

Modification of wood flour/PLA composites by reactive extrusion with maleic anhydride

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ABSTRACT: MA modified wood flour/PLA composites were prepared by one-step reactive extrusion, in which wood flour and poly(lactic acid) (PLA) were used as raw material, maleic anhydride (MA) was used as modifier, and dicumyl peroxide (DCP) was used as initiator. The influences of MA concentration on the morphology, thermal stability, rheological, and mechanical properties of the composites were studied. The addition of MA improved the compatibility of the composites significantly. The thermal and rheological results showed that with the increase of the concentration of MA, the thermal stability of the composites decreased, the storage modulus and complex viscosity of the composites also decreased. The MA modified composites had an enhanced mechanical strength compared to the unmodified one. As the concentration of the MA increased, the tensile and flexural strength of the composites first increased and then decreased, and reached a maximum when the concentration of MA was 1 wt %. The MA modified composites showed a better water resistance than the unmodified ones. © 2015 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* **2016**, *133*, 43295.

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INTRODUCTION

Wood-plastic composites (WPCs) usually refer to the composites prepared by wood fiber or natural fiber reinforced thermoplastic plastics, which is a new type of composite materials instead of traditional plastics. In recent years, the mainly applications and developments of WPCs are fibers reinforced polypropylene, polyethylene, and poly(vinyl chloride). With the increase of environmental concerns and shortage of petroleum resources, more efforts have been driven to product biodegradable materials.¹ Poly(lactic acid) (PLA) is one of the most promising materials with biodegradability and good mechanical properties for industrial applications.^{2–6} Due to its high modulus and strength, PLA has been used to produce fibers, film, vehicle interiors, appliance components, food wares, food/beverage packaging, and so forth.⁶ Nonetheless, its major drawbacks, high cost, and brittleness, still remain the main research focus in both academia and industry.⁷

Polymer blending is a practical and economical method for improving the properties of polymers. Blending PLA with some natural polymers, such as cellulose and starch, can reduce the total cost and ensure the degradability of the composites. Bledzki *et al.* reported the high performance of PLA composites reinforced with short man-made cellulose fibers and softwood flour.⁸ The tensile strength and impact strength of the cellulose

reinforced PLA biocomposites had been significantly improved due to the addition of bioadimide (aromatic carbodiimide) according to the research of Awal *et al.*⁹ Silane was used to improve the properties of PLA/wood flour composites reported by Lv *et al.*¹⁰

Wood flour is an abundant, inexpensive, biodegradable and renewable natural material. It has a large number of hydroxyl groups in its structure, and resulting in a strong hydrophilic. However, its hydrophilic leads to poor compatibility with PLA due to the large difference in their hydrophilicity.^{9,11–13} The interfacial bonding of simple wood flour/PLA composites is fairly weak. Interfacial modifiers containing reactive functional groups are able to generate in situ formed blocks or grafted copolymers at the interface to improve the compatibility.² Grafting maleic anhydride (MA) onto the surface of polymer matrix is one of the potential approaches of interfacial modification. MA is an unsaturated monomer which has a higher reaction activity. Free radical grafting MA onto the surface of PLA has gained wide industrial application as used as the chemical coupling agent or compatibilizer for blend systems. PLA-g-MA has been widely used as a compatibilizer in natural polymer/PLA composites such as starch/PLA^{1,14,15} and fiber/PLA^{16,17} due to the MA groups can react with the natural polymers in some ways. Tsou *et al.* studied the influence of PLA-g-MA on

