

# Modification of Lignin with Silane Coupling Agent to Improve the Interface of Poly(L-lactic) Acid/Lignin Composites

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To improve the mechanical properties of lignin-filled poly(L-lactic) composites, three silane coupling agents, 3-aminopropyltriethoxysilane (KH550),  $\gamma$ -glycidoxypropyltrimethoxysilane (KH560), and g-methacryloxypropyltrimethoxysilane (KH570), were treated systematically with different solvents to modify the interfacial connections. The treatment of lignin with 2 wt.% aqueous KH550 solution was proved to be the most successful. Chemical bonding between the filler and the matrix was formed, according to the FTIR spectra. Furthermore, scanning electron microscope images showed that such treated lignin particles dispersed well in the composites. The tensile strength and Young's modulus of the composite improved significantly from 55.1 and 1589 MPa to 67.0 and 1641 MPa, respectively, with 5 wt.% treated lignin addition. Although its elongation at break decreased from 20.3 to 12.4% after 5 wt.% of the treated lignin was added, it was still better than that of poly(L-lactic acid) without any additive (10.3%).

*Keywords:* Poly(L-lactic) acid/lignin bio-composites; Silane coupling agent; Interfacial modification; Mechanical properties

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## INTRODUCTION

The ongoing depletion of fossil fuel reserves and increasing environmental concerns have resulted in more and more production of fully degradable bio-composites (Zhang and Sun 2004). Degradable bio-composites can be broadly defined as composite materials consisting of natural fillers and biopolymers such as poly( $\epsilon$ -caprolactone), poly(lactic acid), or polyhydroxyalkanoates (Chun *et al.* 2012). Poly(lactic acid) (PLA), which is a racemic mixture, is one of the most promising biopolymers commercially available today (Li *et al.* 2003; Bhardwaj and Mohanty 2007). It is primarily produced *via* the ring-opening polymerization of lactides, which themselves are derived from agricultural products such as corn, beet, or rice (Yao *et al.* 2011). PLA is also considered easy to process in industrial plastic applications (Rangari and Vasanthan 2012). However, its high cost, poor toughness, low glass transition temperature (ranging from 55 to 65 °C), and uncontrollable biodegradation rate have severely limited its application (Dorati *et al.* 2007; Wu 2008; Yeh *et al.* 2008). Developing PLA-based composites with low-cost, renewable, natural fillers with enhanced properties and lower price provides an important class of new biodegradable materials.

Lignin is the second most abundant natural polymer on Earth, after cellulose (Dorati *et al.* 2007; Yeh *et al.* 2008; Rangari and Vasanthan 2012). It serves as a

continuous matrix component in plant cell walls, providing mechanical strength and structural support (Wang *et al.* 2001; El-Wakil 2009; Yu *et al.* 2010; Ouyang *et al.* 2012). Lignin and derivatives chemistry is applicable for use in composites because they have small particle size, are hydrophobic, and can form chemical connections with other materials. While most lignin has been burned for energy recovery for many years (Pilla *et al.* 2008; Chen *et al.* 2010; Wang *et al.* 2011), this produces large amounts of carbon dioxide and wastes a useful natural resource. Researchers (Li *et al.* 2003; Ouyang *et al.* 2012) prepared completely degradable bio-composites by adding lignin to optically pure poly(L-lactic acid) (PLLA). However, the mechanical properties, such as the tensile strength and the elongation at break were obviously decreased compared to the PLLA by itself, mainly because of bad interfacial properties.

