

DEGRADATION OF WOOD FLOUR/POLY (LACTIC ACID) COMPOSITES REINFORCED BY COUPLING AGENTS AND ORGANO-MONTMORILLONITE IN A COMPOST TEST

Ru Liu

Graduate Student
E-mail: 408518486@qq.com

*Jinzhao Cao**†

Professor
E-mail: caoj@bjfu.edu.cn

Liang Ou-Yang

Graduate Student
Faculty of Material Science & Technology
Beijing Forestry University
Qinghua East Road 35
Haidian
Beijing, China 100083
E-mail: 853668656@qq.com

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Abstract. To investigate the degradation properties of wood flour (WF)/poly (lactic acid) (PLA) composites modified with organo-montmorillonite (OMMT) and two types of coupling agents, namely, maleic anhydride grafted polypropylene (MAPP) and silane (γ -methacryloxypropyltrimethoxysilane, KH-570), pure PLA, OMMT/PLA, and WF/PLA composites were prepared with the hot-press molding method and tested in a compost test for 6 mo. After compost tests, samples were also characterized with scanning electron microscopy, Fourier transform infrared spectrum, and differential scanning calorimeter for further understanding. The results showed that 1) introducing WF and OMMT accelerated the degradability of PLA (after 5 mo, all composites were completely degraded, whereas the pure PLA control still had 4.78% residue); 2) the two types of coupling agents had opposite effects on degradation of WF/PLA composites (MAPP delayed the degradation process, whereas silane accelerated it); 3) silane and OMMT had a synergic effect on degradability, which was supported by the complete degradation of WF/PLA composites modified with both silane and OMMT in 4 mo; 4) after a 3-mo compost, many cracks or voids occurred on the surface of PLA, and this compost test also resulted in separated WF. T_m values of PLA and OMMT/PLA decreased and their crystallinity degrees increased, suggesting faster degradation of PLA with WF and OMMT loading.

Keywords: Wood flour/poly (lactic acid) composite, degradation, coupling agent, organo-montmorillonite.

INTRODUCTION

Because of increasing environmental concerns and restricted availability of petrochemical resources, biopolymers have been attracting more and more interest in public research in recent decades. One biopolymer, poly (lactic acid) (PLA), is produced by its monomers and

lactic acids, which are obtained from the fermentation of sugar feed stock (Martin and Averous 2001). Synthesis of PLA from lactic acid is followed by a ring-opening polymerization of the cyclic lactide dimmer. PLA is a “green polymer” because it can be finally degraded into CO_2 and H_2O . Therefore, it is a good material to produce objects such as plastic bags, food packaging, disposable cutlery and cups, slow-release membranes for drug delivery, and a liquid barrier layer in disposable diapers

* Corresponding author

† SWST member

(Petinakis et al 2009). Hydrolytic degradation of PLA is produced by random cleavage of the ester bond, mainly involving four main phenomena: absorption of water, cleavage of ester bond, formation of oligomer fragments, and solubilization of oligomer fragments (Liu et al 2001). The rate largely depends on several factors, such as polymer crystallinity and purity, copolymer type (composition and initial molecular weight), sample size, pH and temperature of the degradation medium, processing and sterilization methods as well as the presence of additives (Mobedi et al 2006). Some researchers found that not only the cleavage of the ester bond, but also the end hydroxyl group played a crucial role in hydrolytic degradation (Shih 1995; de Jong et al 2001). Also, PLA hydrolysis can be catalyzed by some microbes and enzymes, such as *Rhizopus delemere* lipase, *hog pancreatic* lipase, and carboxylic esterase (Fukuzaki et al 1989) and highly accelerated by proteinase K (Reeve et al 1993).

However, because of its complicated process of production, PLA is more costly than other polymers such as polyethylene, polypropylene (PP), poly (vinyl chloride) (PVC), and polystyrene. Furthermore, its brightness, low deformation-at-break, and limited processing approaches also restricts its widespread applicability (Huda et al 2006). Numerous studies have focused on improving its properties, decreasing its price, as well as enhancing its degradability by blending it with natural materials such as starch (Gattin et al 2002; Petinakis et al 2010), plant fibers (Lee and Wang 2006; Takatani et al 2008), synthetic monomers and polymers such as polyethylene glycol (Kulinski and Piorkowska 2009), glycerol (Martin and Averous 2001), maleic anhydride (MA) (Niu et al 2005), lactide (Mobedi et al 2006, 2011), and many kinds of inorganic fillers (Kolstad 1996; Ray et al 2003; Navarro et al 2005; Lewitus et al 2006; Fortunati et al 2012).

Wood flour (WF) usually made by conventional grinding is gaining increasing acceptance as a filler for polymers because it offers many advantages such as low density, high stiffness, biode-

gradability, easy availability, renewability, and relatively low cost. Various types of WF/polymer composites have been widely studied and commercialized. Many investigations have confirmed that adding WF enhances some physical, mechanical, and thermal properties, such as rigidity, stiffness, strength, hardness, and heat resistance (Matuana et al 1998; Marcovich and Villar 2003; Dikobe and Luyt 2010). However, introducing a large amount of polar WF into nonpolar polymer matrix including PLA may cause a decrease in composite physical and mechanical properties caused by weak interfacial adhesion and lack of fiber dispersion because of fiber agglomeration (George et al 2001). Various surface modification techniques on WF have been applied to improve the interaction that occurs at the interface between the polymer matrix and the fibers, including esterification (Mohanty et al 2001), acetylation (Abdul Khalil and Ismail 2000), and cyanoethylation (Sain et al 2005). Using coupling agents or compatibilizers is a more widely accepted method, especially in industrial applications. There are numerous studies focusing on improving the interfacial adhesion by coupling agents such as silane, titanate, aluminate, isocyanate, and polar monomer-grafted polyolefin (Schneider 1994; Oksman 1996; Wang et al 2011), among which maleic anhydride grafted polypropylene (MAPP) and silane are often used types. Concerning the effect of WF on degradation of PLA, Petinakis et al (2009, 2010) reported that WF caused faster degradation of PLA because of increasing water uptake. This is reasonable because natural WF is porous and hydrophilic and vulnerable to decay fungi or bacteria in compost. Meanwhile, the weak interface between WF and PLA could have created a new passage for water penetration and fungi or bacteria growth, which led to the gradual degradation of PLA (Petinakis et al 2010). Also, degradation of WF could generate organic acids that decrease the pH value of the microenvironments, accelerating PLA hydrolysis (Liu et al 2005).

