

# We are IntechOpen, the world's leading publisher of Open Access books Built by scientists, for scientists

6,900

Open access books available

185,000

International authors and editors

200M

Downloads

Our authors are among the

154

Countries delivered to

TOP 1%

most cited scientists

12.2%

Contributors from top 500 universities



WEB OF SCIENCE™

Selection of our books indexed in the Book Citation Index  
in Web of Science™ Core Collection (BKCI)

Interested in publishing with us?  
Contact [book.department@intechopen.com](mailto:book.department@intechopen.com)

Numbers displayed above are based on latest data collected.  
For more information visit [www.intechopen.com](http://www.intechopen.com)



---

# Natural Fibre Bio-Composites Incorporating Poly(Lactic Acid)

---

Eustathios Petinakis, Long Yu, George Simon and  
Katherine Dean

Additional information is available at the end of the chapter

<http://dx.doi.org/10.5772/52253>

---

## 1. Introduction

In recent years increasing awareness in relation to the world's petrochemical resources no longer being finite, the rising cost of oil and concerns surrounding climate change and the necessity for reducing our carbon footprint, are resulting in a renewed demand and expediation of development of polymeric materials that are produced from sustainable and ecologically sound raw material feedstocks that are not petrochemically derived and are generally more abundant. Poly(lactic acid) (PLA), being a compostable synthetic polymer produced using monomer feedstock derived from corn starch, satisfies many of the environmental impact criteria required for an acceptable replacement for oil-derived plastics [1]. PLA exhibits mechanical properties that make it useful for a wide range of applications, but mainly in applications that do not require high performance including plastic bags, packaging for food, disposable cutlery and cups, slow release membranes for drug delivery and liquid barrier layers in disposable nappies [2]. However, the wider uptake of PLA is restricted by performance deficiencies, such as its relatively poor impact properties which arise from its inherent brittleness, but also the limited supply and higher cost of PLA compared with commodity polymers such as polyethylene and polypropylene [3].

Polymer composite materials often possess mechanical and physical properties that make them better suited for a wide range of applications than the individual composite components. The use of natural fibers to produce polymer composites having improved mechanical and impact performance is well-documented, and is of particular interest for enhancing the properties of biodegradable polymeric materials such as PLA [4-6]. The benefits of using natural fibers compared with other potential reinforcing agents, such as glass fibers, talc, or carbon fibers, for improving the performance of biodegradable polymers include the reten-

tion of the biodegradability of the composite, but generally also exhibit lower density, superior performance, and lower cost due to the abundance of many natural fibres. An example of such a product is wood-flour, a bio-waste product produced from the preparation of timber for the building and other related industries.

PLA/natural fibre composites containing less than 30%w/w fiber have been shown to have increased tensile modulus and reduced tensile strength compared with PLA, and this has been attributed to factors that include the weak interfacial interaction between the hydrophobic PLA matrix and the hydrophilic cellulose fibers, and lack of fiber dispersion due to a high degree of fiber agglomeration. Various methods of modifying the surface of the cellulosic fibers have been explored in an effort to improve the interaction that occurs at the interface between the PLA matrix and the fibers, including esterification [7], acetylation [8], and cyanoethylation [9]. It is apparent that the stronger the molecular interactions that occur at the interface between cellulose fibers and polymer matrix, the resulting interfacial adhesion is stronger and the optimal stress transfer efficiency. The use of coupling agents or compatibilisers have proven to be a much more efficient means of improving interfacial interactions between polymer matrices and cellulose fibers. The strongest adhesion can be achieved when covalent bonds are formed at the interface between cellulose fibers and coupling agent as well as molecular entanglement between coupling agent and the polymer itself [10]. Coupling agents also have the benefits of improving fibre dispersion, since they can also induce better flow of the molten polymer during processing, improve melt elasticity and melt strength in the resulting polymer composites [11].

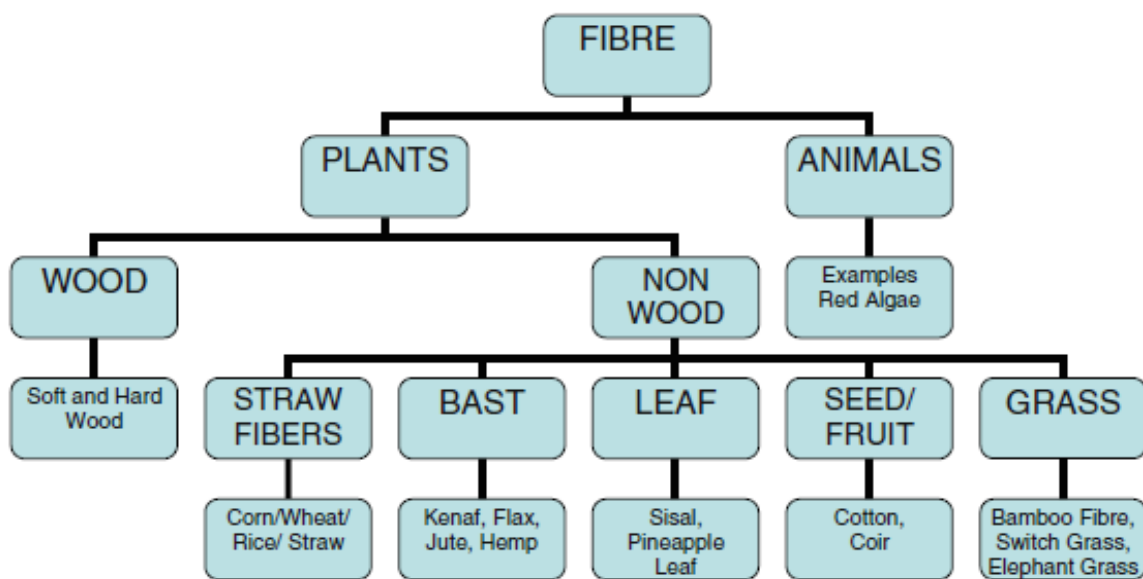
The nature of the interface/interphase in polymer composites incorporating natural fibers is still not well understood, since many of the chemical reagents used in surface modification of natural fibres and/or coupling agents used do not form covalent bonds, but in most cases are rarely created [12]. Therefore, the aims of this book chapter research will attempt to address this issue and provide a fundamental understanding of the surface and adhesion properties of polymer composite systems incorporating natural fibres. The authors of this book chapter will demonstrate such understanding thru their research into PLA based bio-composites incorporating wood-flour as the natural fiber/filler. It has been demonstrated in the preliminary research that the best path forward for developing polymer composites with enhanced physical properties is by modifying the surface of wood-flour particles to induce chemical bonding at the interface and to enhance compatibilisation with the PLA matrix.

## **2. Poly(lactic acid) bio-composites based on natural fibres**

### **2.1. Structure and properties of natural fibres**

Natural fibres can be classified into five major types: bast, leaf, seed, fruit and wood, depending upon the source. In order to develop polymer composites from natural resources it is important to understand the microstructure and chemical composition of natural fibres. Natural fibres comprise of three principal components; cellulose, lignin and hemicellulose. These three hydroxyl- containing natural polymers are distributed throughout the cell wall.

