

Silane Modified Wood Flour Blended with Poly(lactic acid) and its Effects on Composite Performance

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The aim of this work was to study silane-modified wood flour/poly(lactic acid) (PLA) blends and the effect of blending on the properties of the wood flour/PLA composites. The surface of the wood flour used as filler was successfully modified by silane, as demonstrated by Fourier transform infrared spectroscopy (FTIR) results. The influence of silane types and content on the morphology, mechanical properties, and water absorption were studied. Scanning electron microscopy (SEM) results demonstrated that the KH-550 silane was the most effective modifier for improving the compatibility, mechanical properties, and water absorption of the blend. The appropriate additive content was 1.5% (relative to wood flour content). As the KH-550 content increased, the mechanical strength and elongation at the break first increased and then slightly decreased. These properties reached a maximum at 1.5% KH-550. The water resistance of the blend also was improved at a KH-550 content of 1.5%.

Keywords: Poly (lactic acid) (PLA); Wood flour; Silane; Mechanical properties

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INTRODUCTION

Wood-plastic composites (WPCs) are usually the composites prepared by wood (or natural) flour/fibers and thermoplastics, with the goal of generating high performance and high added value. A variety of thermoplastics have been used to produce WPCs, such as polypropylene, polyethylene, and poly(vinyl chloride). However, these thermoplastics are nondegradable petroleum-based polymers, and their inappropriate disposal can lead to serious environmental pollution. As a result, a demand for biodegradable materials to replace the petroleum-based plastics has increased. Among the current biodegradable polymers, poly(lactic acid), or PLA, is one of the most promising candidates to replace the petroleum-based plastics (Martin and Avérous 2001).

In recent years, the interest in PLA as an environmentally friendly biodegradable polymer has increased considerably in research and development (Bhardwaj and Mohanty 2007; Gregorova *et al.* 2011; Arrieta *et al.* 2013). Due to its high strength, biodegradability, biocompatibility, and ease of processing, PLA exhibits great potential for application in many fields (Petinakis *et al.* 2009; Zhao *et al.* 2013). However, its inherent brittleness and high price have restricted wider application. In order to expand its use, extensive strategies have been developed to modify the PLA. Adding wood flour to PLA is an effective approach to lowering the price while still maintaining degradability (Liu *et al.* 2015). However, wood flour and PLA are not compatible due to the hydrophobic properties of PLA and the hydrophilic properties of wood flour. Many methods have been used to improve the compatibility between wood flour and PLA, such

as surface treatment (Altun *et al.* 2013; Csizmadia *et al.* 2013) and the addition of compatibilizing agents (Gregorova *et al.* 2011).

Silanes are recognized as efficient coupling agents and are extensively used to modify the interfacial properties in composites *via* the hydrolyzable and organo-functional reactions (Jariyasakoolroj and Chirachanchai 2014). In the past, the use of silane coupling agents to improve the performance of composites has been reported. For example, the improvement of strength and toughness of silane crosslinked low-density polyethylene/wood composites was successfully demonstrated; in these experiments, the flexural strength was doubled and the interfacial adhesion between the wood and LDPE was improved by the formation of silane-bridges (Grubbström *et al.* 2010).