Montmorillonite (MMT), which is the most widely used type of clay, as another kind of filler reinforcement has attracted a great deal of

interest both in wood products and polymers. It is a layered silicate with a mean layer thickness of 0.96 nm. The simple chemical components of MMT were $\text{Al}_2\text{O}_3 \cdot 4\text{SiO}_2 \cdot 3\text{H}_2\text{O}$ with two layers of tetrahedron of Si-O and one layer of octahedron of Al-O in between. There are three types of structures when the layered silicate is introduced into wood or polymer matrix: 1) a phase-separated structure; 2) an intercalated structure; and 3) an exfoliated or delaminated structure (LeBaron et al 1999). An exfoliated structure is always expected to form a true nanocomposite. Zhao and Lv (2003) proposed a possible way to prepare wood/MMT composites by introducing MMT into the nanoscale wood cavities. Then, they successfully prepared MMT/wood composites using phenol-formaldehyde resin as the intermediate. They found that some exfoliated clay entered the amorphous region of the wood cell wall and the strength of wood after treatment increased (Lv et al 2006). Wang et al (2010) used organo-montmorillonite (OMMT) modified by didecyl dimethyl ammonium chloride to treat wood and found that compared with untreated control, the compression strength of treated wood increased up to 27% and decay resistance of the composite also improved. Jiang et al (2011) studied the micronized clay suspension by combining OMMT with polyvinyl alcohol to treat wood, and the results showed that water sorption, dimension stability, and surface hardness of treated wood were greatly improved. As for polymers, MMT also played a significant role in property enhancements even at contents lower than 10 wt% by acting as a nucleating agent, increasing crystallinity and strength (Bala and Samantaray 2001; Cheng et al 2003; Thellen et al 2005). In recent years, MMT has been used in wood-polymer composites, such as WF/HDPE (Zhong et al 2007), WF/PVC (Matuana 2009), WF/PP (Hemmasi et al 2010), and WF/PLA (Meng et al 2010). The effect of MMT on degradation of PLA has been studied in some investigations. Ray et al (2003) found that degradation of PLA modified by OMMT was accelerated, and they proposed that the presence of terminal hydroxylated edge groups of the silicate layers in OMMT could be

a responsible factor for the degradation behavior. The intercalated silicate layers were homogeneously dispersed into PLA matrix, and these hydroxyl groups started heterogeneous hydrolysis of the PLA matrix after absorbing water from compost. Fukusima et al (2009) also found that OMMT could influence bacterial degradation of PLA depending on the chemical structure and affinity of the bacterium for OMMT.

As previously mentioned, many investigations have been performed on WF/PLA composites modified with either coupling agents or OMMT. However, the focus of these studies was usually reinforcement of physical, mechanical, or thermal properties. Until now, degradation of WF/PLA composites after reinforcement with a coupling agent or OMMT, especially the comparison of degradation effects caused by two types of coupling agents, has not been studied. Therefore, this study proposed to use WF modified with a coupling agent, OMMT, or both to prepare a cost-effective, high-performance, and easily degradable WF/PLA composite, which could be used to make some short-term products indoor use, for example, disposable cutlery. Flexural properties of the composites were tested to ensure the reinforcement effect of the modifications, and a 6-mo compost test was used to evaluate degradation of the composites by comparing weight loss percentages and morphology of the composite residues. Scanning electron microscope (SEM), Fourier transform infrared spectrum (FTIR), and differential scanning calorimeter (DSC) analyses were also performed for further explanation.

MATERIALS AND METHODS

Materials

PLA (AI-1001) (L content) was obtained from Esun, Shenzhen BrightChina Industrial Co., Ltd. (Shenzhen, China). It had a density of about 1.25 g/cm^3 and a melt flow index about 10-20 g/10 min at 190°C . The M_n of PLA was about 80,000. WF of poplar (*Populus tomentosa* Carr.) of a size that passed a 100-mesh sieve was supplied by Xingda Wood Flour Company (Hebei, China). OMMT from modifying natural MMT

with a quaternary ammonium salt was purchased from Zhejiang Hongfeng Clay Chemical Co., Ltd. (Huzhou, Zhejiang, China). The mean interlayer distance of OMMT was 2.217 nm with an average particle size of 76 μm . The coupling agents used in this study included MAPP and silane (γ -methacryloxypropyltrimethoxysilane, $\text{CH}_2 = \text{C}[\text{CH}_3]\text{COOCH}_2\text{CH}_2\text{CH}_2\text{Si}[\text{OCH}_3]_3$) with a density of 1.04 g/cm^3 , which is designated as KH-570 by the Chinese Academy of Science. Polyfluoro-tetraethylene membranes were used in this study as demolding materials to avoid a sticking board during hot-pressing.

Preparation of Samples

Prior to use, WF was dried in an oven at 105°C for 5 h to 1-2% MC. The size of WF/PLA composites with target density of 1.28 g/cm^3 was 270 \times 270 \times 3 mm. Then, PLA, WF, 2 per hundred compounds (phc) of OMMT, and also 2 phc of the two types of coupling agents were weighed and mixed according to formulations given in Table 1 in a high-speed blender at about 2900 rpm for 4 min. For silane-modified groups, silane was first hydrolyzed into silanol solution (pH = 3.6 at 24°C) by deionized water at concentration of 2% and then evenly sprayed on the dried WF. The modified WF was dried in an oven at 105°C to 1-2% MC and mixed with PLA and OMMT in the same process. The mixture was then dried at 105°C for 2 h. After drying, the mixture was extruded via a corotating twin-screw extruder (KESUN KS-20; Kunshan, Jiangsu, China) with a screw diameter of 20 mm

and a length-to-diameter ratio of 36/1. The corresponding temperature profile along the extruder barrel was 150/160/180/180/150°C, and the screw speed was 180 rpm. The extruded rods were cut into small particles about 5 mm, and then the blends were dried again at 105°C for 2 h and taken out for hand matting. A hot-press (SYSMEN-II, made by Chinese Academy of Forestry) was used to produce the composites by compressing the mat at 180°C with a pressure of 4 MPa for 6 min. Prior to demolding, the formed mat was cooled down at 4 MPa for another 6 min at room temperature. The same method was used to prepare the pure PLA, OMMT/PLA, and WF/PLA controls. After that, all mats were cut into required dimensions for further tests.

Mechanical Test

Flexural tests were carried out according to the Chinese standard GB/T 9341-2000 (Standardization Administration of the People's Republic of China 2000), which involves a three-point bending test at a crosshead rate of 1 mm/min. Samples were 60 \times 25 \times 3 mm (thickness). Four replicates were tested in each group.

Compost Test

Degradation of pure PLA, OMMT/PLA, and WF/PLA composites was tested by a compost test performed according to the International Organization for Standardization (2004). Mature compost samples (aged approximately 2-4 mo) were collected from garden fertilizer. The compost

Table 1. Compositions and labeling of studied formulations.

