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REVIEW



Composites of Wood and Biodegradable Thermoplastics: A Review

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ABSTRACT

This paper is an overview of current understanding in the areas of composites made from biodegradable thermoplastics and wood fillers. The review finds that the composite properties depend on the type of wood filler, the choice of polymer matrix, the wood filler content, the compatibilization technique used and the processing parameters. The extent of interfacial adhesion and the filler morphology are identified as the underlying factors that control the composite properties. Future research needs are identified, including establishment of fundamental relationships between quantified interfacial adhesion and end-use properties and advanced modelling of biodegradation processes.

KEYWORDS

Wood polymer composites;
biodegradable polymers;
PHA; PLA; starch

1. Introduction

A composite is a material formed from two or more materials that, when combined, yield a new material with properties different from the individual components. Reinforced plastic composites are a recent class of composite materials in which fibers of high modulus are added to a polymer matrix to overcome the low modulus and thermal instability of plastics. Inorganics such as glass fibers and ceramics have traditionally been used as the reinforcing filler for composites. However, recently, the use of organic fillers, such as lignocellulosic-based fibers, has been emerging into the market, as they give advantages over traditional inorganic fillers such as being low-cost, light weight, renewable, abundantly available, and biodegradable.¹

Wood plastic composites (WPCs) have been burgeoning internationally in the past decades. The WPC market is projected to be worth up to US\$5.8 billion globally by 2021 with a compound annual growth rate of 12.2% between 2016 and 2021.² These composites have many applications, from automotive parts to building structure components such as decking and railing.³ WPCs are typically produced by compounding lignocellulosic fillers with molten polymers and processed to the desired shape. With attractive mechanical properties,

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polyolefins, such as polyethylene (PE) and polypropylene (PP), remain the primary resins used in commercial WPCs. They are also cost effective and durable, with relatively low moisture permeability. However, polyolefin-based WPCs are a mix of synthetic and bio-based materials. Hence, they are difficult to recycle and the encapsulation of the wood by the essentially non-biodegradable polyolefin means that these materials as a whole are non-biodegradable.

In recent years, research has turned to using wholly renewable and biodegradable materials to replace traditional polyolefins in WPCs.^{1,4–6} The reasons for this include: increasing concerns about the environmental impact of polymers and/or composites due to an increased awareness of environmental sustainability and end-of-life management; pressures for reducing the over-dependence on petroleum-based chemical resources; concerns about the volume of waste in landfills; and drives towards a circular economy, in Europe in particular. The use of biodegradable polymers as the matrix for WPCs potentially ensures complete biodegradability of the composite, and the applications of WPCs can, therefore, be extended to relatively short-term uses such as food packaging as well as long-term uses such as pallets and interior furnishing, where recycling and ease of after-life management becomes a valued material attribute.

Until now, the use of biodegradable polymers in composite applications has reportedly been limited by higher cost, poor moisture and gas barrier properties, slow crystallization rate, poor stability and narrow processing windows.⁷ Specific challenges include:

- High production cost of biodegradable polymers;
- Incompatibility between hydrophilic wood and relatively hydrophobic polymer that leads to an overall reduction in mechanical properties and stability;
- Requirement of mechanical and physical stability in selected service environments (particularly with respect to moisture uptake);
- Lack of insight into the rate and extent of biodegradability that constitutes service applicability and the end-of-life environmental impact, particularly in different environments.

These challenges are now being addressed, with current investigations seeking to improve the cost-effectiveness of the production process, deliver a thorough understanding of the whole process from raw materials to end-of-life properties, as well as develop technologies to address the compatibilisation and stability issues. In addition, thorough life cycle analysis has to be performed to assess the environmental impact of this new generation of materials. The strategies that researchers have been using to overcome the above issues are reviewed herein. Recent reviews^{1,5,6} have summarized the literature on biocomposites reinforced with natural fibers. Given the broad range of natural fibers and biodegradable polymers, the present review aims to focus on the more recent literature for wood fiber and wood flour reinforced composites formed using biodegradable thermoplastics. The present work will not address natural fibers from animals (e.g. silk or wool) and plants (e.g. hemp, flax) but does include a detailed discussion of the structure and properties of wood as a background to its use in composite manufacture. The overall picture of the biocomposite mechanical properties and the details of individual studies will also be presented. We present the major challenges and critical issues in the broader context for the future of wood based biocomposites to highlight both challenges and the potential for growth for WPC engineering and applications.

This review is structured based on the flow of the production of biocomposites: from raw materials (biodegradable polymers and wood), through processing methods and composite properties, to the material end-of-life. The following keywords were used as a starting point for this work: biopolymer, polyhydroxyalkanoates, polylactic acid, thermoplastic starch, wood fiber, wood flour, wood plastic composite, biocomposite, processing, and mechanical properties.

2. Wood plastic composites – overview

Wood plastic composites have been emerging in daily life throughout the past decades, from structural components to commodity products. Figure 1a–e highlights current applications of WPCs, which include furniture, screening, containers and car interiors.^{8–11} Typically, WPCs are made up of three components: polymer matrix, wood filler and additives. Polypropylene (PP), polyethylene (PE), and polyvinyl chloride (PVC) remain the most common polymer matrices used in commercial WPC products. The type of wood varies from softwoods such as radiata pine to hardwoods such as oak. The morphology of wood fillers can be particulate flour or longer fibers. With a relatively low production cost, wood fillers are included at high contents ranging from 40 wt% to 60 wt% in commercial products.¹² WPCs are typically stiff and brittle but the incorporation of additives such as plasticizers, lubricants, processing aids, fillers etc. can alter the processing, mechanical and aging properties.¹³ The typical ranges of tensile strength, tensile modulus, and elongation at break of commercial WPCs are 12 – 47 MPa, 0.8 – 5.6 GPa and 1.4 – 5.4%, respectively, values which are also tabulated in section 6 in comparison with biodegradable polymer WPCs. Different types of additives offer individual advantages to the product. Plasticizers and lubricants are used to improve the processing and material properties of WPCs, while the use of coupling agents and inorganic fillers can tailor the properties for specific applications. Protective agents such as antioxidants, flame retardants and UV stabilizers are also used to improve the stability of WPCs.

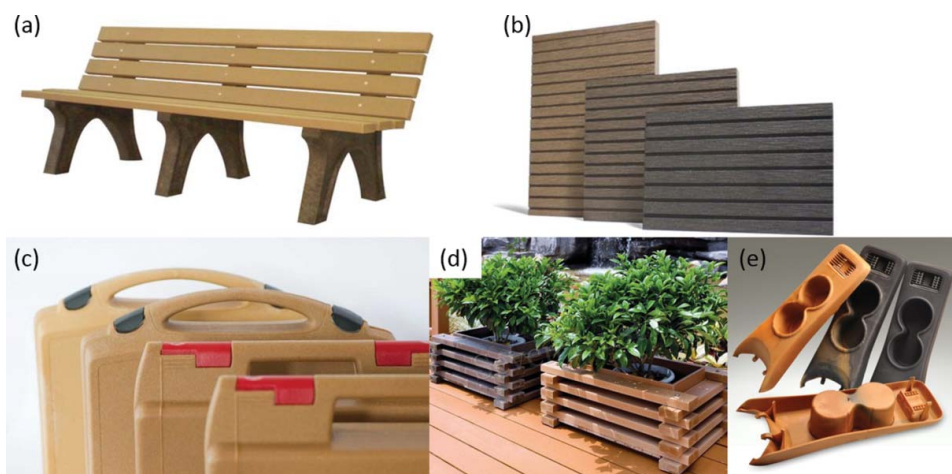


Figure 1. Commercial products made from wood plastic composites (PP, PE and PVC): (a) Park furniture (Integrated Recycling, Australia);⁸ (b) Screening (Integrated Recycling, Australia);⁹ (c) Tool box (JELU-Werk, Germany);¹⁰ (d) Plant boxes (SevenTrust, China);¹¹ and (e) Car interior (JELU-Werk, Germany).¹⁰

3. Biodegradable polymers in WPCs

Biodegradable polymeric materials are polymers that can be converted into carbon dioxide, water and new biomass by bacteria or other living organisms due to biological activity such as enzymatic action. Biodegradable polymers can be synthesized from renewable resources in plants (e.g. PLA via fermentation, starch) and bacteria (e.g. PHA) as well as from non-renewable petroleum (e.g. synthetic polyesters (PLA via chemical synthesis and polycaprolactone (PCL))). The most commonly studied biodegradable polymers have been either polysaccharides (e.g. starch) or aliphatic polyesters (e.g. PHA, PLA and PCL). These biodegradable polymers have been entering the market in different sectors. Examples of commercial products made from biodegradable polymers include: plastic packaging made from starch¹⁴ (Plantic), cutlery made from starch¹⁵ (Biopak), food containers based on PLA¹⁶ (GreenGood) and beach toys made from PHA¹⁷ (Zoebs organics). The typical mechanical and thermal properties of these biodegradable polymers in comparison to PP and PE are summarized in Table 1. Biodegradable polyesters including poly(3-hydroxybutyrate) (P(3HB), a common PHA homopolymer), PLA and PCL have similar mechanical properties to that of PP and PE, with P(3HB) and PLA being more brittle (Table 1). Starch possesses lower tensile strength and elongation at break when compared to PP and PE but the applications of plasticizers and polymer blends can improve its properties.¹⁸ The material properties of P(3HB) can also be tailored through the inclusion of other monomers, such as 3-hydroxyvalerate. The wide range of properties of the resulting random copolymer, poly(3-hydroxybutyrate-co-3-hydroxyvalerate) (P3HB-co-3HV) is also presented in Table 1. The degree of surface hydrophobicity, as indicated by the surface free energy, is also an important property, particularly for WPC applications, as it governs compatibility between the polymer matrix and the relatively hydrophilic wood filler. The surface free energies, as determined by contact angle analysis, of PP, PE and the selected biodegradable polymers are presented in Table 2. When comparing the total surface energy, it is obvious that PHA, PLA and PCL are more hydrophilic than PP and PE, because of the ester groups. Starch is the most hydrophilic of the biodegradable polymers because of the hydroxyl groups that are available for hydrogen bonding.

3.1 Poly(lactic acid) (PLA)

Poly(lactic acid) (PLA), also known as polylactide, is a biodegradable aliphatic polyester that has been widely used in packaging and medical industries. The monomer, lactic acid, can be produced by the fermentation of plant feedstocks such as corn and potato.⁴⁷ It has been extensively researched and widely utilized (see numerous published reviews^{23,48,49} and note that Natureworks has a nominal production capacity of 140,000 tons per annum⁵⁰). There are three stereoisomers of PLA (Figure 2): Poly(*L*-lactide) (PLLA), poly(*D*-lactide) (PDLA) and poly(*D,L*-lactide) (PDLLA).⁵¹ Isotactic PLLA and PDLA are crystalline whereas atactic PDLLA copolymers, with between 5 to 95 mol% *D*-lactide content, are amorphous.⁵² PLA was first synthesized in 1932 by Carothers (Dupont) through condensation polymerization of lactic acid. However, high molecular weight PLA with good mechanical properties is not easy to obtain through this synthetic route. Through extensive research, the ring-opening polymerization of cyclic lactide was developed for the production of high molecular weight PLA.⁵³ Most commercial PLAs are manufactured via ring-opening polymerization using a

Table 1. List of typical properties of selected polymers.

Sample type	Density	Melting temperature, T_m (°C)	Glass transition temperature, T_g (°C)	Tensile strength (MPa)	Tensile Young's modulus (GPa)	Elongation at break (%)	Melt flow index (specified temperature and weight) (g/10 min)
P(3HB) ¹⁹	1.18–1.26	162 – 181	–4–18	19–44	1.2–4	0.8–4.5	12–19 (190 °C, 2.16 kg) ^{20–22}
P(3HB-co-3HV) ¹⁹ (3HV content: 3%–71%)	1.18–1.26	64–171	–13–10	1.8–51	0.14–8.7	1–970	–
PLA ²³	1.21–1.25	150–162	45–60	21–60	0.35–3.5	2.5–6	4–15 (190° C, 2.16 kg) ^{24–27}
PCL ²³	1.11–1.15	58–65	–65––60	21–42	0.21–0.44	300–1000	7 (160 °C, 2.16 kg) ²⁸
Starch ¹⁸	1.26–1.28	Amorphous	31–98	3.1–30	0.17–1.5	0.8–60	3 (150 °C, 2.16 kg) ²⁹
Pp ^{30,31}	0.90–0.91	160–169	–14––6	28–40	1.1–2.0	20–75	4–10 (190° C, 2.16 kg) ^{32–35}
HDPE ^{30,31}	0.95–0.97	130–137	–125––90	20–40	0.70–1.4	100–1000	0.2–11 (230° C, 2.16 kg) ³⁶
LDPE ^{30,31}	0.92–0.93	105–125	–125––90	7–17	0.14–0.30	200–900	0.8–2 (230° C, 2.16 kg) ³⁶

Table 2. Surface free energy of selected polymers determined by contact angle measurement.