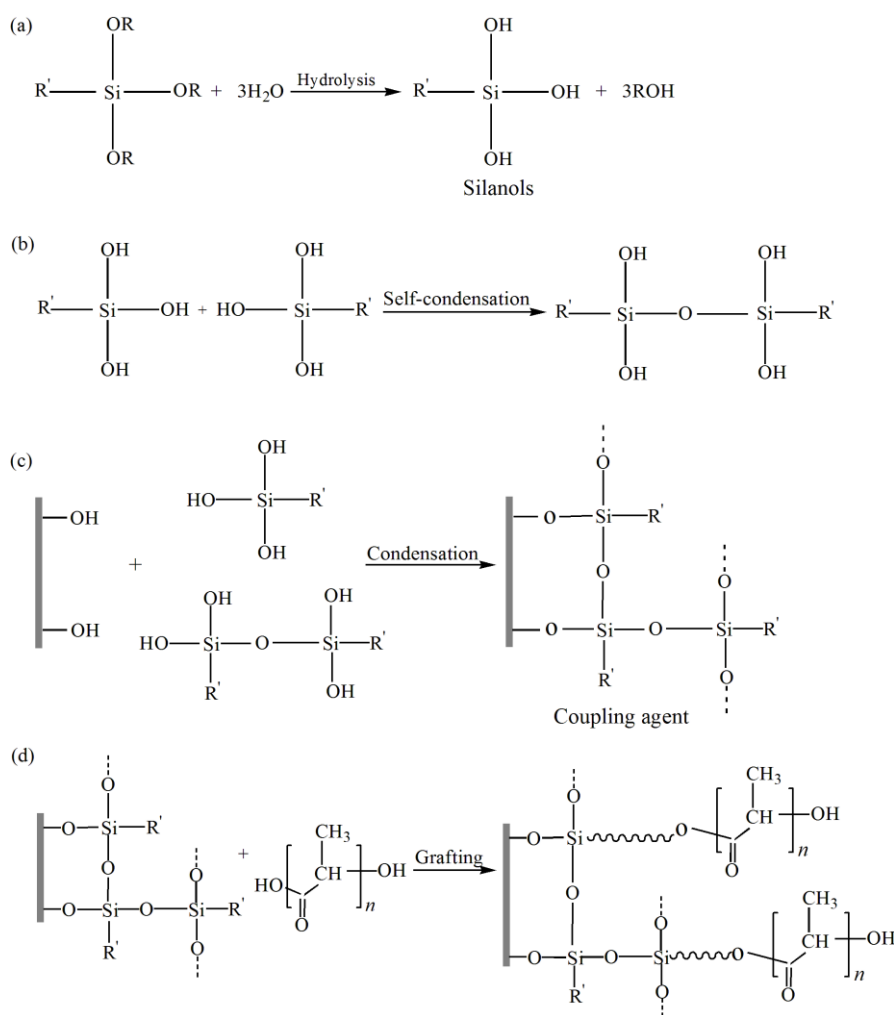


Fig. 1. Interaction mechanism of silane with wood flour and PLA

In the present research, silane coupling agents were used to treat the wood flour prior to blending with PLA. The interaction mechanism between silane, wood flour, and PLA is illustrated in Fig. 1. When the silane is hydrolyzed in solution, it is transformed into silanols, which have a large number of reactive hydroxyl groups (shown in Fig. 1a). During the hydrolysis process, the concomitant self-condensation of silanols also takes place (Xie *et al.* 2010), forming -Si-O-Si- groups that are stable towards hydrolysis (Plueddemann 1991) (shown in Fig. 1b). When the hydrolyzed silane solutions are mixed

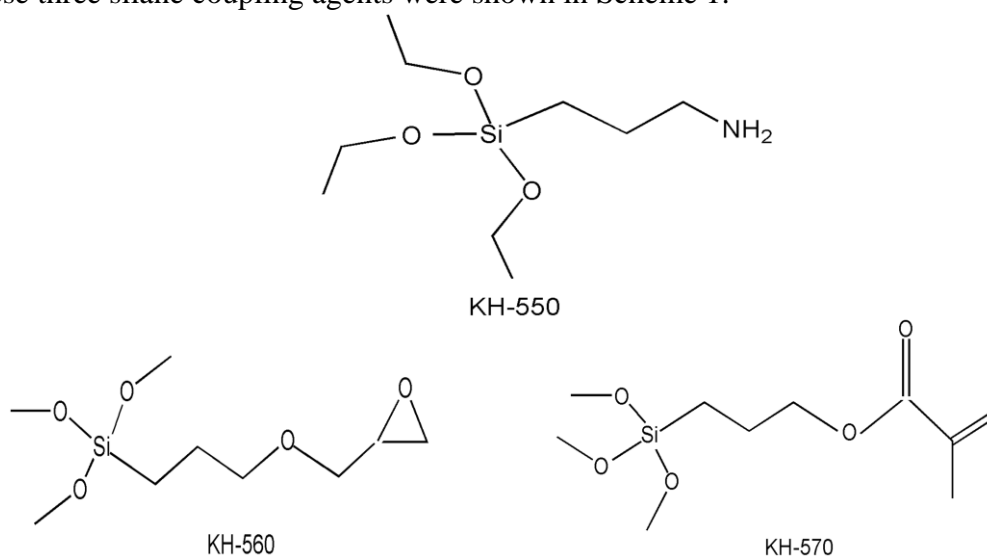
with wood flour, the reactive silanol groups have a high affinity for the hydroxyl groups of wood flour and they become absorbed on to the hydroxyl groups by hydrogen bonds on the surface of wood flour. At the same time, the free silanol groups react with each other to form a linked -Si-O-Si- network structure (shown in Fig. 1c), which serves as a coupling system. The self-condensation rate of silanols can be controlled by adjusting the pH of the hydrolysis system. An acidic pH environment is employed to slow down the condensation rate of silanols while accelerating the hydrolysis rate of silanes, thereby allowing the reactive silanol access to hydroxyl sites in the wood flour cell walls (Xie *et al.* 2010). When the treated wood flour is mixed with PLA, the coupling agents formed in the condensation process (Fig. 1c) are grafted onto the PLA chains, which bond the wood flour and PLA together (Fig. 1d).

The aim of this work is to study the influences of the silane types and contents on the performances of the wood flour/PLA composites prepared by the silane modified wood flour. The morphology, mechanical properties, and water resistance were studied. In addition, the modified effect of the different silanes on wood flour was characterized and demonstrated by Fourier transform infrared spectroscopy (FTIR).

EXPERIMENTAL

Materials

The PLA was purchased from Ningbo Huanqiu Plastic Products Co., Ltd. (Ningbo, Zhejiang, China). The selected grade, PLA 306D, was a semi-crystalline extrusion material. The T_g of PLA was about 60 °C, and its T_m was in the range 147 °C to 156 °C. It was dried at 50 °C for 8 h prior to use in the vacuum oven in order to eliminate moisture. Wood flour with particle sizes between 80 and 100 meshes was supplied by Baiquan Wood plastic composite material base (Heilongjiang, China). Silane coupling agents (AR), γ -aminopropyl triethoxysilane (KH-550), γ -(2,3-epoxypropoxy) propyl trimethoxysilane (KH-560) and γ -(methacryloxypropyl) trimethoxysilane (KH-570), were purchased from Shanghai Yaohua Chemical Plant (Shanghai, China). The structures of these three silane coupling agents were shown in Scheme 1.