Labels	PLA (wt%)	WF(wt%)	OMMT loading (phc)	Loadings of coupling agent (phc)	
				MAPP	Silane
PLA	100	0	0	0	0
PLA-WF	50	50	0	0	0
MA-PLA-WF	50	50	0	2	0
SI-PLA-WF	50	50	0	0	2
PLA-OMMT	100	0	2	0	0
PLA-WF-OMMT	50	50	2	0	0
MA-PLA-WF-OMMT	50	50	2	2	0
SI-PLA-WF-OMMT	50	50	2	0	2

PLA, poly lactic acid; WF, wood flour; MA, maleic anhydride; OMMT, organo-montmorillonite; phc, per hundred compounds; MAPP, maleic anhydride grafted polypropylene.

was a sandy loam texture with organic matter content of 21.66 wt%. The composition of the solid was sand (particle size about 2-0.02 mm) 57.40 wt%, powder (particle size about 0.02-0.002 mm) 29.12 wt%, and clay (particle size less than 0.002 mm) 13.48 wt%. The pH of the solid was 7.98. The compost was passed through a 10-mm sieve, and any glass or stone pieces were manually removed to obtain a homogeneous mix prior to testing. The water content of the substrate was about 50 wt%, and the aerobic conditions were guaranteed by mixing it softly. Before testing, samples were dried at 40°C until constant weight and weighed. Then, they were buried at 40-60 mm depth in perforated bottles containing the prepared mix and incubated at 58°C. The samples were recovered at different disintegration steps, washed with distilled water, completely cleaned of soil and mold, dried in an oven at 40°C until constant weight, and weighed. Degradation of samples was determined by weight loss percentage according to Eq 1:

$$WL = \frac{W_0 - W_1}{W_0} \times 100\% \quad (1)$$

where WL is weight loss percentage of each sample (%) and W_0 and W_1 represent the weight retentions in samples before and after the compost test (g), respectively.

Evaluation of Degradation by Scanning Electron Microscopy, Fourier Transform Infrared, and Differential Scanning Calorimeter Analysis

After a 3-mo compost test, surface and internal microstructures of samples were examined using a Philips (Hitachi S-3400; Tokyo, Japan) SEM with an acceleration voltage of 10 kV. Samples were sputtercoated with gold prior to observation.

The chemical groups of samples before and after degradation were examined by a FTIR spectrum analysis spectrometer (Tensor 27, Bruker, Germany), and potassium bromide (KBr) was used to collect the background. Air-dried powder, passed through a 100-mesh sieve, was

mixed with KBr in a weight ratio of 1:100 before spectrum collection. All spectra were displayed in wavelengths ranging from 400-4000 cm^{-1} .

Thermal behavior of samples before and after degradation were examined by DSC (DSC-204; Netzsch, Selb, Germany). Data were collected by heating from room temperature to 200°C at a constant heating rate of 10°C/min under a constant nitrogen flow of 60 mL/min. Samples weighing about 1 mg were placed in aluminum pans. Values for glass transition temperatures (T_g), melting temperatures (T_m), fusion enthalpies (ΔH_m), and cold crystallization enthalpies (ΔH_c) were evaluated. Crystallinity was estimated by Eq 2 (Gregorova et al 2011).

$$X_c(\%) = \frac{\Delta H_m - \Delta H_c}{\Delta H_m^0} \times \frac{100}{w} \quad (2)$$

where X_c is crystallinity (%); ΔH_m^0 is enthalpy of melting 100% crystallized PLA, which is equal to 93.7 J/g; ΔH_m is enthalpy required for melting each sample; ΔH_c is enthalpy for cold crystallization of each sample; and w is PLA weight fraction of each sample.

RESULTS AND DISCUSSION

Flexural Properties

Flexural modulus of rupture (MOR) and modulus of elasticity (MOE) are listed in Table 2. Adding 50 wt% WF decreased the MOR because of the weak interfacial adhesion between hydrophilic WF and hydrophobic polymer (Table 2). In contrast, MOE improved, which is associated with the increasing stiffness and brittleness caused by WF. Adding OMMT into PLA could dramatically increase the flexural properties of pure PLA from 44.40-64.77 MPa for MOR and 3.02-3.77 GPa for MOE, respectively. However, for an OMMT-modified WF/PLA system, MOR only slightly improved. The results suggested that the strength was largely dependent on the WF factor. The MOR and MOE of WF/PLA composites could also be improved by adding either MAPP or silane because of their coupling

Table 2. Flexural properties of pure PLA, OMMT/PLA, and WF/PLA composites.

Labels	Flexural properties ^a	
	MOR (MPa)	MOE (GPa)
PLA	44.40 (1.99)	3.02 (0.17)
PLA-WF	42.94 (3.81)	4.15 (0.33)
MA-PLA-WF	46.69 (3.03)	4.37 (0.22)
SI-PLA-WF	48.95 (3.26)	4.41 (0.42)
PLA-OMMT	64.77 (1.42)	3.77 (0.13)
PLA-WF-OMMT	45.21 (3.94)	4.73 (0.31)
MA-PLA-WF-OMMT	51.89 (3.26)	4.77 (0.18)
SI-PLA-WF-OMMT	52.60 (1.90)	4.79 (0.01)

^a Values in parentheses are standard deviations of four replicates.

PLA, poly lactic acid; WF, wood flour; MA, maleic anhydride; OMMT, organo-montmorillonite.

effects between WF and PLA. Meanwhile, OMMT and both coupling agents might have a synergetic effect of further improving MOR and MOE of WF/PLA composites (Lee et al 2008). Comparing the two types of coupling agents, silane appeared to perform better than MAPP, which might explain the better compatibility between PLA and WF after modification with silane.

Weight Loss Percentage

Weight loss percentages of pure PLA, OMMT/PLA, and WF/PLA composites after the compost test are listed in Table 3. All groups achieved complete degradation after 6 mo. For all composite groups, this can be decreased to 5 mo, suggesting the positive combined effect of WF, coupling agent, and OMMT on degradation. By comparing the weight losses of PLA-WF and PLA-OMMT with pure PLA, the

individual effects of WF and OMMT on degradation were also clarified. Both WF and OMMT facilitated degradation, which is consistent with results of previous studies (Ray et al 2003; Nieddu et al 2009; Petinakis et al 2009, 2010). The effect of both coupling agents was analyzed by comparing the degradation performance of MA-PLA-WF and SI-PLA-WF with PLA-WF. MAPP showed a negative effect on degradation of WF/PLA composites, namely, the weight loss percentages were lower than those of unmodified controls. After 2 and 3 mo, weight loss percentages of MA-PLA-WF were 52.91 and 74.91%, respectively, which were even lower than pure PLA. This may have been because MAPP could provide a better interfacial adhesion for PLA and WF by decreasing the area exposed to compost. Besides, the nondegradable propylene may have covered the surface of the WF/PLA composites. These two factors would act as barriers to water penetration during degradation. However, silane caused different results, although it could benefit interfacial adhesion of WF/PLA composites as well. Silane is a reagent with two types of groups, namely, both polar and nonpolar groups. The reaction between PLA matrix and WF with silane can be divided into two steps according to Matuana et al (1999). First, the silane agent is easily hydrolyzed to silanol by water and then reacted with the hydroxyl groups on the WF surface; second, the nonpolar long carbon chain of silane twisted and intervened with PLA matrix, acting as a bridge to combine WF and PLA together. Therefore, to some extent, it is possible that the hydrophilic

Table 3. Weight loss percentages of pure PLA, OMMT/PLA, and WF/PLA composites during the compost test.