It is well known that the mechanical properties of composites are closely related to the interfacial connection between the filler and the matrix (Yu *et al.* 2010) and that interfacial adhesion can be improved by adding a reactive compatibilizer or coupling agent (Wang *et al.* 2001; El-Wakil 2009). Silane coupling agents such as 3-aminopropyltriethoxysilane (KH550),  $\gamma$ -glycidoxypropyltrimethoxysilane (KH560), and  $\gamma$ -methacryloxypropyltrimethoxysilane (KH570) have been widely used (Pilla *et al.* 2008; Pilla *et al.* 2009; Chen *et al.* 2010; Wang *et al.* 2011; Zhong *et al.* 2011; Yu *et al.* 2012) and have also been applied in PLA and inorganic composites (Rakmae *et al.* 2012) with natural fillers, such as coconut shell powder (Chun *et al.* 2012), kenaf fiber (Huda *et al.* 2008), cellulose fiber (Frone *et al.* 2011), and wood flour (Pilla *et al.* 2009). Silane coupling agents can be hydrolyzed to produce silanol groups that interact with the filler (Dupraz *et al.* 1996; Zhang *et al.* 2005; Pilla *et al.* 2008). Amine groups in KH550 or epoxy groups in KH560 can react with the terminal carboxylic groups and hydroxyl groups of PLA, respectively. KH550 and KH560 act as bridges to link the PLA matrix with the filler, as shown in Fig. 1. To the best of our knowledge, the use of silane coupling agents as compatibilizers in PLLA/lignin composites as well as the effect of solvent on the properties of the composites have not been previously studied. In this work, the effects of KH550, KH560, and KH570 with various solvents on the interfacial properties of PLLA/lignin bio-composites and their mechanical behavior were comparatively investigated.

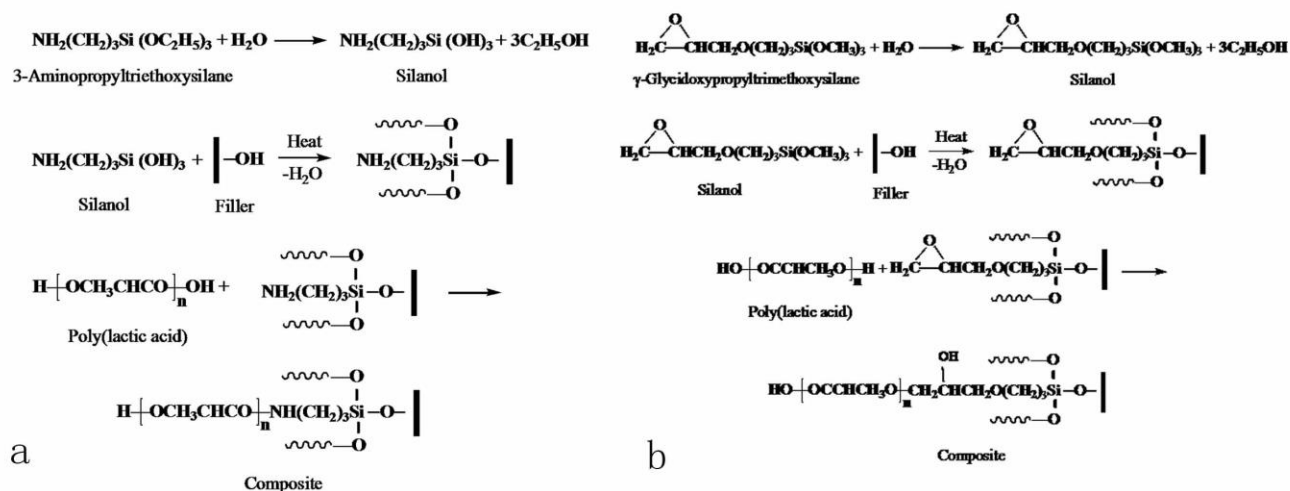


Fig. 1. Schematic of the reactions between (a) KH550 and (b) KH560 with filler and PLA

## EXPERIMENTAL

### Materials

Poly(L-lactic) acid (2003D, D-isomer molar content of 4.3%, MW of  $2.53 \times 10^5$  g/mol) was purchased from Nature Works, USA. Lignin was supplied by the Shandong Shengquan Croup Co., Ltd. It was isolated from corn stalk under high pressure at pH 5.35, contained 1.24% ash, and had an electrical conductivity of 200  $\mu$ S/cm. The lignin was ground into a powder and sieved with 60-mesh screens. Both PLLA and lignin samples were dried at 80 °C for 12 h before use. KH550, KH560, KH570, and all other reagents were of analytical grade and were used without further purification.

