ABSTRACT

To reduce our dependency on depleting fossil fuels and their cost, biocomposites were prepared using polylactic acid (PLA) as a matrix and wood flour (WF) as filler by a twin-screw extrusion method. Because of poor wettability between wood flour and PLA matrix, the properties of the PLA/wood flour composite are not right. Thus, the silane coupling agents (as the surface treatment agent of wood flour) and the interfacial modifiers (various copolymers) have been used to improve their interfacial adhesion. The effects of wood flour content, types of silane coupling agents and their content, interfacial modifiers and their concentration on the properties and morphology of PLA/WF biocomposites were systematically studied in detail, including microstructures, mechanical and rheological properties. The results revealed that the properties of biocomposites were expected to be improved by dispersing wood flour aggregations into microfibrils and improving the interfacial adhesion between PLA and WF with the addition of epoxy silane or ethylene-methyl acrylate-glycidyl methacrylate (EMAGMA). Especially, the interfacial modifier of EMAGMA could improve not only the interfacial action but also the impact strength of PLA. Further studies indicated that the co-interfacial modifiers of epoxy silane and EMAGMA could effectively enhance the interaction between PLA matrix and WF and further improve mainly the impact strength and elongation-at-break of PLA/WF biocomposites.

INTRODUCTION

Advances in synthetic plastics made from petroleum have brought considerable benefits to human life. However, the widespread use of plastics has also become a significant concern due to their negative impact on the environment and the fossil fuels resources. Therefore, there is an immediate need to develop a non-petroleum-based and sustainable feedstock, and this has predominantly shifted the attention of many researchers towards bio-based plastics [1] because they reduce our dependency on depleting fossil fuels and decrease CO₂ release into the atmosphere. One of the most interesting bio-based polymers is polylactide (PLA) which is made from plants and it is readily biodegradable [2].

In general, PLA is synthesized by ring-opening polymerization of lactide and lactic acid monomers, which are obtained from the ferme-
tion of sugar feed stocks [3]. The as-synthesized PLA is a kind of favourable biocompatible, biodegraded, thermoplastic, high-strength and high-modulus polymer [4] which can substitute conventional polymers in many ways, such as barriers for sanitary products and diapers, planting, disposable cups and plates and others [5]. However, its high cost, brittleness, low deformation-at-break and narrow processing windows restrict its widespread applicability. Recently, the combination of PLA with natural materials [6-8] or synthetic polymers [9-11] provides a new way to obtain the tailored properties at low cost. Numerous studies have been devoted to blending PLA with biocompatible plasticizers [12-14] and other polymers, and different kinds of partially biodegradable [15,16] or totally biodegradable composites were obtained [3, 17,18].

Wood flour (WF), usually made by conventional grinding [19] is gaining increasing acceptance as a kind of filler materials for polymers since it offers many advantages, including low density, non-significant damage during processing, biodegradability, high stiffness, noise absorption, availability, and renewability as well as relatively low cost [20]. Furthermore, biocomposites comprised of natural fibres [21] and bio-based plastics [22,23], specifically wood fibres-thermoplastic composites, have also displayed the cost-effective reinforcement of wood fibres in several thermoplastics. Their uses have received considerable attention in industrial fields [19, 24-26] not only as feasible problem solving to growing environmental threats, but also as a sustainable solution to the uncertainty of the world's petroleum supply [1, 19, 27-30].

PLA and wood flours (WF) are two of the most promising biomaterials possessing potentials for the replacement of petroleum-based commodities because of low cost and availability. Furthermore, their biodegradability and compatibility can also be assets in applications where there is a demand for recycled materials [31-33]. However, the poor wettability between hydrophilic wood microfibres and hydrophobic polymeric matrices would lead to their direct mixture with poor interfacial adhesion and mechanical strength and ductility [29,34]. Thus, it is important to find some suitable interface modifiers to improve the interfacial interaction between filler and matrix, and further obtain biocomposites with desirable properties [35-37].