Labels	Weight loss percentages ^a (%)					
	After 1 mo	After 2 mo	After 3 mo	After 4 mo	After 5 mo	After 6 mo
PLA	19.32 (7.16)	53.97 (3.57)	77.67 (2.13)	87.44 (4.85)	95.22 (3.33)	100
PLA-WF	25.78 (2.26)	54.08 (4.69)	79.68 (2.93)	91.55 (3.80)	100	100
MA-PLA-WF	23.18 (5.63)	52.91 (5.65)	74.91 (6.23)	91.12 (2.23)	100	100
SI-PLA-WF	28.73 (6.03)	56.60 (5.88)	82.33 (3.24)	93.20 (2.32)	100	100
PLA-OMMT	27.34 (8.31)	60.34 (4.73)	84.65 (6.14)	94.47 (2.27)	100	100
PLA-WF-OMMT	36.55 (6.75)	66.08 (5.51)	84.71 (2.01)	95.51 (1.09)	100	100
MA-PLA-WF-OMMT	29.98 (7.79)	54.38 (4.33)	78.71 (4.63)	93.15 (3.31)	100	100
SI-PLA-WF-OMMT	62.79 (7.49)	84.81 (4.33)	93.43 (6.20)	100	100	100

^a Values in parentheses are standard deviations of six replicates.

PLA, poly lactic acid; WF, wood flour; MA, maleic anhydride; OMMT, organo-montmorillonite.

WF could enter into the PLA matrix and break the regularity of PLA molecular arrangements and then finally lead to fast hydrolysis of PLA. SI-PLA-WF-OMMT with both silane and OMMT obtained the fastest weight loss. The weight decreased to 62.79% after 1 mo, which was more than three times faster than pure PLA. After 4 mo, it was completely degraded. Thus, the combined effects of OMMT and silane facilitated degradability the most in the compost.

Morphology Analysis

Degradability in composting conditions was then evaluated by visual observation of the PLA and PLA composites. The appearance of pure PLA, OMMT/PLA, and WF/PLA composites during compost testing are shown in Fig 1. It is obvious that all samples degraded severely as composting proceeded. Pure PLA was first cracked into several fragments after 1 mo of degradation and was finally degraded into powders that would pose minimal burden to the environment. OMMT played a significant role in degradability of PLA. It accelerated the degradation process, showing very little residue after 3 mo. Adding WF accelerated degradation compared with pure PLA. Although the samples kept their original shape after 1 mo of composting, there were more voids inside the com-

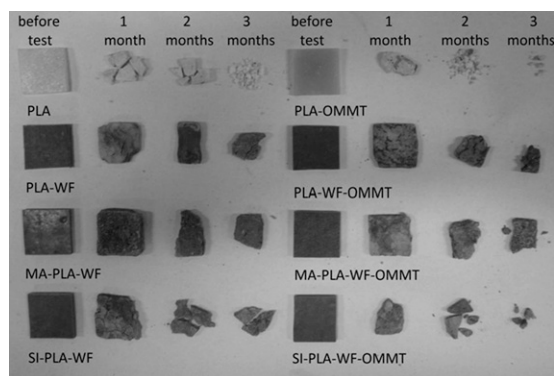


Figure 1. Images of pure PLA, OMMT/PLA, and WF/PLA composites before testing and after different stages of disintegration during compost testing. PLA, poly lactic acid; WF, wood flour; MA, maleic anhydride; OMMT, organo-montmorillonite.

posites. This was further indicated by SEM analysis. However, WF/PLA still exhibited fairly good degradability judging from the results after 3 mo. For samples modified with MAPP, some PP might cover the surface of MAPP-modified WF/PLA composites, restricting the degradation progress of PLA. Consistent with the results of weight loss percentages, silane-modified WF/PLA composites exhibited rapid degradation, especially the SI-PLA-WF-OMMT group, which showed the least residue of all groups. The appearance of PLA/WF composites in Fig 1 might be a deviation from the weight loss data in Table 3. There were two reasons for this. First, the thickness of samples was hard to observe and it was not shown in Fig 1. Second, the predominant WF in the composites after degradation had relatively lower density (about 0.4 g/cm^3) than PLA.

Scanning Electron Microscopy Analysis

The SEM images for surface and internal microstructures of PLA, OMMT/PLA, and WF/PLA composites after a 3-mo compost test are shown in Fig 2. Compared with pure PLA, PLA modified with OMMT showed deeper fractures on its surface and also more voids inside, which suggests that OMMT improved PLA degradability, whereas for WF/PLA composites, the disintegration appeared to be more severe than pure PLA, showing more fractures and granules on the surfaces with tremendous depressions. Also, the inside of WF/PLA composites exhibiting less continuous matrix and the filler of WF were separated alone, indicating that more PLA had been degraded. With respect to the effects of the two types of coupling agents, MAPP appeared to have a negative effect on degradability of WF/PLA composites. A continuous gel-like substance covered the surface, and big bulks existed inside the WF/PLA composite (see arrow in Fig 2). These objects were considered to be the non-degradable PP. Adversely, silane-modified WF/PLA composites showed totally different microstructures compared with MAPP-modified groups. In silane-modified composites, more voids appeared on the surface, although smaller cracks still existed and individual wood fibers were