### Methods

#### *Surface treatment of lignin with silane coupling agent*

Set amounts of silane coupling agent were dissolved in water, ethanol, or a water-ethanol mixture to make the silane coupling agent solutions. The prepared solution was then slowly transferred onto the dried lignin powder with continuous stirring. The treated lignin was dried at 105 °C for 12 h. The formulations of the silane coupling agent and the treated lignin samples are summarized in Table 1.

#### *Preparation of PLLA/lignin bio-composites*

Dried PLLA granules and lignin or silane-treated lignin powders were weighed and placed in plastic bags to be manually mixed. The mixture was subsequently fed into a twin-screw extruder (SHJ-30, China) operating at a screw speed of 120 rpm at 120 to 165 °C from hopper to die. The extruded splines were chopped into pellets and dried in a convection oven first at 55 °C for 24 h and then at 80 °C for 12 h. The dried pellets were subsequently injected into an injection-molding machine (NISSEIPS40E5A5E, Japan). The melt temperature was set to 160 to 170 °C, the mold temperature was set to 23 °C, and the cooling time was 40 s. Finally, the samples were aged for one week at room temperature before being tested.

**Table 1.** Formulations of Lignin Samples Treated with Silane Coupling Agents

Silane	Silane Content <sup>1</sup>	Water: Ethanol (wt:wt)	Lignin Sample
KH550	25 wt.%	95:5	Lignin treated with 25 wt.% KH550 with water-ethanol solvent
KH550	2 wt.%	100:0	Lignin treated with 2 wt.% KH550 with water solvent
KH550	2 wt.%	0:100	Lignin treated with 2 wt.% KH550 with ethanol solvent
KH550	2 wt.%	95:5	Lignin treated with 2 wt.% KH550 with water-ethanol solvent
KH560	2 wt.%	95:5	Lignin treated with 2 wt.% KH560 with water-ethanol solvent
KH570	2 wt.%	95:5	Lignin treated with 2 wt.% KH570 with water-ethanol solvent

<sup>1</sup> wt.% based on dry weight of lignin

#### *Characterization and analysis*

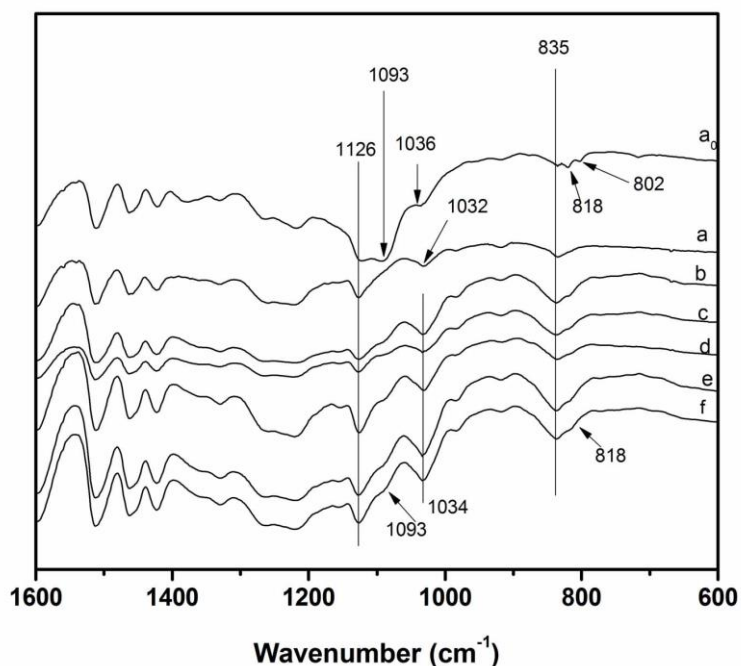
The tensile strength was measured according to ASTM D638 (1999) at room temperature (23±2 °C) using an Instron Universal Tester (Model 3365, Shimadzu AGS-J, Japan) at a tensile speed of 50 mm/min. At least five replicates were tested, and the average values were recorded. Fourier transform infrared spectroscopy (FTIR) was performed in a Nicolet-5700 spectrometer by direct transmittance using the KBr pellet