Polymer type	Sample type	Dispersive component of surface energy, γ_s^D (mJ/m ²)	Polar component of surface energy, γ_s^P (mJ/m ²)	Total surface energy, γ_s^T (mJ/m ²)	References
PE	Plaque	28.4	0.4	28.8	37
PE	Plaque	26.8	4.2	31.0	38
PP	Hot melt pressed sheet	28.4	3.0	31.4	39
PP	Plaque	27.1	0.9	28.0	40
PLA	Extruded film	30.3	11.0	41.3	41
PLA	Solvent-cast film	34.5	5.6	40.1	42
PLLA	Solvent-cast film	40.0	9.4	49.4	42
PDLLA	Solvent-cast film	37.9	6.8	44.7	42
P(3HB)	Solvent-cast film	29.8	11.3	41.1	43
P(3HB)	Solvent-cast film		Not specified	36.2	44
P(3HB-co-3HV) with 4% 3HV	Solvent-cast film		Not specified	36.2	44
P(3HB-co-3HV) with 4% 18HV	Solvent-cast film		Not specified	34.7	44
P(3HB-co-3HV) with 30% 3HV	Solvent-cast film		Not specified	34.9	44
PCL	Monofilaments from melt spinning	25.4	9.7	35.1	45
Potato starch plasticized by glycerol	Extruded sheet	5.4	65.2	70.6	46
Water	Liquid	21.8	51.0	72.8	46

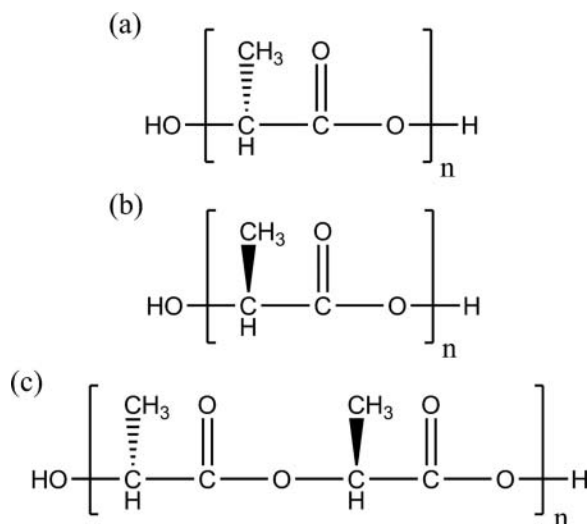


Figure 2. Chemical structure of (a) poly(L-lactide) (PLLA); (b) poly(D-lactide) (PDLA); (c) poly(D, L-lactide) (PDLLA).

single-step reactive extrusion technology.⁴⁸ The type of initiator has been shown to have a significant effect on the reaction rate and the molecular weight of the as-produced PLA.^{48,54} Direct biosynthesis of PLA from the fermentation of metabolically engineered *E. coli* has also been reported.⁵⁵

PLA is competitive among biodegradable polymers for composite applications due to low cost of production,⁵⁶ high mechanical strength and stiffness²³ and water resistance.²³ However, PLA homopolymers are subject to thermal degradation through hydrolysis at temperatures above 200°C.⁵⁷ With a melting temperature of around 175°C,⁵⁷ PLA homopolymers therefore have a narrow processing window. This can be improved through incorporating lactide enantiomers of opposite configuration to obtain PDLLA. However, the resulting depression in T_m was shown to be accompanied by a decrease in crystallinity and rate of crystallization⁵⁸ and associated loss of mechanical properties.⁵⁹ Different stereoisomers of PLA have different mechanical properties, e.g. the tensile strength of PDLLA copolymer decrease as D-lactide content increases from 0 to 50 mol%, which is due to differences in the overall crystallinity.⁶⁰ The properties of PLA can also be tailored through controlling the proportion of the enantiomers of lactide monomer and the arrangement of blocks and branched copolymers.⁶¹

PLA does have its drawbacks, including an elongation at break of less than 10%, which limits its use in applications that require flexibility at high strain. Also, the biodegradation rate of PLA upon disposal in the environment is slow. PLA degrades mainly through hydrolysis and chain scission. However, the hydrolysis rate of PLA is relatively low due to the presence of alkyl groups that hinder the attack by water.⁶² Furthermore, PLA has been shown to be relatively resistant to attack by microorganisms in soil since there are few natural PLA degrading enzymes produced by soil bacteria.⁵⁰ For example, Ohkita and Lee observed no degradation in PLA sheets after 6 weeks in soil.⁶³ On the other hand, PLA degrades rapidly in both aerobic and anaerobic composting environments, with complete biodegradation of PLA sheets being observed after 40 days in compost at 60°C (i.e. above its

glass transition temperature).⁵⁴ The biodegradation rate also depends on the ratio between the enantiomers of lactide monomer, or more specifically, the crystallinity of PLA, with elevated crystallinity leading to slower degradation.⁶⁴ Further, Urayama et al. showed that the molecular weight of PLA films with 99 wt% and 70 wt% *L*-lactide units decreased by 20% and 75%, respectively, after 20 months in soil.⁶⁴ Overall, the biodegradability of PLA has been found to be dependent on factors such as the disposal environment, conditions of water permeability, molecular weight, and crystallinity.

3.2 Polyhydroxyalkanoates (PHAs)

Polyhydroxyalkanoates (PHAs) are a family of polyesters (Figure 3a) that are synthesized intracellularly by more than 300 species of bacteria and archaea in the presence of excess carbon source, often with one of the elements necessary for growth, such as oxygen, nitrogen or phosphorus, being in some form of limitation.⁶⁵ The most common homopolymer of PHAs is poly(3-hydroxybutyrate) (P(3HB)) (Figure 3b). Poly(3-hydroxybutyrate-co-3-hydroxyvalerate) (P(3HB-co-3HV)) (Figure 3c), a random copolymer of 3-hydroxybutyrate (3HB) and 3-hydroxyvalerate (3HV), is also commonly stored by bacteria. The state-of-the-art for commercial PHA production is the use of microbial fermentation of sugar or glucose in pure cultures.⁶⁶ Due to the high costs for sterilizing equipment, in combination with a refined carbon source, the productivity limitations for biological processes and the need for an extraction stage, the market price of PHA is considered to be relatively high when compared to the costs of conventional polymers such as polypropylene and polyethylene.

PHAs exhibit a number of properties which make them promising candidates as the polymer matrix for WPCs. They have higher melt flow indices than most other thermoplastic polymers (see Table 1) and hence there exists potential for better distribution and contact between wood fibers and the biodegradable polymer than for polypropylene and polyethylene.

PHAs can be degraded by natural microflora through enzymatically driven hydrolytic scission reactions, producing water-soluble monomers and oligomers which can be further

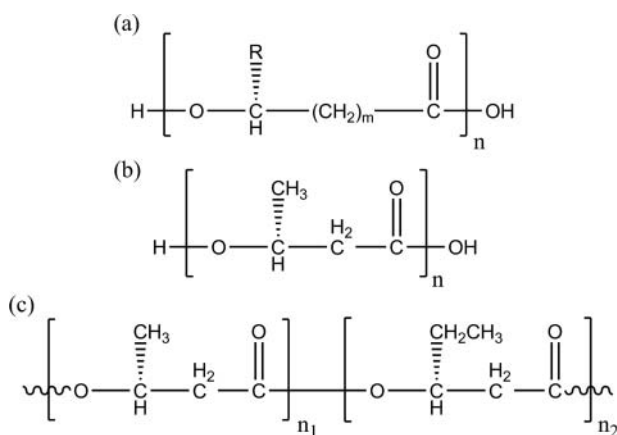


Figure 3. Chemical structure of (a) polyhydroxyalkanoates (PHA) in general; (b) poly(3-hydroxybutyrate) (P(3HB)); (c) poly(3-hydroxybutyrate-co-3-hydroxyvalerate) (P(3HB-co-3HV)).

metabolized to carbon dioxide and water under aerobic conditions and to methane under anaerobic conditions.⁶⁷ Complete biodegradation of PHA films can occur within a few months in many environments,⁶⁷ such as in fresh or marine waters,⁶⁸ activated sludge,⁶⁹ and soil.⁷⁰ However, since an active microbial environment is required for degradation, PHAs were found to be otherwise stable on moisture and air exposure.⁷¹ Rates of degradation are modulated by crystallinity (also related to type of PHA), surface quality, and the kinds of additives in bioplastic formulations.

On the downside, unlike polyolefins, some PHAs have low thermal stability in the melt. Studies have shown that the molecular weight may decrease during processing due to random chain scissions,⁷² although this effect can be much reduced by using relevant pretreatment such as acid washing⁷³ and the use of an antioxidant.⁷⁴ Scission rates are more a function of the kind of trace impurity associated with the polymer rather than an inherent property of the polymer.⁷⁵

Tensile strength of P(3HB-*co*-3HV) has been shown to be constant upon the loss in molecular weight until below 100 kg/g-mol at which point it decreases dramatically, as the degree of chain entanglement decreases.⁷⁶ A graph of the ultimate tensile strength versus molecular weight of P(3HB-*co*-3HV) is presented in Figure 4.

Other processing challenges for some PHAs include a slow crystallization rate and the changes in mechanical properties on aging due to secondary crystallization at room temperature, which has been shown to make the materials more brittle but which can also be modified and controlled through limitation of spherulite size on processing.⁷⁷ The homopolymer poly(3-hydroxybutyrate) (P(3HB)) in particular was reported to have a narrow processing temperature window and the material can be brittle in nature.⁷⁸ In order to overcome such challenges, researchers have explored the properties of other homopolymers or random copolymers of PHA. In particular, the P(3HB-*co*-3HV), is considered to be a candidate for composite applications. The melt flow is higher with elevated 3HV content. For example, a

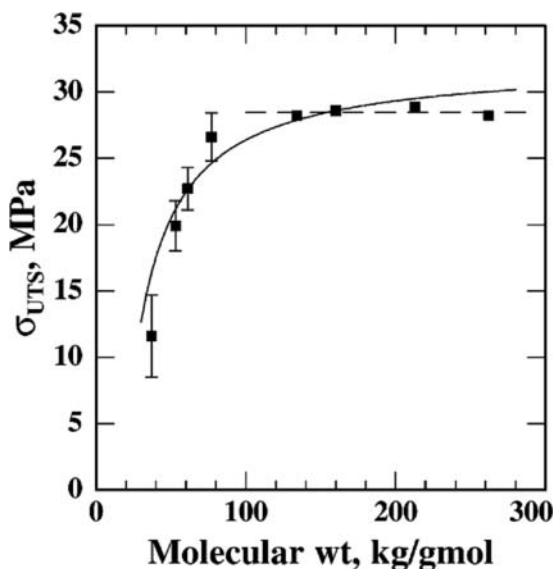


Figure 4. Ultimate tensile strength of P(3HB-*co*-3HV) at different molecular weight.⁷⁶ © Elsevier. Reproduced by permission of Elsevier. Permission to reuse must be obtained from the rights holder.

150% increase in melt flow index was achieved when the 3HV content was increased from 0 to 15 mol%.⁷⁹ P(3HB-*co*-3HV) has higher impact strength at a cost of lower flexural modulus with increasing 3HV content from 0 to 28%.^{71,80} P(3HB-*co*-3HV) was also reported to become soft, flexible and tough within the 30–60 mol% 3HV composition range.⁸¹ In addition, the melting temperature of P(3HB-*co*-3HV) decreased with increasing 3HV content: e.g. it has been reported that the mean melting temperature decreased from 180°C to 132°C when the 3HV content increased from 0 mol% to 25 mol%.⁸⁰

It should be noted that while P(3HB-*co*-3HV) is usually treated as a random copolymer with well-defined 3HV content and reproducible properties, it can be difficult to produce P(3HB-*co*-3HV) with a narrow 3HV content distribution. It has been reported that both as-produced and commercially available P(3HB-*co*-3HV) can have a broad chemical compositional distribution.^{82,83} For example, Yoshie et al. used solvent fractionation technique to analyze a commercial P(3HB-*co*-3HV) with a specified 3HV content of 21.8 mol% purchased from Aldrich and found out that it had a range of 3HV content of 10 – 34.4%.⁸³ Thus it is important to characterize the actual chemical compositional distribution of P(3HB-*co*-3HV) polymers in use in order to understand their material properties. Any high melting copolymer component present may result in higher melting requirements during extrusion, and thus an early higher temperature stage.

Aside from P(3HB-*co*-3HV), several other copolymers of PHA that are commercially available, including poly(3-hydroxybutyrate-*co*-3-hydroxyhexanoate) (P(3HB-*co*-3HHx)) and poly(3-hydroxybutyrate-*co*-4-hydroxybutyrate) (P(3HB-*co*-4HB)), also offer potential for use as-is or in composite applications.⁶⁶ Studies have been performed to fully characterize such random copolymers. Li et al. successfully synthesized P(3HB-*co*-3HHx) with 12% 3-HHx through bacterial cultivation.⁸⁴ The as-synthesized P(3HB-*co*-3HHx) exhibited a dramatically higher elongation at break (400%) but lower tensile strength (7 MPa) and modulus (0.39 GPa) when compared to a P(3HB) homopolymer. It was also reported in a study on the characterization of commercial PHA that P(3HB-*co*-4HB) with unspecified 4HB content from Telles, USA had mechanical properties similar to P(3HB-*co*-3HV) with 5 mol% 3HV from TianAn Biopolymer, China.⁸⁵

In recent years, researchers have focused on reducing the cost of PHA production. One option is the use of waste organics as feedstocks rather than refined substrates.⁸⁶ An extension to this approach is to use mixed culture bacterial production, which is robust to the use of a variety of waste carbon streams. With mixed cultures, the costs associated with the sterilization requirements of pure culture methods and the purchase of refined substrates can both be avoided. PHA could even be produced from carbon-rich pulp and paper waste streams,^{87,88} which would be associated with wood fiber and flour production. PHA extracted from bacterial biomass produced from wastewater streams has been shown to have properties comparable to commercial PHAs.⁸⁹ With high PHA productivities, at up to 89 wt% cellular content within 7.6 h, having been achieved in enriched mixed cultures,⁹⁰ mixed culture production of PHA is becoming increasingly anticipated as a commercially viable technology.

Overall, PHAs can be tailored through the alteration of copolymer ratio to exhibit a wide combination of properties to target specific applications. However, only a small fraction of the PHA family has been incorporated in WPC material testing and development activities so far.

3.3 Thermoplastic starch (TPS)

Starch is a natural polysaccharide which can be obtained from a great variety of crops such as cassava and corn. It is considered to be one of the most abundant renewable materials known to man. It is edible and biodegradable, which makes it an attractive material for food packaging. The processing of starch is challenging as it is not a true thermoplastic, but studies have shown that starch can be modified by grafting with vinyl monomers, by blending with other polymers, or by processing with plasticizers. It can exhibit thermoplastic properties in the presence of plasticizers such as water and glycerol at high temperatures (90 – 180°C) and under shear. Such thermoplastic starch (TPS) readily melts and flows, enabling it to be injection moulded or extruded, and used as polymer matrix in composites. Being bio-renewable and biodegradable in soil⁹¹ and compost⁹² environments, TPS is a potential candidate to substitute conventional plastics in packaging applications. However, its sensitivity to moisture and poor mechanical stability are the main disadvantages when compared to other commercial bioplastics. The tensile strength and modulus of TPS is in the range of 0.2 – 5.8 MPa and 0.01 – 1 GPa,⁹³ which are much lower than that of PHA and PLA. Upon storage, TPS loses mechanical strength and stiffness due to an aging effect through hydrolysis brought about by the sorption and diffusion of water into the matrix,⁹⁴ and to the recrystallization of amylopectin, with this latter process known as retrogradation.¹⁸ Throughout the past decades, studies have been focused on improving the mechanical properties, reducing the water absorption, and suppressing the retrogradation of TPS, where the incorporation of nanoparticles and other fillers comes into play.