Cellulose and hemicellulose are polysaccharides. Cellulose is a highly crystalline polymer with a regular structure, which comprises of thousands of anhydroglucose units with a DP (degree of polymerisation) around 10,000 [13]. Cellulose is the major component which is responsible for the inherent strength and stability of the natural fibre. Hemicellulose is a shorter branched polymer composed of various five- and six- carbon ring sugars. The molecular weight is much lower than cellulose but still hemicellulose still contributes to the structure of natural fibres. Lignin is an amorphous, cross-linked polymer network, which consists of an irregular array of variously bonded hydroxy- and methoxy- substituted phenyl propane units. The chemical structure of lignin depends on the source of the wood. Lignin is not as polar as cellulose and the major function of lignin is to function as a chemical adhesive between cellulose fibers.

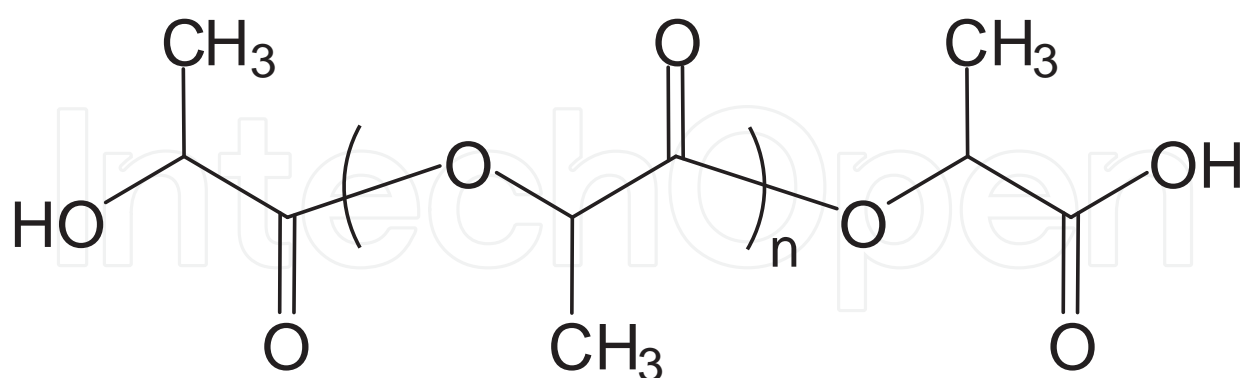


**Figure 1.** Classification of natural fibres (courtesy of Mohanty et al [14])

Natural fibres also consist of varying amounts pectin, wax and other low molecular weight compounds or extractives. Extractives are described as non-structural components in wood, which are composed of extra cellular and low molecular weight compounds. There are three types of lipophilic extractive compounds: terpenes (and terpenoids), aliphatics (fatty acids and their esters) and phenolic compounds [15]. Aliphatic compounds include alkanes, fatty alcohols, fatty acids, fat esters and waxes. Terpenoids include turpentine and resin acids. Phenolic compounds include tannins, flavonoids, lignans, stilbines and tropolones. Extractives can diffuse to the surface of natural fibres during drying, which can influence the degree of adhesion. This is an important factor to consider during the processing of polymer composites incorporating lignocellulosic fillers, since extractives may influence the degree of interfacial adhesion between polymer matrix and lignocellulosic filler. Extractives can be typically removed by solvent extraction or steam distillation or even water treatment if compounds are water soluble. Steam distillation can be used to remove the volatile terpenes, whereas solvent extraction can remove resin acids, fatty alcohols, fatty acids and waxes.

## 2.2. Structure and properties of PLA

Polymers from renewable resources can be classified into three major groups: natural polymers such as starch and cellulose; synthetic polymers from natural monomers such as polylactic acid (PLA); polymers from microbial fermentation such as polyhydroxybutyrate (PHB). Polylactic acid is one of the most promising biodegradable polymers, which can be derived from natural feedstocks such as corn starch but can also be derived from rice, potatoes, sugar beet and other agricultural waste. Initially, PLA synthesis involves conversion of the raw material feedstock into dextrose, which then undergoes conversion into lactic acid or lactide via a fermentation process in the presence of a catalyst. The lactide undergoes further processing in order to purify the monomer and this is followed by conversion of the purified monomer into a polymeric form of PLA through polymerisation in the presence of a suitable catalyst [16]. Polylactic Acid (PLA) can be processed by conventional methods such as injection moulding, blow moulding, extrusion and film forming operations, since PLA has a  $T_g$  of 55-65°C and a melting temperature between 150-175°C. The mechanical properties of PLA are similar or in most cases are superior to petrochemical polymers, such as polypropylene. Therefore, PLA has attracted great interest as a commodity polymer which is capable of replacing petrochemical polymers like polypropylene and polyethylene, particularly in the area of single use packaging applications. However, PLA exhibits low toughness due to its brittle nature, but also the molecular weight in comparison to conventional polymers, is much lower. In order to overcome the brittle nature of PLA it is useful to incorporate natural fillers into the polymer matrix. It has already been stated that incorporation of natural fillers into polymer matrices can optimise mechanical properties but from an economical viewpoint, natural fillers can make the composites more cost competitive due to their high abundance and lower cost.



**Figure 2.** Structure of Poly(lactic acid)

## 2.3. Natural fibres used in PLA based bio-composites

The major factors that can influence the development of polymer composites using natural fibers are listed as follows [17]:

1. Thermal stability
2. Moisture Content
3. Processability
4. Fibre dispersion in polymer matrix
5. Fibre-matrix adhesion
6. Surface modification of natural fibers
7. Fiber aspect ratio

Oksman et. al. incorporated cellulose fibres as reinforcement in PLA [18]. Due to the brittle nature of PLA, triacetin was used as a plasticizer for the matrix as well as PLA/flax composites in order to improve the impact properties. Plasticizers can be used during processing in order to lower the viscosity of the matrix polymer, which can then facilitate better fiber dispersion within the matrix polymer. Fiber dispersion is a critical factor to be considered during the development of biodegradable natural fibre composites. Shibata et. al. evaluated the use of short abaca fibres in the development of biocomposites using biodegradable polyesters. In this study it was shown that strength and modulus increase with decreasing fibre diameter for both untreated and treated abaca fibre[19].

Wollerdorfer et. al. investigated the influence of plant fibres such as flax, jute, ramie, oil palm fibres and fibres made from regenerated cellulose on the mechanical properties of biodegradable polymers. The so-called biocomposites produced by embedding natural fibres, e.g. flax, hemp, ramie, etc. into a biopolymeric matrix made of derivatives from cellulose, starch, lactic acid, etc., new fibre reinforced materials were developed [20]. Huda et. al. evaluated the use of recycled cellulose in the development of “green” composites using PLA as the matrix and recycled cellulose from newsprint. The physico-mechanical properties of the composites as well as the morphological properties were investigated as a function of varying amounts of recycled cellulose [21]. Bax et al [22] investigated the impact of cordenka and flax fibres on the impact and tensile properties. The study showed that PLA composites with cordenka fibres with a maximum fibre loading of 30% show promise as alternative biocomposites for industrial applications due to optimisation in impact properties. However, both biocomposites showed evidence of poor interfacial adhesion between the PLA matrix and the cordenka and flax fibres, respectively.