Scheme 1. Structures of different silane coupling agents

Methods

Surface modification of wood flour

Wood flour was dried first at 80 °C for 24 h in a vacuum oven to remove water and low molecular weight organic materials (Pilla *et al.* 2009). Then 5 wt% silane was added into a 95 wt% ethanol aqueous solution, and a pH of 4.5 was attained by the addition of acetic acid to promote the hydrolysis of silane (except for KH-550). The hydrolysis silane solution was sprayed on the surface of the dried wood flour and mixed in a high-speed mixer to get modified wood flour. After being mixed for about 15 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 silane. In this work, the different types of silane addition amount was 1%, and the different KH-550 content was 0.5%, 1.0%, 1.5%, and 2.0% respectively. All of the silane percentages in this study were mass percentages relative to the wood flour content in the formulation.

Preparation of wood flour/PLA composites

The wood flour and PLA (the weight ratio of wood flour to PLA was 3:7) were well mixed for 15 min using a high-speed mixer. Then the final mixture was fed into a co-rotating twin-screw (L/D ratio of 40/1) set at 100 rpm to obtain the granules. The temperatures at each stage were 135-150-170-170-135 °C (from the inlet to the outlet). Finally, the granules were molded by a single-screw extruder. The extrusion temperature profile was 150-170-170-120 °C from the feeder to the mold. The nominal width and thickness of the strip specimens were 10 mm and 3 mm, respectively. The final specimens were moisture conditioned at 23 °C in a 60% RH chamber for one week before determining all the properties.

Fourier transform infrared spectrometer (FTIR)

FTIR spectroscopy was conducted on a Nicolet 6700 FT-IR spectrometer (Thermo Fisher, USA) to provide a detailed report of the functional groups present at the wood flour surface before and after modification by the silane coupling agent. Scans were run at a resolution of 4 cm⁻¹. For each sample, 32 scans were recorded in absorbance units from 4000 cm⁻¹ to 700 cm⁻¹. The spectra were obtained using attenuated total reflectance (ATR).

Morphological characterization

The morphology of the composites was characterized using a QUANTA 200 (FEI, Netherlands) scanning electron microscope (SEM), operating at an acceleration voltage of 10 kV. The samples were cooled in liquid nitrogen, and then broken into pieces. The brittle fracture surfaces were then sputter-coated with gold for SEM observation.

Mechanical properties

All of the mechanical property measurements were performed at room temperature using a CMT-5504 Universal Testing Machine (Shenzhen SANS Test Machine Co., Ltd. China). The tensile strength and elongation at break of the materials were tested according to the ASTM D638-10 method at a crosshead speed of 20 mm/min. The three-point flexural strength was measured according to the ASTM D790-10. A minimum of five specimens were tested to obtain an average value.

Water absorption

The water absorption of the materials was evaluated according to the ASTM D570-98 (Reapproved 2005). The specimens were dried at 50 °C for 24 h, then cooled in desiccators and weighed (W_1) quickly. The dried specimens were immersed in distilled water at 23 °C for 24 h. Then, the specimens were removed from the distilled water and placed on a dry filter paper to remove the excess free water on the specimen surfaces. The wet weight (W_2) was immediately measured. The water absorption of the materials was calculated as follows: water absorption = $(W_2 - W_1)/W_1 \times 100\%$. All of the tests were replicated five times to get an average value.

RESULTS AND DISCUSSION

Characterization of Silane Modified Wood Flour

In order to make the modified changes more visible, a larger magnification of two interest ranges of the FTIR wavenumber for unmodified wood flour and modified wood flour are shown in Fig. 2. In Fig. 2a, the broad peak that occurs at 3400-3200 cm^{-1} is associated with -OH stretching in hydroxyl groups, originating mainly from cellulose (Stark *et al.* 2004; Dominkovics *et al.* 2007; Deka and Maji 2010) in wood flour. The intensity of absorption for hydroxyl groups of modified wood flour decreased, indicating that the hydroxyl groups were consumed in the modification process as expected. Besides the decrease in the intensity of the hydroxyl vibration, the shapes of the absorption peaks became narrower due to the decrease in the number of hydrogen bonds formed between the hydroxyl groups (Dominkovics *et al.* 2007).