3.4 Other biodegradable polymers

Several other biodegradable polymers have also been incorporated into WPCs. These biodegradable polymers include a synthetic polyester, polycaprolactone (PCL), and natural materials, such as cellulose esters, e.g., cellulose acetate. PCL is a petroleum based polymer which is completely biodegradable in aerobic soil and compost environments.⁹⁵ It was reported that the biodegradation rate of PCL was higher than that of P(3HB-co-3HV) while PLA had the lowest biodegradability among the three, as evidenced by the weight loss after 180 days of soil burial.⁹⁶ Guo et al. presented similar findings, although in their case the soil biodegradation rate was ranked from highest to lowest as starch > P(3HB-co-3HV) > PCL > PLA.⁹⁷ PCL is generally prepared through the ring-opening polymerization of ϵ -caprolactone. It has been widely used in the biomedical industry as a biomaterial for implantation and drug delivery. PCL has similar mechanical properties to PLA but the low glass transition (-60°C) and melting temperature (60°C) remain major challenges that reduce its broader application.⁹⁸ With relatively higher elongation at break and toughness, PCL and its WPCs pose unique advantages for applications that require flexibility and toughness.⁹⁹

Cellulose esters such as cellulose acetate (CA) are chemically modified forms of cellulose that are obtained from esterification of cellulose using acids or anhydrides. Cellulose is an abundant natural polymer that can be extracted from plant cells. Recent reports have also demonstrated the production of cellulose through bacterial fermentation.¹⁰⁰ In general, pure CA has mechanical properties similar to common biodegradable polyesters but a higher melting temperature (230°C) and a lower melt flow index (2.1 at 230°C with a load of 2.16 kg) than biodegradable polyesters.¹⁰¹ CA is often plasticized or blended with other

thermoplastics for composite applications.^{102,103} The addition of plasticizer has been proven to improve the melt flow and the elongation at break of the in exchange of a lower tensile strength.^{104,105} The slow biodegradation of pure CA films in both soil and compost has been reported, with the addition of triacetin-based plasticizers very significantly accelerating the rate.^{101,104,105}

4. Wood as filler

Wood has received substantial attention as the reinforcing filler for polymer systems. It brings advantages over traditional inorganic fillers (e.g. glass fiber and ceramics): it is low-cost, light weight, renewable, abundantly available, biodegradable, and less abrasive to processing equipment. Commonly used wood species include softwoods (pine, spruce) and hardwoods (beech, birch, eucalyptus), although other applied species are reported in the literature.¹ They are categorized by their reproducing method where hardwoods are produced by angiosperm trees that reproduce by flowers and softwoods come from seed-reproducing trees called gymnosperm. Hardwoods are not necessarily harder or more rigid than softwoods. It has been shown that, in general, hardwoods shrink and swell more than softwoods when in contact with water.¹⁰⁶

In order to be effective as a filler in a wood-polymer composite, the raw wood matrix needs to be refined into particles of appropriate morphology and chemical functionality. In general, the wood fillers can be divided into wood fibers from the pulping process and wood particles or flour from the hammer milling process. Different types and morphologies of wood fillers have different reinforcing effects. Therefore, a deepened understanding of the structural and chemical properties of wood is important for optimizing the mechanical properties of wood bioplastic composites.

4.1 Structure and properties of wood

Wood has a complex multi-layer structure. The schematic structure of wood in three different levels are visually presented in [Figure 5](#). At the macroscopic level ([Figure 5a](#)), wood consists of elongated hollow cells called wood cells or tracheids. These cells have a thick lignified cell wall which gives wood its strength, stiffness, and toughness.¹⁰⁷ They are squeezed and packed parallel to the axis of the tree from the bottom up. Wood growth occurs from the outer-most layer of the wood just below the bark, which is called cambium, and leads to the formation of radial growth rings. The physical properties of wood differ along the growth rings, or more generally the different types of wood cells across the wood log.¹⁰⁸ The outer-most layers of the wood stem consist of dead tissues, called bark, which is a hard surface that protects the inner wood tissues. At the microscopic level ([Figure 5b](#)), the wood cell walls have a multi-layer structure. The outermost layer is the middle lamellar (ML) which consists of mainly lignin. The inner three-layered secondary cell wall (Inner, middle and outer wall in [Figure 5b](#)) is made up of two parts: cellulose microfibrils and a matrix of lignin-hemicellulose. The mechanical properties of wood and wood fiber are governed by the complex hierarchical structure of cellulose microfibrils. The types of cells, their orientation or direction and the properties of the cell wall layers play a role in determining the mechanical properties.¹⁰⁹ The highly crystallized cellulose microfibrils are oriented to a certain framework/direction in each layer of the secondary cell wall. This gives wood anisotropic properties. The microfibrils

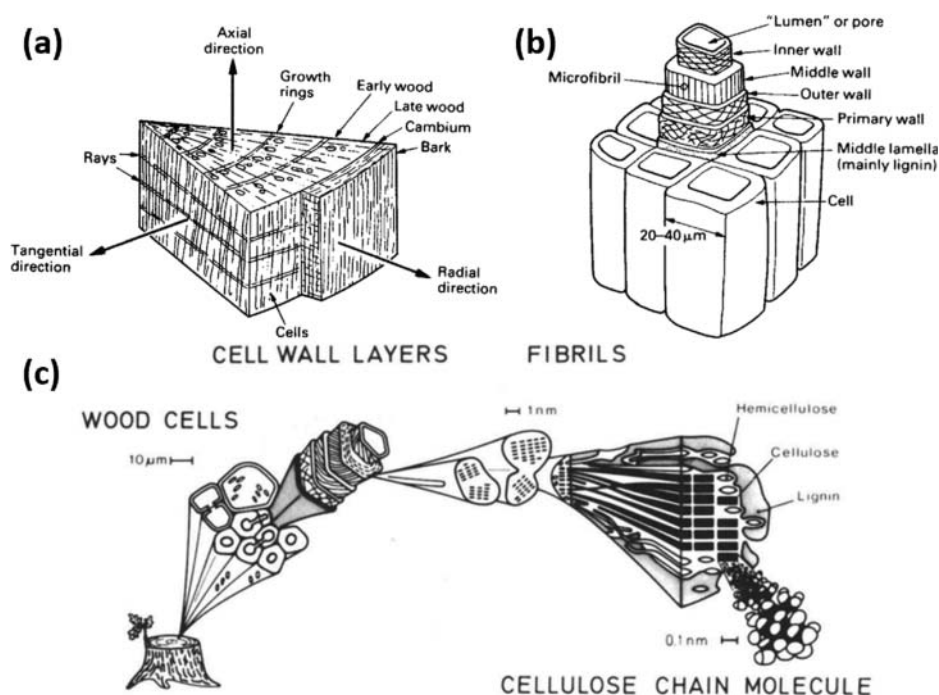


Figure 5. Typical structure of wood (a) macroscopic log level; (b) microscopic cell level; (c) molecular level.^{108,112} (a), (b) © 2013. Adapted with permission from Elsevier Ltd.; (c) © 1989. Adapted with permission from American Chemistry Society. Permission to reuse must be obtained from the corresponding rights holders.

are oriented in a direction nearer to the cell axis (vertical) rather than across it (horizontal). A schematic orientation model is shown in Figure 5a. This gives the wood a much higher axial strength than transverse strength.¹⁰⁸ The wood cell walls have a structure at a molecular level (Figure 5c) that is mainly comprised of cellulose (40–45% by dry weight), hemicelluloses (25–35%), and lignin (20–30%). Some minor constituents include extractives (2–5%) and inorganics (0.1–1%).¹¹⁰ Cellulose is a linear polymer that can be arranged into microfibrils with high tensile strength. Hemicellulose is a branched polymer which consists of shorter chains than cellulose. It has an amorphous structure with little strength. The role of lignin, an amorphous polymer, is as a glue to bind cellulose and hemicellulose. The remaining extractives and inorganics have no mechanical value but give wood its color and smell. Their removal have shown to benefit the mechanical properties of wood plastic composites due to the enhanced interfacial adhesion when the extractive masking was removed.^{33,111} However, the use of extractive-free wood flour increased the water uptake of the resulting WPC.³³ The chemistry of each wood components is discussed below.

4.2 Wood chemistry

In bulk, wood is chemically inert to the action of most chemicals. Cellulose is the major component of wood. The bulk structure is closely packed with a large amount of covalent and hydrogen bonds, which results in a stiff, insoluble, and chemically

resistant bulk structure.¹¹⁰ Interestingly, the surface chemistry of wood is different from the bulk. Hydroxyl groups on the surface of cellulose and hemicellulose are open to chemical reactions, which provides potential for surface modification.¹¹³ The hydroxyl group-rich surfaces also give rise to the hydrophilic characteristic of wood, which is a challenge for compatibility with traditional hydrophobic polyolefins such as PP and PE. The lower hydrophobicity of biodegradable polyesters, as shown in Table 2, partially addresses this problem, but even they are still significantly more hydrophobic than wood.

4.2.1 Cellulose

Cellulose (Figure 6a) is made up of long, unbranched chains of β -D-glucose, forming highly crystalline polymers with a typical degree of polymerization of 10,000.¹¹⁰ The extended (straight chain) arrangement of the cellulose molecules is driven by the orientation of the $\beta(1\rightarrow4)$ glycosidic linkages between molecules. These long glucose chains form microfibrils or parallel arrays, which are held together by the hydrogen bonds between and within the chains. Microfibrils are packed in a highly regular manner, leading to high crystallinity, stiffness and strength, and chemical resistance; water molecules can hardly penetrate the crystalline regions of cellulose. At the same time, the hydroxyl groups on the surface of cellulose are responsible for its reactive and hygroscopic nature.

4.2.2 Hemicelluloses

Hemicelluloses are mixed polymers that are derived from pentose sugars and hexose sugars with short-side chains (Figure 6b). Because of the random packing nature of mixed polymers, hemicelluloses have a more loosely-packed structure and lower crystallinity when compared to cellulose. Therefore, they are more hydrophilic than cellulose and lignin. Thus, hemicellulose is relatively more soluble and easily degraded. When wood is exposed to water, water molecules readily penetrate through the amorphous regions of hemicellulose and form hydrogen bonds with the more accessible hydroxyl groups on the surface. The removal of hemicelluloses remains as the most commonly applied wood modification technique to decrease the hydrophilicity of wood, and thereby improve the compatibility with hydrophobic polymers.¹¹⁴

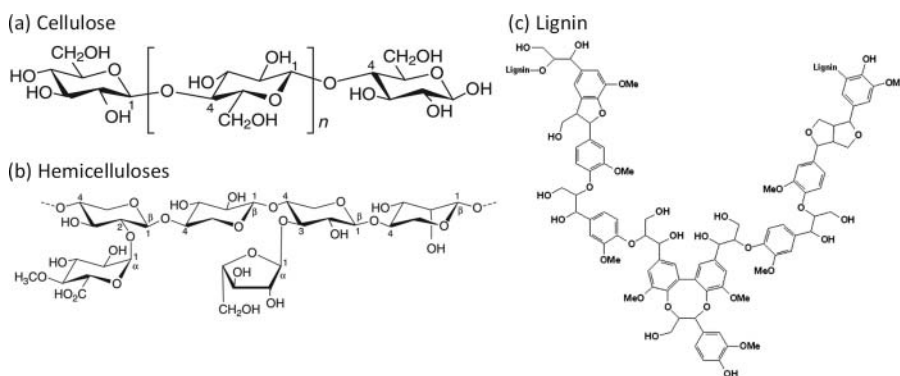


Figure 6. General chemical structure of (a) cellulose, (b) hemicelluloses and (c) lignin.

4.2.3 Lignin

Lignin is an amorphous molecule containing aromatic substances with aliphatic linkages that serves as a natural adhesive and stiffening agent in cell walls (Figure 6c). It is insoluble in most solvents. Unlike cellulose and hemicelluloses, lignin is hydrophobic because of the aromatic units found within its chemical structure and has a high degree of cross-linking. Lignin is also not as reactive as cellulose and hemicelluloses due to the low incidence of reactive surface (particularly hydroxyl) groups.

4.2.4 Wood chemistry of different wood species

The chemical compositions of some common wood species are listed in Table 3. Notably, birch and eucalyptus contain more extractives than other species. It was reported that the removal of wood extractives from eucalyptus wood flour improved the tensile and flexural properties of the resulting PP-based WPC.³³ Similar results were obtained from poplar³³ and pine wood floor.¹¹¹ Improvements in interfacial adhesion upon the removal of extractives were proposed to be responsible.³³ Another notable difference between wood species is the higher cellulose content of eucalyptus. Cellulose content impacted the properties of the resulting WPC such that a higher tensile strength was achieved in PE-based WPC when pine wood floor was used over that of eucalyptus.¹¹⁵ The difference was interpreted to be due to pine having a lower cellulose content which gives the fibers their mechanical strength. A lower water absorption rate was observed from PE/pine wood flour composites than that of eucalyptus.¹¹⁵ A tighter bonding between PE and pine was proposed to explain the result.

4.3 Wood processing – grinding and pulping

Wood processing can be classified into two major categories: grinding and pulping.¹¹⁷ Various grinding and pulping processes, which are summarized in Figure 7, have been developed to yield different filler grades. Grinding involves crushing wood chips into smaller pieces by repeated impact from rotary hammers or stone without changing their chemical composition. Generally, it does not involve the use of any chemicals. Grinding usually yields wood fillers with relatively lower aspect ratios than pulping.¹¹⁸ Pulping, which is predominantly associated with the production of paper, is a process to separate wood fiber from solid wood. Wood pulping can be classified as mechanical, chemical or semichemical.¹¹⁹ Different pulping processes yield wood pulp with different chemical composition and properties. The chemical compositions and fiber dimensions of some typical wood pulp are presented in Table 4. Thermomechanical pulp (TMP), by which pulp is produced through the use of heat and mechanical refining, has been widely used in the paper industry; its use is emerging in

Table 3. Typical chemical composition of various wood species.