technique. Each spectrum was recorded over four scans in the range from 4000 to 400  $\text{cm}^{-1}$  with a resolution of 2  $\text{cm}^{-1}$ . The thermal stabilities of the lignin samples before and after treatment were measured using an EXSTAR 6000 instrument (Japan) running dynamic scans from 30 to 600  $^{\circ}\text{C}$  at 10  $^{\circ}\text{C}/\text{min}$  in an air atmosphere. The morphologies of the lignin samples before and after treatment, and the fracture surfaces from the tensile tests, were examined with a scanning electron microscope (SEM, Fei Inspect FEI, Netherlands) at an accelerating voltage of 5.0 kV. The particle distributions in the original and treated lignin samples were measured by a laser particle analyzer (ZEN3690, Malvern, UK). All samples were dried at 80  $^{\circ}\text{C}$  for 12 h before analysis.

## RESULTS AND DISCUSSION

### Lignin Surface Treatment

The FTIR spectra of the original and silane coupling agent-treated lignin are shown in Fig. 2. The absorptions at 1126 and 835  $\text{cm}^{-1}$  can be attributed to C-H deformation vibrations of lignin. In spectrum (a), the peak at 1032  $\text{cm}^{-1}$  is due to the primary alcohol C-O stretching vibrations of lignin.

