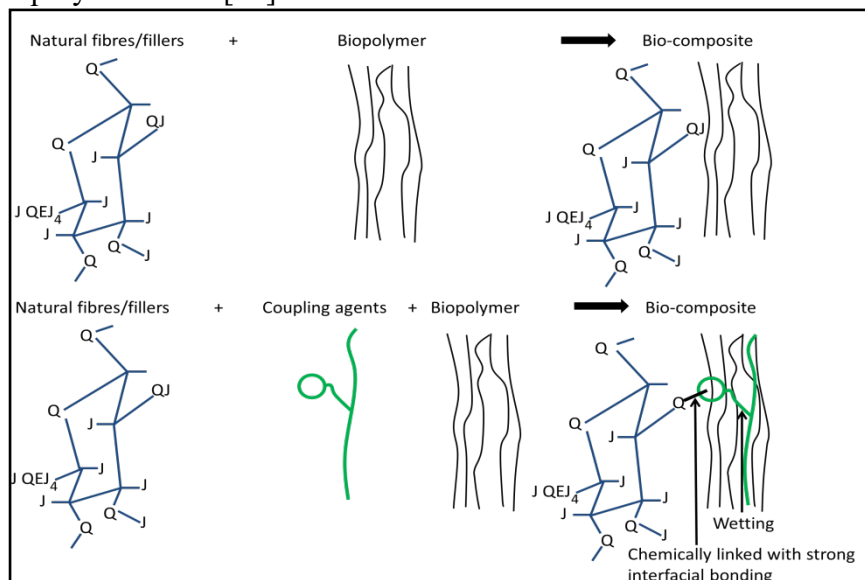
Fig. 10 Coupling mechanism between hydrophilic fibre/filler and hydrophobic biopolymer matrix

4.1.1. Bio-based coupling agents

356 Biopolymers, such as chitin, chitosan and zein, have been used as coupling agents for bio-

357 composites production. The benefits of chitin, chitosan and zein are their wide availability,

358 non-toxicity, biocompatibility and lower price in comparison to synthetic coupling agents.

Zein, extracted protein from corn, possesses many functional groups on its molecular chain, which makes it suitable as a coupling agent. Polar groups such as carboxyl and amino groups in zein react with the hydroxyl group of biofibres via hydrogen bonds, while the alkyl and aryl groups react with a polymer matrix through hydrophobic interactions [100]. Lysine-based diisocyanate (LDI) is another example of bio-based coupling agent which has proved to enhance the tensile properties, water resistance, and interfacial adhesion of bio-composite from PLA and poly (butylene succinate) (PBS) with bamboo fibre as reinforcements [101]. LDI reacts with hydroxyl or carboxyl groups in PLA or PBS, leading to the establishment of urethane bonds that can be completely hydrolysed into raw materials. The polyurethane synthesised from LDI, glycerol, and ascorbic acid can be biodegraded in aqueous solution and yield the non-toxic breakdown products of lysine, glycerol, and ascorbic acid [102].