Type name (species)	Radiata pine (Pinus radiata ¹¹⁶)	Norway spruce (Picea abies ¹¹⁶)	Common beech (fagus sylvatica ¹¹⁶)	Silver birch (Betula verrucosa ¹¹⁶)	Red gum (Eucalyptus camaldulensis ¹¹⁶)
Cellulose (wt%)	37.4	41.7	39.4	41.0	47.0
Hemicellulose (wt%)	33.2	28.3	33.3	32.4	19.2
Lignin (wt%)	27.2	27.4	24.8	22.0	31.3
Extractives (wt%)	1.8	1.7	1.2	3.2	2.8

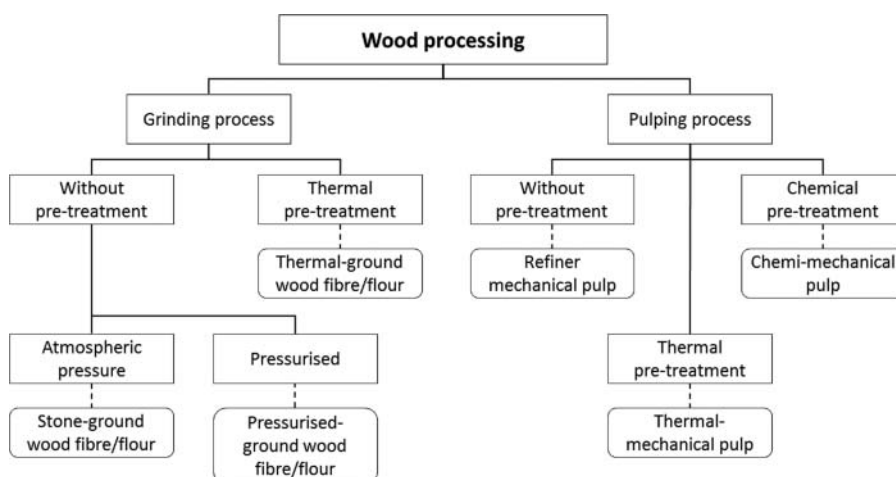


Figure 7. Common mechanical pulping processes for producing lignocellulosic fibers.¹¹⁷ © 2016 John Wiley and Sons. Reproduced with permission from John Wiley and Sons. Permission to reuse must be obtained from the rights holder.

the composites space.^{120,121} Being produced without the use of additional chemicals, lignin is typically preserved in TMP pulp and the fibers are as a result quite rigid (Table 4). Chemi-thermomechanical pulping (CTMP) uses the pretreatment of wood with chemical such as caustic before refining of the wood, leading to some lignin removal and less rigid fibers. Chemical processes include soda, soda-AQ, kraft and sulphite pulping and in general yield longer fibers with lower lignin and higher cellulose content when compared to mechanical pulping.¹²² Soda pulping involves the use of sodium hydroxide as the cooking chemical; the kraft process breaks down wood chips with help of sodium hydroxide and sodium sulfide; the sulphite process applies treatment with sulphite and bisulphite salts. The other major difference between mechanical and chemical pulping is that mechanical pulping has a dramatically higher yield (> 90%) than chemical processes (45 – 50%) because the chemical pulping process involves the removal of lignin and extractives from the bulk.¹²³ Peltola et al. compared the properties of PP WPCs reinforced by spruce wood fibers from two pulping methods (bleached kraft and thermomechanical) and found that composites made with TMP had higher water absorption and lower impact strength,¹²⁰ likely due to agglomeration and the relatively shorter length of the TMP fibers.

Table 4. Chemistry and fiber dimensions of softwood after different pulping and bleaching processes.

	Cellulose (wt%)	Hemicellulose (wt%)	Lignin (wt%)	Extractives (wt%)	Fiber length (mm)	Fiber width (μm)
Original softwood ¹²⁸	40 – 45	25 – 30	26 – 34	0 – 5	2.5–3.0	34
Unbleached kraft softwood pulp ¹²²	69.0	22.0	8.8	0.2	2.09	30.8
Bleached kraft softwood pulp ¹²²	79.2	20.0	0.8	0.0	2.4	30.4
Thermo-mechanical softwood pulp ¹²²	37.7	29.2	31.2	1.9	1.52	34.2

Bleaching of wood pulp is often carried out to achieve a higher paper grade in the paper industry due to improved pulp brightness from further removed lignin. As presented in Table 4, the lignin content of bleached pulp is the lowest among the pulp fibers produced using the different processes. Traditionally, wood pulp has been treated with chlorine, chlorine dioxide and sodium hypochlorite during the bleaching process. In response to the environmental and health concerns over by-product formation of chlorinated organic compounds, elemental chlorine free (ECF) and total chlorine free (TCF) bleaching processes have been increasingly introduced. The ECF process is based around chlorine dioxide bleaching with peroxide stages, while typical TCF bleaching involves oxygen, ozone and hydrogen peroxide stages in sequence.¹²⁴ It was reported that these bleaching stages led to the partial removal of wood extractives¹²⁴ and improvement in pulp strength¹²⁵ of kraft wood pulp. It has been demonstrated that the tensile strength of pulp was directly proportional to cellulose content.¹²⁶ Composites with fibers of higher cellulose content have also been shown have better mechanical properties.¹²⁷ The better adhesion between more-reactive cellulose and the polymer matrix was the proposed reason.¹²⁷

4.4 Wood morphology

4.4.1 Wood fiber morphology

Softwood fibers such as pine are longer than hardwoods such as eucalyptus and birch. Furthermore mechanical pulping, in general, reduces the fiber length of a given fiber more than that with chemical pulping. Table 5 shows fiber dimensions after kraft pulping. Notably, pine yields fibers with relatively high aspect ratio (length/width or diameter ratio) after pulping. The incorporation of fibers with higher aspect ratio has been shown to yield composites with higher strength and stiffness.^{129,130} The details of the effect of fiber dimensions on properties of WPCs will be given in Section 4.4.3.

4.4.2 Wood flour morphology

Wood can be refined into small particulates through different grinding processes including hammer milling and stone, which were discussed in section 4.3. The resulting wood flour is in the form of a particle with aspect ratio close to 1.¹¹⁸ Researchers have performed a comparative study on the reinforcing effect between wood flour and wood pulp using PP as the matrix.¹³⁵ Thermomechanical pulp yielded composites with higher tensile strength and impact strength but similar tensile modulus and elongation at break when compared to those made using wood flour.

4.4.3 Effect of particle size and fiber dimensions on composite properties

It has been shown in various WPC systems, including P(3HB-co-3HV) with 8% 3HV/spruce,¹³⁶ PLA/osage orange,¹³⁷ and TPS/cypress¹³⁸ wood flour, that, at every wood loading

Table 5. Dimensions of kraft pulp produced from different wood species.

	Fiber length (mm)	Fiber width (μm)	Aspect ratio
Radiata pine (<i>Pinus radiata</i>) ¹³¹	2.7	34	79:1
Scots pine (<i>Pinus sylvestris</i>) ¹³²	2.15	33	65:1
Red gum (<i>Eucalyptus camaldulensis</i>) ¹³³	0.80	15	55:1
Silver birch (<i>Betula verrucosa</i>) ¹³⁴	0.84	17	48:1

from 10 wt% to 50 wt%, an increase in wood particle size resulted in a decrease in the composite mechanical strength and stiffness for particle sizes up to around 250 μm ; there was no observed effect for particle size above 250 μm . The gradual decrease in mechanical properties was attributed to the polymer matrix being less continuous with larger particles and thus less able to evenly distributed load.^{137,138}

Further, a loss of tensile strength is attributable to an increased probability for many large defects in the composite matrix around larger particles,¹³⁷ which was also evidenced by the decrease in elongation at break when larger wood particles (250 μm in diameter) were used.^{136,137} Once particles reach a certain size, there is no further loss because the defects around the particles reach a critical limit such that failure is dominated by filler-matrix interface cracking.¹³⁹

It was also reported that the notched impact strength increased but the unnotched impact strength decreased with increasing wood particle size from 50 μm to 500 μm .¹⁴⁰ The author used crack initiation and propagation mechanisms to explain the result, whereby notched impact strength is a measure of crack propagation, while unnotched impact strength is a measure of both. Larger particles introduced more flaws and voids at interfaces for easier initiation. Therefore, the decrease in impact strength was only observed in unnotched samples. However, another study pointed out that fiber reinforced materials did not fail by the initiation and propagation of a single dominant crack in most situations.¹⁴¹ They instead failed through the accumulation of distributed damage brought about by the combined effect of internal flaws and defects, interfacial de-bonding, matrix cracking, fiber fracture and delamination.¹⁴¹ Flaws and damage caused by the applied load can be evenly distributed among the fillers when the filler is well-dispersed in the matrix.¹⁴² Thus, the reduced distribution of load can be used to explain the decrease in mechanical properties with increasing particle size as smaller particles were easier to disperse in the polymer matrix than larger particles.^{136,138}

The use of smaller wood particles may also deliver an advantage when a semi-crystalline polymer is used as the matrix. For example, the crystallinity of PLA increases with decreasing wood particle size as smaller particles can provide nucleation sites for more perfect crystals towards expectations of enhancing matrix mechanical properties.¹³⁷

Apart from the particle size of wood flour, the length of wood fiber also provides different reinforcing effects to the polymer matrix. Migneault et al. extruded composites using HDPE and birch chemi-thermomechanical pulp with three fiber length classes: long (0.48 mm, $L/D = 21$), medium (0.30 mm, $L/D = 13$) and short (0.20 mm, $L/D = 8.3$). It was found that an increasing fiber length had beneficial effects on tensile and flexural properties of the resulting WPC.¹³⁰ The toughness and impact resistance of the composites were also improved by longer fibers, as they imposed an interpreted higher degree of mechanical interlocking and thus more efficient load transfer between the polymer matrix and the fiber. Moreover, it was shown in a study on short-term flexural creep behavior of wood fiber/HDPE composites that composites with longer wood fibers had a greater creep resistance than those made using shorter fibers.¹⁴³ Overall, longer wood fibers with higher aspect ratios are expected to provide for better interfacial mechanical interlocking and, thus, improved mechanical properties of WPCs.^{129,130}

5. Processing aspects of WPCs

5.1 Processing technologies for biocomposites

High processing temperatures can facilitate melt flow and thus good mixing in composites. However, the low thermal stability of biodegradable polymers limits this approach, making process optimization a critical area for biodegradable polymer based WPCs. In general, two steps are involved in the processing of WPCs: melt compounding of the wood filler, the polymer, compatibilisers and/ or other additives, and subsequent sample processing to yield products with the desired shape.⁴ It should be noted that this review of processing techniques will be focused on those used for production of composites with randomly distributed short fibers from wood, as opposed to laminate structures with oriented fibers and/or thermoset resin composites.

Brabender rheology mixers and twin-screw extruders are commonly used to melt mix the wood flour with biodegradable polymers at the laboratory scale. “Dogbone” shaped specimens or other shapes with specific dimensions for standard tensile testing are then prepared using either compression moulding followed by cutting, or injection moulding. Single-step extrusion using a slit die, which combines the compounding and sample processing steps, has also been used for melt compounding of WPCs. Commercially, extruded pellets are produced by compounders, and these are supplied to manufacturers to make final products by extrusion or injection moulding.

5.1.1 Brabender mixing

Brabender mixing is a batch process involving the mixing of filler and molten polymer in a torque rheometer using selected temperatures, rotor speeds, and time. Mixing temperatures have been shown to be the most important factor for controlling mechanical properties of WPCs.²⁹ Higher temperatures and longer processing times have resulted in reduced tensile and flexural strengths while rotor speed has been reported to have mixed effects on the mechanical strength of the composites. As an example, in a wood flour/starch-polyester (Mater-Bi®) composite it was found that a processing temperature of 160°C for 4 mins and 60 min⁻¹ rotor speed was ideal.²⁹

5.1.2 Extrusion

Extrusion is a continuous mixing process that pushes molten materials through a die of selected cross-section. Extrusion can be further classified into twin-screw and single-screw extrusion. The former is primarily for melt mixing of two components whereas a single-screw is used for forming products of defined geometry.

Given its complexity and industrial-relevancy, composite extrusion has been widely studied. Screw speed, temperature profile, screw configuration, and feed rates are the principal parameters.¹⁴⁴ Higher screw speeds enhance fiber dispersion, through thorough mixing, but higher speeds also decrease the tensile and impact strength, as shear heating may degrade both wood filler and biodegradable polymer.¹⁴⁵ An increase in extrusion temperature lowers the melt viscosity, thus producing better mixing but, on the other hand, increasing temperatures increase thermal degradation rates.

The screws can be made up of different elements including: forward elements, which push the material through; reverse elements, which provide for backward flow of material; and kneading blocks, which facilitate mixing. The material residence time, which is defined as

the time required for material to flow from the feed to the die, has also been shown to affect the final properties of, for example, P(3HB-co-3HV)-based WPCs.^{146,147} Extrusion is usually used to produce strands that are pelleted and fed to another process for moulding into more complex geometries. It is also capable of producing a range of end products such as pipes and other long articles.