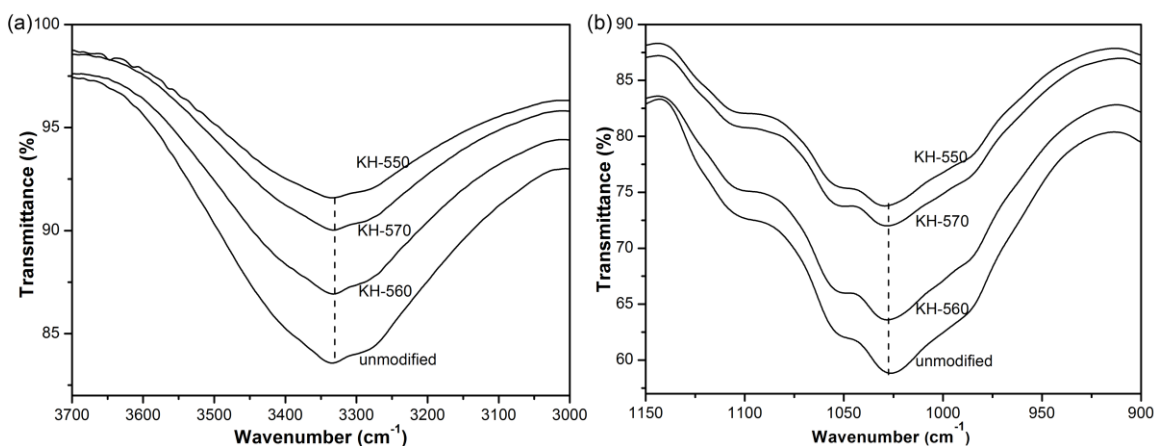


Fig. 2. FT-IR spectra of wood flour modified by different types of silane

The peak at 1026 cm^{-1} shown in Fig. 2b is assigned to C-O stretching in the primary alcohols of lignin in wood flour. Similar to the changes of hydroxyl absorption shown in Fig. 2a, less intense vibration characteristics for the modified wood flour can be detected in the spectra at the corresponding range of 1026 cm^{-1} , *i.e.*, the number of primary alcohols on the surface of wood flour were reduced. The peaks at 3331 cm^{-1} and 1026 cm^{-1} were greatly diminished for each of the modified wood flours, indicating a reduction in polarity at the surface of wood flour.

It may be concluded from this analysis that one can successfully modify wood flour, causing a significant reduction in the polarity of wood flour, which is a benefit for blending with PLA. Moreover, as shown in Fig. 2, the effect of KH-550 modification was much greater than that of other silanes because the KH-550 modified wood flour has fewer polar hydroxyl groups than other wood flour. This means that the KH-550 modified wood flour would have better compatibility with PLA and the mechanical properties of final composites would be improved.

Morphology of Silane Modified Wood Flour/PLA Composites

Effect of silane types on the morphology of wood flour/PLA composites

The mechanical properties of blends are closely related to their morphology and the wettability between the hydrophilic wood flour and hydrophobicity PLA. Figure 3 shows the morphology of wood flour/PLA composites with different types of silane as the surface modifier. As can be seen from Fig. 3, different types of silane modifiers had different effects on the interfacial modification of wood flour/PLA composites. As shown in Fig. 3(a), the clear boundary between the wood flour and the PLA matrix indicated the non-wettability of wood flour/PLA composites prepared with unmodified wood flour. Both the clear exposed and irregularly distributed wood flour in the PLA matrix demonstrated the lack of compatibility of these two components in composites, *i.e.*, there was a poor interaction between the wood flour and PLA.

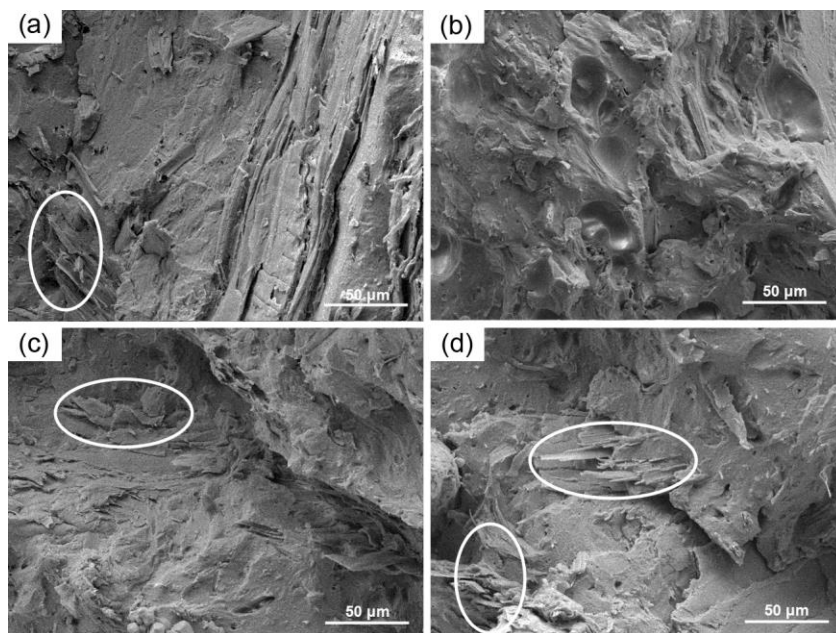


Fig. 3. SEM images of wood flour/PLA composites with different types of silane, (a) unmodified; (b) KH-550; (c) KH-560; (d) KH-570

Unlike the composites prepared with unmodified wood flour, the silane modified wood flour/PLA composites had a better morphology with less exposed wood flour, which indicated that the silane was an effective modifier for the improvement of compatibility between wood flour and PLA. This must be related to the decrease in surface tension that was caused by the disappearance of free hydroxyl groups from the

surface of the modified wood flour. Comparing the morphology of the composites modified by KH-550, KH-560, and KH-570, it was clear that the morphology of composites modified by KH-550 was smooth and there was no visible boundary observed in the morphology. However, the morphologies of the composites modified by KH-560 and KH-570 were coarse, and the aggregations of wood flour, marked by the white circles, were apparent (Figs. 3c and d). All of these observations indicated poor compatibility between wood flour and PLA.

In view of these analyses, the best modification effect was achieved by KH-550. There was no clear phase interface or boundary. This implied that KH-550 may be more effective for improving the interface interaction between wood flour and the PLA matrix, which could, in turn, improve the mechanical properties of wood flour/PLA composites.