4.1.2. Silane

Silane is a multifunctional molecule which is used as a coupling agent to modify fibre surfaces. The effectiveness of silane is dependent on a number of parameters including hydrolysis time, organo-functionalised silane, temperature, and pH. It undergoes several stages of hydrolysis, condensation and bond formation during the treatment process of the biofibre [103]. Silane chemical structure could be represented as $R-Si-X_3$, where R is the functional organic group and X is the hydrolysable group that forms silanols in the presence of moisture [98,104]. Silanols and hydroxyl groups of biofibres could then form covalent bonds of –Si-O-C [105,106]. The functionality of the R group plays a major role in the reactivity of silane towards biopolymer matrix. Trialkoxysilanes have been applied extensively for biopolymer-based bio-composites to enhance the interfacial bonding quality [98]. The physical blending of the silane-treated biofibres with thermoplastic matrices improves their mutual adherence through inter-molecular entanglement, or acid–base interactions. Aminosilanes, especially (3-aminopropyl) triethoxysilane (APS), are used as coupling agents between biofibres and biopolymer-PLA [98,107–109]. For example, silane treatment was used for kanaf fibres reinforced PLA laminated composites [108], where the compatibility between kenaf fibre and biopolymer matrix was enhanced. An improved interfacial interaction (Fig. 11b) resulted in high mechanical performance of pre-treated fibres (alkali-NaOH 5% w/v for 2 hours at room temperature, followed by silane 5% wt APS). Fig 11a shows the aggregation at the surface and fibre breakage and pull out which is an indication of poor fibre/matrix adhesion.
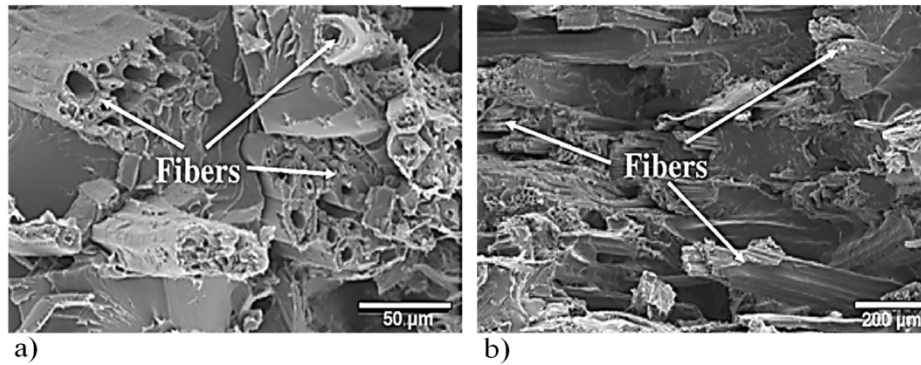
Fig. 11 Micrographs of impact fracture surface of PLA composite (PLA/fibres= 60/40 wt%): (a) untreated fibres and (b) alkali followed by silane treated fibres [108]

Additionally for other biopolymers apart from PLA, the use of the silane coupling agent, as the adhesion promoter, has been proved, where an improvement of the storage modulus of PHB–flax bio-composites of up to 106% was observed [110]. The various methods to pre-treat biofibres with silane can be divided into: i) fibre surface pre-treatment and ii) cell wall modification. Spraying is a simple method to pre-treat the biofibre surface with a silane solution, although, this only leads to a coating where the inner cell walls structure is not affected. Silane solution and initiator can directly be pumped into an extruder during extrusion process [111]. The extruded composites can subsequently be exposed to high humidity and temperature environment in order to facilitate the hydrolysis and condensation processes of the silane. Nonetheless, this strategy can be long process for the hydrolysis and condensation stages. In comparison, for the impregnation strategy, the penetration of silanes into cell walls depends significantly on the molecular size of silane. Incomplete hydrolysis processes may lead to a fast condensation of silanols, and hence prematurely increasing the molecular size of the silanes, where as a results, the diffusion of silanes into the cell walls becomes very limited. The bulking pre-treatment of biofibre cell walls can change their characteristics and stimulate the performance enhancement of the resultant bio-composites. In comparison to the surface treatment, i.e. spraying, the impregnation process can cause problems for fine and short fibres/fillers, as they may aggregate and therefore, not be evenly mixed in the solution.

4.1.3. Maleated coupling agents

Maleated coupling agents lead to the effective interaction of maleic anhydride (MA) with the functional surface of biofibres [112]. MA is grafted to the equivalent biopolymer being used as the matrix for compatibility improvements. Issaadi et al. [113] studied the effects of MA grafted PLA on morphology, thermal and barrier properties of PLA/graphene oxide (GO) nanocomposites. The nanocomposite containing 3 wt% GO and 3 wt% MA grafted PLA

420 yielded the highest elastic modulus. This proves the better distribution of GO as a result of

421 coupling agent, which in turn also led to better thermal and barrier properties. Petersson et al.

422 [114], used MA grafted PLA as coupling agent for layered-silicate nanocomposites. The

423 outcome of using MA grafted PLA differed amongst the two layered silicates because of the

424 alteration in the organic pre-treatment. The bentonite layered silicate showed a more distinct

425 improvement in exfoliation and an upsurge in the mechanical properties because of the

426 addition of MA grafted PLA, in comparison with a hectorite layered silicate.