5.1.2.1 Breaker plates. A breaker plate is a metal puck with holes drilled through it which is placed between the extruder barrel and the die. In composite extrusion, the breaker plate serves to create back pressure in the extruder barrel for better packing and to randomize the distribution and orientation of fillers.¹⁴⁸

Back pressure is defined as the pressure opposed to the flow direction of the fluid in the barrel. Back pressure facilitates the mixing and packing of the composite blend and prevents the build-up of trapped air bubbles that may lead to void defects in the final product.¹⁴⁹ Apart from the addition of a breaker plate, back pressure can also be introduced by decreasing the die melt temperature and by reducing the cross sectional area of the extruder barrel downstream.¹⁵⁰ However, in one case the application of back pressure during polypropylene extrusion resulted in increased tensile strength but less uniform mechanical properties, as evidenced by differences in shear banding depending on the applied back pressure levels.¹⁵¹

In the processing of wood plastic composites, efficient mixing is essential for ensuring good mechanical performance, which can be achieved by tailoring the design of the breaker plate. The typical design provides only shear type of flow which produces only distributive mixing that separates solid agglomerates.¹⁵² Rios et al. designed a new mixing breaker plate that can enhance both the distributive and dispersive mixing (breakup of solid agglomerates) between plastic and additives, as evidenced by computational flow simulation.¹⁵³

5.1.3 Injection moulding

Injection moulding takes pre-mixed and/or pre-melt blended samples and forcibly pumps the melted materials into a mould. It has been widely-used in industry as it is capable of forming products with complex geometries. Injection pressure, holding time, and barrel temperature are identified as the key parameters.¹⁵⁴

5.1.4 Compression moulding

Compression moulding is a process whereby heat and pressure are applied to melt press pre-mixed powder or pellets to form thin planar and contoured sheets of composites. The desired product outer dimensions and shape can then be obtained by cutting. Compression moulding has been widely used in the production of engineering products such medium density fibreboards. Recently, its use has been extended to random short fiber composites but a melt mixing step is required beforehand to achieve random distribution. The platen temperature, consolidation pressure, and pressing time are the important parameters. WPCs processed using compression moulding at lower temperatures (but still higher than melt temperature), lower pressures and shorter times yielded better tensile properties.¹⁵⁵ Among the process parameters, mould temperature was found to exhibit the most significant effect. However, due to the complexity of the processes involved, compression moulding is restricted to products with more simple geometries. It also does not deliver any microstructural orientation effects, and mixing is poor if samples are not pre-blended. Hence, the materials produced by compression moulding can be poor models of full-scale extruded products.

5.1.5 Comparison between processing methods

As discussed above, there are advantages and disadvantages of the different processing methods for WPC production. Some studies have been performed to compare the properties of WPCs with the same formulations but made using different processing techniques. For example, higher values of tensile strength and modulus were observed for injection molded specimens over extruded then cut specimens.¹⁵⁶ The higher pressure during the injection moulding process could explain this result, since the injection molded specimens also had a higher density. La Mantia et al. compared the mechanical properties between starch-based WPCs with 15 wt% of wood flour from four different processing methods: Brabender mixing, twin-screw extrusion, single-screw extrusion, and injection moulding.¹⁵⁷ Mechanical results suggest that twin screw co-rotating extrusion and injection moulding are the preferred processing methods when compared to single-screw extrusion and Brabender mixing for producing such composites.

5.2 Processing challenges

From the discussion so far, we find that an appropriate choice of processing parameters can principally define the compounding quality and the composite properties. The balance between fiber dispersion and degradation or fiber breakage has been cited as the key for process optimization.¹⁵⁸ In practice, more care and attention needs to be taken in the processing of biodegradable polymers because of the risk of hydrolytic and thermal degradation during processing.²³

5.2.1 Fiber breakage

The breakage of fiber during processing has been a major concern for the processing of synthetic or natural fibers with thermoplastics. Studies have revealed that most fiber breakage occurs in the mixing section, especially during extrusion or Brabender mixing.^{159,160} The resulting shear force brought about by the combination effects from the mixing configuration, molten polymer viscosity and fiber dimensions has been shown to govern the degree of fiber breakage. The reduction in fiber length is often more pronounced than the reduction in width resulting in a loss in aspect ratio and thus reductions in composite strength and stiffness.^{129,161} A detailed study on the effect of the initial fiber dimensions on the resulting degree of fiber breakage after processing has been undertaken on thermomechanical pulp from aspen wood.¹⁶¹ It was reported that the loss in aspect ratio values was less pronounced in smaller fibers (1.5 mm in length and 36 μm in width) than for larger fibers (1.7 mm in length and 48 μm in width) after processing with PP in a Brabender mixer. The authors extended the study to the effect of processing conditions and found that higher extrusion temperature, faster screw speed and higher wood content are conducive to more fiber breakage.¹⁶² The high shear forces from faster screw speed and the higher chance of additional breakage through rough fiber–fiber contacts from higher wood content were suggested to explain the observed more severe fiber breakage. The worsened mechanical properties of wood fibers at elevated temperature could further promote fiber breakage during processing. To combat these challenges, optimization has to be done to achieve well-dispersed fibers while minimizing shear and processing temperatures when producing wood fibers with thermoplastics.

5.2.2 Moisture

Drying is the usual step before processing biodegradable polymer based WPCs.^{163,164} Ndazi et al. characterized the mechanical properties and molecular weight of PLA in the presence of 100% relative humidity and found that the molecular weight, flexural strength and ductility decreased after exposure to moisture.¹⁶⁵ For polyesters, water can cause hydrolytic chain scission reactions leading to the increased rate of loss of molecular weight at elevated temperature.¹⁶⁵ However, to the best of our knowledge no attempts have been made to systematically compare the properties of biodegradable polyester WPCs prepared using dried versus non-dried materials. Water has a different effect on starch (TPS)-WPCs since it acts as a plasticizer for starch-based material.¹⁶⁶ It was observed that the drying of such materials caused an improvement in tensile modulus but a decrease in elongation at break due to the loss of plasticizing effect of water.¹⁵⁷

5.2.3 Thermal degradation

As discussed in section 3, unlike polyolefins, biodegradable polymers such as PHA and TPS are more thermally-sensitive and may undergo thermal degradation at elevated temperatures which can in turn reduce mechanical properties of polymer composites.¹⁶⁷ Methods to improve thermal sensitivity, as well as precautions taken when processing biocomposites, are required to prevent thermal degradation and, thereby, preserve the mechanical properties. The positive effect of better melt flow can only be isolated from a negative effect of thermal degradation if the initial polymer molecular mass and thermal stability are sufficiently high, while the time at higher temperatures is commensurably not too long. Even if it is known that degradation of polymer may reduce mechanical performance for the polymer, these effects are not well-understood within the WPC matrix because of the difficulty of isolating the balance of influences from fibers, matrix, and composite interface regions, that are all contributing factors affecting the overall matrix WPCs.

6. Properties of biodegradable polymer based WPCs (without modification)

The reported range of mechanical properties of biodegradable polymer based WPCs are shown in Table 6, and these are comparable to commercial polyolefin-based WPCs. In the following sections, details of properties of selected biodegradable polymer based WPC composite combinations are reviewed.

6.1 Properties of PLA-based wood plastic composites

Given the attractive properties of PLA, extensive research has been undertaken on optimizing the processing and characterizing the properties of PLA-based WPCs, which have mechanical properties comparable to commercial polyolefin-based WPCs. The tensile strength, modulus and elongation at break of PLA-based WPCs are summarized in Figure 8. As can be seen, the majority of the studies on PLA-based WPCs have focused on optimizing the mechanical properties through various compatibilisation techniques.

The trend-lines in Figure 8 suggest that wood filler has mixed effects on tensile strength but the stiffness of PLA-based WPCs improves and the elongation at break decreases with increasing wood filler content. Nevertheless, there is considerable variation between studies

Table 6. Typical range of tensile properties of biodegradable polymer based WPCs and commercial PP- and PE-based WPCs (with a wood filler content of 40 – 50 wt%).

Composite type	Tensile strength (MPa)	Tensile Young's modulus (GPa)	Elongation at break (%)	References
Wood-PHA	13 – 26	0.4 – 5.9	0.5 – 6.6	136,164,168–171
Wood-PLA	37 – 71	1.2 – 8.9	1.0 – 3.1	172–178
Wood-starch	14 – 36	0.7 – 4.8	1.1 – 2.9	91,179,180
Commercial wood-PP	18 – 47	1.8 – 5.6	1.6 – 5.4	Data obtained from FKUR (Germany), Jeluplast (Germany), wood force (France)
Commercial wood-HDPE	12 – 39	0.8 – 4.7	1.4 – 2.9	Data obtained from Perth wood plastic composite (Australia), ChoiceDek (USA), TimberTech (USA), Fomeida (China) and Jeluplast (Germany)

for all properties and for all formulations. The different grades of PLA, origin of wood, and processing methods are likely contributing factors to the observed variation of outcomes in general. Overall, no trends are identifiable from the summarized literature with respect to the effect of compatibilisers, and between fiber and flour, among PLA-based WPCs.

The addition of wood filler had a mixed effect on mechanical strength but the type and origin of wood filler has a significant influence on composite properties. Peltola et al. compared the properties of PLA-based and PP-based composites reinforced by four different types of wood-based fillers (bleach kraft pulp from pine, eucalyptus and birch, thermomechanical spruce pulp and pine flour).¹²⁰ In general, the fibers dispersed better in PLA than PP leading to a higher improvement in tensile strength and tensile modulus but lower impact strength.

The strength of the interfacial adhesion between wood and the PLA matrix was generally suggested to be the governing factor controlling mechanical properties. Bogren et al. modelled the dynamic mechanical properties of PLA/bleached sulphite softwood pulp composites to predict the loss factors.¹⁹⁰ The predicted values were lower than those obtained from experiments. Since the model did not account for energy losses in the material, the results implied poor interfacial adhesion with restrained stress transfer. However, contradictory results were found with film-grade PLA/maple wood fiber composites.¹⁸² The authors in this case suggested mechanical interlocking between wood and PLA as evidenced by the observation (by Scanning Electron Microscopy (SEM)) of fiber breakage as the dominating failure mechanism.

Attempts have been made to produce microcellular foamed PLA (modified with a Joncryl[®] branching agent)/maple wood flour containing up to 40 wt% of wood flour using extrusion with supercritical carbon dioxide. It was found that the expansion ratio for PLA in foamed samples decreased with increasing wood content.¹⁹¹ Under the same foaming process, the void fraction of PLA reduced from 91% to 47% when the wood flour content was increased from 0 to 40 wt%. Microcellular foamed PLA/maple wood flour composites with uniform morphologies were successfully produced by matching the melt viscosity of the composites to that of neat PLA through use of a rheology modifier.¹⁹² This development could help to deliver a new generation of composite materials for wider applications at low cost. Further investigation into the fundamental relationships between foam structure and mechanical performance and on improving the compatibility between PLA and wood is required.

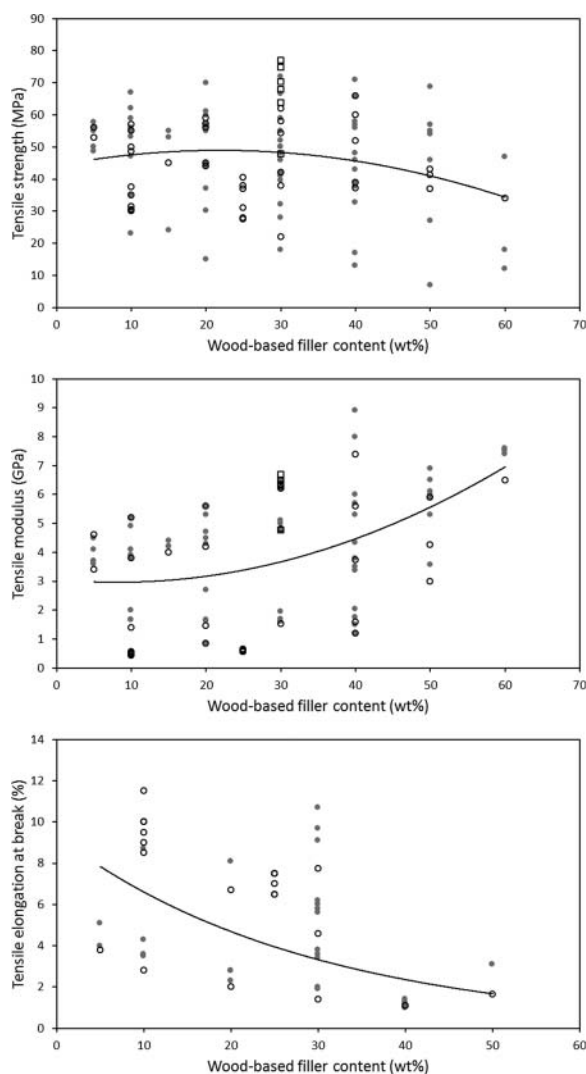


Figure 8. Tensile strength (top), modulus (middle) and elongation at break (bottom) of PLA-based composites reinforced with wood-based fillers; Solid squares (■) represent compatibilised composites with wood fiber; Open squares (□) represent uncompatibilised composites with wood fiber; Solid circles (●) represent compatibilised composites with wood flour; Open circles (○) represent uncompatibilised composites with wood flour.^{120,137,172–178,181–189}

6.2 Properties of PHA-based wood plastic composites

The properties of a range of P(3HB) and P(3HB-co-3HV)-based WPCs have been characterized (Figure 9). As shown by the trend-lines, the addition of wood filler may improve the stiffness of both neat P(3HB) and P(3HB-co-3HV) but those composites exhibit a lower tensile strength and elongation at break. The presence of wood filler can provide nucleating sites, promoting rapid polymer crystallization from the melt, hence helping to overcome one limitation with PHA, especially for P(3HB-co-3HV), which is slow crystallizing.⁷²

To distinguish the influence of 3HV content on composite properties, the data points associated with the blends containing P(3HB-*co*-3HV) with relatively higher 3HV content (8 – 10%) are marked with a cross. As can be seen in Figure 9, those composites show much higher elongation at break but lower tensile strength and modulus. Two different trends are observed between composites with P(3HB-*co*-3HV) at a 3HV content of < 8% (solid lines) and that at 3HV content of 8 – 10% (dashed lines). Both lines obey similar trends for tensile strength and elongation at break. However, unlike the case of composites with P(3HB-*co*-3HV) (<8% 3HV), the addition of wood filler shows no improvement in tensile modulus of composites with P(3HB-*co*-3HV) (8 – 10% 3HV). The stiffness of the composite material is dominated by the matrix, which has low stiffness.