Effect of KH-550 content on the morphology of wood flour/PLA composites

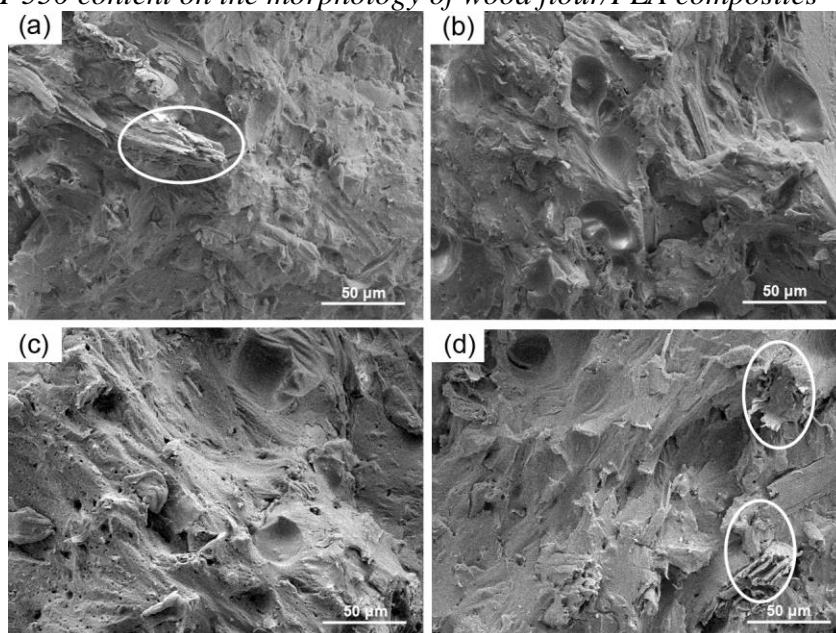


Fig. 4. SEM images of wood flour/PLA composites with different KH-550 contents, (a) 0.5%; (b) 1.0%; (c) 1.5%; (d) 2.0%

Figure 4 shows the morphologies of wood flour/PLA composites with different KH-550 content. Unlike the morphology of unmodified wood flour/PLA composites, the morphology of KH-550 modified wood flour/PLA composites had no visible gaps between the wood flour and PLA matrix, suggesting better interfacial adhesion for modified composites compared to the unmodified composites. As the content of KH-550 increases, the morphology of the composites also changes. When the KH-550 content was 0.5% (Fig. 4a), the morphology of the composites was coarse and wood flour particles, marked by white circles, can be seen in the PLA matrix, exhibiting the weak interaction between wood flour and PLA matrix. When the content of KH-550 reached 1.0% (Fig. 4b), the morphology of the composites became smooth and the visible wood flour particles disappeared, *i.e.*, the wood flour particles were enveloped by the PLA matrix. With the further increase of the content of KH-550 (Fig. 4c), the morphology also became smooth and there was no obvious phase interface, suggesting that interfacial adhesion had been achieved between the fillers and PLA matrix.

The smooth morphology demonstrated the improvement of the compatibility between the wood flour and PLA matrix. Of course, the improved compatibility will enhance the mechanical strength and reduce the water absorption of the wood flour/PLA composites. However, when the content of KH-550 was 2.0% (Fig. 4d), the morphology turned back to coarse and exposed wood flour, marked by the white circles, can be observed. These results indicate that the use of a moderate silane modifier was beneficial for the improved compatibility of wood flour/PLA composites.