In this paper, PLA/WF biocomposites were prepared as a means to reduce the overall material cost and tailor the material properties through a twin-screw extrusion method. To improve the interfacial interaction between PLA and WF and processability, some low molecular weight silane coupling agents were used to treat the surface of wood flours and some copolymers were used as interfacial modifiers. The properties of biocomposites can be improved by dispersing wood flour aggregations into microfibrils and improving the interfacial adhesion between PLA and WF with the addition of epoxy silane or ethylene-methyl acrylate-glycidyl methacrylate (EMAGMA), while it is not easy to break the extruded bar. The effect of wood flour content, the types of interfacial modifiers and their concentration on the properties of PLA/WF biocomposites has been studied in detail, including the mechanical, thermal and rheological properties. Moreover, the co-interfacial modifiers of epoxy silane and EMAGMA have been used in the PLA/WF biocomposites where they could effectively enhance the interaction between PLA matrix and WF and further improve mainly the impact strength and elongation-at-break of PLA/WF biocomposites.

EXPERIMENTAL

Materials

PLA (3051D) was obtained from Natureworks Co. Ltd. (USA), and was polymerized mainly from L-lactic acid. It had a specific gravity of 1.25 g/cm³ and a melt flow index about 25 g/10 min (210°C/2.16 Kg). Its glass transition was in the range of 55-65°C and melting temperature was in the range of 150-165°C. Pine wood flour (nominal 80 mesh, moisture content ~10%, specific gravity ~0.25 g/cm³, and the aspect ratio of fibril ~102) was supplied by Linan Mingzhu Bamboo & Wood Flour Co. Ltd., China) whose composition was cellulose (42±2%), hemicellulose (27±2%), lignin (28±2%) and volatile matter (3±1%). Vinyltrimethoxysilane (vinyl silane), γ-aminopropyl triethoxysilane (amino silane), γ-glycidoxypropyltrimethoxysilane (epoxy silane) and γ-methacryloxypropyltrimethoxysilane (allyl ester
silane) were purchased from National Medicines Co. Ltd., China and used as wood flour surface treatment agents. LDPE-g-MAH (grafting degree 0.8%) and POE-g-MAH (grafting degree 1.0%) were prepared by our group. Grafting reactions were carried out in the molten state with a TSE-35 co-rotating twin-screw extruder (Ruiya Group, Nanjing, China) at 170°C. LDPE (722, Dow Chemical Co., Unite States) or ethylene-octene copolymer (POE) (Exact 4049, Exxon Mobil Co., USA), MAH, initiators, solvents, and co-monomers were simultaneously introduced into the twin-screw extruder after dry blending which was similar to that of the preparation of ABS-g-MAH [38]. Ethylene methyl acrylate copolymer (EMA, 24MA005, MA content 24%) or ethylene-methyl acrylate-glycidyl methacrylate (EMAGMA, AX8900, GMA content 8%) resins were used as interfacial compatibilizers and supplied by Arkema Investment Co., Ltd., China.

Sample Preparation
Surface Treatment of Wood Flour
Pine wood flour (WF) was dried first at 80°C for 24 h in a vacuum oven to remove water and low molecular weight organic materials [5,39]. Then, silane (5 wt% silane in 95% ethanol aqueous solution) was added into a fixed amount of dried wood flour in a high-speed mixer. The silane content (2 wt%) employed in this study was a percentage amount relative to WF content in the formulation, and thus the higher the WF content, the higher was the silane content. After being mixed for about 10 min, the wood flour was removed and dried at 120°C in a vacuum oven for 2 h to complete the reaction of wood flour with coupling agent, and then cooled to 105°C and held for 12 h.

Table 1. Formulations of PLA/WF biocomposites.