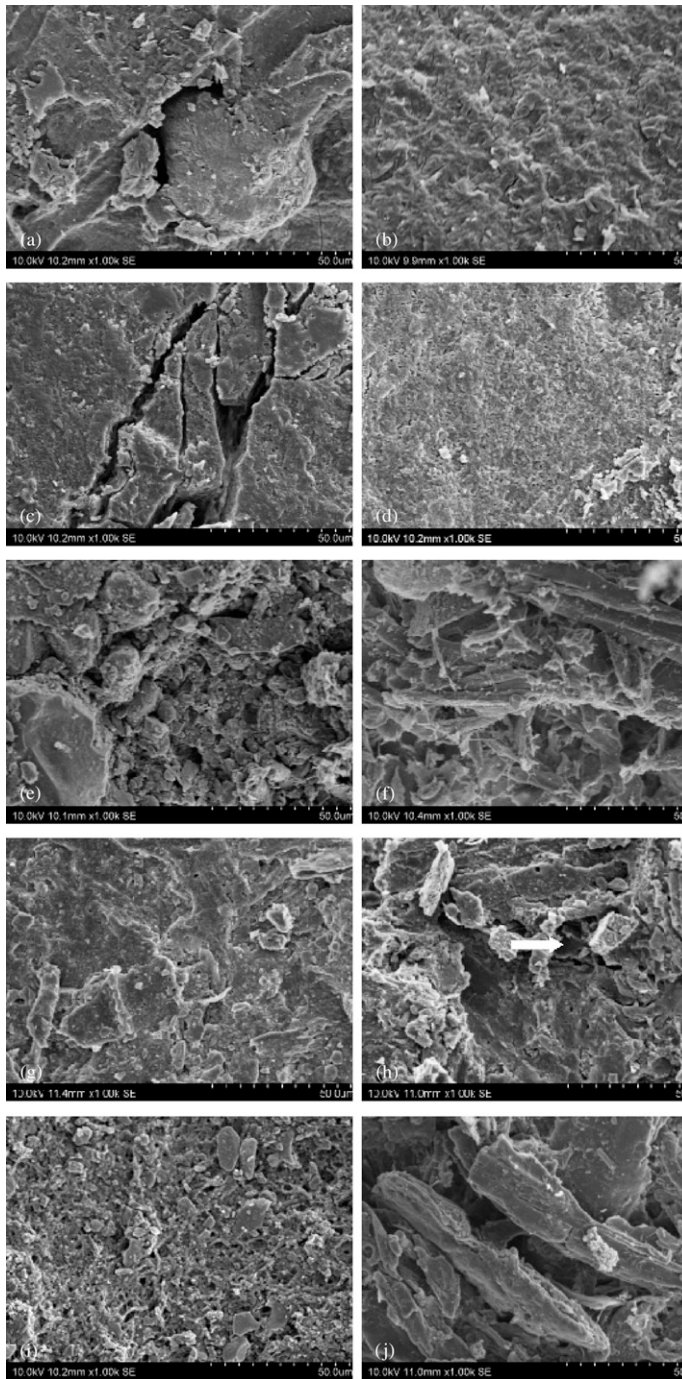


Figure 2. Scanning electron micrograph images of surface and interior of PLA, OMMT/PLA, and WF/PLA composites after 3 mo in a compost test: (a) PLA surface; (b) PLA inside; (c) PLA-OMMT surface; (d) PLA-OMMT inside; (e) PLA-WF surface; (f) PLA-WF inside; (g) MA-PLA-WF surface; (h) MA-PLA-WF inside; (i) SI-PLA-WF surface; (j) SI-PLA-WF inside. PLA, poly lactic acid; WF, wood flour; MA, maleic anhydride; OMMT, organo-montmorillonite. Scale bars of all images are $\times 1000$.

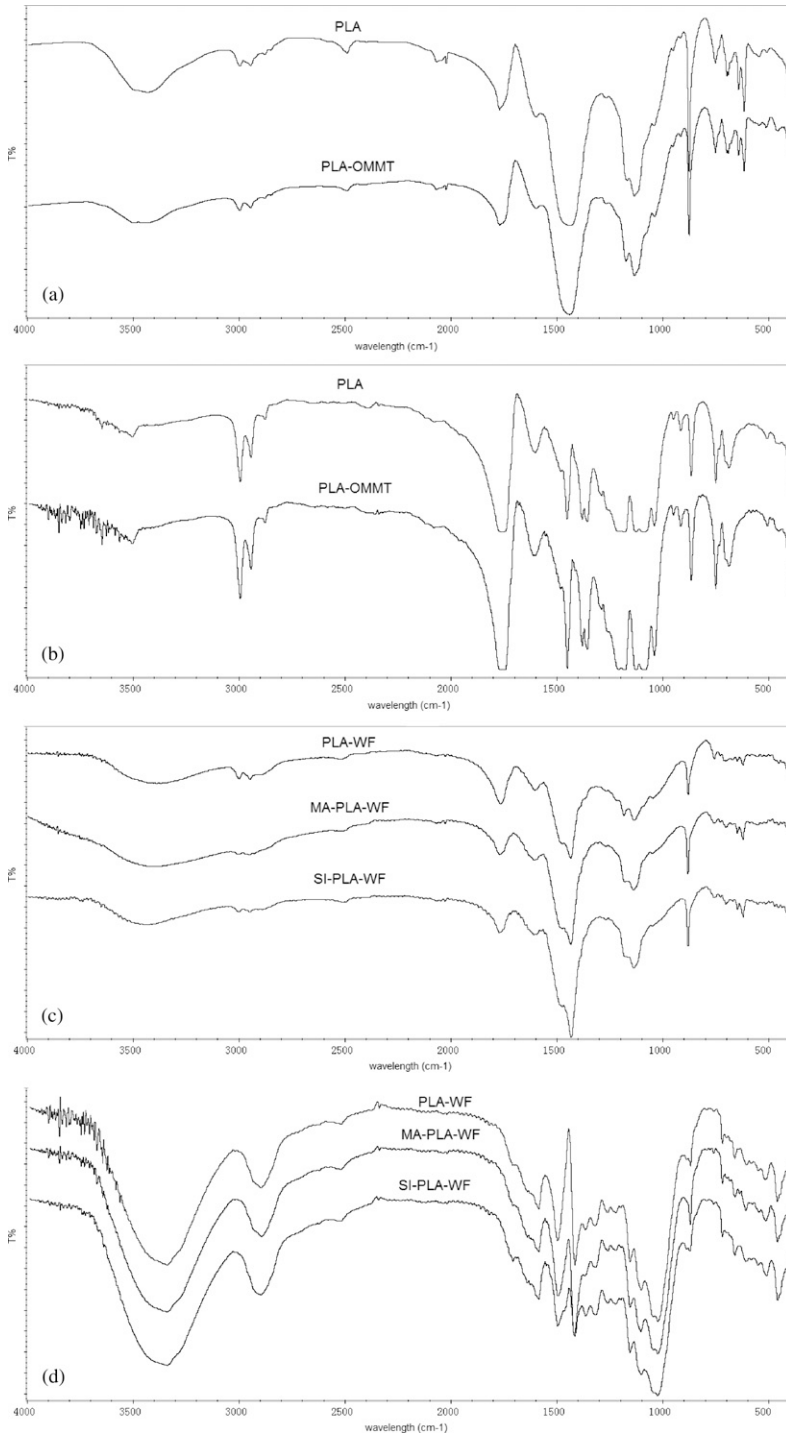


Figure 3. Fourier transform infrared images of pure PLA and OMMT/PLA before (a) and after (b), WF/PLA composites before (c) and after (d) 3 mo in a compost test. PLA, poly lactic acid; WF, wood flour; MA, maleic anhydride; OMMT, organo-montmorillonite.

separated in the interior. These results provided evidence that better interfacial adhesion and more homogeneous advanced degradation of WF/PLA composites during compost testing were achieved.