427 Blending PLA with MA grafted wheat starch was carried out with a lab-scale co-extruder,

428 where the interfacial adhesion between PLA and starch was significantly improved and

429 hence, mechanical properties increased in comparison to the virgin composites of PLA/starch

430 [115]. MA grafted PHA was used for evaluating the thermal properties and biocompatibility

431 of composites of PHA and hyaluronic acid (HA) [116]. The lower melt torque of the MA

432 grafted PHA and HA composites facilitated their processing. The water resistance of PHA

433 grafted MA and HA was also higher. It was reported that the glass transition temperature and

434 crystallinity of PLA films diminished with adding of the MA, due to chain branching as a

435 results of the grafting reaction between PLA and MA, leading to a upsurge in the segmental

436 mobility of the PLA chain [117].

4.1.4. Isocyanates

438 Isocyanates function is by the establishment of covalent bonds between the hydroxyl groups

439 of biofibres and the functional groups, i.e. N=C=O via urethane linkage. Some of the most

440 common isocyanate coupling agents are shown in Table 2 [118].

441 **Table 2 Isocyanate coupling agents for bio-based polymer composites**

Name	Structure
Methylenediphenyl diisocyanate (MDIC)	
Polymethylene polyphenyl isocyanate (PMPPIC)	
Toluene 2,4-diisocyanate (TDIC)	
Hexamethylene diisocyanate (HMDIC)	

442 Isocyanates coupling agents, such as methylene diisocyanate (MDI), toluene diisocyanate

443 (TDI), 4-4′-methylenedicyclohexyl diisocyanate (hydrogenated MDI), and hexamethylene

444 diisocyanate have been used [119–121]. These coupling agents however, have found limited

445 use because their ultimate hydrolysis products, i.e. their corresponding diamines, such as

446 4,4'- methylenedianiline and 2,4-diaminotoluene are a cancer suspect agent or produce

447 hepatitis [101]. Isocyanates are prone to hydrolysis in the presence of moisture, which

448 requires blocked isocyanates to be implemented for stopping hydrolysis reaction prior to the

449 reaction with biofibre's hydroxyl groups [122]. In corn starch-PLA composites, isocyanates

450 groups react with hydroxyl or carbonyl groups of PLA along with the hydroxyl groups of

451 corn starch to form urethane linkages [123]. The use of isocyanate coupling agents has shown

452 to enhance the mechanical properties and reduce the water uptake of composites such as

453 methylenediphenyl diisocyanate (MDIC) pre-treated wheat starch-PLA [120,123] and MDIC-

454 pre-treated pine fibre-polystyrene [122].

455 ## 5.   Additives for biopolymer-based bio-composites

456 An additional route to enhance properties such as creep and stiffness is through the

457 incorporation of inorganic fillers, e.g. calcium carbonate, calcium sulphate, and mica. The

458 influence of talc (magnesium silicate) on the engineering properties of PHBV-wood

459 composites resulted in an almost 200% improvements in both the Young's and flexural

460 modulus, as a consequence of enhanced compatibility between PHBV and wood due to

461 addition of talc [124]. Nanoclay can have a positive influence on the mechanical properties,

462 scratch resistance, glass transition temperature and stiffness, in addition to influencing the

463 thermal and flammability properties of the biopolymer-based bio-composites [125]. The

464 incorporation of citric acid as a crosslinker with montmorillonite nanoclay resulted in an

465 increase in the mechanical properties by more than 10% [126]. Bioamidie™ which is a bio-

466 additive also resulted in significant enhancement in the mechanical properties where the

467 tensile modulus of biopolymer-based bio-composites was improved by 26% and the impact

468 strength by 20% (Izod test) as the interface generated a strong network [127].