<table>
<thead>
<tr>
<th>Composites</th>
<th>PLA (phr)</th>
<th>WF (phr)</th>
<th>Coupling agent (phr)</th>
<th>Compatibilizer (phr)</th>
</tr>
</thead>
<tbody>
<tr>
<td>WU10</td>
<td>100</td>
<td>10</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>WU20</td>
<td>100</td>
<td>20</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>WU30</td>
<td>100</td>
<td>30</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>W30-a</td>
<td>100</td>
<td>30</td>
<td>0.6 (Amino silane)</td>
<td>0</td>
</tr>
<tr>
<td>W30-b</td>
<td></td>
<td></td>
<td>0.6 (Epoxy silane)</td>
<td>0</td>
</tr>
<tr>
<td>W30-c</td>
<td></td>
<td></td>
<td>0.6 (Allyl ester silane)</td>
<td>0</td>
</tr>
<tr>
<td>W30-d</td>
<td></td>
<td></td>
<td>0.6 (Vinyl silane)</td>
<td>0</td>
</tr>
<tr>
<td>WP10</td>
<td>100</td>
<td>10</td>
<td>0.2 (Epoxy silane)</td>
<td>0</td>
</tr>
<tr>
<td>WP20</td>
<td>100</td>
<td>20</td>
<td>0.4 (Epoxy silane)</td>
<td>0</td>
</tr>
<tr>
<td>WP30-b</td>
<td>100</td>
<td>30</td>
<td>0.6 (Epoxy silane)</td>
<td>0</td>
</tr>
<tr>
<td>WP40</td>
<td>100</td>
<td>40</td>
<td>0.8 (Epoxy silane)</td>
<td>0</td>
</tr>
<tr>
<td>WU30</td>
<td>100</td>
<td>30</td>
<td>0</td>
<td>0  LDPE-g-MAH/15 EMA/15 POE-g-MAH/15 EMAGMA/15</td>
</tr>
<tr>
<td>WCO30-B</td>
<td>100</td>
<td>30</td>
<td>0</td>
<td>0  LDPE-g-MAH/15 EMA/15 POE-g-MAH/15 EMAGMA/15</td>
</tr>
<tr>
<td>WCO30-C</td>
<td></td>
<td></td>
<td>0</td>
<td>0  LDPE-g-MAH/15 EMA/15 POE-g-MAH/15 EMAGMA/15</td>
</tr>
<tr>
<td>WCO30-D</td>
<td></td>
<td></td>
<td>0</td>
<td>0  LDPE-g-MAH/15 EMA/15 POE-g-MAH/15 EMAGMA/15</td>
</tr>
<tr>
<td>WCO30-E</td>
<td></td>
<td></td>
<td>0</td>
<td>0  LDPE-g-MAH/15 EMA/15 POE-g-MAH/15 EMAGMA/15</td>
</tr>
<tr>
<td>WMA10</td>
<td>100</td>
<td>10</td>
<td>0.2 (Epoxy silane)</td>
<td>0</td>
</tr>
<tr>
<td>WMA20</td>
<td>100</td>
<td>20</td>
<td>0.4 (Epoxy silane)</td>
<td>0</td>
</tr>
<tr>
<td>WMA30</td>
<td>100</td>
<td>30</td>
<td>0.6 (Epoxy silane)</td>
<td>0</td>
</tr>
<tr>
<td>WMA40</td>
<td>100</td>
<td>40</td>
<td>0.8 (Epoxy silane)</td>
<td>0</td>
</tr>
<tr>
<td>AX13</td>
<td>100</td>
<td>26</td>
<td>0.52 (Epoxy silane)</td>
<td>0</td>
</tr>
<tr>
<td>AX26</td>
<td></td>
<td></td>
<td></td>
<td>0</td>
</tr>
<tr>
<td>AX52</td>
<td></td>
<td></td>
<td></td>
<td>0</td>
</tr>
</tbody>
</table>
Preparation of Biocomposites

Different interfacial modifiers were used in the PLA/WF system with varied ratio in order to modulate the properties of the obtained biocomposites. Table 1 shows the formulas in terms of WF and interfacial compatibilizers.

After PLA was dried in a vacuum oven at 80°C for 24 h, PLA, dried WF and other agents were added into a high-speed mixer. Then they were mixed for 10 min and extruded through a ZE 25A twin-screw extruder (Berstorff GmbH, Germany) with a screw diameter of 25 mm and a length-to-diameter ratio of 36/1. The corresponding temperature profile along the extruder barrel was 20/120/140/160/170/175/170°C, the temperature at the die was 165°C, and the screw speed was 150 rpm. The extruded rods were cut into short cylinders of about 10 mm in length, and then the blends were dried again in the vacuum oven at 80°C for 24 h before moulding.

The short cylinders were pressed into thin plates by a hot press at 170°C and 20 MPa for 8 min, and then cut into bars for tensile and impact strength tests.

Characterization

Mechanical Testing

Tensile tests were performed on an Instron testing machine (Instron 4465, Instron Corp., USA) according to ASTM D882 with a crosshead speed of 10 mm/min. The specimen for tensile test was dumbbell-shaped with a dimension of 2×6×80 mm under 50% humidity and 23°C. All samples were pre-conditioned at 23°C and 50% RH for 16 h. At least five replicate specimens were tested for each formulation.