Mechanical Properties of Silane Modified Wood Flour/PLA Composites

Effect of silane types on the mechanical properties of wood flour/PLA composites

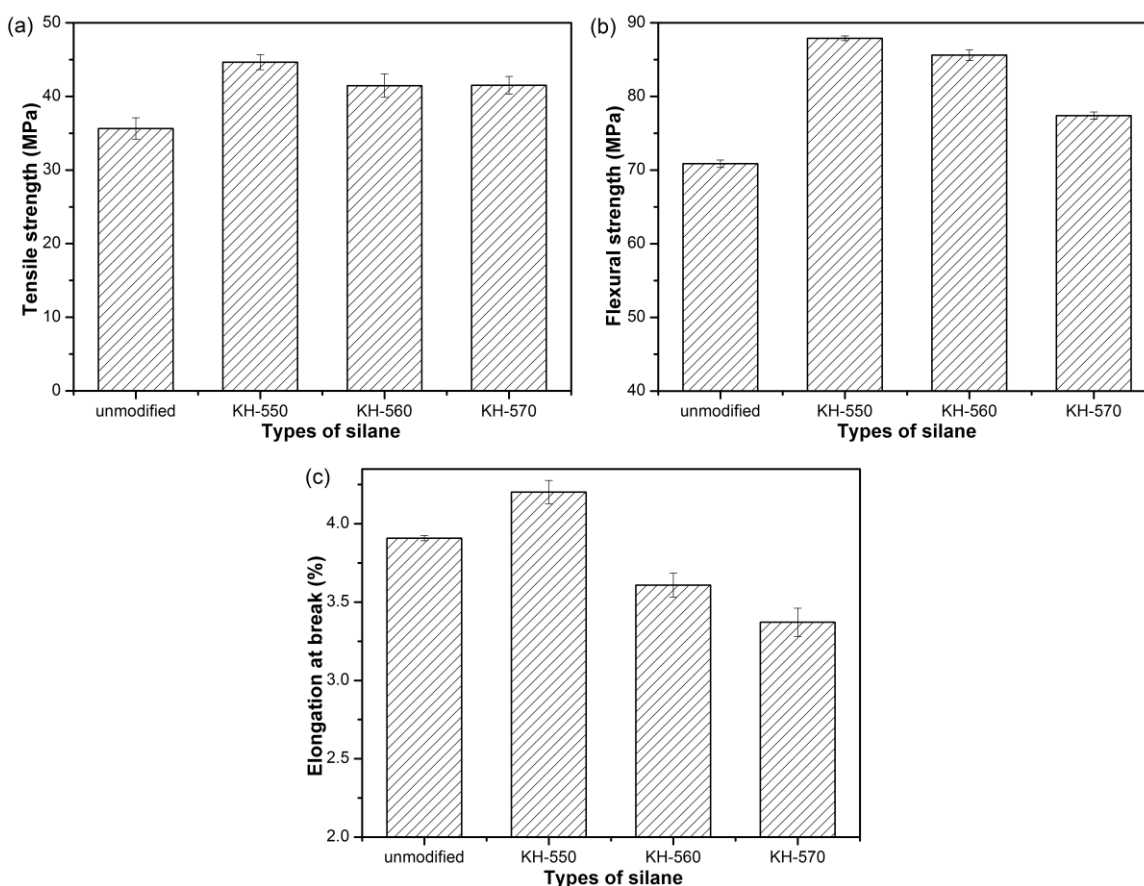


Fig. 5. Mechanical properties of wood flour/PLA composites with different types of silane

Figure 5 illustrates the tensile strength, flexural strength, and elongation at the break of wood flour/PLA composites with and without silane coupling agent treatment. The composites prepared by modified wood flour exhibited better mechanical properties than that of composites prepared by unmodified wood flour.

The mechanical properties exhibited a dependence on the interfacial adhesion of the composites. A better interfacial adhesion enhanced the mechanical properties. The morphological analysis results demonstrated that the surface treatment of wood flour with a silane coupling agent improved the compatibility of the composites. The improvement of compatibility might result in an enhanced interaction between the wood flour and PLA

matrix, *i.e.*, the interfacial adhesion of the modified wood flour/PLA composites would increase compared to the unmodified ones. In this case, the load transfer capacity of the fillers was enhanced, and more energy was needed to distribute the interaction between each component of the composites. As a result, the mechanical strengths of modified wood flour/PLA composites increased compared to that of the unmodified composites.

As shown in Figs. 5a and b, the mechanical strengths of the modified composites were indeed higher than the unmodified ones. For the KH-550 modified composites, the tensile strength were increased from 35.6 to 44.6 MPa, which corresponded to a 25.3% increase, and the flexural strength were increased from 70.8 to 87.9 MPa, which corresponded to an increase of 24.2%. The mechanical strengths of the blends modified by KH-560 and KH-570 were slightly lower than that of the KH-550 modified composites. Nevertheless, the mechanical strengths of these two blends were higher than the unmodified ones.

Figure 5c shows the elongation at break of the unmodified and modified wood flour/PLA composites. Comparing with the unmodified wood flour/PLA composites, the KH-550 modified composites exhibited a better elongation at break, while the KH-560 and KH-570 modified composites exhibited lower elongation at break than the unmodified ones. The compatibility of KH-550 modified composites was improved greatly, and the filler particles of wood flour were better enveloped by the polymer matrix. As a result, the stress concentration caused by the wood flour was reduced, increasing the deformation of the composites before the failure of the materials. Therefore, the KH-550 modified wood flour/PLA composites showed an increased elongation at break. Wood flour is a natural polymer with high crystallinity, which led to the stiffness of this filler. Although the KH-560 and KH-570 silane improved the compatibility of composites, the effects were not obvious. The crosslinking network and aggregations formed by the stiff wood flour prevented the deformation of the materials, resulting in a decrease of elongation of the composites.

Effect of KH-550 content on the mechanical properties of wood flour/PLA composites

Figure 6 shows the mechanical properties of wood flour/PLA composites when the wood flour was modified by different contents of KH-550. The tensile strength, flexural strength, and elongation at break of the composites exhibited the same trend. These three parameters (Fig. 6) increased first and then decreased, and they reached a maximum of 49.8 MPa, 90.6 MPa, and 6.14%, respectively, at a KH-550 content of 1.5%. As known from the above discussion in section 3.2.2, the wood flour/PLA composites exhibited the greatest compatibility when the KH-550 content was 1.5%. This meant that the interaction between the wood flour and PLA chains was stronger when the KH-550 content was 1.5% than at other concentrations. Therefore, the mechanical properties of the composites reached the maximum at the KH-550 content of 1.5%. With the increase of KH-550 content, more hydroxyl groups of wood flour were substituted by the KH-550. The KH-550 played a bridging role between the wood flour and PLA matrix, thus the interfacial adhesion between wood flour and PLA was increased with the increase of KH-550 content. The interaction between wood flour and PLA was also improved with the increase of KH-550 content. At this concentration the wood flour was better enveloped by the PLA matrix. As a result, a load placed on the blends was better transferred by the wood flour particles. The mechanical strength of the wood flour/PLA composites was improved with increased KH-550 content. With the increase of the interfacial adhesion between the two components of the composites, there was more intermolecular force per

unit area between the wood flour and PLA chains to prevent the failure of the composites. Thus, it had a larger deformation before the break of the composites, *i.e.*, the elongation at break of the composites increased with an increase of the content of KH-550.