Mathew et. al. conducted a study towards developing PLA based high performance nanocomposites using microcrystalline cellulose as reinforcement. The study was concerned with achieving the best possible outcome for dispersion of the MCC within PLA during processing. Comparisons were also made with using wood flour and wood pulp as an alternative reinforcement for PLA [23]. Tzerki et. al. investigated the usefulness of lignocellulosic waste flours derived from spruce, olive husks and paper flours as potential reinforcements for the preparation of cost-effective bio-composites using PLA as the matrix [24]. Petinakis et al studied the effect of wood-flour content on the mechanical properties and fracture behaviour of PLA/wood-flour composites. The results indicated that enhancements in tensile

modulus could be achieved, but the interfacial adhesion was poor [25]. Therefore, it can be seen that incorporation of lignocellulosic materials into biodegradable polymer matrices, such as PLA, has the affect of improving mechanical properties, such as tensile modulus. But the strength and toughness of these bio-composites are not necessarily improved. This can be attributed to several reasons, such as the hydrophilic nature of natural fillers, compatibility with the hydrophobic polymer matrix can be problematical. In addition to the poor interaction between the phases, the hydrophilic nature of natural fibres leads to a tendency for fibres to mingle or form agglomerations, which can generally result in low impact properties, especially at high fibre loadings.

In order to overcome these shortcomings a variety of chemical and physical treatments can be utilised to improve fibre-matrix adhesion in biodegradable polymer composites as well as improve dispersion of natural fibres within biopolymer matrices. There are many articles in the public domain that have reported the use of coupling agents and compatibilisers for improving fibre-matrix interfacial adhesion in polymer composite systems incorporating a polyolefinic matrix, such as polypropylene and polyethylene.

### **3. Strategies for improving interfacial adhesion in PLA/natural fibre composites**

Surface modification of natural fillers can be classified into two major types; chemical and physical methods. Surface modification is a critical processing step in the development of biopolymer composites, since natural fillers tend to be highly hydrophilic in nature and in order to improve the compatibilisation with the hydrophobic polymer matrix this level of processing is required. The use of surface modification techniques can facilitate fibre dispersion within polymer matrix as well as improve the fibre-matrix interaction [26]. Some of the techniques that have been previously reported in the literature for improving fibre-matrix adhesion include: treatment of fibres by bleaching, acetylation, esterification, grafting of monomers and the use of bi-functional molecules [27]. The use of coupling agents and compatibilisers has also been widely reported in the development of conventional polymer composites. Coupling agents include silanes, isocyanates, zirconates, titanates and chitosan [28]. One of the most widely reported compatibilisers in the literature has been the use of functional polyolefins such as maleated polypropylene (MAPP) [29-34]. More recently, Xu et al synthesised a novel graft copolymer, polylactide-graft-glycidyl methacrylate (PLA-GMA), which was produced by grafting glycidyl methacrylate onto the PLA chain via free radical polymerisation, which was then used to produce biocomposites using PLA and bamboo flour [35]. All techniques have proven successful in improving the fibre-matrix interactions, which have resulted in polymer composites with greatly improved mechanical properties.

### 3.1. Chemical techniques

#### 3.1.1. Alkaline treatment

Alkaline treatment is one of the most widely used chemical treatments for natural fibres for use in natural fibre composites. The effect of alkaline treatment on natural fibres is it disrupts the incidence of hydrogen bonding in the network structure, giving rise to additional sites for mechanical interlocking, hence promoting surface roughness and increasing matrix/fibre interpenetration at the interface. During alkaline treatment of lignocellulosic materials, the alkaline treatment removes a degree of the lignin, wax and oils which are present, from the external surface of the fibre cell wall, as well as chain scission of the polymer backbone resulting in short length crystallites. The treatment exposes the hydroxyl groups in the cellulose component to the alkoxide.

In alkaline treatment, wood fibres/flour is immersed in a solution of sodium hydroxide for a given period of time. Beg et. al. studied the effect of the pre-treatment of radiate pine fibre with NaOH and coupling with MAPP in wood fibre reinforced polypropylene composites. It was found that fibre pre-treatment with NaOH resulted in an improvement in the stiffness of the composites (at 60% fibre loading) as a function NaOH concentration, however at the same time, a decrease was observed in the strength of the composite [36]. The reason for a reduction in the tensile strength was attributed to a weakening of the cohesive strength of the fibre, as a result of alkali treatment. The use of alkali treatment in conjunction with MAPP was found to improve the fibre/matrix adhesion. However, it seems that only small concentrations of NaOH can be used to treat fibres, otherwise the cohesive strength can be compromised. Ichazo et. al also studied the addition of alkaline treated wood flour in polypropylene/wood flour composites. It was shown that alkaline treatment only improved fibre dispersion within the polypropylene matrix but not the fibre-matrix adhesion. This was attributed to a greater concentration of hydroxyl groups present, which increased the hydrophilic nature of the composites. As a result, no significant improvement was observed in the mechanical properties of the composites and a reduction in the impact properties [37]. From previous studies it is shown that the optimal treatment conditions for alkalization must be investigated further in order to improve mechanical properties. Care must be taken in selecting the appropriate concentration, treatment time and temperature, since at certain conditions the tensile properties are severely compromised. Islam et al studied the effect of alkali treatment on hemp fibres, which were utilised to produce PLA biocomposites incorporating hemp fibres. This study showed that crystallinity in PLA was increased due to the nucleation of hemp fibres following alkaline treatment. The degree of crystallinity had a positive impact on the mechanical and impact performance of the resulting composites with alkaline treated hemp fibres as opposed to the composites without treated hemp fibres.

#### 3.1.2. Silane treatment

Silane coupling agents have been used traditionally in the past in the development of conventional polymer composites reinforced with glass fibres. Silane is a class of silicon hydride with a chemical formula  $\text{SiH}_4$ . Silane coupling agents have the potential to reduce the inci-

dence of hydroxyl groups in the fibre-matrix interface. In the presence of moisture, hydrolysable alkoxy groups result in the formation of silanols. Silanols react with hydroxyl groups of the fibre, forming a stable, covalently bonded structure with the cell wall. As a result, the hydrocarbon chains provided by the reaction of the silane produce a cross-linked network due to covalent bonding between fibre and polymer matrix. This results in a hydrophobic surface in the fibre, which in turn increases the compatibility with the polymer matrix. As mentioned earlier silane coupling agents have been effective for the treatment of glass fibres for the reinforcement of polypropylene. Silane coupling agents have also been found to be useful for the pre-treatment of natural fibres in the development of polymer composites. Wu et. al. demonstrated that wood fibre/polypropylene composites containing fibres pre-treated with a vinyl-tri methoxy silane significantly improved the tensile properties. It was discovered that the significant improvement in tensile properties was directly related to a strong interfacial bond caused by the acid/water condition used in the fibre pre-treatment [38].

In a study by Bengtsson et al. the use of silane technology in crosslinking polyethylene-wood flour composites was investigated [39]. Composites of polyethylene with wood-flour were reacted in-situ with silanes using a twin screw extruder. The composites showed improvements in toughness and creep properties and the likely explanation for this improvement was that part of the silane was grafted onto polyethylene and wood, which resulted in a cross-linked network structure in the polymer with chemical bonds occurring at the surface of wood. X-ray microanalysis showed that most of the silane was found within close proximity to the wood-flour. It is known that silanes can interact with cellulose through either free radical or condensation reaction but also through covalent bonding by the reaction of silanol groups and free hydroxyl groups at the surface of wood, however the exact mechanism could not be ascertained. In a study by González et al, focused on the development of PLA based composites incorporating untreated and silane treated sisal and kraft cellulose fibres [40]. The tensile properties of the resulting composites did not present any major statistical difference between composites with untreated cellulose fibres and silane treated cellulose fibres, which suggested that silane treatment of the cellulose fibres did not contribute to further optimisation in the reinforcing affect of the cellulose fibres. The analysis of the high resolution C1s spectra (XPS) indicates that for C<sub>1</sub> (C-C, C-H), the percentage of lignin in the intreated sisal fibres was higher, in comparison with kraft fibres. But after modification with silanes, the C<sub>1</sub> signal decreases for sisal fibres, which shows that attempted grafting with the silane has resulted in removal of lignin and exposed further cellulose. The higher C<sub>1</sub> signal reported for kraft fibres suggested some grafting with silane as a result of the contribution from the alkyl chain of the attached silanol, but no further characterisation was provided to support grafting of silanes to kraft fibres.