In specific examples:

Ren *et al.* reported that P(3HB)/pulp composites had a higher tensile properties but lower impact strength when compared to similar composites made with PP.³⁵ Peterson *et al.* produced pressed sheets of P(3HB-*co*-3HV) (8% 3HV) composites containing 18 wt% high temperature mechanical pulp fiber based on *Pinus radiata* using different processing parameters¹⁵⁵ and found that the processing temperature imparted the largest influence on mechanical properties. Fernandes *et al.* investigated the thermal degradation and thermal stability of plasticized (poly(ethylene glycol))/P(3HB)/10 wt% beech wood flour composites.²⁰ The molecular weight of P(3HB) was found to be halved after processing at high temperature (170°C for 7 min and 180°C for 4 min) during the production of the composite. The addition of plasticizers mitigated the loss in molecular weight. Singh *et al.* evaluated the mechanical performance of extruded WPCs containing P(3HB-*co*-3HV) with 8% 3HV and maple wood fiber (0 – 40 wt%) and showed that the tensile modulus increased with increasing wood fiber content (from 1.02 to 2.73 GPa) but decreases in tensile strengths were observed (from 21.4 to 16.8 MPa).¹⁹⁶ These decreases were interpreted to be due to poor interfacial adhesion, as demonstrated by the visualization of fiber pullouts and gaps from fractured surfaces. The incorporation of wood flour improved the thermal stability. However, the dimensional stability deteriorated as shown by the reduction of the coefficient of linear thermal expansion from 182 to $154 \times 10^{-6}/^{\circ}\text{C}$. Singh *et al.* further extended this work to explore the performance of novel hybrid composites with the additional reinforcement from micro sized talc and showed a pronounced enhancement of 200% in the Young's and flexural modulus with the dual reinforcement of 20 wt.% talc and 20 wt.% wood fiber in P(3HB-*co*-3HV) matrix.¹⁷⁰ In another study, the addition of oak wood flour also showed a reinforcing effect in a P(3HB-*co*-3HV) (3% 3HV)/oak wood flour (0 – 40 wt%) composite.¹⁶⁹ The addition of 20 and 40 wt% of wood flour improved the neat P(3HB-*co*-3HV) stiffness by 114 and 127% to a tensile modulus of 3.8 and 4.3 GPa, respectively. However, the tensile strength decreased from 34.8 MPa for neat P(3HB-*co*-3HV) to 21.4 MPa at a wood loading of 40 wt%. At the same loading, the elongation of break decreased by half to 0.8%. Similar trends were observed from flexural 3-point bending tests. Upon exposure to moisture, both the flexural mechanical stiffness and strength of the composites decreased, with a more pronounced effect on the composite with higher wood content. Based on these data, the authors constructed a model that suggested that macroscale cracks induced hydrothermal related deterioration in WPCs, showing good agreement with experimental results from literature.¹⁹⁵ Wood flour reduced the overall degree of crystallinity of the composite but the crystallization rate was not characterized.

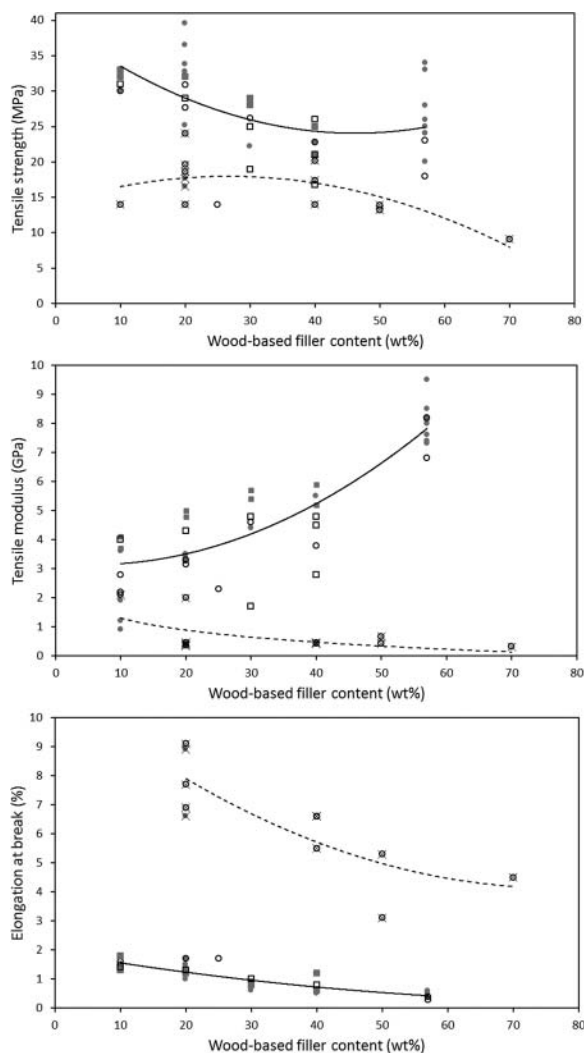


Figure 9. Tensile strength (top), modulus (middle) and elongation at break (bottom) of P(3HB) and P(3HB-co-3HV)-based composites reinforced with wood-based fillers. Solid squares (■) represent compatibilised composites with wood fiber; Open squares (□) represent uncompatibilised composites with wood fiber; Open circles (○) represent uncompatibilised composites with wood flour; Solid circles (●) represent compatibilised composites with wood flour; Data points marked with a cross (X) represent composites containing P(3HB-co-3HV) with a 3HV content between 8% and 10%; Solid line is the trend-line for composites with P(3HB-co-3HV) with a 3HV content of <8% and dashed line is the trend-line for composites with P(3HB-co-3HV) a 3HV content between 8% and 10%.^{20,35,136,156,164,168–170,193–195}

To date, most research has been based on commercially available, pure culture P(3HB)s and P(3HB-co-3HV)s, generally using different wood-based fillers, with wood contents lower than those of commercial WPCs (which are typically ~50 wt%).^{169,196} Only a few attempts have been made to study the effect of P(3HB-co-3HV) properties, particularly 3HV content, on the overall composite properties. It is known that the copolymer composition has a significant effect on the crystallization behavior of wood PHA composites produced

using P(3HB-*co*-3HV) with up to 24 mol% 3HV.⁷² No study has been reported to extend the insights on P(3HB-*co*-3HV) with 3HV contents higher than 25%.

In addition, only a few studies have been made on the utilization of non-extracted PHA-rich biomass in WPCs. One such study used commercially available purified P(3HB) and hammer milled cell debris (68 wt% of particles <150 μm) produced from wastewater to model the incorporation of PHA-rich biomass in WPCs.¹⁵⁶ The mechanical properties and water resistance of the composites were found to decrease with increasing cell debris content. Another study demonstrated that unpurified P(3HB)-rich biomass produced biologically in *Azotobacter vinelandii* UWD (24% P(3HB) content) could be utilized in the production of WPC with 10, 20 and 30 wt% of pine wood floor.¹⁹⁷ The incorporation of P(3HB)-rich biomass resulted in a significant decrease in flexural strength but had no measured effect on the modulus of elasticity.

Overall, with attractive mechanical properties and biodegradability, PHA is promising as the polymer matrix in wood plastic composites. It is believed that fundamental insights concerning the structure-property relationships of wood PHA composites will help deliver the optimum formulations and processing methods for targeted biocomposite applications.

6.3 Properties of thermoplastic starch-based wood plastic composites

Starch has not been extensively used for composite applications when compared to PHA and PLA because of its poor mechanical and water barrier properties. The tensile strength, modulus and elongation at break of TPS-based WPCs at different wood loading from the literature are summarized in Figure 10. Despite the poor matrix properties, improvements in mechanical strength and modulus and the decrease in elongation at break upon addition of wood fillers to TPS are much more notable than for biodegradable polyesters. This is due to the chemical similarities between TPS and wood and thus better compatibility between them. At various wood loadings, composites with wood fibers give higher tensile strength and modulus when compared to WPCs reinforced with wood floor. The increases in tensile strength and modulus with increasing wood filler content are more pronounced in wood fiber/TPS composites than that with wood floor as suggested by the solid and dashed trendlines in Figure 10, respectively.

Muller et al. used a mechanical strength model to quantify the interfacial adhesion between corn starch and wood fibers and found that such an interface demonstrated a stronger adhesion than that of PP and PLA.¹⁷⁹ Also, FTIR analyses demonstrated compatibility between cassava starch and wood particles, which was attributed to the association by hydrogen bonding of OH groups.¹⁸⁰ Therefore, unlike the focus for PLA and PHA, research into TPS-based WPCs has been concentrated on understanding the reinforcing effects of various wood fillers rather than improving the interfacial adhesion through the addition of compatibilisers.

The addition of 16 wt% of bleached *E. urograndis* pulp to corn starch (plasticized with 30% of glycerin) resulted in a 100% increase in tensile strength and 150% increase in modulus.²⁰⁰ It was also shown that the tensile strength of wood fibers/plasticized corn starch composites improved with increasing wood content then deteriorated when the wood content was above 40 wt%.^{138,179} Other types of starches, including potato¹⁹⁸ and cassava starch,¹⁸⁰ have also been used in composites. The addition of wood fillers to plasticized (using 30% glycerol) potato and cassava starch resulted in similar improvement in tensile strength and

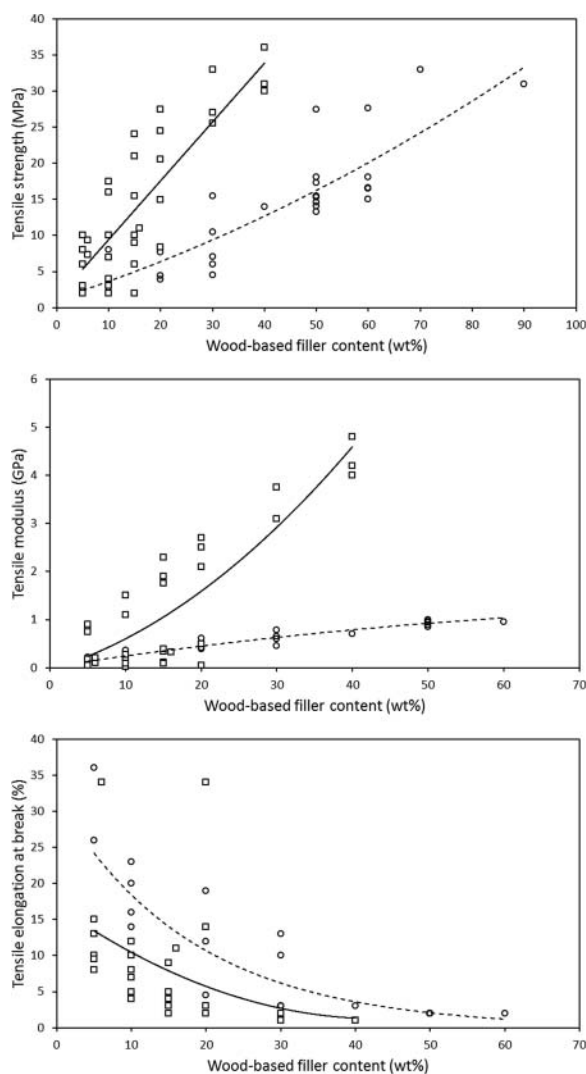


Figure 10. Tensile strength (top), modulus (middle) and elongation at break (bottom) of TPS-based composites reinforced with wood-based fillers; Open squares (□) represent uncompatibilised composites with wood fiber; Open circles (○) represent uncompatibilised composites with wood flour; Solid line is the trend-line for composites with wood fiber and dashed line is the trend-line for composites with wood flour.^{91,138,179,180,198,199}

modulus as seen in corn starch-based WPCs.^{180,198} One commercially available TPS/polyester copolymer is Mater-Bi®. Similarly to pure starch-based composites, the incorporation of wood flour resulted in increases in tensile strength and modulus but a decrease in elongation at break of the Mater-Bi-based composites.^{91,166}

The wood species may also affect the properties of the composites, with spruce and pine giving better mechanical properties and thermal stability than beech and poplar.⁹¹ These species effects were correlated to the specific axial and bending strength of each species. Furthermore, decreasing the particle size from 750 μm to 150 μm appeared to increase the tensile strength and decrease the water absorption of the composites.^{91,138} Overall, the addition

of wood filler improved the mechanical properties of TPS but a sensitivity of these composites to moisture still limits the scope of the material use in practical applications.

6.4 WPCs with other biodegradable polymer

The synthetic biodegradable polyester, polycaprolactone, has been applied to wood flour reinforced composites in a study of mechanical properties and soil biodegradation behavior.²⁸ The resulting composites had poor mechanical properties and a dramatically lower melting point (58°C) when compared to PLA and PHA.²³ Nitz et al. successfully used reactive extrusion to graft maleic anhydride to PCL chains to improve compatibility with wood floor.²⁰¹ The addition of 5 wt% of maleic anhydride grafted-PCL improved the yield stress and impact strength of the composites at various wood loadings (10 to 50 wt%) but exhibited minimal effect on tensile modulus.

Apart from PCL, plasticized cellulose esters have also been used in WPC applications. The effect of fiber loading on the mechanical properties of plasticized cellulose acetate butyrate/yellow poplar wood fiber composites has been reported.²⁰² The tensile modulus and impact strength increased but the elongation at break decreased with increasing wood content, which supports the general trend of wood reinforcement. Researchers have also explored the use of biodegradable polymer blends in WPCs. Cunha et al. extruded composites containing a commercial starch-cellulose acetate based blend and from 0 to 60 wt% of pine wood flour.¹⁰² The tensile properties in both the radial and tangential directions increased with wood flour content up to 50 wt% but then deteriorated. Overall, however, there is limited literature on WPCs containing other biodegradable thermoplastics when compared to the major three: PHA, PLA and TPS. The production of biodegradable polymer based WPCs remains a wide-open playing field in scope and opportunity for research and development.

7. Modifications to improve adhesion between wood fillers and polymer matrix

Strong interfacial adhesion and efficient stress transfer across phases are governing factors in achieving good composite properties.²⁰³ Poor interfacial interactions between hydrophilic wood and hydrophobic polymer matrices such as polyolefins and polyesters may result in voids and thus poor contact and inferior stress transfer.¹³⁶ In general, the addition of wood filler negatively affects the mechanical strength of polyester-based composites. Based on this principle, it is well known that improving the interfacial interactions through compatibilisation is an effective means to mitigate such negative effects of poor interfacial adhesion and to further improve the performance of WPCs.²⁰³

7.1 Surface treatment of wood

Wood pretreatments and modifications are well established in the literature as a means for improving the compatibility and stress transfer efficiency between hydrophilic wood and hydrophobic thermoplastics. The underlying principle is to reduce the hydrophilicity of wood to more closely match the surface energy of the polymer. Common modification

techniques include alkali and thermal pretreatments, and chemical modifications such as acetylation and silane treatment.