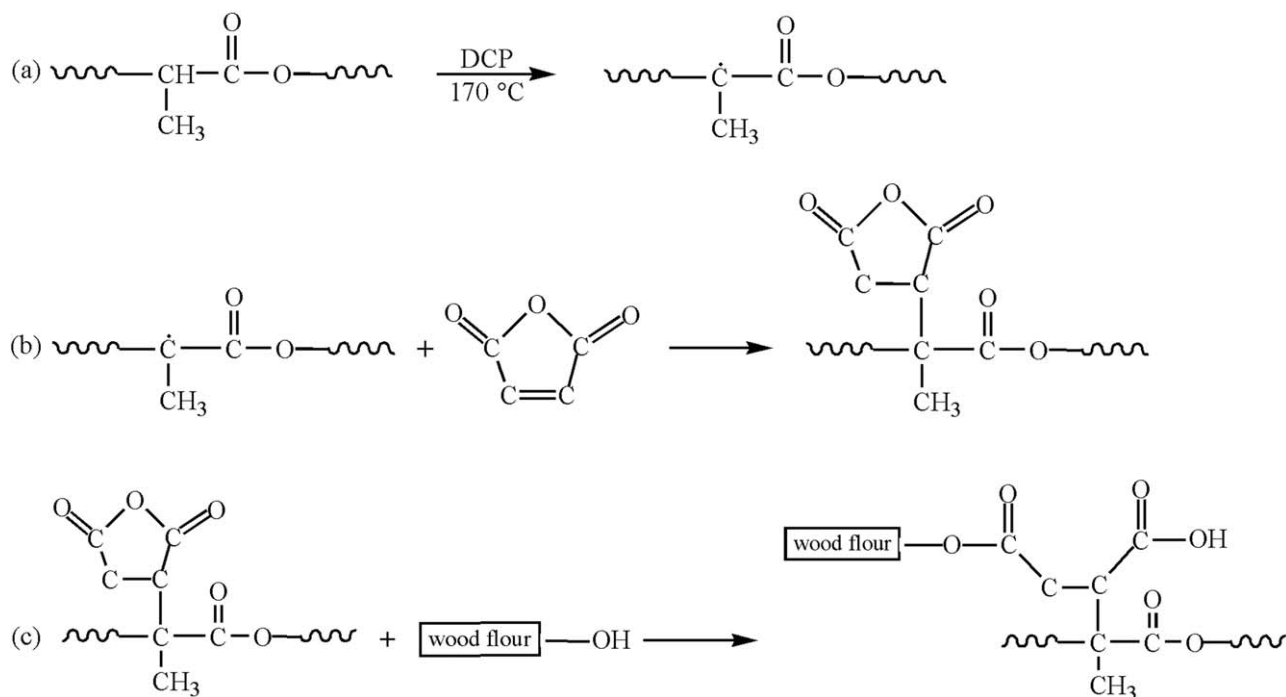


Figure 1. Mechanism of chemical reaction among PLA, wood flour and MA.

the compatibility and mechanical properties of the PLA/WF (wood flour) composites. They reported that the interfacial adhesion had been enhanced after MA was grafted onto the PLA, and the PLA-g-MA/WF had optimum tensile strength than the PLA/WF composites.¹⁸ The results of that the MA grafted unsaturated polyester composites had better mechanical properties and thermal stability were demonstrated by Rahman *et al.*¹⁹

The mechanisms of MA reacting with PLA and wood flour are shown in Figure 1. First, the PLA chains form primary free radicals induced by an initiator of dicumyl peroxide [shown in Figure 1(a)]. Then, the free radicals react with the unsaturated carbon-carbon bond in the MA structure and forming PLA-g-MA [shown in Figure 1(b)]. And the anhydride groups in PLA-g-MA can reactive with the hydroxyl groups of starch to form ester linkages [shown in Figure 1(c)]. At the same time, the carboxylic groups which arising from the hydrolyzed anhydride of MA can form hydrogen bonding with the hydroxyl groups at the surface of wood flour. MA acts as a role of “bridge” between the wood flour and PLA matrix. The interfacial adhesion between PLA and wood flour has a large improvement due to the crosslink between wood flour and PLA caused by reaction with MA.

In this study, the MA modified wood flour/PLA composites were prepared by reactive extrusion, and the concentration of MA varied from 0 to 3 wt %. In order to confirm the effect of MA on the compatibility of wood flour/PLA composites, the morphology of the fracture surface was observed and compared to the unmodified composites. Meanwhile, the thermal stability, rheological properties, mechanical properties, and water resistance of the composites were studied. The ultimate purpose of this work was to optimize a suitable concentration of the MA.

EXPERIMENTAL

Materials

Wood flour with the mesh size of 40–60 mesh used in this study was supplied by Baiquan wood plastic composite material base (Heilongjiang, China). PLA (L-PLA, 306 D), with a weight average molecular weight of approximately 1.0×10^6 – 1.2×10^6 , was purchased from Ningbo Huanqiu Plastic Products (Ningbo, Zhejiang, China). The density of PLA was $1.2 \pm 0.05\text{ g cm}^{-3}$, and the melting index was 16 – $19\text{ g }10\text{min}^{-1}$. The tensile strength of PLA $\geq 45\text{ MPa}$, and the elongation at break $\geq 3.0\%$. The T_g and T_m of PLA was 55 – 60°C and 150 – 160°C , respectively. The PLA was dried at 50°C for 8 h prior to use in the vacuum oven in order to eliminate the moisture. Maleic anhydride (MA) (AR) was provided by Tianjin Guangfu Chemical Reagent (Tianjin, China). Dicumyl peroxide (DCP) was used as the initiator of the grafting reaction between PLA and MA.

Preparation of Wood Flour/PLA Composites

PLA and wood flour were premixed using a high-speed mixer at room temperature for 15 min. Then, DCP and MA were added into the wood flour/PLA system at various MA concentrations, the compositions of various wood flour/PLA composites were shown in Table I. Whereafter, the blend was evenly mixed for another 15 min. The final mixture was pelletized by using a co-rotating twin-screw with a screw-diameter of 21.7 mm and a process length of 40 D (Nanjing Giant SHJ-20). The screw speed of the extruder was set at 100 rpm (the throughput was 2 kg/h). The temperatures of each zone were set at $135^\circ\text{C}/150^\circ\text{C}/170^\circ\text{C}/170^\circ\text{C}/135^\circ\text{C}$ (from the feeder zone to the die). Finally, the granules were fed into a single-screw extruder (The screw-diameter was 20 mm and the process length was 25 D, Harbin special plastic products) with a standard three-section screw. The temperatures of the three sections

Table I. Compositions of Various Wood Flour/PLA Composites

PLA (wt %)	Wood flour (wt %)	Relative to the weight of PLA	
		DCP (wt %)	MA (wt %)
70	30	0.4	0
70	30	0.4	1
70	30	0.4	2
70	30	0.4	3

were set at 150°C/170°C/170°C and the die temperature was 120°C. After the single-screw extrusion, the strip specimen was cut into dumbbell-shaped (Scheme 1) samples to test the mechanical properties. The composites were placed for one week before determining all the properties.