Fourier Transform Infrared Analysis

FTIR results of PLA, OMMT/PLA, and WF/PLA composites before and after 3 mo of compost testing are shown in Fig 3a-d. In Fig 3a, the peaks of PLA modified with OMMT were almost the same as pure PLA except for an emerging small peak at 467 cm^{-1} assigned to the absorption of the Si-O group in OMMT. This indicated that OMMT had been introduced into the PLA matrix but did not change the main structure of PLA. After 3 mo in compost (Fig 3b), most characteristic peaks of PLA remained, eg the absorption of CH_2 stretching vibration at 3000 and 2950 cm^{-1} , C=O vibration at 1773 cm^{-1} , CH_3 bending vibration around 1450 cm^{-1} , and C-O stretching vibration at 1140 cm^{-1} . However, the intensity of absorption assigned to CH_3 bending vibration was much lower than that of pure PLA before degradation, and the peak also became narrower, shifting to a higher wavelength at 1460 cm^{-1} . Also, shoulder peaks at 1392 and 1364 cm^{-1} assigned to the symmetrical deformation of CH_3 appeared. Generally, absorption of CH_3 groups was associated with the length of the polymer main chain. Longer polymer chains usually had more intense CH_3 bending vibrations at lower wavelengths. Meanwhile, when combined with the C=O group, especially the ester bond, it could shift to a much lower wavelength and overlap the symmetrical deformation of CH_3 . During the degradation process, a great amount of ester bonds of PLA was broken, which was shown by the weakened and broadened peaks at 1140 and 1180 cm^{-1} assigned to C-O of the ester bond in PLA. These peaks might overlap the absorption assigned to hydroxyl groups at 1200 and 1100 cm^{-1} . The peak at 1773 cm^{-1} was also broadened. This could have resulted from overlapping the C=O in the generated carboxyl groups.

Figure 3c gives the FTIR results of WF/PLA composites with or without a coupling agent.

Compared with pure PLA in Fig 3a, introducing WF did not influence the structure of PLA greatly with very close curves, except for two increased peaks, namely, absorption at 1434 cm^{-1} assigned to CH_2 groups from cellulose or hemicelluloses and absorption around 3450 cm^{-1} assigned to free hydroxyl groups. This was considered to be caused by the fact that WF was well covered by the PLA matrix during processing. The difference between WF/PLA composites with and without a coupling agent was insignificant. After the 3-mo compost test (Fig 3d), the curves were very different from those of PLA but similar to those of WF. The strong and broad absorption around 3360 cm^{-1} was assigned to vibration of hydroxyl groups in WF. Absorption around 2900 cm^{-1} was assigned to C-H stretching in cellulose, and the peaks at 1182 and 1044 cm^{-1} were assigned to stretching vibration of C-O-C and C-O of acetyl from cellulose or hemicelluloses. Some small emerging peaks around 1450 cm^{-1} were assigned to benzene derivatives in lignin. This could imply that WF accelerated the degradation of PLA and resulted in more separated WF. However, WF also degraded when exposed to compost. The characteristic C=O in carboxylic acid groups in hemicelluloses disappeared, suggesting hemicelluloses had been degraded as well.

Differential Scanning Calorimeter Analysis

Figure 4 demonstrates the DSC curves of PLA, OMMT/PLA, and WF/PLA composites before and after 3 mo of compost testing. Thermal properties values, such as glass transition temperatures (T_g), melting temperatures (T_m), fusion enthalpies (ΔH_m), cold crystallization enthalpies (ΔH_c), and degrees of crystallinity (X_c), are listed in Table 4. For pure PLA, the T_g value could be plainly seen at 64.6°C , whereas after 3 mo in compost testing, the T_g value was not clear. Tsuji and Tezuka (2005) studied the enzymatic degradation properties of PLA. They also found the decreasing T_g value after degradation, and they attributed it to increasing mobility of the polymer chains caused by a plasticizing effect of lactic acid oligomers formed during degradation. T_m value of PLA shifted

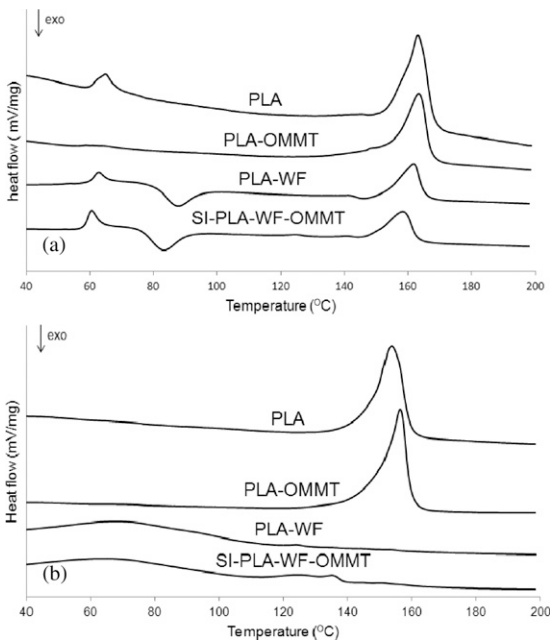


Figure 4. Differential scanning calorimeter curves of pure PLA, OMMT/PLA, and WF/PLA composites before (a) and after (b) 3 mo in a compost test. PLA, poly lactic acid; WF, wood flour; MA, maleic anhydride; OMMT, organo-montmorillonite.

from 162.9 to 153.6°C as a consequence of the breaking of molecular chains in the compost test. However, ΔH_m value increased greatly from 53.39 to 73.15 J/g corresponding to the increasing degree of crystallinity. In a previous study, Fischer et al (1973) reported that during hydrolytic degradation of PLA, water diffused into the amorphous region, resulting in random hydrolytic scission of ester bonds. Therefore, the degree of crystallinity could even increase as degradation proceeded. The results of this study are consistent with their results.

After introduction of OMMT into PLA, the heat-retardant property of the sample before the compost test was improved compared with that of pure PLA by showing an indistinct T_g value and a higher T_m value. This might be associated with the barrier effect of OMMT on heat flow during heating. Another difference between PLA and OMMT/PLA composites was the degree of crystallinity, which was higher in OMMT/PLA composites than in pure PLA. This was attributed to the nucleating effect of OMMT on improving the crystallization degree of PLA (Lewitus et al 2006). After 3 mo of degradation, the PLA modified with OMMT also showed lower T_m values but a higher degree of crystallinity, which was the same as pure PLA. However, the T_m value and degree of crystallinity of OMMT/PLA composites were still higher than those of pure PLA even after degradation.

With regard to the effect of WF, WF/PLA composite samples before the degradation test showed slightly decreasing T_g and T_m values compared with pure PLA. Also, ΔH_m value sharply dropped and the cold crystallinity temperature was about 87°C. This might be caused by the combination of WF preventing PLA from crystallizing during the heat-pressure cycle. Therefore, a big part of PLA was in the amorphous phase, which could be proven by the much lower degree of crystallinity (18.84%) of WF/PLA composites compared with pure PLA. After 3 mo in compost, none of the values of thermal properties of PLA could be found in Fig 4d, suggesting most of PLA had degraded and the residue was mainly composed of WF. The broad peak from 40-80°C might have been related to water volatilization during heating, showing much water had permeated into WF/

Table 4. Thermal property values of pure PLA, OMMT/PLA, and WF/PLA composites before and after 3 mo in a compost test.