7.1.1 Physical pre-treatment

7.1.1.1 Thermal treatment. The thermal pretreatment of wood particles involves the removal of hemicelluloses and the enhancement of crystallinity index through steam explosion, hot water extraction or heat treatment under an inert atmosphere.¹¹⁴ Hemicellulose removal results in a decrease in the wettability of wood by polar solvents i.e. increased hydrophobicity.²⁰⁴ Thermally treated pine wood flour has also been found to exhibit a better thermal stability compared to untreated flour.²⁰⁵ This outcome was taken as a promising indication of the removal of hemicelluloses, which has the lowest thermal resistance among cellulose, hemicelluloses and lignin. The inclusion of such thermally treated wood flour into polypropylene composites was shown to improve the tensile strength, water resistance and mould resistance.²⁰⁵ However, contradictory results were presented in a study conducted on P(3HB) where limited improvements in tensile properties were observed with hydrothermally treated beech wood flour when compared to PHA WPCs made with untreated wood flour.¹⁹⁴

7.1.1.2 Plasma treatment. Plasma treatment utilizes the energy from an electric discharge to modify the chemical and physical structures of the surfaces of natural polymeric substrates without altering the bulk properties of the materials. It improves the fiber–matrix adhesion mainly by providing polar or excited groups, or even a different polymer layer on the fiber surface, that interacts with the matrix.²⁰⁶ It has also been reported that plasma radiation roughens the wood fibers, increasing the mechanical interlocking between the fiber and the matrix²⁰⁷ and increases the oxygen/carbon ratios of wood fibers thus generating more functionality for better adhesion.²⁰⁸ The incorporation of such plasma-treated wood fibers in PP composites has shown improvement in tensile strengths and moduli.²⁰⁸ However, contradictory results were again obtained from a study on spruce wood flour filled P(3HB-co-3HV) with 8% 3HV composites such that plasma treatment had an insignificant effect on mechanical properties for some biodegradable polymers.¹³⁶

7.1.2 Chemical modification

7.1.2.1 Alkaline treatment. Several studies have found that alkali pretreatment increased the aspect ratio of wood fibers and removed the amorphous hemicellulose.²⁰⁹ It also improved the wettability and physical, mechanical and thermal properties of the treated fibers over untreated fibers.²¹⁰ Such improvements were interpreted as being due to a larger effective surface area for chemical interaction and mechanical interlocking with polymer matrix in composite materials.²¹⁰ However, excessive alkali treatment can damage the radiata pine wood fibers as evidenced by SEM analysis, which leads to a reduction in fiber strength.²¹¹ The incorporation of such fibers in PP composites resulted in a reduction in strength but an improvement in stiffness.²¹¹ Similar results were presented in a study conducted on P(3HB) systems that showed enhanced tensile modulus but worsened tensile strength from composites with alkali treated beech wood flour.¹⁹⁴

7.1.2.2 Silane treatment. Silane-based compatibilisers are compounds with different groups attached to the central silicon such that one end can bond to the filler and the other end contains an organo-functional group. The organo-functionality can be classified into two types: a non-reactive alkyl group that increases the compatibility with non-polar polymer matrix based on similar polarities or a reactive organo-functionality that can covalently bond to the polymer matrix and establish physical linkages.²¹²

Silane pretreatment is well-established in composite applications²¹³ with extensive recent research to investigate the potential in natural fiber and wood fiber systems.²¹² Most of the established silanes used for wood fibers composites are trialkoxysilanes, which can react with the hydroxyl groups on the wood, with organo-functionalities that can reduce the hydrophilicity of the fiber such as long alkyl, vinyl, and methacryloxy groups. Typically, alkoxy silane treatment of natural fibers proceeds through the following steps (Figure 11): hydrolysis, self-condensation, adsorption and chemical grafting.²¹²

The polarity of wood flour was shown to be reduced by alkoxy silane treatment.^{188,214} However, the incorporation of organosilane treated wood filler has had mixed effects on composite properties when using PLA. Lv et al. and Pilla et al. for example showed that the mechanical properties and water resistance of PLA composites containing 10 to 30 wt% of treated wood flour improved.^{183,188} With increasing silane content, the tensile strengths of the composites first increased then decreased, with a maximum value at 1.5% silane.¹⁸⁸ On the other hand, silane treatment had an insignificant effect on the mechanical and thermal properties of PLA/40 wt% pine wood flour.¹⁷⁴

7.1.2.3 Acetylation. Acetylation is a method for modifying the chemistry of lignocellulosic-based fibers and making them more hydrophobic.²¹⁵ It involves chemical reactions of acetic anhydride with the hydroxyl groups on wood surfaces, hindering them from forming hydrogen bonds with water molecules. Tserki et al. performed acetylation and propionylation functionalization on wood fibers, improving the tensile strength and water resistance of biodegradable polyester composites made from these fibers.²¹⁶ Similar results were also obtained from a study on a biocomposite based on acetylated wood particles and cellulose ester, in that acetylated composites had higher tensile strength and water resistance but lower impact strength than the unmodified composite.¹⁰³

7.1.3 Isocyanate functionalization

Isocyanate containing reagents are another set of potential functionalization chemicals for natural fiber composites, due to their clean chemical reaction with the hydroxyl groups on the wood-based filler surfaces (Figure 12). Two major types of isocyanate compounds used in the WPC field include isocyanates and diisocyanates. The former modify the surface of wood fillers to make them more compatible with the matrix whereas the latter are coupling agents that establish physical linkage between wood and polymer. Some of the types of isocyanates that have already been explored include m-isopropenyl- α,α -dimethylbenzyl isocyanate (m-TMI) grafting,^{217–219} poly(methylene)-poly(phenyl) isocyanate (PMPPIC)^{121,220} and polybutadiene isocyanate (PBNCO)²²¹ as well as diisocyanates such as toluene diisocyanate (TDI)¹²¹ and methylene diphenol diisocyanate (MDI),¹²¹ and polymethylene diphenyl diisocyanate (pMDI).^{156,222} In general, improvements in mechanical properties were observed in wood flour^{156,218,219,222} and wood fiber^{121,217,221} reinforced polymer composites after the addition of isocyanate reagents, predominantly in the tensile, flexural and impact

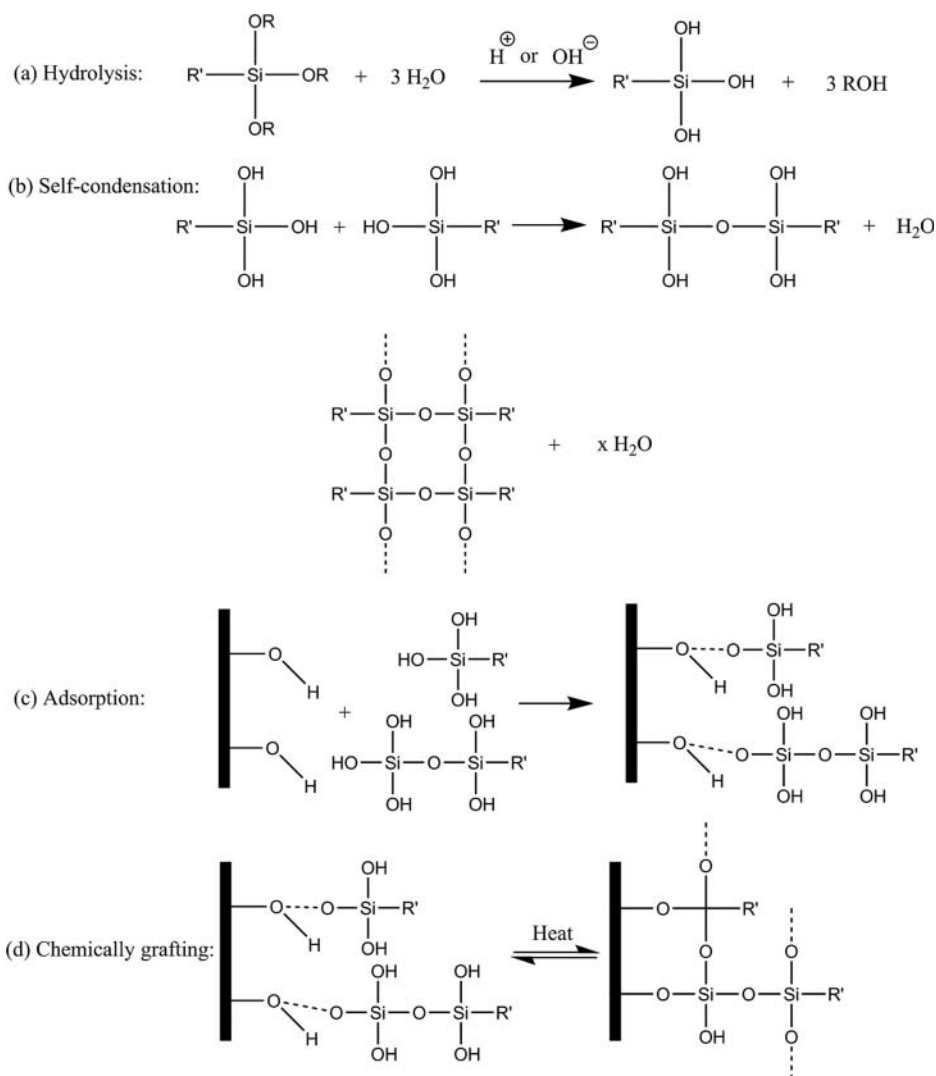


Figure 11. Silane treatment of natural fibers by hydrolysis process.²¹² © 2010 Elsevier Ltd. Adapted with permission from Elsevier Ltd. Permission to reuse must be obtained from the rights holder.

strengths, but as well in improved water resistance. However, the use of the functionalizing, not coupling, agent PMPPIC on pine wood fiber/PP composites produced no significant effect on strength.²²⁰ By contrast, other polymeric isocyanates have been shown to be more effective in improving the tensile strength of thermomechanical pulp reinforced PE composites than diisocyanate compounds.¹²¹

A recent study proposed that isocyanates are more effective than other compatibilisers in PLA and P(3HB-co-3HV) systems, as binding can be established between the isocyanate and the hydroxyl groups on wood plus the isocyanate and the carboxylic acid end-groups of the biodegradable polyester.¹⁵⁶ Petinakis et al. introduced MDI or poly(ethylene-acrylic acid) (PEAA) at a loading of 1 and 3 wt% respectively to PLA/wood flour composites containing

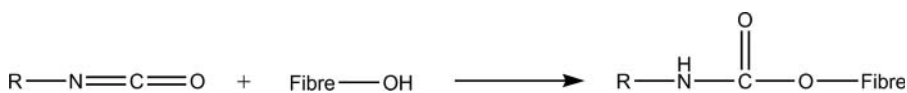


Figure 12. Generic chemical reaction between isocyanate group and the hydroxyl groups of wood fibers.

40 wt% of wood.¹⁷⁵ The addition of MDI resulted in improvements in tensile strength (10% increase), tensile modulus (20% increase) and impact strength (25% increase) of the composite providing evidence of enhancement in interfacial adhesion. The addition of pMDI as a coupling agent in pine wood flour/P(3HB)¹⁵⁶ resulted in improved composite strength and fiber interface interactions. A better understanding of the bonding mechanisms between isocyanate and PHA would help towards further systematic (rather than trial and error) developments of wood/PHA composites with properties comparable to conventional polyolefin WPCs.

7.1.3.1 Other chemical treatments. Other chemical treatments of wood have also been utilized. Csizmadia et al. modified the wood flour through resin impregnation using a solution of 1 wt% phenolic resin and observed considerable increase in the mechanical strength of the composite, but the treatment had a detrimental effect when wood was treated with a concentration higher than 1%.¹⁷⁷

Organo-montmorillonite treated wood flour has also been incorporated into PLA-based WPCs containing 50 wt% of wood flour wherein significant improvement in stiffness and water resistance was observed.^{178,187}

Finally, stearic acid treatment of compression moulded P(3HB)/20 wt% bleached beech wood flour composites led to improvements in crystallization rate, Young's modulus and storage modulus.¹⁹⁴ Among the various wood pretreatment methods that were tested (alkali, thermal and stearic acid), stearic acid treated wood flour had the most pronounced effect on the tensile and dynamic mechanical properties.

7.2 Chemical compatibilisers

Besides surface treatment of wood, researchers have explored chemical compatibilisers, aiming to improve the interfacial strength through the establishment of chemical bonds at the interfaces between wood and polymer matrix phases. This technique involves chemical reaction with the hydroxyl groups in wood at one end and with the polymer, at the other, through radical or other reactions. With a more reactive surface, polyesters deliver advantages over polyolefins when using this approach.

7.2.1 Maleic anhydride grafting on matrix

Maleic anhydride (MA) graft copolymerization involves modification of the polymer matrix through addition of an anhydride group using dicumyl peroxide (DCP) as an initiator. MA-grafted thermoplastics are able to not only wet and disperse the wood fiber efficiently in the matrix, but to also form an ester link between maleic anhydride and the hydroxyl groups of wood (Figure 13).^{32,223}

MA-grafted polyolefins have received widespread application in wood fiber reinforced PP^{32,223,224} and PE^{225,226} composites. In general, the addition of a MA-grafted

polymer matrix improved the mechanical properties, especially tensile and impact strengths, of the composites at a low loading of less than 5 wt% polymer.^{32,225} Enhanced interfacial adhesion was proposed to explain the observation as evidenced by the change in deformation mechanism from de-bonding to fracture of wood particles.²²⁴ Inverse gas chromatography²²³ and a model of composition dependence of tensile strength²²⁴ have also been used to quantitatively show the improvement in interfacial adhesion upon the addition of MA-grafted polymers.