Characterization

Scanning Electron Microscopy. The morphologies of wood flour/PLA composites were characterized with a scanning electron microscope (SEM) (QUANTA 200; FEI). The SEM was operated at an acceleration voltage of 10 kV. The samples were cooled in liquid nitrogen to have a brittle failure and got a flat fracture surface. Then, the fracture surfaces were sputter-coated with gold prior to SEM observation.

X-ray Diffraction. The X-ray diffraction (XRD) data were determined by using a X-ray diffraction equipment (Rigaku D/max220, Japan). The generator was set up at 32 kV and 30 mA, using Cu-K α radiation ($\lambda = 0.1542$ nm) as the X-ray source, together with a Ni-filter to extract the K α radiation. The data were collected over a range of scattering angles (2θ) of 5°–40°. All the measurements were carried out at room temperature under atmospheric pressure.

Thermo Gravimetric Analysis. Thermo gravimetric analysis (TGA) was carried out to determine the thermal stability of the wood flour/PLA composites. TGA data were obtained on the TG 209 F3 (NETZSCH) from room temperature to 600°C with 10°C/min of heating rate and 50 mL/min of argon gas flow.

Rheological Properties. The rheological properties of the wood flour/PLA composites were analyzed on a rheometer AR2000ex (TA Instrument) using a parallel plate geometry with small amplitude. The parallel plate diameter was 25 mm and the plate spacing was 2 mm. The storage modulus (G') and complex viscosity (η^*) of the composites were obtained from the dynamic frequency sweep. In order to make sure the measurements were



Scheme 1. Profile of the wood flour/PLA composites. (a) without MA; (b) with MA. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

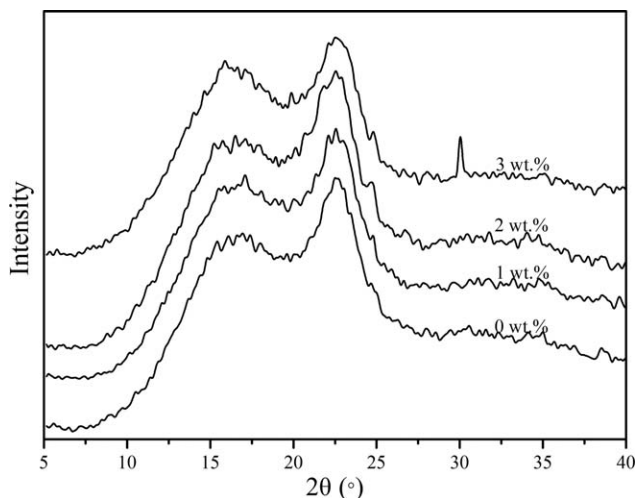


Figure 2. XRD diffraction pattern of the wood flour/PLA composites with different concentrations of MA.

performed in the range of linear viscoelasticity, the strain was kept at 0.1%. All the samples were characterized in the frequency scanning range from 0.1 rad/s to 628.3 rad/s at 190°C. All of the experiments were performed under a nitrogen atmosphere, in order to prevent thermo-oxidative degradation.

Mechanical Properties. The mechanical properties of the composites were tested on a CMT-5504 Universal Testing Machine (Shenzhen SANS Test Machine, China). The tensile strength and elongation at break of the composites were tested according to the ASTM D638-10 method at a crosshead speed of 20 mm/min. The flexural strength was measured according to the ASTM D790-10 at a crosshead speed of 2 mm/min. The specimen geometry was 100 × 10 × 3 mm³ (length × width × thickness). At least five replicates were tested for each sample to obtain an average value.

Water Absorption. The water absorption of the composites was evaluated according to the ASTM D570-98 (Reapproved 2005). The specimens were vacuum dried at 50°C for 24 h, then cooled in desiccators and weighed (W_1) quickly. The dried specimens were soaked in distilled water at room temperature for 24 h. Then, the specimens were removed from the distilled water and placed on a dry filter paper to blot the excess water on the specimen surfaces, and then immediately weighed the wet weight (W_2). The water absorption of the composites was calculated as eq. (1):

$$\text{Water absorption} = \frac{W_2 - W_1}{W_1} \times 100\% \quad (1)$$

At least five specimens were tested to obtain an average value.

RESULTS AND DISCUSSION

XRD Analysis

Figure 2 depicts the influence of MA concentration on XRD diffraction pattern of the composites. The crystallinity of the composites obtained from the XRD data is shown in Table II. As can be seen in Table II, the crystallinity of the composites decreased with the increase of MA concentration. When the MA was added into the composites, the PLA molecular chains and

Table II. The Crystallinity of the Composites with Different MA Concentration

MA concentration (wt %)	0	1	2	3
X_c	33.7%	26.1%	24.7%	17.4%

wood flour were bounded by the MA monomer through the chemical reaction, and a crosslinked network-like structure was formed. Therefore, the mobility of the molecular chains was slowed down by the crosslinked structure, resulting in a decrease of the crystallinity.