Notched Izod impact testing was performed on a universal pendulum impact tester (RAY-RAN Test Equipment Ltd., UK) according to ASTM D256 (samples of 4×10×80 mm dimensions and notch depth of 2 mm). The impact resistance was calculated through dividing the total energy required to break the sample by the area of impact specimens. The specimens were pre-conditioned at 23°C and 50% RH for 16 h. Both tests were conducted on five samples and the average values were recorded.

Morphology

Scanning electron microscope (SEM) was used to observe the microstructure of composites. The extruded rods were cooled in liquid nitrogen for 20 min and then broken to obtain fracture surfaces. The fracture surfaces were vacuum-coated with gold for SEM observation. The instrument was a Hitachi S-2150 SEM (Hitachi High-Technologies Corp., Japan) with an accelerated voltage of 15 kV.

Rhological Behaviours

Dynamic measurements (G’ and G”) were accomplished using the cone and plate feature of a Gemini 200 HR (Bohlin Instruments, UK). The cone angle and the cone diameter were 0.1 radians and 25 mm, respectively. Preliminary studies were conducted to ensure that the dynamic properties were measured in the linear viscoelastic region. The measurements were conducted in a frequency range 0.1-100 s⁻¹ at an applied strain of 1%. All samples were dried in an oven at 60°C for 24 h prior to being tested.

RESULTS AND DISCUSSION

Mechanical Properties

Effect of WF Content

The high cost and low deformation-at-break limit the wide applications of PLA, and the addition of wood flour can provide the cost reduction and combination of properties. To obtain high performance PLA/WF biocomposites, different interfacial modifiers were used in the PLA/WF system with varied ratio in order to modulate the properties of the obtained biocomposites. Table 1 shows the formulas in terms of WF and interfacial compatibilizers.

Table 1. The effect of WF content on the mechanical properties.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Tensile strength (MPa)</th>
<th>Elongation-at-break (%)</th>
<th>Notched Izod impact strength (KJ/m²)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pure PLA</td>
<td>54.9±1.1</td>
<td>2.5±0.3</td>
<td>2.3±0.2</td>
</tr>
<tr>
<td>WU10</td>
<td>37.4±0.8</td>
<td>2.6±0.3</td>
<td>3.0±0.2</td>
</tr>
<tr>
<td>WU20</td>
<td>34.0±0.8</td>
<td>1.8±0.2</td>
<td>2.6±0.2</td>
</tr>
<tr>
<td>WU30</td>
<td>27.6±0.7</td>
<td>1.3±0.2</td>
<td>2.4±0.2</td>
</tr>
</tbody>
</table>
composites, the influence of wood flour content on mechanical properties, tensile strength, elongation-at-break (EB) and impact resistance were initially investigated. Table 2 shows the effect of WF content on the mechanical properties (PLA/WF biocomposite formulations are listed in Table 1). Pure PLA is a kind of brittle and stiff material because its elongation-at-break is as low as 2.5%. Based on the results in Table 2, it is evident that both tensile strength and elongation-at-break values of PLA/WF biocomposites are lower than those of pure PLA which decrease with increased WF content. This may imply that there is a poor interfacial interaction between reinforcing fibre and polymer matrix because of the poor stress transformation across interphase, which can be also observed in the traditional thermoplastic composites with the addition of fibres [40]. Unlike tensile strength, the impact strength increased initially and then dropped with higher WF content, where the maximum value of WF content was achieved at 10 phr. On the whole the impact strength of all the PLA/WF biocomposites is slightly higher than that of pure PLA. This is because a small amount of wood flour would increase the free volume in the composites and segmental movements are facilitated when composites are subjected to an impact force [41]. However, excessive wood flour could lead to its aggregation due to poor interfacial interaction between WF and PLA, resulting in lower impact strength.