In recent years, the application of MA has been extended to biodegradable polymer based WPCs. The addition of 10 wt% MA-PLA improved the tensile strength and modulus of a PLA/50 wt% wood flour composite by 66% and 19%, respectively.¹⁷² The composite also became more flexible.¹⁷² Csikos et al. extended the study to the effect of the MA-PLA content,¹⁶³ with increased amounts of MA-PLA enhancing the interfacial adhesion parameter, and thus the tensile strength of PLA/wood flour composites, with a more pronounced effect with increasing number of functionality and compatibiliser amount. However, contradictory results were reported by Lv et al. who found that the compatibiliser amount exhibited an insignificant effect on mechanical properties of PLA/30 wt% wood flour composites produced using a single-step reactive extrusion.¹⁸⁹

The application of MA graft copolymerization has been extended to improve the tensile, flexural and impact strengths oak wood flour/P(3HB-co-3HV) (2 wt% MA-grafted P(3HB-co-3HV))^{169,195} and pine wood flour/P(3HB) (1 – 4 wt% MA-grafted P(3HB-co-3HV))¹⁵⁶ composites. However, interestingly, the use of MA grafting imparted negligible improvements in flexural strength and stiffness, moisture resistance and durability in P(3HB-co-3HV)-based wood flour composites.¹⁹⁵

The surface properties of P(3HB)s have also been modified using acrylic acid,²²⁷ improving composite processability due to the lower melt temperatures and torque values of these mixes. Such compatibilised composites also showed higher tensile strength and a slightly lower biodegradation rate than the uncompatibilised blend.

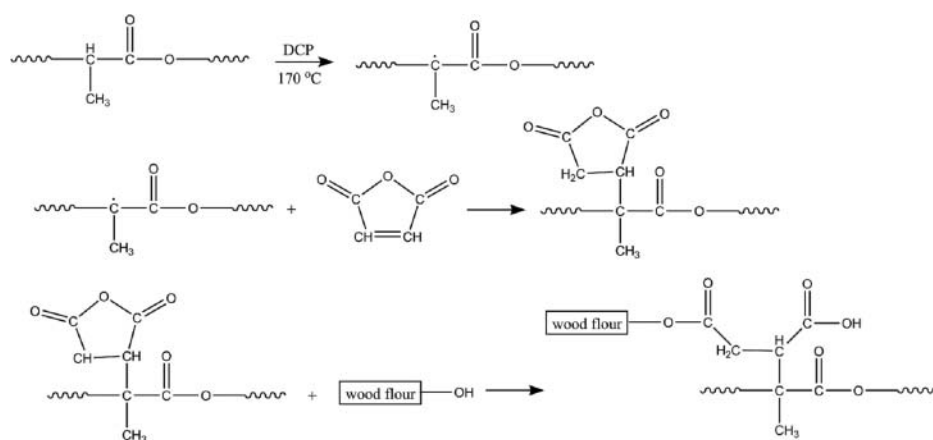


Figure 13. Generic chemical reaction between MA-grafted PLA and the hydroxyl groups of wood flour.¹⁸⁹
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7.2.2 Silane-based coupling agents

On top of reducing the hydrophobicity of wood fiber, silane coupling agents used in the WPC field have also been used to establish physical linkage between wood and polymer. The organo-functional group on the silane in this case is carefully chosen such that it can covalently bond to the corresponding polymer matrix thus improving the interfacial adhesion. Figure 14 provides examples of siloxanes that have been commonly applied to natural fiber systems.²¹²

Several workers have investigated the effect of silane treatment on biodegradable polymer based WPCs properties and reported that organo-silane treated wood reinforced PLA^{173,176} and P(3HB-co-3HV)¹⁶⁹ composites had improved mechanical properties and water resistance when compared to the untreated wood fillers. Silane treatment proved in one study to be the most effective among hydrothermal, maleic anhydride, silane and stearic acid treatments in improving the storage and loss moduli, which indicates that intramolecular and intermolecular interactions between wood fibers and PLA took place.¹⁷⁶ However, contradictory results have been reported in another study based on PLA, where no significant difference in mechanical strength was observed between WPCs with silane-treated and untreated fibers.¹⁷⁴

Silane coupling agents have similarly been tested for PHA-based composites, but mixed results were again observed. Srubar et al. used a novel thermochemical vapor deposition technique for the functionalization of oak wood floor by octadecyl-trimethoxysilane to ensure that silane was sufficiently chemisorbed onto the particles.^{169,195} In contrast to the results from PP and PE matrices, the mechanical results revealed that silane treatment slightly improved the tensile, flexural and storage moduli of the P(3HB-co-3HV) with 3% HV-based composites.¹⁹⁵ However, there was negligible improvement in the strength and moisture resistance.¹⁹⁵ It was proposed that the silane may react with both cellulosic hydroxyl groups and matrix polymer chains, thereby enhancing particle wettability and improving dispersion, but further characterization is required to confirm this hypothesis.¹⁶⁹ A comparative study of the effects of silane on

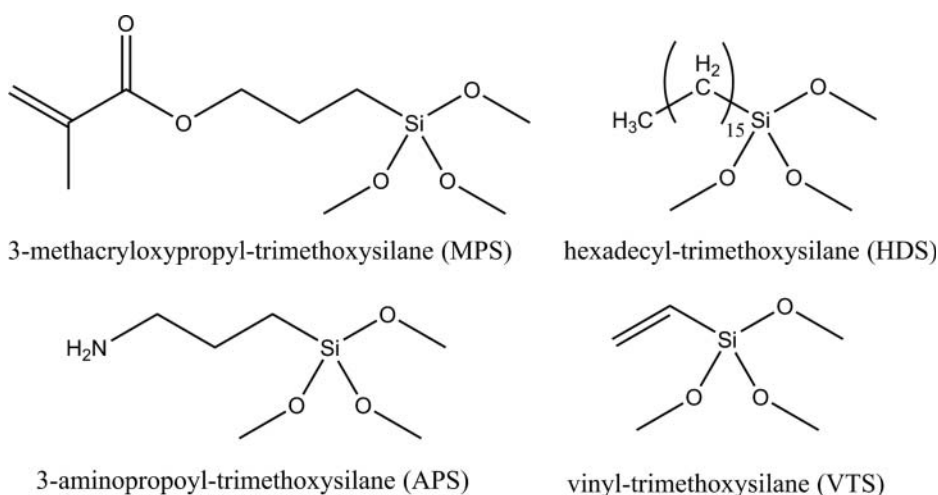


Figure 14. Commonly used silanes for wood fiber applications.

the mechanical performance between pulp fiber reinforced P(3HB) and PP was reported in Ren et al.³⁵ The results indicated that the silane-based compatibilising agent was more effective in PP based pulp fiber composites than for P(3HB)-based composites. The authors suggested that the pulp fibers are already adequately dispersed into P(3HB) matrixes such that the use of silane coupling agents is not necessary. Overall, the effectiveness of silane coupling agent on PHA-based composites is not well-studied and further investigations into the effect on interfacial adhesion between wood and PHA upon addition of different types of silane to wood should provide deepened insights into the differences and mechanisms.

8. WPC Biodegradation

Biodegradability has been highlighted in most studies as the unique advantage of biocomposites over traditional petroleum-based WPCs. However, degradation studies are limited.

In one study, the biodegradation rates of P(3HB-*co*-3HV)/straw fiber composites with 10, 20 and 30 wt% of wood filler were similar to those of P(3HB-*co*-3HV) after incubation in a liquid environment (Modified Sturm test) (Figure 15).²²⁸ It was also reported that P(3HB-*co*-3HV)/peach palm particle biocomposites degraded faster than neat P(3HB-*co*-3HV) in soil,¹⁹³ where it was suggested that the poor adhesion between wood particles and matrix increases accessibility to both moisture and microorganisms from the soil, thus accelerating biodegradation. A similar result was obtained in another study, such that the introduction of wood flour accelerated the biodegradation as evidenced by the larger weight loss on soil burial from composite samples.²²⁷ However, the biodegradation of wood-PHA biocomposites is complex and not well-studied. A better understanding on the effect of filler type, morphology and content, void content, and incubation environment on biodegradation rate would help to unravel the mix of influencing mechanisms and factors.

The only investigation into the biodegradation of PLA-based WPCs, to the best of our knowledge, was done on PLA/70 wt% pine wood fiber composites made using four different commercial PLAs before and after 6-month soil burial.¹⁸⁴ The mechanical strength and molecular weight analyses indicated that the composites degraded more extensively than neat PLA. The flexural strength of the composite decreased by an average of 88% and the number-average molecular weight of the PLA in such composites decreased by an average of 40% after 6 months of soil burial.¹⁸⁴ Further studies on the biodegradation of PLA-based WPCs upon composting and burial in landfill would provide a more thorough end-of-life analysis for such material.

Unlike PHA, it has been shown that pure TPS degrades faster than composites with wood flour.⁹¹ A series of 50/50 Mater-Bi/wood flour composites lost 30 – 37% of their weight, depending on the wood species, after 10 months burial in soil whereas pure Mater-Bi lost 45% of its weight during the same period.⁹¹ A good adhesion between TPS and wood could explain this observation.

Overall, biodegradability of WPCs was highlighted in most studies but the kinetics and mechanisms were not thoroughly studied explicitly. Research on the combination of macroscopic (mechanical properties), microscopic (surface cracking), and chemical (molecular weight and CO₂ evolution) changes of biocomposites upon biodegradation would provide for a deeper understanding of the environmental impact of this material and exploitation of biodegradation in service as a function or in management after product useful life.

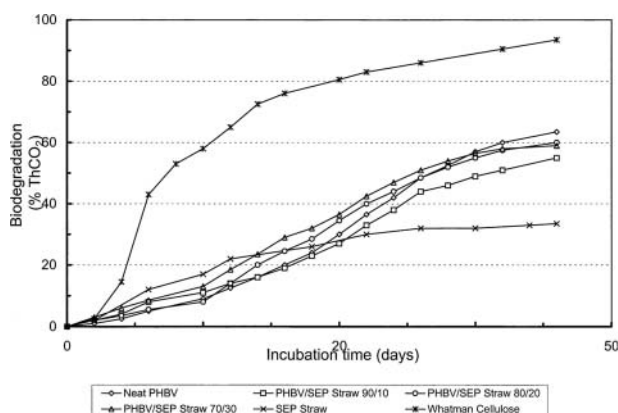


Figure 15. Biodegradation rate of P(3HB-co-3HV) and P(3HB-co-3HV)/ straw fiber composites based on % of CO₂ evolved with respect to theoretical upon incubation in liquid environment.²²⁸ © 2000 Springer. Adapted with permission from Springer. Permission to reuse must be obtained from the rights holder.

9. Conclusions and recommendations for future research in biodegradable polymer based WPCs

9.1 Summary and conclusions

Research into biodegradable polymer based WPCs is on the rise due to concerns about the accumulation of plastics wastes in the environment and the instability of the petroleum price. Different types of biodegradable thermoplastics including both bio-derived (e.g. PLA via fermentation PHAs, starch and cellulose esters) and petroleum derived (PLA via chemical synthesis and PCL) are commercially available and well-studied. They have many general properties comparable to traditional polyolefins and possess the advantage of being compostable and/or biodegradable. Wood-based fillers are emerging rapidly in composite applications due to their low-cost, light weight, abundance and biodegradability. The resulting composites deliver advantages over other composites such as glass fiber and thermoset composites in terms of their full biodegradability and mouldability. However, their relatively high cost of production and susceptibility to thermal degradation have been their limitations when compared to other composites.

Research has been underway to characterize the properties of biodegradable WPCs in order to explore the potential applications of this material. Although there is variability in composite properties related to the initial polymer properties and wood fiber origin, as well as the processing conditions, consistency was achieved throughout the literature on the reinforcing effect of wood fillers. General trends of improvement in composite stiffness and reduction in elongation at break were observed with increasing wood content. The composite strength is governed by the strength of interfacial adhesion between the polymer and the wood fillers, which depends on the nature of the polymer. From this review, it is shown that the tensile strength of hydrophobic biodegradable polyester WPCs decreases with increasing wood content but contradictory results were obtained when hydrophilic TPS was used as the polymer matrix. Such limitations have been addressed through compatibilisation techniques.

The majority of the studies on biodegradable polyester based WPCs have been focused on improving the interfacial adhesion between wood and polymer through various compatibilisation techniques, mainly based on modifying the hydrophilicity of wood, the hydrophobicity of polymer, and the chemical linkages between composite components. Overall, compatibilisation techniques have shown promise with respect to further improving the composite properties and providing an understanding of the mechanical behavior of such materials.

9.2 Questions and research gaps

However, while there is a considerable body of literature on the production of wood composites based on biodegradable polymers, several fundamental concepts still need to be investigated for broader implementation of such technology and further commercial development of such materials. In particular, a deeper understanding of the structure-property relationships and interfacial optimization strategies as well as a more thorough end-of-life analysis are needed. Therefore it is suggested that efforts be placed on the following areas:

9.2.1 Effect of wood fiber/particle properties on composite properties

Wood fibers and powders have very significantly different properties depending on species, age, sampling period and processing method, resulting in distinct chemistries, morphologies and particle dimensions of the resulting particles, which all will influence the composite material properties. However, the wood component in biodegradable polymer based WPCs has usually been treated as a generic ingredient. A more thorough understanding of the relationship between wood properties and overall composite properties is needed.

9.2.2 Process optimization and its influence on WPC properties

The influence of process parameters on composite material properties has been underrated. It is important for the development of effective process control that further fundamental research into the effect of processing parameters and composite properties be undertaken, particularly when thermally-sensitive biodegradable polymers are in use.

9.2.3 Modelling and quantification of interfacial adhesion in WPCs

Although the interfacial strength is often suggested as the controlling factor for composite mechanical properties, the quantification of the interfacial adhesion in these WPCs is lacking, and a clear literature gap. Much more work is needed on both characterizing and modifying the interfacial adhesion in WPCs.

9.2.4 Full characterization of the biodegradability and stability of WPCs

In spite of the claim for biodegradability as a highlighted benefit in most studies, there has been limited research into the biodegradation kinetics and mechanisms of biodegradable polymer based WPCs. It is important to demonstrate the biodegradability of these materials in practical real-life contexts such as household landfill for clarifying their end-of-life environmental impact. It is also necessary to identify their product life-time in use.

In many ways these opportunities for future research are all interlinked and fit into process and property optimizations for the production of low-cost high-performance biodegradable polymer based WPCs. Significant research is underway to overcome the above-mentioned literature gaps. These studies feed into the development of a higher performance, cost effective biodegradable composite material. Clearly the extensive amount of research in this area has shown the great potential for global application of biodegradable wood plastic composite materials.

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