Morphology Characterization

The morphologies of the wood flour/PLA composites with different MA concentrations are shown in Figure 3. As shown in Figure 3(a), without the addition of MA, the interstices between wood flour and PLA matrix were clearly observed and the wood flour was unevenly distributed, indicating phase separation has occurred between the wood flour and PLA. Without the addition of MA, the surface of the composites was coarse and most of the wood flour was kept detached from the PLA matrix, implying the weak interfacial adhesion and poor compatibility between wood flour and PLA matrix. The poor compatibility of the composites without MA would be confirmed by the poor mechanical properties in the follows. By contrast, with the

presence of MA [Figure 3(b–d)], the wood flour was enveloped by the PLA matrix and the interface between the two phases was closely connected. Moreover, the concentration of MA exhibited influences on the morphology and phase structure of the composites. With the presence of 1 wt % MA [Figure 3(b)], the interstices between wood flour and PLA became blurry and the wood flour distributed evenly in the matrix, the phase separation phenomenon was not so obvious compared with that of the composites without MA, indicating the compatibility of the composites was improved. With the further increase of MA concentration [Figure 3(c,d)], the surface of the composites became smooth gradually. The unsaturated carbon-carbon bonds in the structure of MA were likely to graft onto the surface of PLA, while the anhydride groups were likely to reactive with the hydroxyl groups of wood flour, resulting in the reduce of the dispersion size and the enhancement of the interfacial adhesion.²⁰ Therefore, the MA played a key role in the improvement of compatibility between wood flour and PLA.

Thermal Stability of Wood Flour/PLA Composites

Figure 4 shows the typical temperature-dependent weight loss (TGA) curves of the raw materials and wood flour/PLA composites, and the temperatures of thermal degradation of composites are shown in Table III. In Figure 4(b), as the concentrations of MA in the composites increased, the onset temperature for decomposition of the composites decreased gradually (The temperature can be seen in Table III). This can

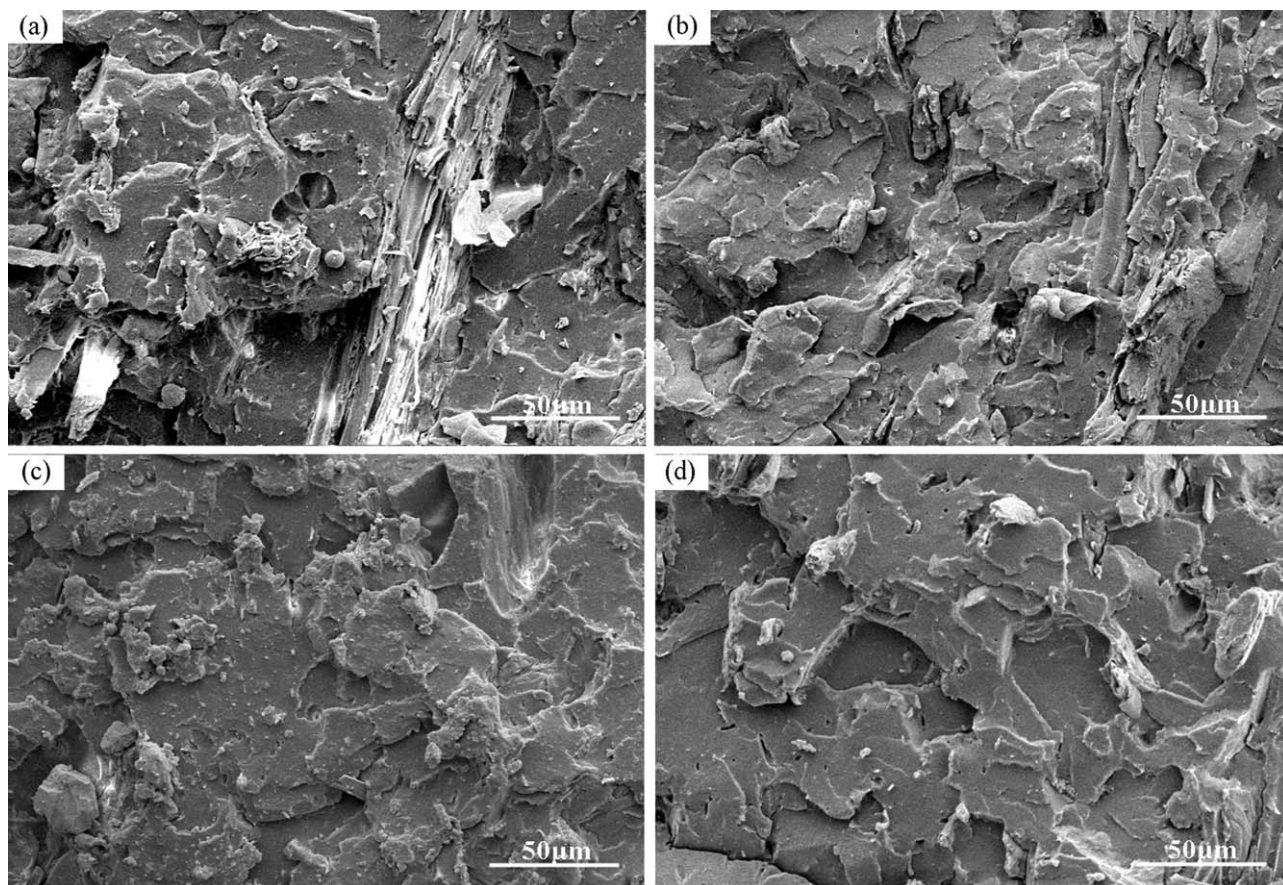


Figure 3. SEM images of wood/PLA composites with different concentrations of MA. (a) 0 wt %; (b) 1 wt %; (c) 2 wt %; (d) 3 wt %.