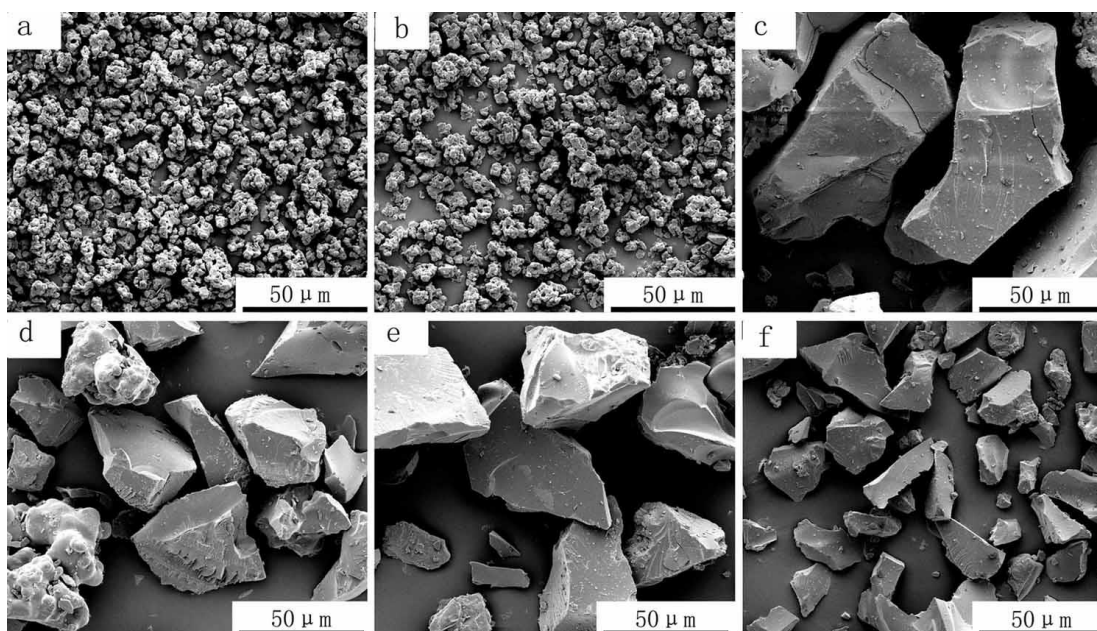


**Fig. 2.** FTIR spectra of original and treated lignin: (a<sub>0</sub>) lignin treated with 25 wt.% KH550 using water-ethanol as the solvent, (a) lignin, (b) lignin treated with 2 wt.% KH550 using water as the solvent, (c) lignin treated with 2 wt.% KH550 using ethanol as the solvent, (d) lignin treated with 2 wt.% KH550 using water-ethanol as the solvent, (e) lignin treated with 2 wt.% KH560 using water-ethanol as the solvent, and (f) lignin treated with 2 wt.% KH570 using water-ethanol as the solvent.

To better observe the interactions between lignin and the silane coupling agent, the FTIR spectrum of lignin treated with 25 wt.% KH550 using water-ethanol as the solvent was investigated (spectrum a<sub>0</sub>). Compared with the spectrum of original lignin (spectrum a), two new peaks at 1093 and 818  $\text{cm}^{-1}$  appeared in the spectrum of the treated lignin, corresponding to asymmetric and symmetric stretching of the Si-O-C bond,

indicating there was chemical interaction between the silane and lignin. Furthermore, the peak of primary alcohol C-O of lignin shifted from 1032 to 1036  $\text{cm}^{-1}$  after treatment because of the enlarged steric hindrance of the silanol linked to the lignin. The weak peak at 802  $\text{cm}^{-1}$  in spectrum (a) is associated with the deformation vibrations of N-H in the KH550 silane. When the amount of silane was decreased to 2 wt.%, the chemical interactions between the lignin and the silane coupling agents KH550, KH560, and KH570 still existed, as shown in spectra (b) to (f).

After the lignin was treated with KH560 or KH570, its microstructure was seriously changed, as shown in Fig. 3. The surface of the lignin treated with KH550 using only water as the solvent (Fig. 3b) had the smallest particle size, which was further confirmed by the laser particle analysis described in Table 2.

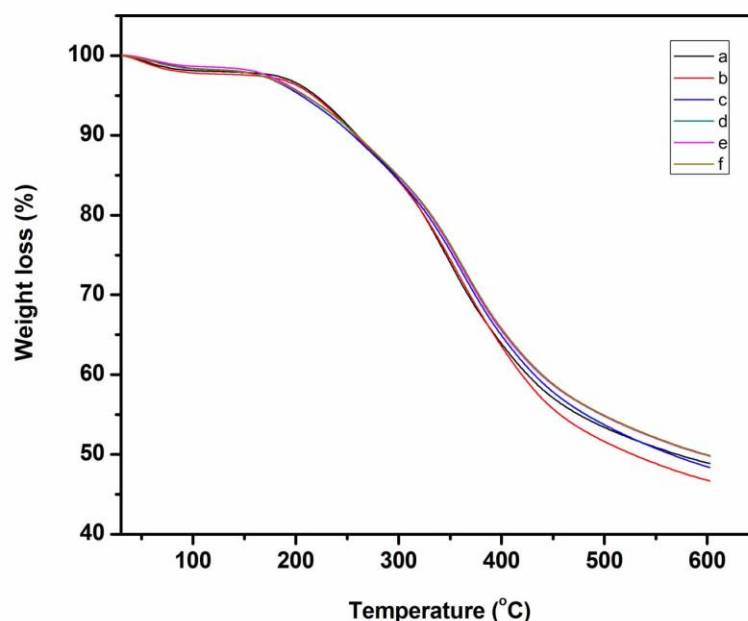


**Fig. 3.** SEM images of lignin and silane coupling agent-treated lignin: (a) lignin, (b) lignin treated with 2 wt.% KH550 using water as the solvent, (c) lignin treated with 2 wt.% KH550 using ethanol as the solvent, (d) lignin treated with 2 wt.% KH550 using water-ethanol as the solvent, (e) lignin treated with 2 wt.% KH560 using water-ethanol as the solvent, and (f) lignin treated with 2 wt.% KH570 using water-ethanol as the solvent