### 3.1.3. Esterification of natural fibres

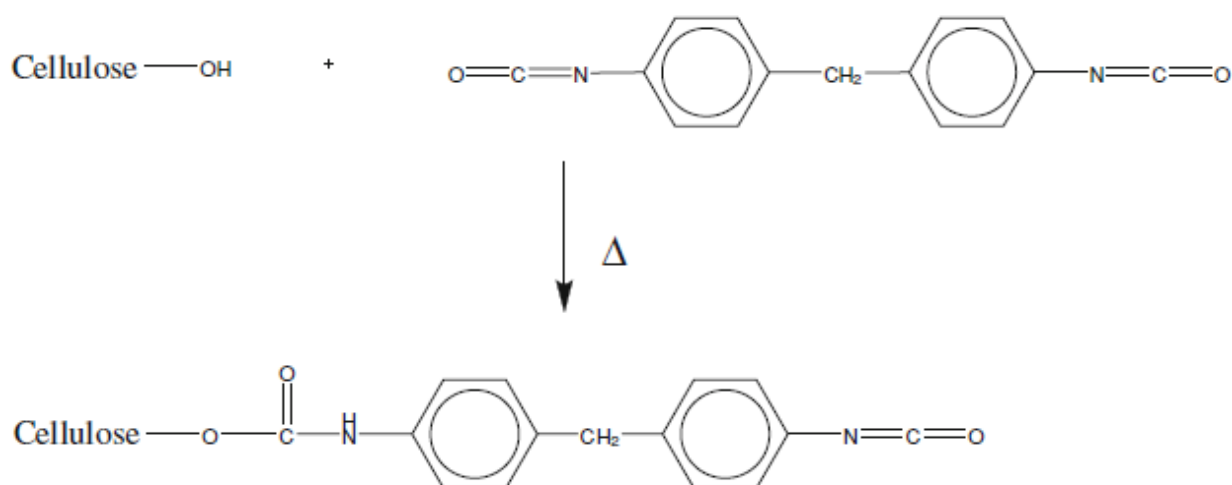
This section reviews research into the modification of wood constituents with organic acid anhydrides. Anhydrides can be classified into two major groups: non-cyclic anhydrides (i.e. Acetic) and cyclic anhydrides (i.e. Maleic). Of the non-cyclic anhydrides, Acetylation with Acetic Anhydride is the most widely reported [41-43]. The reaction involves the conversion

of a hydroxyl group into an ester group by the chemical affiliation of the carboxylic group of the anhydride with the free hydroxyl groups in cellulose. Reactions involving non-cyclic anhydrides are quite cumbersome as there are several steps involved during the treatment. These reactions also require the use of strong bases or catalysts to facilitate the reaction. Although the use of non-cyclic anhydrides can generally lead to good yields a large proportion of the treated cellulose can contain free anhydride, which cannot be easily removed from the treated cellulose. Generally, the modified cellulose may comprise of a distinct odour, which suggests the presence of free anhydride. The other drawback of the use of non-cyclic anhydrides is the formation of acid by-products, which are generally present in the modified cellulose. Pyridine, a catalyst used in the reaction, acts by swelling the wood and extracting lignin to expose the cellular structure of the cellulose. This facilitates the exposure of the free hydroxyl groups in cellulose to the anhydride. However, due to the aggressive nature of pyridine, it can also degrade and weaken the structure of the cell wall, which may not allow efficient modification. The effect of esterification on natural fibres is it imparts hydrophobicity, which makes them more compatible with the polymer matrix.

Tserki et. al. investigated the reinforcing effect of lignocellulosic fibres, incorporating flax, hemp and wood, on the mechanical properties of Bionolle, an aliphatic polyester [44]. The use of acetic anhydride treatment of the fibres was proven not to be as effective for improving the matrix tensile strength, compared with other techniques such as compatibilisation; however it did reduce the water absorption of the fibres. Lower tensile strengths were reported for composites reinforced with wood fibre, compared with flax and hemp. This may be attributed to the nature of the fibres, since flax and hemp are fibrous, whereas wood fibre is more flake like in nature with an irregular size and shape. The type and nature of lignocellulose fibres (chemical composition and structure) is of paramount importance in the development of polymer composites. It is shown that different fibres behave differently after various treatments. On the other hand, reactions of cellulose with cyclic anhydrides have also been performed [45]. Reactions involving cyclic anhydrides generally do not result in the formation of by-products and reactions can be performed with milder solvents, which don't interfere with the cell wall structure of cellulose. In order to facilitate reactions of wood flour with cyclic anhydrides it is important that the wood flour be pre-treated. Pre-treatment requires immersion of the wood flour in a suitable solvent, such as NaOH. This process is otherwise known as Mercerization, which is thought to optimise fiber-surface characteristics, by removing natural impurities such as pectin, waxy substances and natural oils. It is widely reported that the wood alone does not readily react with esterifying agents, since the hydroxyl groups required for reaction are usually masked by the presence of these natural impurities.

#### 3.1.4. Isocyanate treatment

Isocyanates are compounds containing the isocyanate functional group  $\text{-N=C=O}$ , which is highly reactive with hydroxyl groups in lignocellulose materials. The general reaction for cellulose with an isocyanate coupling agent is shown Equation 1:

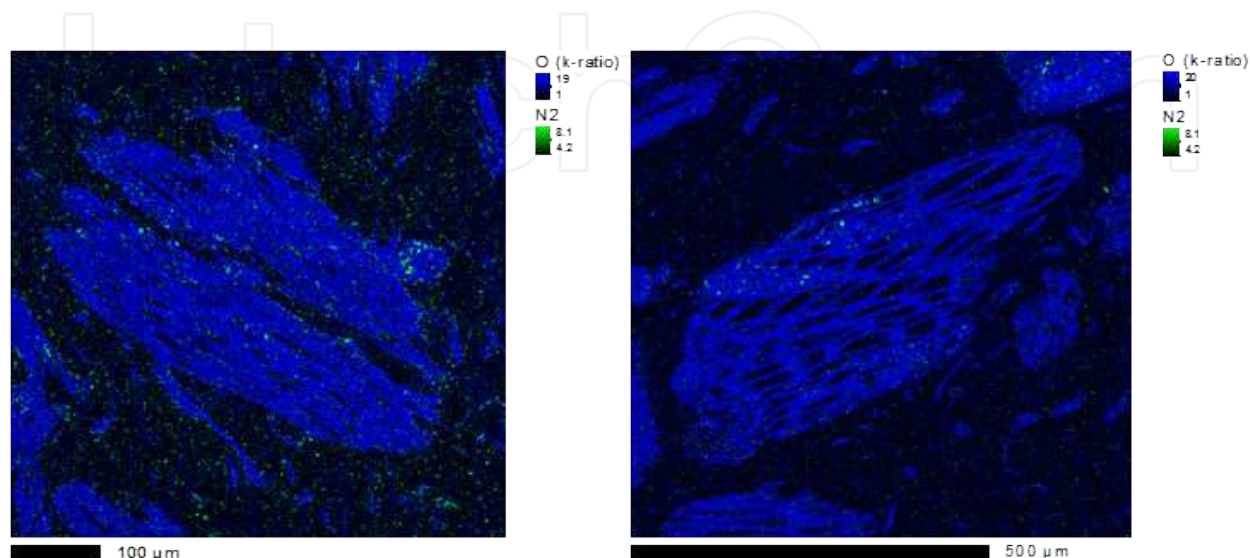


**Equation 1.** Possible reaction mechanism of MDI with wood-flour

R can represent any chemical group, such as alkyl or phenyl. Pickering et al studied the effects of Poly[methylene(polyphenyl isocyanate) and maleated coupling agents on New Zealand radiata pine fibre-polypropylene composites. A modest improvement in strength (4%) was reported with the addition of isocyanate to the polymer matrix over the matrix alone. When the radiata pine was treated with isocyanate and added to matrix, the strength improved by 11.5% over untreated radiata pine, and the modulus exhibited a significant improvement of 77% [46]. It appears that lignin content in wood fibres plays a significant role in relation to the ability of certain functional groups to interact with the cellulose component. The modest gains in tensile strength with the isocyanate can be attributed to the greater percentage of lignin in radiata pine.

X-ray mapping using Electron Probe Microanalysis presents a useful technique for evaluating the extent of cross-linking with MDI in biopolymer composites. Analysis of polished cross-sections was performed on unmodified wood-flour composite and the composites with MDI-mediated wood-flour. The aim of this was to detect the presence of nitrogen in the composites, which would indicate the extent of cross-linking in the modified PLA/wood-flour composites with MDI. The micrographs with the X-ray mapping of micro-composite with unmodified wood-flour composite and (b) micro-composite with MDI-modified wood-flour are shown in Figure 3. The nitrogen in the composite is depicted in the micrograph by the regions colored in green. The composite with unmodified wood-flour (Figure 3(a)) shows some nitrogen but this was expected since wood in its native form comprises traceable amounts (<0.75%) of nitrogen. Figure 3(b) depicts the composite with MDI-modified wood-flour and shows a greater concentration of nitrogen, presumably associated with MDI, in close proximity to the particle and the fibre lumen (cells) of the wood-flour particles and some concentrated areas at the interface. Similar observations were also reported by Bengtsson et al., which demonstrated the X-ray mapping of silicon from the silane used to modify wood-flour for polyethylene composites[47]. This suggests some reaction of the MDI-modified wood-flour with the PLA matrix creating a cross-linked structure with chem-

ical bonds joining MDI-modified wood-flour with the PLA matrix. This provides further evidence of the improvement in the mechanical properties as a result of an improvement in the interfacial interaction between PLA and the wood-flour particles. MDI appears to be also spread throughout the PLA matrix suggesting that part of it remains un-reacted within the host polymer.



**Figure 3.** Electron Probe Microanalysis of PLA/wood-flour micro-composites containing (a) unmodified wood-flour (b) MDI-mediated wood-flour (wood-flour content = 30% w/w)

Ecotoxicity is an important factor to consider when developing polymer composites from renewable resources. Isocyanate compounds, such as MDI, may not be regarded as a viable treatment method for natural fibres. Isocyanates upon decomposition in water can result in the formation of diamines. The decomposition products, such as 4, 4'-methylenedianiline and 2,4-diaminotoluene are suspected to be cancer causing agents and may also cause hepatitis in humans [48]. An alternative isocyanate that has been reported in the literature is lysine-based di-isocyanate. Lee et al reported the use of LDI as a coupling agent in the development of biodegradable polymers produced from poly lactic acid/bamboo fibre and poly(butylene succinate)/bamboo fibre. LDI is based upon Lysine, a naturally occurring amino acid with two amino groups and one carboxylic group. LDI can react with hydroxyl groups in cellulose, forming an isocyanate bridge, which can then readily react with the carboxylic and hydroxyl groups of the matrix polymer. MDI has previously been reported in the compatibilization of PLA and starch blends [49]. Wang discovered that blends of PLA with 45% wheat starch and 0.5% MDI resulted in composites with the highest tensile strength. It was also shown that moisture absorption increased as a function of increasing starch content. Water absorption can influence the mechanical properties of the composite. The moisture in the composite can react with MDI, which can effect interfacial interaction between starch mediated MDI with the PLA matrix by reducing the tensile strength or having a limited improvement. The reaction of moisture with MDI has also been reported in another paper [50] by Yu et al. It was interesting to note that the highest strength was achieved

at 45%. This can be attributed to two major reasons: the level of water in the blend can aid processing of the PLA, whereby the water behaves as a plasticiser, and secondly, the viscosity of the PLA at this level of water content maybe just sufficient to allow optimum dispersion of the starch particles within the PLA matrix. However, in order to utilise these materials in commercial applications such as for short term packaging these materials would require water proofing on the surface in order to prevent the rapid degradation.