Labels	Before test					After 3 mo				
	T_g (°C)	T_m (°C)	ΔH_m (J/g)	ΔH_c (J/g)	X_c (%)	T_g (°C)	T_m (°C)	ΔH_m (J/g)	ΔH_c (J/g)	X_c (%)
PLA	64.6	162.9	53.39	—	56.98	—	153.6	73.15	—	78.07
PLA-OMMT	—	163.2	54.12	—	57.76	—	156.2	74.67	—	79.96
PLA-WF	62.9	161.9	20.87	12.04	18.84	—	—	—	—	—
SI-PLA-WF-OMMT	60.3	158.4	20.01	13.16	14.62	—	—	—	—	—

PLA, poly lactic acid; OMMT, organo-montmorillonite; WF, wood flour.

PLA composites after 3 mo in compost. These results all confirmed that WF could accelerate the degradation process of PLA.

To investigate the effect of silane coupling agent and OMMT on the thermal properties of WF/PLA composites, the optimal group SI-PLA-WF-OMMT was also analyzed by DSC. The results showed that before the compost test, all values of thermal properties were the lowest among all the samples. For example, T_g and T_m values shifted to 60.3 and 158.4°C, respectively, and the degree of crystallinity was only 14.82%. This suggested that silane-modified WF could lead to more irregular molecular arrangements of PLA leading to larger parts of PLA being in amorphous phases compared with other samples. This was in agreement with Bengtsson and Oksman (2006) who reported that silane treatment of WF increased the degree of crosslinking in WF/HDPE composites but decreased the crystallinity value. After 3 mo in compost, thermal property values of PLA also disappeared, consistent with the PLA-WF group.

CONCLUSION

Both OMMT and WF used in this study had an accelerating influence on the degradation of PLA compared with pure PLA. Composites were completely degraded after 5 mo. Also, MAPP and silane influenced the degradability of WF/PLA composites. MAPP had a negative effect on the degradation properties because of some nondegradable polymer PP covering the surface during the degradation process. In contrast, because of the interruption of WF and silane on regularity of PLA molecular arrangement, silane increased the rate of degradation of PLA. The fastest degradation occurred for WF/PLA composites modified with both OMMT and silane. It could be completely degraded after 4 mo. SEM analysis showed some cracks on PLA, although it was degraded more seriously after modification with OMMT. After introducing WF, more voids existed on the surface and individual fibers were separated after 3 mo in compost. FTIR analysis indicated that many

ester bonds were broken during degradation of PLA, whereas for WF/PLA composites, the curves were similar to those of PLA before composting but close to WF after the compost test. DSC analysis indicated the increase in degrees of crystallinity of PLA and PLA modified with OMMT, suggesting degradation mostly took place in the amorphous region of PLA. For WF/PLA composites, thermal property values of PLA matrix were not obvious. All these results suggested the great losses of PLA and therefore the predominant percentage of WF in the composites after a 3-mo compost.

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REFERENCES

- Abdul Khalil HPS, Ismail H (2000) Effect of acetylation and coupling agent treatments upon biological degradation of plant fibre reinforced polyester composites. *Polym Test* 20(1):65-75.
- Bala P, Samantaray BK (2001) Effect of alkylammonium intercalated montmorillonite as filler on natural rubber. *J Mater Sci Lett* 20:563-564.
- Bengtsson M, Oksman K (2006) Silane crosslinked wood plastic composites: Processing and properties. *Compos Sci Technol* 66:2177-2186.
- Cheng FO, Mong TH, Jia RL (2003) The nucleating effect of montmorillonite on crystallization of PET/montmorillonite nanocomposites. *J Polym Res* 10:127-132.
- de Jong SJ, Arias ER, Rijkers DTS, van Nostrum CF, Kettenes-van den Bosch JJ, Hennink WE (2001) New insights into the hydrolytic degradation of poly(lactic acid): Participation of the alcohol terminus. *Polymer (Guildf)* 42(7):2795-2802.
- Dikobe DG, Luyt AS (2010) Morphology and thermal properties of maleic anhydride grafted polypropylene/ethylene-vinyl acetate copolymer/wood powder blend composites. *J Appl Polym Sci* 116:3193-3201.
- Fischer EW, Sterzel HJ, Wegner G (1973) Investigation of the structure of solution grown crystals of lactide copolymers by means of chemical-reactions. *Colloid Polym Sci* 251(11):980-990.
- Fortunati E, Armentano I, Iannoni A, Barbale M, Zaccheo S, Scavone M, Visai L, Kenny JM (2012) New multifunctional