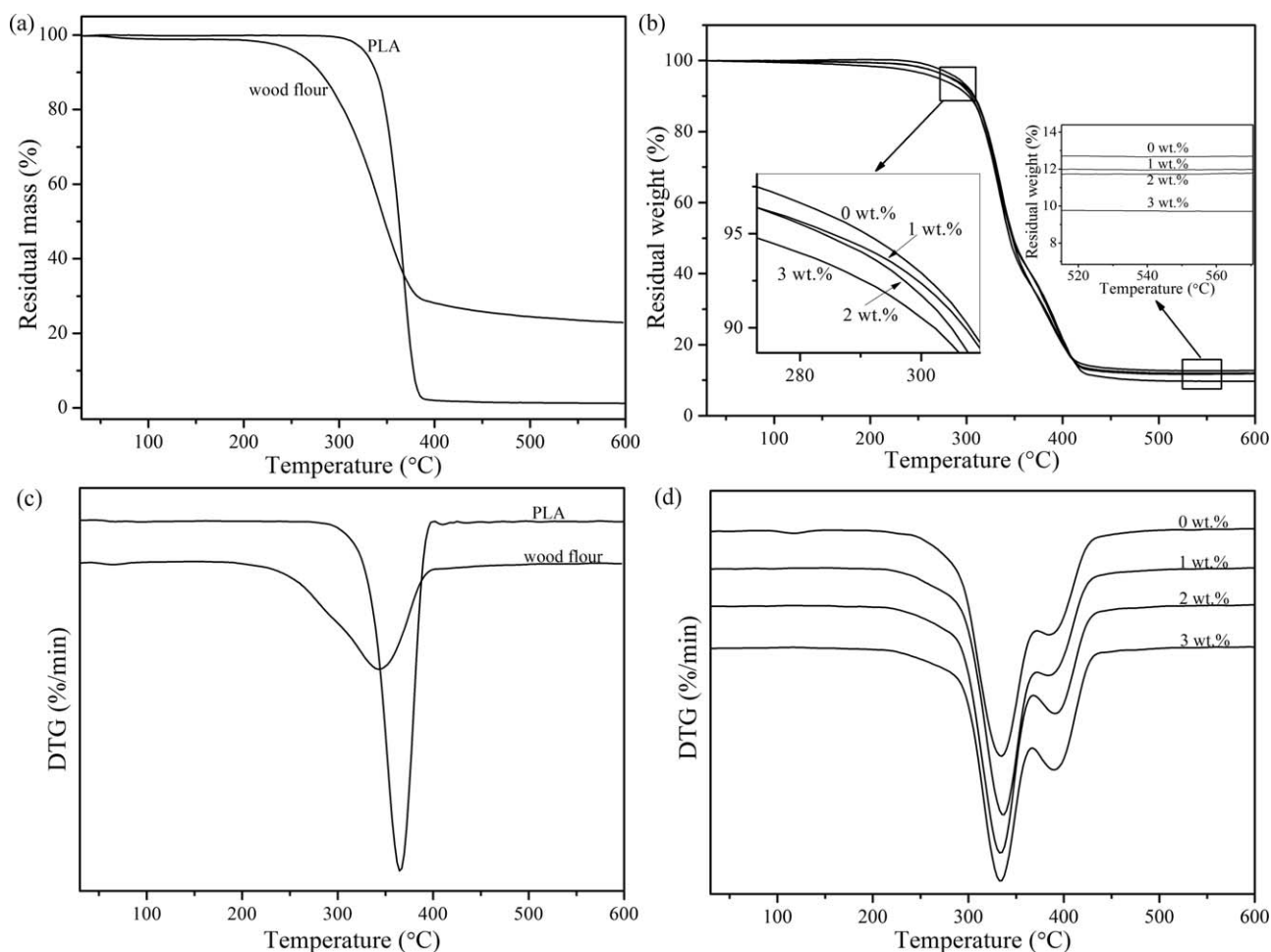


Figure 4. TGA and DTG curves of the materials. (a) TGA curves of PLA and wood flour; (b) TGA curves of wood flour/PLA composites with different concentrations of MA; (c) DTG curves of PLA and wood flour; (d) DTG curves of wood flour/PLA composites with different concentrations of MA.

be attributed to the decrease of the crystallinity of the composites with higher MA concentration. As a result, the thermal stability of the composites has a decline with the increase of the concentration of the MA. The onset temperature of the composites with 3 wt % MA was 277.4°C, while the onset temperature of other modified composites were 290.1 and 287.6°C, respectively. The decrease of the onset temperature of the composites modified by 3 wt % MA was larger than other modified composites (The decrease was 10–12°C compared to other composites modified by 1 and 2 wt % MA). The possible reason for this phenomenon was that more MA in the reactive extrusion system may cause more degradation of the PLA molecular. In addition, the DCP used during grafting of MA, may also cause some degradation of PLA.