**Effect of Silane Coupling Agents**

In general, tensile strength is more sensitive to the properties of matrix and the interfacial interaction between the fibres and matrix. The same happens in all the wood composites where there is a weak

---

**Figure 1.** Mechanical properties of PLA/WF biocomposites as a function of different silane coupling agents: (a) tensile strength, (b) elongation-at-break, and (c) notched Izod impact strength.
interfacial interaction between highly hydrophilic wood flour and weakly hydrophilic plastics [29]. As expected, the addition of WF into PLA matrix without any interfacial compatibilizers would also reduce the tensile strength and elongation-at-break values of the composites given in Table 2. Moreover, in the extrusion process, it is difficult to add fluffy wood flour into PLA matrix, as the extrudate bar is easily broken, and thus, it prevents a smooth process. To improve interfacial interactions, wood flour is usually treated by some silane coupling agents before mixing procedure. Herein, different kinds of silane are chosen as surface treatment agent and their effects on the mechanical properties are studied for PLA/WF biocomposites (the content of wood flour is fixed at 30 phr as given in Table 1). In the process, due to the addition of coupling agent, wood flour becomes dense, more easily mixed with polylactic acid and the extrudant bar is not easily broken.

From Figure 1, it is observed that the incorporation of silane coupling agents into the formulations can suitably improve the tensile strength and the elongation-at-break values of composites compared to those of PLA/WF biocomposites prepared without any surface treatment agent. The slight improvement in impact strength of composites with silane coupling agent also suggests the positive influence of silane on PLA/WF biocomposites. There are two aspects on the role of silane coupling agent on mechanical properties of biocomposites. First, the active group of silane coupling agent can react with the hydroxyl group of WF (route II in Scheme I) [42,43], weaken the polarity of WF and further improve its wettability with PLA matrix. Secondly, the long carbon chain of silane coupling agent can twist with matrix PLA. The combined effect makes the silane coupling agent to act as a bridge between PLA and WF in the composites, which may improve the interfacial interaction between WF and PLA and then strengthen the mechanical properties of the composites. Among silane coupling agents, epoxy silane is a more effective surface treatment agent for the PLA/WF system. This might be due to the following reactions between epoxy group and PLA [44-47] (Scheme I (route III)) which could further increase the compatibility of the system.

Thus, epoxy silane is chosen as the typical surface treatment agent for further investigation. Therefore, the coupling reaction of epoxy silane with filler potentially increases the adhesion between polymer matrix and the filler surfaces.

**Effect of Copolymer as Interfacial Modifiers**

Although silane coupling agents can to some extent
improve the interfacial interaction between wood flour and matrix, the mechanical properties of the composite are still unsatisfactory. It is well known that the mechanical behaviour of heterogeneous materials depends on four main parameters:

- modulus of each component;
- volume fraction of each component;
- morphology and aspect ratio of the filler, length distribution, and orientation of fibres in composite and;
- interface properties due to its liability in load transfer. The latter parameter depends mainly on the degree of interactions between the phases, i.e., fibre treatment for fibre-filled composites [42].

In order to further improve the interfacial interaction between WF and PLA matrix, functionalized or polar copolymer modifiers were also used as compatibilizer and toughening agent, such as LDPE-g-MAH, EMA, POE-g-MAH and EMAGMA. The effect of various types of copolymer compatibilizers on the mechanical properties of WF/PLA biocomposites has been investigated with wood flour fixed at 30 phr (formulations listed in Table 1) and the results are given in Figure 2.

From Figure 2, it may be seen that all copolymer compatibilizers can improve the mechanical properties of PLA/WF composites. Among them, the impact strength of EMAGMA-modified composites is higher than that of other compatibilizers which is due to the rich epoxy functional groups reacting with carboxyl or hydroxyl functional groups of PLA and wood flour (the reaction is similar to (route III in Scheme I)). Furthermore, after adding compatibilizer, the bar is not easily broken which indicates that the
processability can be improved even though not very significantly.

**Effect of Co-interfacial Modifiers of Epoxy Silane and EMAGMA**

In order to further improve the properties of PLA/WF biocomposites, EMAGMA was also used as a co-modifier with epoxy silane in the present work. The ratios of silane to WF and EMAGMA contents are fixed (WP and WMA series in Table 1) and the results are shown in Figure 3. From Figure 3a, we can find that the tensile strength of PLA/WF composites with or without EMAGMA exhibits the same trend, but the tensile strength of PLA/WF composites without EMAGMA is more sensitive towards WF content. Tensile strength is higher compared to that of PLA/WF composites with EMAGMA which under 28 phr WF content, it reaches that of PLA. This phenomenon could be attributed to the low tensile strength of EMAGMA (its tensile strength-at-break is 4 MPa). However, the addition of EMAGMA leads to significant improvements in elongation-at-break and impact strength because the epoxy functional groups can improve the distribution and wetting of WF and further lead to high impact resistance with strain energy dissipation mechanism (Figures 3b and 3c).