- poly(lactide acid) composites: Mechanical, antibacterial, and degradation properties. *J Appl Polym Sci* 124:87-98.
- Fukushima K, Abbate C, Tabuani D, Gennari M, Camino G (2009) Biodegradation of poly(lactic acid) and its nanocomposites. *Polym Degrad Stabil* 94:1646-1655.
- Fukuzaki H, Yoshida M, Asano M, Kumakura M (1989) Synthesis of copoly (D, L-lactic acid) with relative low molecular weight and in vitro degradation. *Eur Polym J* 25:1019-1026.
- Gattin R, Copinet A, Bertrand C, Couturier Y (2002) Biodegradation study of a starch and poly(lactic acid) co-extruded material in liquid, composting and inert mineral media. *Int Biodeterior Biodegradation* 50:25-31.
- George J, Sreekala MS, Thomas S (2001) A review on interface modification and characterization of natural fiber reinforced plastic composites. *Polym Eng Sci* 41(9):1471-1485.
- Gregorova A, Hrabalova M, Kovalcik R, Wimmer R (2011) Surface modification of spruce wood flour and effects on the dynamic fragility of PLA/wood composites. *Polym Eng Sci* 51:143-150.
- Hemmasi AH, Khademi-Eslam H, Talaiepoor M, Kord B, Ghasemi I (2010) Effect of nanoclay on the mechanical and morphological properties of wood polymer nanocomposite. *J Reinf Plast Comp* 29:964-971.
- Huda MS, Drzal LT, Mohanty AK, Misra M (2006) Wood-fiber-reinforced poly (lactic acid) composites: Evaluation of the physicomechanical and morphological properties. *J Appl Polym Sci* 102:4856-4869.
- International Organization for Standardization (2004) *Plastics—Determination of the degree of disintegration of plastic materials under simulated composting conditions in a laboratory-scale test. ISO 20200:2004* [United Kingdom].
- Jiang XH, Cao JZ, Luo GQ (2011) Physical and mechanical properties of MMT/PVA/wood composites. *Chemistry and Industry of Forest Products* 31(1):41-46.
- Kolstad JJ (1996) Crystallization kinetics of poly (L-lactide-co-meso-lactide). *J Appl Polym Sci* 62(7):1079-1091.
- Kulinski Z, Piorkowska E (2009) Crystallization, structure and properties of plasticized poly (L-lactide). *Polymer (Guildf)* 46:10290-10300.
- LeBaron PC, Wang Z, Pinnavaia TJ (1999) Polymer-layered silicate nanocomposites: An overview. *Appl Clay Sci* 15:11-29.
- Lee SH, Wang S (2006) Biodegradable polymers/bamboo fiber biocomposite with bio based coupling agent. *Compos, Part A Appl Sci Manuf* 37:80-91.
- Lee SY, Kang IA, Doh GH, Kim WJ, Kim JS, Yoon HG, Wu Q (2008) Thermal, mechanical and morphological properties of polypropylene/clay/wood flour nanocomposites. *Express Polym Lett* 2:78-87.
- Lewitus D, McCarthy OA, Kenig S (2006) The effect of nanoclays on the properties of PLLA-modified polymers part 1: Mechanical and thermal properties. *Journal of Polymers and the Environment* 14:171-177.
- Liu JW, Zhao Q, Wan CX (2001) Research progresses on degradation mechanism in vivo and medical applications of polylactic acid. *Space Med Med Eng (Beijing)* 14(4):308-312.
- Liu LS, Fishman LM, Hicks BK, Liu AK (2005) Biodegradable composites from sugar beet pulp and poly(lactic acid). *J Agric Food Chem* 53:9017-9022.
- Lv WH, Zhao GJ, Xue ZH (2006) Preparation and characterization of wood/montmorillonite nanocomposites. *For Stud China* 8(1):35-40.
- Marcovich NE, Villar MA (2003) Thermal and mechanical characterization of liner low density polyethylene/wood flour composites. *J Appl Polym Sci* 90(10):2775-2784.
- Martin O, Averous L (2001) Poly (lactic acid): Plasticization and properties of biodegradable multiphase systems. *Polymer (Guildf)* 42:6209-6219.
- Matuana LM (2009) Rigid PVC/(layered silicate) nanocomposites produced through a novel melt-blending approach. *J Vinyl Addit Technol* 10:77-86.
- Matuana LM, Balatinecz JJ, Park CB, Sodhi RNS (1999) X-ray photoelectron spectroscopy study of silane-treated newsprint-fibers. *Wood Sci Technol* 33(4):259-270.
- Matuana LM, Park CB, Balatinecz JJ (1998) Cell morphology and property relationships of microcellular foamed PVC/wood-fiber composites. *Polym Eng Sci* 38(11):1862-1872.
- Meng QK, Hetzer M, De Kee D (2010) PLA/clay/wood nanocomposites: Nanoclay effects on mechanical and thermal properties. *J Composite Mater* 45(10):1145-1158.
- Mobedi H, Mashak A, Nekoomanesh M, Orafi H (2011) L-lactide additive and in vitro degradation performance of poly(l-lactide) films. *Iran Polym J* 20:237-245.
- Mobedi H, Nekoomanesh M, Orafaei H, Mivehchi H (2006) Studying the degradation of poly(l-lactide) in presence of magnesium hydroxide. *Iran Polym J* 15:31-39.
- Mohanty AK, Misra M, Drzal LT (2001) Surface modifications of natural fibers and performance of the resulting biocomposites: An overview. *Compos Interfaces* 8(5):313-343.
- Navarro M, Ginebra MP, Planell JA, Barrias CC, Barbosa MA (2005) In vitro degradation behavior of a novel bioresorbable composite material based on PLA and a soluble CaP glass. *Acta Biomater* 1:411-419.
- Nieddu E, Mazzucco L, Gentile P, Benko T, Balbo V, Mandrile R, Ciardelli G (2009) Preparation and biodegradation of clay composites of PLA. *React Funct Polym* 69:371-379.
- Niu XF, Wang YL, Luo YF, Pan J, Shang JF, Guo LX (2005) Synthesis of the biomimetic polymer: Aliphatic diamine and RGDS modified poly (D, L-lactic acid). *Chin Chem Lett* 16(8):1035-1038.
- Oksman K (1996) Improved interaction between wood and synthetic polymers in wood/polymer composites. *Wood Sci Technol* 30:197-205.
- Petinakis E, Liu X, Yu L, Way C, Sangwan P, Dean K, Bateman S, Edward G (2010) Biodegradation and thermal decomposition of poly(lactic acid)-based materials reinforced by hydrophilic fillers. *Polym Degrad Stabil* 95:1704-1707.

- Petinakis E, Yu L, Edward G, Dean K, Liu H, Scully A (2009) Effect of matrix-particle interfacial adhesion on the mechanical properties of PLA/wood-flour microcomposites. *Journal of Polymer and Environmental* 17:83-94.
- Ray SS, Yamada K, Okamoto M, Ueda K (2003) New poly(lactide)-layered silicate nanocomposites. 2. Concurrent improvements of material properties, biodegradability and melt rheology. *Polymer (Guildf)* 44:857-866.
- Reeve MS, McCarthy SP, Gross RA (1993) Preparation and characterization of (r)-poly(β -hydroxybutyrate)-poly(ϵ -capro-lactone) and (r)-poly(β -hydroxybutyrate)-poly(ϵ -lactide) degradable diblock copolymers. *Macromolecules* 26(5):888-894.
- Sain M, Suhara P, Law S, Bouilloux A (2005) Interface modification and mechanical properties of natural fiber-polyolefin composite products. *J Reinf Plast Comp* 24(2):121-130.
- Schneider M (1994) Wood polymer composites. *Wood Fiber Sci* 26(1):142-151.
- Shih C (1995) Chain end scission in acid catalyzed hydrolysis of poly(D,L-lactide) in solution. *J Control Release* 34:9-15.
- Standardization Administration of the People's Republic of China (2000) *Plastics—Determination of flexural properties*. GB/T 9341-2000. China.
- Takatani M, Ikeda K, Sakamoto K, Okamoto T (2008) Cellulose esters as compatibilizers in wood/poly (lactic acid) composite. *J Wood Sci* 54:54-61.
- Thellen C, Orroth C, Froio D, Ziegler D, Lucciarini J (2005) Influence of montmorillonite layered silicate on plasticized poly (L-lactide) blown films. *Polymer (Guildf)* 46(25):11716-11727.
- Tsuji H, Tezuka Y (2005) Alkaline and enzymatic degradation of L-lactide copolymers, 1. Amorphous-made films of L-lactide copolymers with D-lactide, glycolide, and epsilon-caprolactone. *Macromol Biosci* 5(2):135-148.
- Wang L, Cao JZ, Jiang XH, Liu R (2010) Properties and characterization of poplar wood treated with the montmorillonite-DDAC compound preservative. *Journal of Beijing Forestry University* 32(4):242-246.
- Wang Y, Cao JZ, Zhu LZ (2011) Stress relaxation of wood flour/polypropylene composites at room temperature. *Wood Fiber Sci* 43(3):262-270.
- Zhao GJ, Lv WH (2003) Nanoscale in wood, nanowood and wood-inorganic nanocomposite. *For Stud China* 5(1):44-48.
- Zhong Y, Poloso T, Hetzer M, De Kee D (2007) Enhancement of wood/polyethylene composites via compatibilization and incorporation of organoclay particles. *Polym Eng Sci* 10:797-803.