The process of the decomposition depended on the structure of the composites, that is, the interaction between the two components in the composites. The interaction between the two phases was influenced by the compatibility of the composites, resulting in the complex degradation process of the composites. As can be seen from Figure 4(c,d), both of the PLA and wood flour exhibited a single degradation process, while the wood flour/PLA composites exhibited a two-step degradation process. This also demonstrated the typical immiscibility of the

composites, which was in accord with the discussion of morphology. As can be seen in Table III, the MA concentration had less influence on the lower peak temperature (T_{p1}) of the maximum decomposition of the composites, while the higher peak temperature (T_{p2}) shifted to the higher temperature when the MA concentration was increased. In Figure 4(a), the residue of wood flour was much higher than that of PLA, while PLA was almost complete decomposition (the residual was about 1.2%). When blending the wood flour and PLA together into the composites, the residue of the materials was intermediate to the PLA and wood flour, which exhibited a residual around 9~13% [shown in Figure 4(b)]. With the increase of the concentration

Table III. Thermal Degradation Temperatures of the Raw and Composites

	T_{on} (°C)	T_{p1} (°C)	T_{p2} (°C)
PLA	345.1	364.6	—
WF	290.8	344.7	—
0 wt %	292.5	335.1	384.9
1 wt %	290.1	337.7	384.6
2 wt %	287.6	334.5	388.9
3 wt %	277.4	334.0	391.2

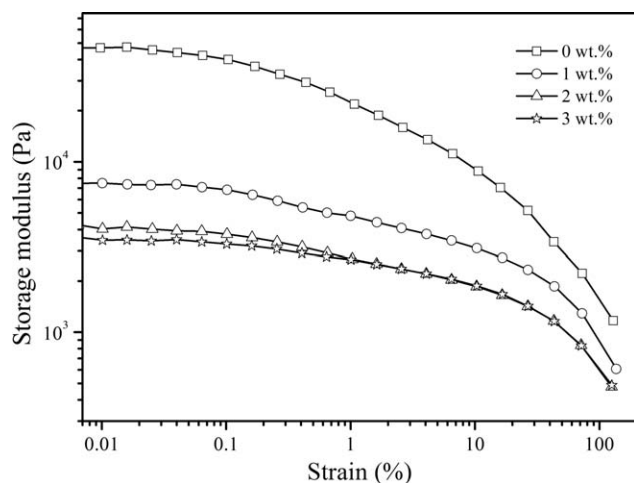


Figure 5. The relationship between the storage modulus and strain of the composites with different MA concentration.

of MA, the residue of the composites reduced, indicating that the introduction of MA has assisted the decomposition of the composites.

Rheological Properties of Wood Flour/PLA Composites

The linear dynamic rheological properties of polymers are very sensitive to the changes in the macromolecular chain structure.²¹ There is a critical strain exist for the viscoelastic of the composites. When the strain is less than the critical value, the materials exhibit a linear viscoelastic behavior; when the strain exceeds the critical value, the storage modulus of the materials decrease abruptly, the materials show a nonlinear viscoelastic behavior. The transformation of the storage modulus during this process reflects the structure changes of the composites melt, which is corresponding to the disentanglement of the molecular chains at the higher strain.²² In order to study the rheological properties in the range of linear viscoelastic region, the strain sweep test of the composites was carried out first. The relationship between the storage modulus and strain is shown in Figure 5. As can be seen in Figure 5, all of the

composites exhibited a linear viscoelastic behavior when the strain was lower than 0.1%. When the strain was higher than 0.1%, it showed an obvious decrease in the storage modulus of the composites. Therefore, the strain in the process of frequency sweep for the composites with different MA concentrations was kept at 0.1%. The storage modulus (G'), loss modulus (G''), and complex viscosity (η^*) as a function of frequency for the composites are shown in Figure 6.

The G' of the materials can be enhanced by the deformation of the dispersed phase in the composites. As shown in Figure 6, with the increase of the concentration of MA, the G' of the composites decreased, which was attributed to the changes of the relaxation process. With the addition of MA, the interaction between wood flour and PLA was enhanced, and a network-like structure was formed. Therefore, the molecular chains couldn't slide from each other easily in the melting state, and the deformation of the wood flour was weakened. As a result, the G' of the composites decreased with the increase of the concentration of MA. In the short-time relaxation region (high frequency region), the difference of the structure could not be reflected completely. Therefore, the difference of G' of the composites wasn't obvious at high frequency region, while the G' of the modified composites had a clear separation compared to the unmodified composites in the low frequency region (long-time region).

As can be seen from Figure 6(a), at low frequency region, the G' of the melts was lower than the G'' of the melts for the composites, indicating a viscous response in the molten state. This can be attributed to the fact that there was sufficient time for the polymer chains to have an enough relaxation rather than an elastic deformation.²³ At a higher frequency, there was an intersection point of G' and G'' for the composites appeared, indicating a transition from viscous to elastic behavior.²⁴ Beyond the intersection point, G' became higher than the G'' of the materials, implying an elastic behavior of the melts. This behavior was due to the polymer chains had no sufficient time to relax. With the increase of the concentration of MA, the intersection point shifted towards higher frequency slightly,