Further studies reveal that the content of EMAGMA has some effects on the mechanical properties of PLA/WF biocomposites. AX series in Table 1 show the formulations of composites under study. Table 3 presents the mechanical properties versus EMAGMA content for PLA/WF biocomposites. The tensile

![Figure 3. Mechanical properties of PLA/WF biocomposites as a function of WF content. (PLA 100 phr; WF/silane 100/2; EMAGMA zero or 15 phr): (a) tensile strength, (b) elongation-at-break, and (c) impact resistance.](image-url)
strength of the obtained composite is slightly lowered with higher EMAGMA content, while the impact strength and the elongation-at-break values increase with the increased EMAGMA content due to efficient wettability between the plastics and wood flour because of the reaction of epoxy groups in EMAGMA and PLA.

**Morphology and Microstructures**

Mechanical properties of a composite are closely related to its morphology, and the wettability between strong hydrophilic WF (containing many hydroxyl groups) and weakly hydrophilic PLA. The clear boundary between wood flour and PLA matrix at the ratio of 100/30 (PLA/WF) indicates non-wettability of PLA/WF biocomposites prepared without any interfacial modifiers (Figure 4a).

In Figure 4a we can also find that wood flour in the form of wood fibre constitutes the disperse phase and PLA as the continuous phase. This result also

<table>
<thead>
<tr>
<th>Sample</th>
<th>Tensile strength (MPa)</th>
<th>Elongation-at-break (%)</th>
<th>Impact strength (KJ/m²)</th>
</tr>
</thead>
<tbody>
<tr>
<td>AX13</td>
<td>31.3±0.6</td>
<td>6.9±0.4</td>
<td>3.4±0.2</td>
</tr>
<tr>
<td>AX26</td>
<td>27.4±0.6</td>
<td>11.7±0.6</td>
<td>3.8±0.2</td>
</tr>
<tr>
<td>AX52</td>
<td>21.0±0.5</td>
<td>24.4±0.6</td>
<td>4.1±0.2</td>
</tr>
</tbody>
</table>
indicates that there is a poor interaction between the matrix and fibres, which further leads to poor mechanical properties of PLA/WF biocomposites. However, the phase boundaries in the PLA/WF biocomposites become blurred when epoxy silane or EMAGMA is used as an interfacial compatibilizer (Figures 4b and 4c) implying that both epoxy silane and EMAGMA can improve the interface interaction between wood flour and PLA matrix which in turn could improve the mechanical properties of PLA/WF biocomposites.

Moreover, as shown in Figure 4d, wood flour can be embedded within PLA matrix when both epoxy silane and EMAGMA are used as interfacial modifiers, implying that the combination of epoxy silane with EMAGMA may be more effective for improving the wettability and interfacial interaction between wood flour and PLA matrix.

Rhological Properties
In general, the increase in wood flour content in PLA increases the melt viscosity of PLA/WF composites. The influence of wood flour content on complex viscosity is shown in Figure 5a. One can see that complex viscosity ($\eta^*$) increases with increased wood flour content and some differences appear at low frequencies. For example, PLA/WF biocomposites exhibit a Newtonian plateau in the low frequency region and shear thinning at higher frequencies, while the complex viscosity-frequency curve of pure PLA is almost flat and does not show distinct shear thinning property within the entire frequency range. For more exact comparison and data interpretation, eqn (2) is presented as follows:

$$\eta^* = m\gamma^{n-1}$$  \hspace{1cm} (1)

where, $m$ is a constant index, $n$ is the power-law
Figure 5. Plots of (a) complex dynamic viscosity ($\eta^*$), of PLA/WF composites as a function of frequency: (A) pure PLA, (B) WMA20, (C) WMA30, and (D) WMA40 and (b) storage modulus ($G'$) and loss modulus ($G''$).

The exponent, and $\dot{\gamma}$ is the frequency. From Table 4, we can find that the values of $n$ drops with increased wood flour content, meaning that wood flour enhances the shear thinning behaviour due to solid fillers requiring higher shear rate to achieve the critical shear flow [48]. The constant index $m$ considerably increases with increased wood flour content, indicating that the addition of wood flour causes a tremendous increase of melt viscosity.