469 ### 5.1.   Plasticisers

470 Plasticisation is often used for biopolymers to improve their process-ability. It's one route to

471 overcome the brittleness and low impact resistance of the biopolymers [128]. Plasticisers

472 exchange the intermolecular bonds among biopolymer chains to bond between the

473 macromolecules and the small molecular weight compound, hence, promoting

474 conformational changes and leading to increased deformability. Both the glass transition and

475 the processing temperature of the material decrease, therefore enabling the melt processing of

476   heat-sensitive biopolymers, like PHB, at lower temperatures [129]. Several compounds have

477   been identified as possible plasticisers for PLA, e.g. different esters [128,130], glycerol [131],

478   poly(ethylene glycol) (PEG) [132], citrates [128] and oligomeric lactic acid [131].

479   Triacetin was attempted as a plasticiser for PLA and kenaf composites where tensile strength

480   and stiffness was improved with the addition of 5% triacetin. Interestingly, the strength

481   deteriorated after addition of more than 5% [133], on the other hand, the effect was not

482   significant below 5%, as observed in another study with biofibre reinforced PLA composites

483   [134].

484   Fig. 12a shows the fibre pull out of samples without triacetin, whereas Fig.12b illustrates

485   plasticised PLA/kenaf composites where crazes were evident.

486
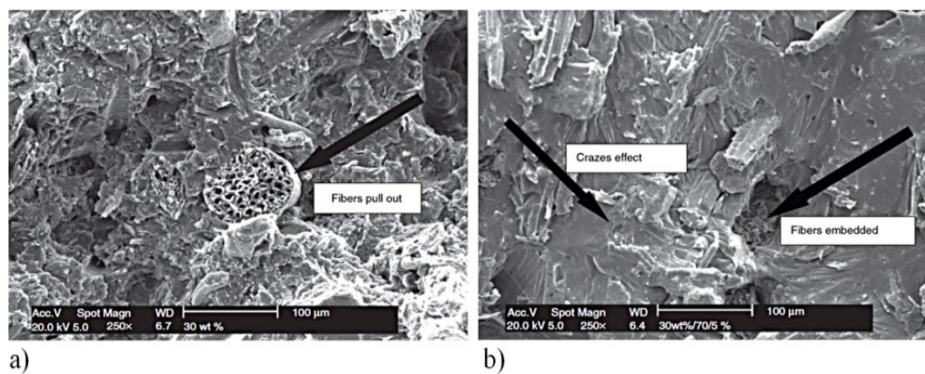
Fig. 12 Fracture surfaces of PLA/kenaf bio-composites at 30 wt%: (a) un-plasticised and (b)
487
plasticised with 5% triacetine [133]**.**
488

489   A suitable strategy to modify the biopolymers can be the plasticisation and physical blending.

490   The chemical modifications of the components or reactive compatibilisation are often used to

491   achieve holistic property combinations needed for a specific applications. An example of

492   chemical modification is the copolymerisation of PHB. With changing co-monomer type and

493   amount, the characteristics and performance of PHA can be altered to a fairly wider range

494   [135].

495   **5.2.   Fire retardant additives**

496   Composites that incorporate cellulosic materials as a filler are extremely vulnerable to

497   burning as a result of the hydrocarbons that will ignite indirectly during combustion, while

498   the biopolymer matrix will begin to degrade with an increase in temperature into various

499   volatile gases that may react with oxygen and further contribute to the combustion behaviour

500   [125]. The most common method to render cellulosic fibres fire retardant is by using P-

501   containing compounds, such as phosphoric acid (PA), tributyl phosphate (TBP), triallyl

502   phosphate (TAP), triallyl phosphoric triamide (TPT), ammonium polyphosphate (APP) ,

503   monoammonium phosphate (MAP) and diammonium phosphate (DAP) , also the addition of

intumescent zeolites, natural clays, organoclays and zinc borates have been investigated to design flame retardant polymer nanocomposites which drastically enhance fire performance [79,136]. The implementation of APP to produce biopolymer-based bio-composites has shown to significantly improve the flame retardancy and limit oxygen index measurements with minimal influence on the mechanical properties [96]. The addition of APP showed no significant changes to microstructure (Fig. 13) suggesting that the APP is well dispersed into the biopolymer-based bio-composite and did not inhibit the interfacial bonding.