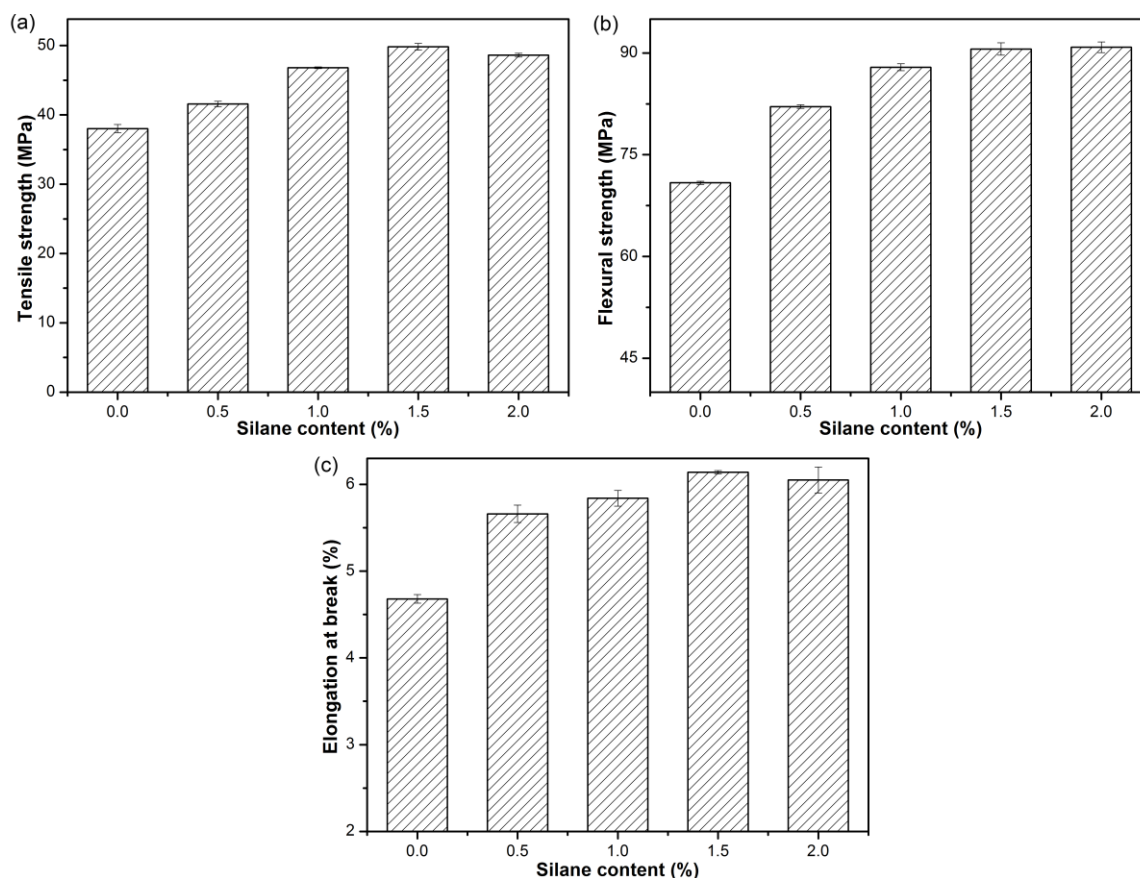


Fig. 6. Mechanical properties of wood flour/PLA composites with different KH-550 contents

When the KH-550 content was higher than 1.5%, the mechanical strength and elongation at break were slightly decreased. This is probably because the content of KH-550 reached saturation at the interface of the blends, the intermolecular distances between the wood flour and PLA matrix were increased by the KH-550, and the intermolecular interaction was reduced, as well as the interaction of wood flour, silane coupling agent, and PLA. As a result, the mechanical properties of the composites are poorer than that of the composites with 1.5% silane content. In addition, the remaining $\text{R}'\text{-Si}(\text{OH})_3$ species have an interaction with PLA and WF, interfering the bonding potential of PLA-Si-O-wood flour (Lee *et al.* 2008). Therefore, the mechanical strength at 2% silane was lower than that at 1.5% silane.

Water Absorption of Silane Modified Wood Flour/PLA Composites

Effect of silane types on the water absorption of wood flour/PLA composites

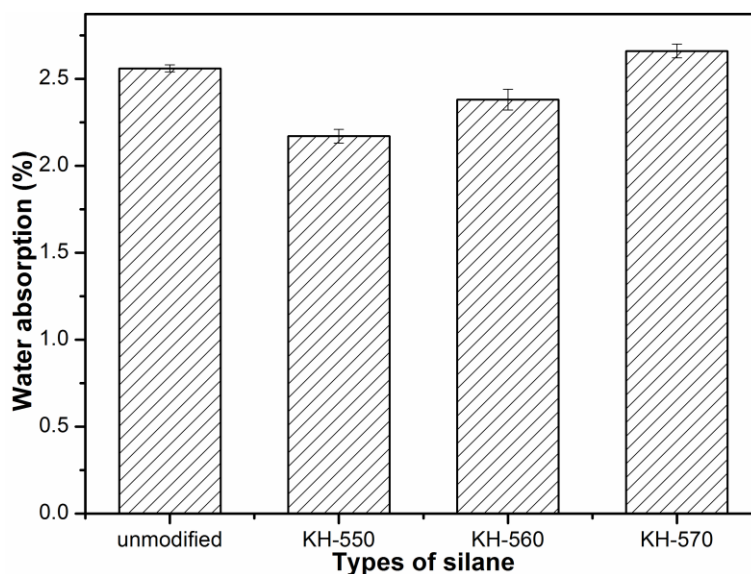


Fig. 7. Water absorption of wood flour/PLA composites with different types of silane