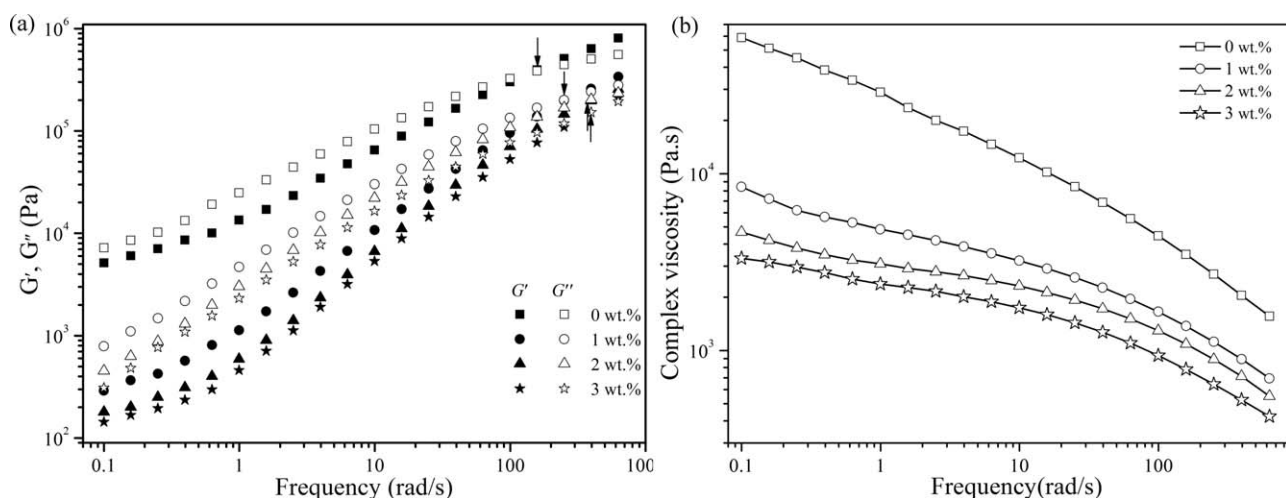


Figure 6. Rheological properties of the wood flour/PLA composites with different concentrations of MA: (a) storage modulus (G') and loss modulus (G'') vs frequency; (b) complex viscosity (η^*) vs frequency.

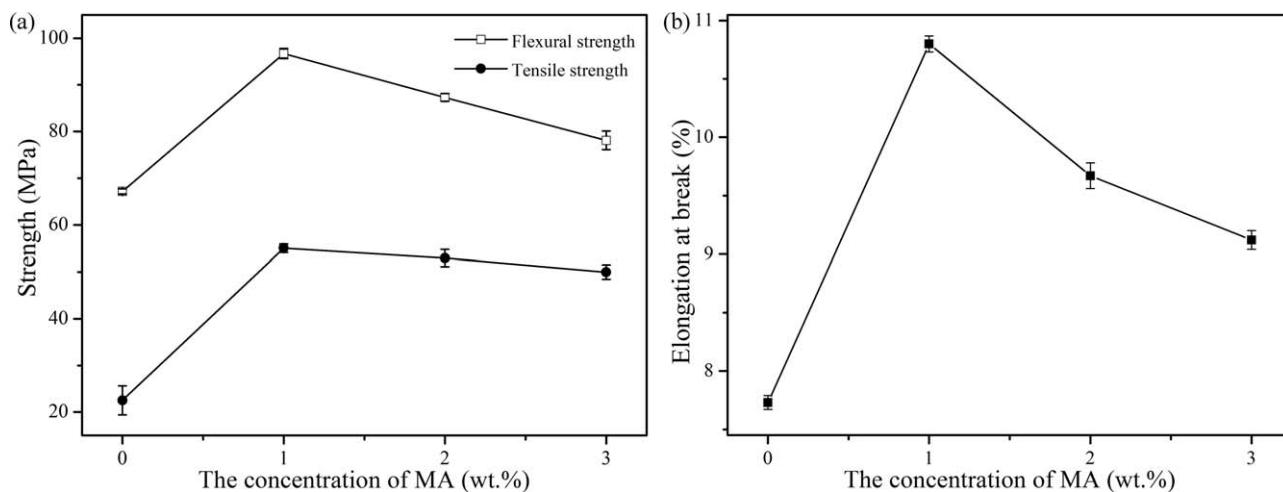


Figure 7. Mechanical properties of wood flour/PLA composites with different concentrations of MA (a) strength; (b) elongation at break.

indicating a hysteresis of the transition from viscous to elastic behavior. At low frequency region, the composites exhibited a plateau-like behavior, in other words, the frequency dependence of the G' was decreasing [Figure 6(a)].

It can be observed that the η^* of the composites decreased with the increase of frequency, exhibiting a shear thinning behavior [Figure 6(b)], which was a typical characteristic of the branched or entangled polymer melts.²¹ This could be explained that there was sufficient time to allow the disentanglements of the polymer chains to rebuild at low frequency, while there was not enough time for the polymer chains to reform original distribution of the wood flour particles when the frequency increased.²⁵ In addition, the η^* of the MA modified composites decreased greatly compared to the unmodified composites. The possible reason for this phenomenon was that the matrix molecular weight was decreased during grafting procedure,²⁶ and the phenomenon was also confirmed by TGA results.