**Table 2.** Particle Distributions of Lignin and Silane-Treated Lignin

Lignin Sample	D50 ( $\mu\text{m}$ )	D(4,3) ( $\mu\text{m}$ )	D3 ( $\mu\text{m}$ )	D97 ( $\mu\text{m}$ )	Surface Area ( $\text{m}^2/\text{cm}^3$ )
Lignin	2.164	4.409	0.241	15.973	4.847
Lignin treated by 2 wt.% KH550 using water as the solvent	2.330	4.662	0.246	16.599	4.663
Lignin treated by 2 wt.% KH550 using ethanol as the solvent	48.228	99.820	4.107	362.935	0.383
Lignin treated by 2 wt.% KH550 using water-ethanol as solvent	36.354	55.211	2.858	228.740	0.453
Lignin treated by 2 wt.% KH560 using water-ethanol as the solvent	34.967	50.832	2.688	213.809	0.471
Lignin treated by 2 wt.% KH570 using water-ethanol as the solvent	35.650	53.418	3.132	221.348	0.441

The thermal stability of the treated lignin did not clearly change, according to the TGA curves shown in Fig. 4.



**Fig. 4.** TGA curves of lignin and silane coupling agent-treated lignin: (a) lignin, (b) lignin treated with 2 wt.% KH550 using water as the solvent, (c) lignin treated with 2 wt.% KH550 using ethanol as the solvent, (d) lignin treated with 2 wt.% KH550 using water-ethanol as the solvent, (e) lignin treated with 2 wt.% KH560 using water-ethanol as the solvent, and (f) lignin treated with 2 wt.% KH570 using water-ethanol as the solvent

### PLLA/Lignin Bio-Composites Modified with Various Silane Coupling Agents

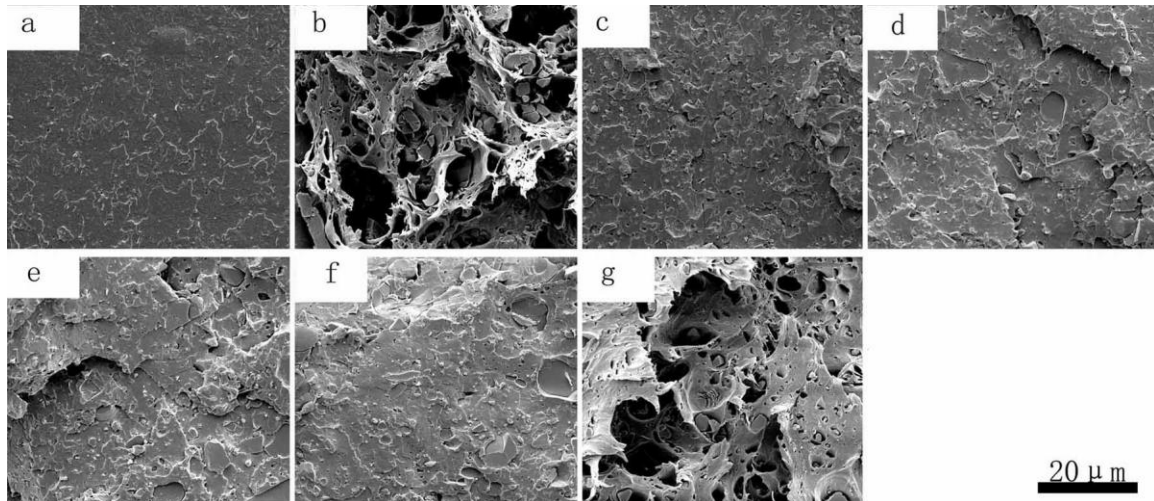
The effects of various silane coupling agents on the tensile properties and morphologies of the PLLA/lignin bio-composites were investigated with 20 wt.% lignin content in the bio-composites.