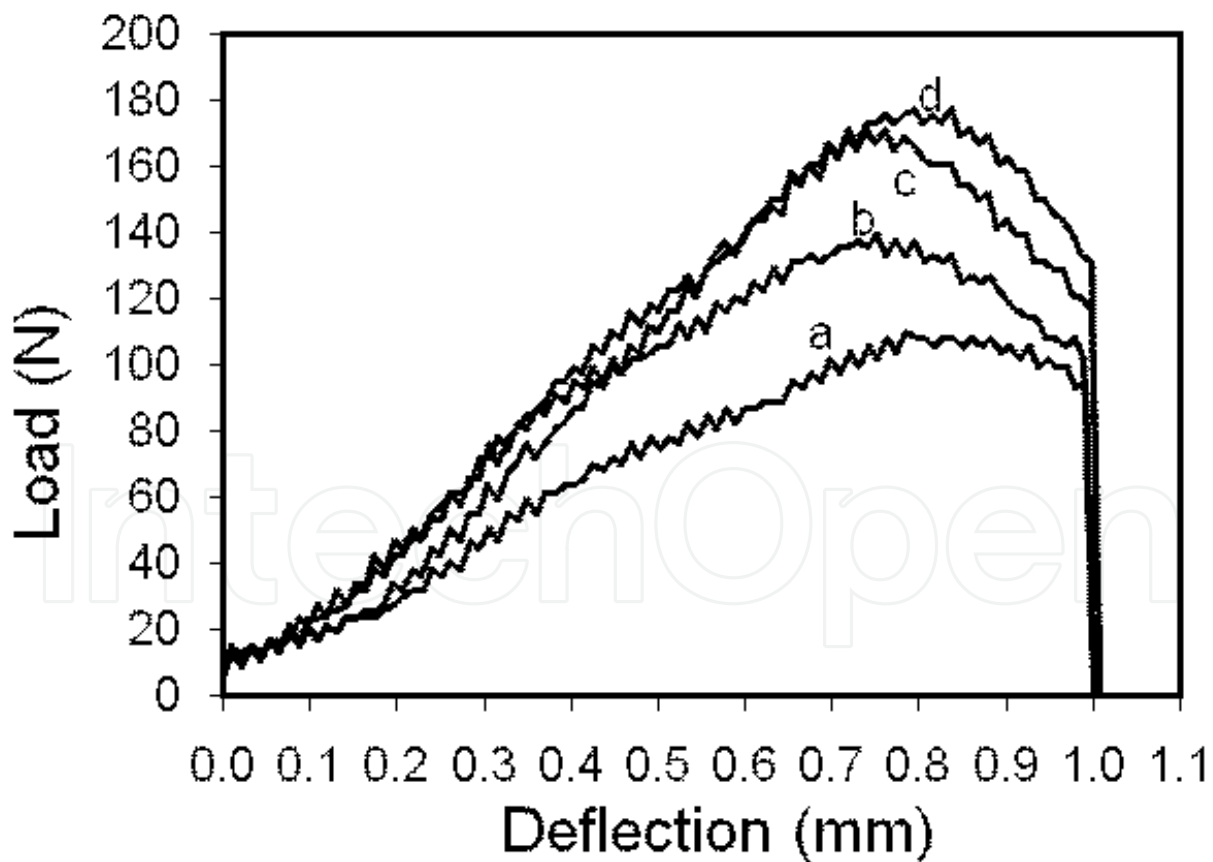
### 3.2. Physical techniques

Physical methods [51-54] reported in the literature are the use of corona or plasma treaters for modifying cellulose fibres for conventional polymers. In recent years the use of plasma for treatment of natural fibres has gained more prominence as this provides a more “greener” alternative for the treatment of natural fibres for the development of polymer composites, but is of particular interest to polymer composites incorporating biopolymer matrices, since this technique provides further credence to the whole idea of “green materials. Sustainability and end of life after use are important considerations to make when developing polymer composites from renewable resources is the toxicity and environmental impact of using various chemical or physical methods for improving the properties of these materials. Some chemical techniques may be toxic, e.g. isocyanates are carcinogenic, and therefore, the use of such agents may not be feasible for the development of polymer composites from renewable resources. Physical methods involving plasma treatments have the ability to change the surface properties of natural fibres by formation of free radical species (ions, electrons) on the surfaces of natural fibres [55]. During plasma treatment, surfaces of materials are bombarded with a stream of high energy particles within the stream of plasma. Properties such as wettability, surface chemistry and surface roughness of material surfaces can be altered without the need for employing solvents or other hazardous substances. Alternative surface chemistries can be produced with plasmas, by altering the carrier gas and depositing different reactive species on the surfaces of natural fibres [56]. This can then be further exploited by grafting monomeric and/or polymeric molecules on to the reactive natural fibre surface, which can then facilitate compatibilisation with the polymer matrix.

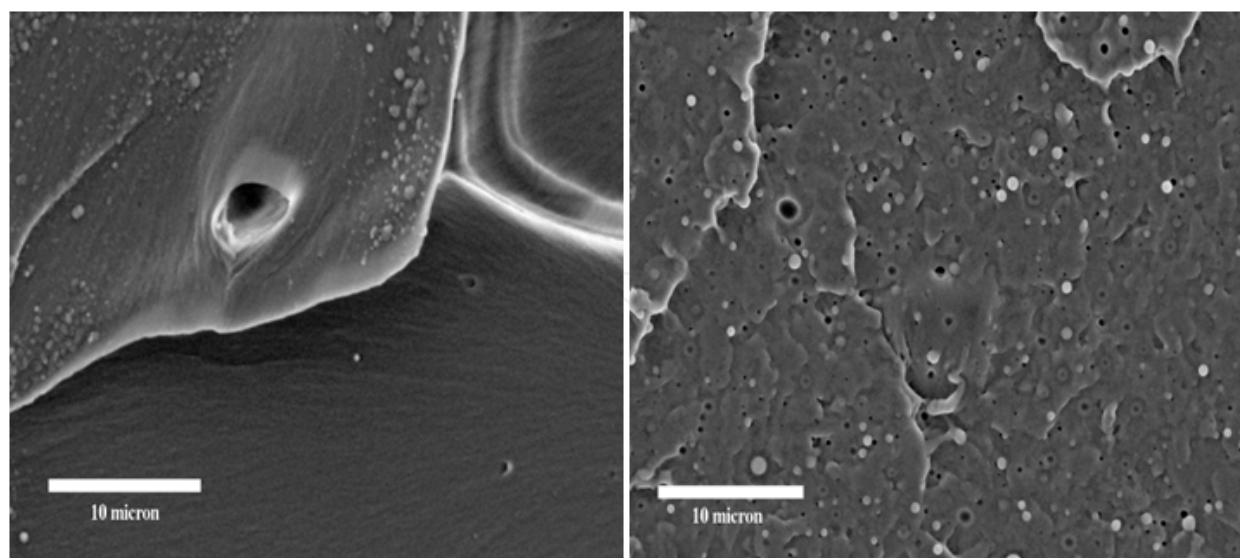
### 3.3. Toughening mechanisms in PLA/wood-flour composites

Physical modification of PLA can be achieved with the incorporation of softer polymer segments, which can attach to the polymer backbone. An example of an impact modification of PLA was performed with the addition of Poly (ethylene) acrylic acid (PEAA). The effect of impact modification can be observed in the load-deflection curves depicted in Figure 4. The load-deflection curve for PLA is almost linear and displays a rapid decrease in load once the peak load is reached, which is indicative of the well-known low resistance of PLA to crack propagation and its susceptibility to brittle fracture, with the smooth impact fracture surface of PLA (Figure 5) being typical of brittle failure. The load-deflection curve

for the PLA/wood-flour micro-composite containing 20%w/w wood-flour shown in Figure 4(b) displays an increased peak load compared with PLA, and the less rapid decrease in the load after peak load is reached is further evidence for effective stress transfer from the PLA matrix to the wood-flour particles. The load-deflection result for the PLA/wood-flour micro-composite containing MDI shown in Figure 4(c) indicates that the addition of MDI leads to a higher peak load compared with the equivalent micro-composite with no added MDI (Figure 4(b)), and the shape of the load-deflection curve is consistent with typical elastic-plastic deformation dominated by unstable crack growth. The increase in the peak load and width of the load-deflection profile, shown in Figure 4(d) indicates extensive plastic deformation of the PLA/wood-flour micro-composite containing PEAA. This increase in plastic deformation is attributed primarily to the increase in the rubbery nature of the blended PLA/PEAA matrix compared with PLA alone, resulting in more efficient dissipation of the energy associated with crack initiation and propagation [57].