a)   b)
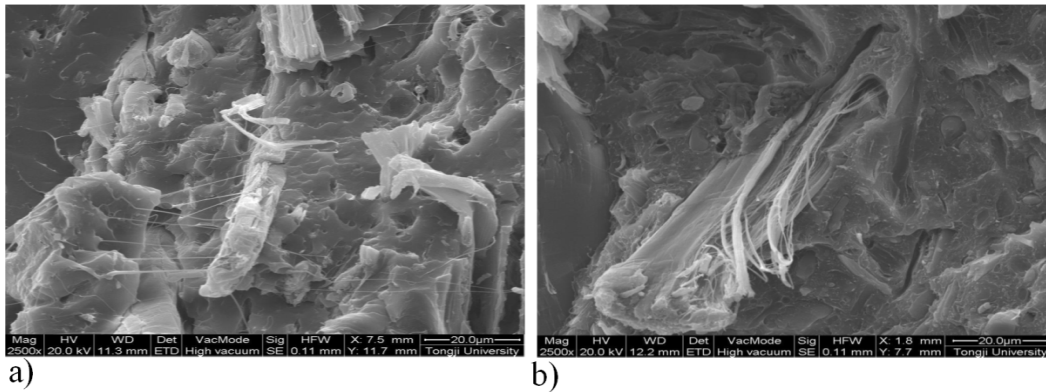
Fig. 13 Micrographs of impact fracture surface of fiber-reinforced PLA biocomposites (a) untreated fibers (b) fibers treated with APP

The addition of nanoclay into short biofiber reinforced PLA composites witnessed higher thermal stability with lower weight loss rate than that of the pure PLA and improved fire behaviour due to the inorganic nature of clay particles as well as nano dispersion, which leads to more homogeneity between the biofibre and the clay, thus inhibiting access to oxygen and preventing combustion process from being sustained [126].

5.3. Durability additives

Mould, mildew, and stains can impede the performance of biopolymer-based bio-composites and this has driven manufacturers to consider antifungal biocides that protect either the biopolymer component and maintain its surface appearance or that preserve the biofibre component from decay and moisture absorption. The inclusion of coupling agents and compatibilisers (additives) can lead to a slower moisture uptake of biopolymer-based bio-composites [137], as a result of stronger interfacial bonds and the limiting of moisture pathways. An increase in micro cracks translates into additional pathways for moisture, enzymatic, and microbial ingress which leads to biofiber swelling, increased damage at the biofiber-matrix interface, propagation of cracking, and further accelerating degradation. A common method to enhance the durability of thermoplastic composites has been through the addition of anti-microbial agents such propertiespoly-diallyl-dimethyl - ammonium chloride (PolyDADMAC), cetyltrimethylammonium bromide (CTAB), and silver (Ag) which

can be easily implemented into biocomposites to enhance the anti-microbial properties and increase their life span [138]. The addition of silver base inorganic filler tended to markedly increase the degree and rate of biodegradation in which the degradation of PLA involved the hydrolysis reaction and subsequent enzymatic-biodegradation by microorganism [139], however, due to a lack of diffusivity with silver, tiiclosan, which is a bacterial and antifungal agent found in some consumer products, including toothpaste, soaps, and surgical cleaning treatments acted as a more efficient anti-bacterial promotor for PLA/wood composites [140].

6. Conclusions and future prospective

Considerable research efforts have been made to narrow the performance gap between biopolymer-based bio-composites and their synthetic counterparts by improving the compatibility, i.e. interfacial bonding quality. The blending of biopolymers can represent a relatively cheaper and faster strategy to tailor the properties of biopolymer-based bio-composites, changing glass transition temperature, improving fracture resistance, flexibility, process-ability and other properties like optical characteristics or flammability. The chemical structure of biopolymers could open up possibilities for their reactive modification, such as copolymerisation, grafting, trans-esterification and the use of coupling agents to achieve biopolymers and blends with improved characteristics. With the intention of tailoring biopolymer-based bio-composites to fit the requirements of structural or functional materials, an in-depth investigation into a wide range of coupling agents and additives must be carried out while at the same time, novel processing protocols must be developed and assessed for industrially feasible pre-treatments of biofibres and manufacturing of biopolymer-based bio-composites.

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