Mechanical Properties of Wood Flour/PLA Composites

The mechanical properties of the wood flour/PLA composites with different concentration of MA were shown in Figure 7. As can be seen in Figure 7(a), the tensile strength and flexural strength of the MA modified composites were enhanced effectively, and reached to a maximum at 1 wt % of the MA concentration. Compared with the unmodified composites, the modified composites with 1 wt % MA exhibited ~144% increase in tensile strength and ~44% increase in flexural strength. The anhydride groups were likely to reactive with PLA and the hydroxyl groups in wood flour, therefore greatly enhanced the interfacial adhesion which played a key role in improving the compatibility. The enhanced interfacial adhesion made the molecular chains not easily slide from each other, leading to an increase in the tensile and flexural strength. Meanwhile, it was difficult to wreck the network structure which was formed during the reactive extrusion. This also contributed to the increase in the tensile and flexural strength. In addition, the inflexibility of the composites was improved by the network structure, resulting in the increase in the flexural strength of the composites. Nevertheless, the increasing trend of tensile strength

and flexural strength leveled off when the MA concentration was above 1 wt %. A similar trend to jute/PLA composites was observed via extrusion reactive.²⁷ With the increase of MA concentration, the excess MA monomer stayed at the interface between wood flour and PLA, made the molecular chains easier to slide from each other, which induced the decrease of the tensile strength and flexural strength.²⁶ It is well known that, in reactive blending, only a certain concentration graft copolymer is required to saturate the interface and produce optimum compatibilization.² As the reference reported the size of the dispersed phase showed an initial significant drop with the addition of the copolymer followed by an equilibrium value at a high concentration of the copolymer.²⁸ Therefore, excess MA couldn't exhibit significant effect on the mechanical properties. The excess MA stated at the interface of the composites, leading to an increase of the distance between the molecular chains and the grafting effect of MA on unit area was decreased, which caused a decrease in the tensile and flexural strengths. In addition, more MA concentration may cause more side reaction and

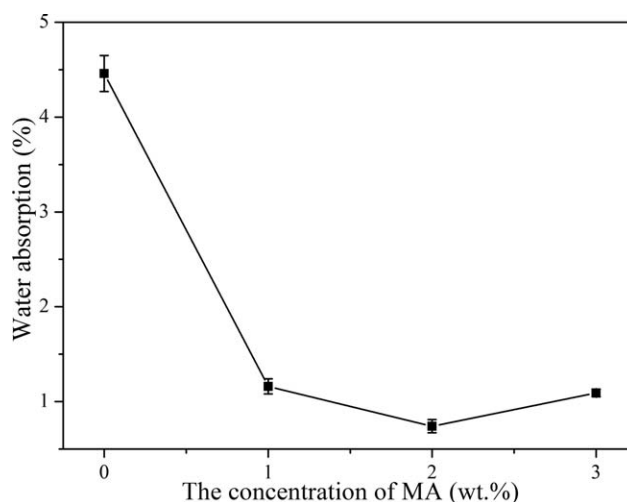


Figure 8. Water absorption of wood flour/PLA composites with different concentrations of MA.

degradation during the processing, which would also cause deterioration of the mechanical properties.

The elongation at break of the wood flour/PLA composites as a function of the concentration of MA was shown in Figure 7(b). The elongation at break showed a maximum value at the MA concentration of 1 wt % followed by a significant drop when the MA concentration was above 1 wt %. The unmodified composites had an elongation at break of 7.7%, while the MA modified composites all showed a higher elongation at break than that of unmodified composites. The addition of MA enhanced the interfacial adhesion, and improved the compatibility between wood flour and PLA, resulting in an enhancement of the molecular interaction. Therefore, the composites need more energy to fracture when the load was applied. In addition, the elongation at break exhibited an obvious dependence on the MA concentration. It showed a similar trend to the flexural strength which was first increased and then decreased. However, the decrease rate of the elongation at break slowed down [as shown in Figure 7(b)]. The possible reason was that the unreacted MA groups in the system during the twin-screw reactive extrusion would react later during the further thermo-mechanical processing, which may increase the crosslinking between wood flour and PLA matrix. As a result, the decrease rate of the elongation at break was slowed down when the MA concentration was further increased.

Water Absorption of the Wood Flour/PLA Composites

The water absorption of the composites with different concentrations of MA was shown in Figure 8. The water resistance of the composites modified by MA was improved obviously compared to the unmodified one. The water absorption of the unmodified composites was 4.5%, while the modified composites showed its water absorption around 1%, which was 1/4 to the water absorption of the unmodified composites. In the composites, the PLA matrix was hydrophobic, while the wood flour was hydrophilic. Therefore the water absorption of the composites was determined by the wood flour. Due to the immiscibility of the unmodified composites, the water molecules could get into the composites easily, leading to the higher water absorption. When the composites were modified by MA, the compatibility was improved and the interfacial adhesion between wood flour and PLA was enhanced, resulting that the diffusion of the water molecular into the composites was restricted. In addition, lower water absorption values could be also related with some crosslinking reaction between MA, PLA, and WF.

CONCLUSIONS

Reactive melt blends of wood flour/PLA and MA was prepared by two-screw extrusion, and the influences of MA concentrations on their morphological, rheological and mechanical properties were investigated. The compatibility of the composites was improved significant after the addition of MA due to the efficient grafting and crosslink between MA, wood flour and PLA. When the MA concentration was 1 wt %, the mechanical strength reached a maximum value, and the maximum had an increase of ~144 and ~44% in the tensile strength and flexural

strength compared to the unmodified composites, respectively. As the concentration of MA increased, the G' of the composites decreased, which was attributed to the changes of the relaxation process. The point of the transition from viscous to elastic behavior shifted to a higher frequency when the MA concentration increased, indicating a hysteresis of the transition from viscous to elastic behavior. The η^* of the MA modified composites decreased greatly compared to the unmodified composites due to the decrease of the molecular weight of the matrix during the reactive extrusion process. The addition of MA also improved the water resistance of the composites.

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