**Figure 4.** Load-deflection curves for a) PLA, (b) PLA/wood-flour, (c) PLA/wood-flour containing MDI, (d) PLA/wood-flour containing PEAA wood-flour content=20%w/w



**Figure 5.** SEM micrograph of impact fracture surface of PLA for (a) Pure matrix and (b) blended with 3% w/w PEAA

## 4. Conclusions

Increasing concerns and awareness of the environment and the impact of human activity on the environment is currently the driving force for developing materials that are sustainable, more ecologically sound and are purely produced from renewable resources. PLA based composite materials have been widely recognised as a noble replacement to more conventional polymer composites derived from petrochemical feedstocks, such as polyolefins. PLA based composites are biodegradable and have high mechanical performance compared with conventional polymer composites. However, the wider uptake of PLA is restricted by performance deficiencies, such as its relatively poor impact properties which arise from its inherent brittleness, but also the limited supply and higher cost of PLA compared with commodity polymers such as polyethylene and polypropylene. It is expected that in the coming years PLA based materials will become more competitively priced as the demand increases and supply of abundant feedstock material becomes more widely available. The use of natural fibres presents a useful technique for developing PLA based composites, which are low-cost, biodegradable and can have properties that can be tailored for their specific application. PLA/natural fibre composites have been shown to have increased tensile modulus and reduced tensile strength compared with PLA, and this has been attributed to factors that include the weak interfacial interaction between the hydrophobic PLA matrix and the hydrophilic natural fibers, and lack of fiber dispersion due to a high degree of fiber agglomeration. Various methods of modifying the surface of the cellulosic fibers have been explored in an effort to improve the interaction that occurs at the interface between the PLA matrix and natural fibres. Better development of processing technologies and improvements in natural fibre treatments will facilitate the production of PLA based composites with opti-

imum mechanical and physical performance but also generate high cost competitiveness and greater acceptance of these materials in the market place.

## Author details

Eustathios Petinakis<sup>1,2\*</sup>, Long Yu<sup>1</sup>, George Simon<sup>2</sup> and Katherine Dean<sup>1</sup>

\*Address all correspondence to: [steven.petinakis@csiro.au](mailto:steven.petinakis@csiro.au)

1 CSIRO, Materials Science and Engineering, Melbourne, Australia

2 Department of Materials Engineering, Monash University, Melbourne, Australia

## References

- [1] Mukherjee T, Kao N. PLA Based Biopolymer Reinforced with Natural Fibre: A Review. *Journal of Polymers and the Environment*. 2011;19(3):714-25.
- [2] Psomiadou E, Arvanitoyannis I, Biliaderis CG, Ogawa H, Kawasaki N. Biodegradable films made from low density polyethylene (LDPE), wheat starch and soluble starch for food packaging applications. Part 2. *Carbohydrate Polymers*. 1997;33(4):227-42.
- [3] Perego G, Cella GD. *Mechanical Properties. Poly(Lactic Acid): John Wiley & Sons, Inc.*; 2010. p. 141-53.
- [4] Bajpai PK, Singh I, Madaan J. Development and characterization of PLA-based green composites: A review. *Journal of Thermoplastic Composite Materials*. 2012 March 22, 2012.
- [5] Yu L, Dean K, Li L. Polymer blends and composites from renewable resources. *Progress in Polymer Science*. [Article]. 2006;31(6):576-602.
- [6] Yu T, Ren J, Li S, Yuan H, Li Y. Effect of fiber surface-treatments on the properties of poly(lactic acid)/ramie composites. *Composites Part A: Applied Science and Manufacturing*. [doi: 10.1016/j.compositesa.2009.12.006]. 2010;41(4):499-505.
- [7] Mohanty AK, Misra M, Drzal LT. Surface Modifications of natural fibres and performance of the resulting biocomposites: An Overview. *Composite Interfaces*. 2001;8(5):31.
- [8] Abdul Khalil HPS, Ismail H. Effect of acetylation and coupling agent treatments upon biological degradation of plant fibre reinforced polyester composites. *Polymer Testing*. 2000;20(1):65-75.

- [9] Sain M, Suhara P, Law S, Bouilloux A. Interface modification and mechanical properties of natural fiber-polyolefin composite products. *Journal of Reinforced Plastics and Composites*. 2005;24(2):121-30.
- [10] Huda MS, Drzal LT, Misra M, Mohanty AK. Wood-Fibre reinforced Poly(lactic acid) Composites: Evaluation of the Physicomechanical and Morphological Properties *Journal of Applied Polymer Science*. 2006;102:14.
- [11] Xie Y, Hill CAS, Xiao Z, Militz H, Mai C. Silane coupling agents used for natural fiber/polymer composites: A review. *Composites Part A: Applied Science and Manufacturing*. [doi: 10.1016/j.compositesa.2010.03.005]. 2010;41(7):806-19.
- [12] Zafeiropoulos NE. Interface engineering of natural fibre composites for maximum performance. Zafeiropoulos NE, editor: Woodhead Publishing Limited; 2011.
- [13] Klyosov AA. Composition of Wood-Plastic Composites: Cellulose and Lignocellulose Fillers. In: Klyosov AA, editor. *Wood-Plastic Composites*. New Jersey: John Wiley and Sons; 2007. p. 75-122.
- [14] Mohanty AK, Misra M, Drzal LT. Sustainable Bio-Composites from Renewable Resources: Opportunities and Challenges in the Green Materials World. *Journal of Polymers and the Environment*. 2002;10(1):19-26.
- [15] Nzokou P, Pascal Kamdem D. X-ray photoelectron spectroscopy study of red oak- (*Quercus rubra*), black cherry- (*Prunus serotina*) and red pine- (*Pinus resinosa*) extracted wood surfaces. *Surface and Interface Analysis*. 2005;37(8):689-94.
- [16] Groot W, van Krieken J, Sliekersl O, de Vos S. Production and Purification of Lactic Acid and Lactide. *Poly(Lactic Acid)*: John Wiley & Sons, Inc.; 2010. p. 1-18.
- [17] George J, Sreekala MS, Thomas S. A review on interface modification and characterization of natural fiber reinforced plastic composites. *Polymer Engineering & Science*. 2001;41(9):1471-85.
- [18] Oksman K, Skrivars M, Selin JF. Natural Fibres as reinforcement in polylactic acid (PLA) composites. *Composites Science and Technology*. 2003;63:8.
- [19] Shibata M, Ozawa K, Teramoto N, Yosomiya R, Takeishi H. Biocomposites made from Short Abaca Fiber and Biodegradable Polyesters. *Macromolecular Materials Engineering*. [Journal]. 2003;288:9.
- [20] Wollerdorfer M, Bader H. Influence of mechanical properties of biodegradable polymers *Industrial Crops and Products*. 1998;8:8.
- [21] Huda MS, Drzal LT, Misra M, Mohanty AK, Williams K, Mielewski DF. A Study on Biocomposites from Recycled Newspaper Fiber and Poly(lactic acid). *Ind Eng Chem Res*. 2005;44(15):5593-601.
- [22] Bax B, Müssig J. Impact and tensile properties of PLA/Cordenka and PLA/flax composites. *Composites Science and Technology*. [doi: 10.1016/j.compscitech.2008.01.004]. 2008;68(7-8):1601-7.