Wood flour is a natural hydrophilic polymer with a large number of hydroxyl groups in its molecular chains. When the materials prepared by wood flour are used in a humid environment, hydrogen bonds will be formed between the hydrogen groups of wood flour and the moisture in the humid environment, which will increase the water absorption and reduce the lifetime of the materials. Figure 7 shows the water absorption of the unmodified and modified wood flour/PLA composites. As can be seen from Fig. 7, the water absorption of the composites modified by KH-550 and KH-560 were lower than the unmodified ones, while the KH-570 modified composites had slightly higher water absorption than that of the unmodified composites. Obviously, the KH-550 was the most effective modifier to enhance the water resistance of the wood flour/PLA composites. The compatibility of the wood flour/PLA composites modified by KH-550 was improved extensively, and the interfacial adhesion between the two phases of the composites was enhanced. Consequently, the enhanced adhesion prevented water from permeating the interior of the composites.

In addition, as can be seen from Fig. 3b, the morphology of the KH-550 modified composites was smooth, implying that the wood flour particles were enveloped better by the hydrophobic PLA matrix. The number of hydroxyl groups on the surface of wood flour modified by KH-550 was greatly reduced when compared with the unmodified ones (Fig. 2a). Therefore, the water resistance of the KH-550 modified wood flour/PLA composites was enhanced.

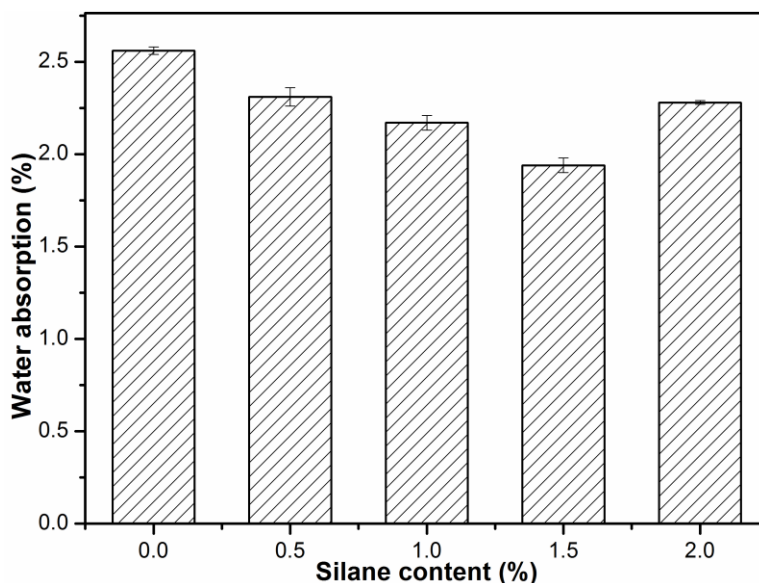
Effect of KH-550 content on the water absorption of wood flour/PLA composites

Fig. 8. Water absorption of wood flour/PLA composites with different KH-550 contents

Figure 8 illustrates the influence of KH-550 content on the water absorption of the modified wood flour/PLA composites. With the increase of the content of KH-550, the water absorption first decreased and then increased, and it reached a minimum value of 1.94% at the content of 1.5%. This phenomenon corresponded to the compatibility of the modified wood flour/PLA composites with different contents of KH-550. As the KH-550 content increased, the compatibility of the blends got better, the interaction between wood flour and PLA increased, and more wood flour particles were enveloped by the PLA matrix. As a result, the opportunity for the water to permeate into the composites decreased. As known from the discussion in section 3.2.2, the wood flour/PLA composites had the highest compatibility when the KH-550 content was 1.5%. Therefore, the water absorption of the composites reached a minimum value at a content of 1.5%. With the further increase of the content of KH-550, the excess KH-550 could not improve the interaction between the wood flour and PLA matrix, and the wood flour was prone to slip from the PLA matrix, resulting in the permeation of water (Deka and Maji 2010). Hence, when the KH-550 content was in excess, the water resistance of the composites decreased.

CONCLUSIONS

1. The polarity of the wood flour was extensively reduced by treatments with silane coupling agents because the active hydroxyl groups at the surface of the wood flour were replaced by silanol groups.
2. The decreased polarity of wood flour increased the affinity between wood flour and poly-(lactic acid) (PLA), leading to considerable changes in the interactions between the wood flour and PLA matrix, and increased compatibility between wood flour and the PLA.

3. The silane modification caused a considerable improvement of mechanical properties and a reduction of water absorption.
4. KH-550 silane was the most effective modifier to improve the compatibility, mechanical properties, and water resistance of the wood flour/PLA composites.
5. With the increase of KH-550 content, the mechanical strengths of the composites first increased then decreased, and reached the maximum value at a content of 1.5%. As the KH-550 content increased, the water absorption also increased at first but then lessened.

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