The storage modulus ($G'$) and loss modulus ($G''$) of the wood flour-filled composites increase greatly with higher wood flour content (Figure 5b). From Figure 5b, one can also deduce that PLA exhibits liquid type viscoelastic behaviour ($G''>G'$) in the whole region. While composites WMA20 and WMA30 have intersecting point; exhibiting liquid type viscoelastic behaviour ($G''>G'$) in large frequency region, and solid type viscoelastic behaviour ($G''<G'$) in small frequency region. Furthermore, $G'$ is higher than $G''$ with the entire frequency region for composite WMA40. These can be attributed to improved interactions between wood flour and matrix at high filler loadings and low frequencies, similar to some sorts of network systems.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Ratios of PLA/WF/epoxy silane/EMAGMA</th>
<th>$m$ (Pa.s)$^n$</th>
<th>$n$</th>
</tr>
</thead>
<tbody>
<tr>
<td>PLA</td>
<td>100/0/0/0</td>
<td>142.4</td>
<td>0.97</td>
</tr>
<tr>
<td>WMA20</td>
<td>100/20/0.4/15</td>
<td>476.7</td>
<td>0.49</td>
</tr>
<tr>
<td>WMA30</td>
<td>100/30/0.6/15</td>
<td>1059.2</td>
<td>0.30</td>
</tr>
<tr>
<td>WMA40</td>
<td>100/40/0.8/15</td>
<td>2068.6</td>
<td>0.27</td>
</tr>
</tbody>
</table>

Table 4. Power-law model parameters at 180°C.

CONCLUSION

PLA/WF biocomposites were prepared using polylactic acid (PLA) as a matrix and wood flour (WF) as filler by a twin-screw extrusion method. The effects of different factors on the properties of PLA/WF biocomposites were investigated in detail. The important results are summarized as follows:

- PLA/WF biocomposites, prepared without any interfacial modifiers, result in poor mechanical properties due to their non-wettability property.
- Silane or EMAGMA can enhance the wettability and interfacial interactions between wood flour and matrix. Moreover, the co-modifiers of epoxy silane and EMAGMA are more effective in PLA/WF biocomposites and notably improve the impact strength and elongation-at-break of PLA/WF biocomposites.

- The increase in WF content leads to a substantial increase in $\eta^*$ value which is favourable for PLA extrusion or blow moulding processes.

ACKNOWLEDGMENTS

This work was financially supported by Shanghai
Leading Academic Discipline Project (No. B202). The authors thank Mr. Yongan Gu for enthusiastic discussion.

SYMBOLS

\( \eta^* \): Complex dynamic viscosity

\( G' \): Storage modulus

\( G'' \): Loss modulus

\( m \): Constant index

\( n \): Power-law exponent

\( \dot{\gamma} \): Frequency

ABBREVIATIONS

<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>PLA</td>
<td>Polylactic acid</td>
</tr>
<tr>
<td>WF</td>
<td>Pine wood flour</td>
</tr>
<tr>
<td>Vinyl silane</td>
<td>Vinyltrimethoxysilane</td>
</tr>
<tr>
<td>Amino silane</td>
<td>( \gamma )-Aminopropyl triethoxysilane</td>
</tr>
<tr>
<td>Epoxy silane</td>
<td>( \gamma )-Glycidoxypropyltrimethoxysilane</td>
</tr>
<tr>
<td>Allyl ester silane</td>
<td>( \gamma )-Methacryloxypropyltrimethoxysilane</td>
</tr>
<tr>
<td>LDPE-g-MAH</td>
<td>Maleic anhydride grafting low density polyethylene copolymer</td>
</tr>
<tr>
<td>POE-g-MAH</td>
<td>Maleic anhydride grafting poly(ethylene 1-octene)</td>
</tr>
<tr>
<td>EMA</td>
<td>Ethylene methyl acrylate copolymer</td>
</tr>
<tr>
<td>EMAGMA</td>
<td>Ethylene-methyl acrylate-glycidyl methacrylat</td>
</tr>
</tbody>
</table>

REFERENCES


38. Qi RR, Qian JL, Zhou CX, Modification of ...