- [23] Mathew AP, Oksman K, Sain M. Mechanical properties of biodegradable composites from poly lactic acid (PLA) and microcrystalline cellulose (MCC). *Journal of Applied Polymer Science*. 2005;97(5):2014-25.
- [24] Tserki V, Matzinos P, Panayiotou C. Novel Biodegradable composites based on treated lignocellulosic waste flour as filler Part II. Development of Biodegradable composites using treated and compatibilized waste flour. *Composites: Part A*. 2006;37:8.
- [25] Petinakis E, Yu L, Edward G, Dean K, Liu H, Scully A. Effect of Matrix-Particle Interfacial Adhesion on the Mechanical Properties of Poly(lactic acid)/Wood-Flour Micro-Composites. *Journal of Polymers and the Environment*. 2009;17(2):83-94.
- [26] Netravali AN. Fiber/Resin Interface Modification in "Green" Composites. In: Bhattacharyya SFaD, editor. *Handbook of Engineering Biopolymers Homopolymers, Blends and Composites*. Munich: Hanser; 2007. p. 847-68.
- [27] Gandini MNBaA. The surface modification of cellulose fibers for use as reinforcing elements in composite materials. *Composite Interfaces*. 2004;12(1-2):41-75.
- [28] Bhavesh L. Shah, Susan E. Selke, Michael B. Walters, Patricia A. Heiden. Effects of wood flour and chitosan on mechanical, chemical, and thermal properties of polylactide. *Polymer Composites*. 2008;29(6):655-63.
- [29] Kazayawoko M, Balatinecz JJ, Matuana LM. Surface Modification and Adhesion Mechanisms in Woof Fibre-polypropylene composites. *Journal of Materials Science*. 1999;34:11.
- [30] Lu JZ, Negulescu II, Wu Q. Maleated wood-fibre/high density polyethylene composites: Coupling mechanisms and interfacial characterization. *Composite Interfaces*. 2005;12(2):16.
- [31] Wang Y, Yeh F-C, Lai S-M, Chan H-C, Chen H-F. Effectiveness of Functionalised Polyolefins as Compatibilizers for Polyethylene/Wood Flour Composites. *Polymer Engineering and Science*. 2003;43(4):13.
- [32] Oksman K, Lindberg H. Influence of thermoplastic elastomers on adhesion in polyethylene-wood flour composites. *Journal of Applied Polymer Science*. 1998;68(11):1845-55.
- [33] Sun-M. Lai F-CY, Yeh Wang, Hsun-C. Chan, Hsiao-F. Shen. Comparative Study of Maleated Polyolefins as Compatibilizers for Polyethylene/ Wood Flour Composites. *Applied Polymer Science*. 2003;87:487-96.
- [34] X. Colom FC, P. Pages, J. Canavate. Effects of different treatments on the interface of HDPE/lignocellulosic composites. *Composites Science and Technology*. 2003;63:161-9.
- [35] Xu T, Tang Z, Zhu J. Synthesis of polylactide-graft-glycidyl methacrylate graft copolymer and its application as a coupling agent in polylactide/bamboo flour biocomposites. *Journal of Applied Polymer Science*. 2012;125(S2):E622-E7.

- [36] Pickering MDHBaKL. Fiber Pretreatment and Its Effects on Wood Fiber Reinforced Polypropylene Composites. *Materials and Manufacturing Processes*. 2006;21:303-7.
- [37] Ichazo MN, Albano C, Gonzalez J, Perera R, Candal MV. Polypropylene/wood flour composites: treatments and properties. *Composite Structures*. 2001;54:207-14.
- [38] Wu J, Yu D, Chan C-M, Kim J, Mai Y-W. Effect of fiber pretreatment condition on the interfacial strength and mechanical properties of wood fiber/PP composites. *Journal of Applied Polymer Science*. 2000;76(7):1000-10.
- [39] Oksman MBaK. The use of silane technology in crosslinking polyethylene/wood flour composites. *Composites Part A: applied science and manufacturing*. 2006;37:752-65.
- [40] González D, Santos V, Parajó JC. Silane-treated lignocellulosic fibers as reinforcement material in polylactic acid biocomposites. *Journal of Thermoplastic Composite Materials*. 2011 September 7, 2011.
- [41] Hill CAS. Chemical Modification of Wood (I): Acetic Anhydride Modification 3.1. In: Hill CAS, editor. *Wood Modification: Chemical, Thermal and Other Processes*. New Jersey: John Wiley and Sons 2006. p. 45-76.
- [42] Bogoeva-Gaceva G, Avella M, Malinconico M, Buzarovska A, Grozdanov A, Gentile G, et al. Natural fiber eco-composites. *Polymer Composites*. [Article]. 2007;28(1): 98-107.
- [43] Li X, Tabil L, Panigrahi S. Chemical Treatments of Natural Fiber for Use in Natural Fiber-Reinforced Composites: A Review. *Journal of Polymers and the Environment*. 2007;15(1):25-33.
- [44] Tserki V, Matzinos P, Zafeiropoulos NE, Panayiotou C. Development of Biodegradable Composites with Treated and Compatibilized Lignocellulosic Fibres. *Journal of Applied Polymer Science*. 2006;100:8.
- [45] Doczekalska B, Bartkowiak M, Zakrzewski R. Modification of sawdust from pine and beech wood with the succinic anhydride. *Holz als Roh- und Werkstoff*. 2007;65(3): 187-91.
- [46] Ji KLPaC. The Effect of Poly[methylene(polyphenylisocyanate)] and Maleated Polypropylene Coupling Agents on New Zealand Radiata Pine Fiber-Polypropylene Composites. *Journal of Reinforced Plastics and Composites*. 2004;23(18):2011-24.
- [47] Bengtsson M, Oksman K. The use of silane technology in crosslinking polyethylene/wood flour composites. *Composites Part A: Applied Science and Manufacturing*. 2006;37(5):752-65.
- [48] Lee SH, Wang S. Biodegradable polymers/bamboo fiber biocomposite with bio-based coupling agent. *Composites Part A*. [Article]. 2006;37(1):80-91.

- [49] Wang H, Sun X, Seib P. Mechanical properties of poly(lactic acid) and wheat starch blends with methylenediphenyl diisocyanate. *Journal of Applied Polymer Science*. 2002;84(6):1257-62.
- [50] Yu L, Dean K, Yuan Q, Chen L, Zhang X. Effect of Compatibilizer Distribution on the Blends of Starch/Biodegradable Polyesters. *Journal of Applied Polymer Science*. 2006;103:7.
- [51] Dong S, Saphieha S, Schreiber HP. Mechanical Properties of Corona-Modified Cellulose/Polyethylene Composites. *Polymer Engineering and Science*. 1993;33(6):4.
- [52] Dong S, Saphieha S, Schreiber HP. Rheological Properties of Corona Modified Cellulose/ Polyethylene Composites. *Polymer Engineering and Science*. 1992;32(22):6.
- [53] Olaru N, Olaru L, Cobillac G. Plasma Modified Wood Fibres as Fillers in Polymeric Materials *Romanian Journal of Physics*. 2005;50(9):7.
- [54] Baltazar-y-Jimenez A, Bistriz M, Schulz E, Bismarck A. Atmospheric air pressure plasma treatment of lignocellulosic fibres: Impact on mechanical properties and adhesion to cellulose acetate butyrate. *Composites Science and Technology*. [doi: 10.1016/j.compscitech.2007.04.028]. 2008;68(1):215-27.
- [55] Lee K-Y, Delille A, Bismarck A. Greener Surface Treatments of Natural Fibres for the Production of Renewable Composite Materials Cellulose Fibers: Bio- and Nano-Polymer Composites. In: Kalia S, Kaith BS, Kaur I, editors.: Springer Berlin Heidelberg; 2011. p. 155-78.
- [56] Nguyen MH, Kim BS, Ha JR, Song JI. Effect of Plasma and NaOH Treatment for Rice Husk/PP Composites. *Advanced Composite Materials*. [doi: 10.1163/092430411X570112]. 2011;20(5):435-42.
- [57] Hristov VN, Vasileva ST, Krumova M, Lach R, Michler GH. Deformation mechanisms and mechanical properties of modified polypropylene/wood fiber composites. *Polymer Composites*. 2004;25(5):521-6.