Generally, the interfacial connection between PLLA and lignin or other fillers were bad (Frone *et al.* 2011; Chun *et al.* 2012). Compared with pure PLLA (Fig. 5a), when untreated lignin was added, agglomerated lignin particles appeared and caused phase separation, as shown in Fig. 5b. This demonstrated the poor miscibility of lignin with the PLLA matrix and it was consistent with the findings of Ouyang *et al.* (2012). Pretreatment of lignin with KH550 or KH560 considerably improved the miscibility between the PLLA and lignin (Figs. 5c to 5f) because KH550 and KH560 react with the hydroxyl groups on the surfaces of the lignin particles to form covalent or hydrogen bonds with the PLLA matrix. As can be seen in Fig. 5g, only KH570 improved the dispersion of lignin in the PLLA matrix. According to Fig. 2f, chemical interactions formed between lignin and KH570. It is reasonable to suggest that the intra- or intermolecular hydrogen bonds among the lignin were broken by KH570 and that the dispersion of lignin in the PLLA matrix was improved. However, KH570 could not improve the miscibility between the PLLA and lignin, as shown in Fig. 5g.

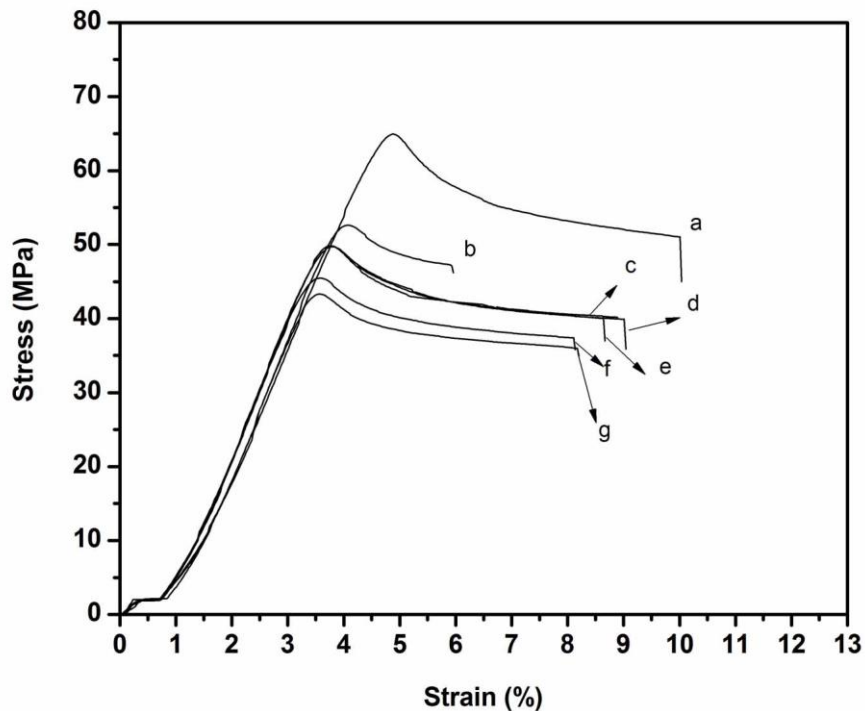
Figure 6 shows the stress-strain curves of the PLLA/lignin bio-composites with 20 wt.% unmodified or treated lignin. The direct blending of the original lignin/PLLA composite led to a sharp decrease in its tensile strength, as seen in Fig. 5g, because of weak adhesion and poor dispersion of the lignin in the hydrophobic PLLA matrix



(illustrated in Fig. 5b). After the lignin was treated with a silane coupling agent, the tensile strength of the composites increased to a certain extent. Compared with pure PLLA or the PLLA/unmodified lignin bio-composites (Fig. 6g), the PLLA/lignin treated with KH550 composite exhibited better strength and toughness (Figs. 6c to 6e).



**Fig. 5.** SEM images of tensile-fractured surfaces of PLLA/lignin bio-composites: (a) pure PLLA, (b) PLLA/lignin composite, (c) PLLA/lignin treated with KH550 using water as the solvent, (d) PLLA/lignin treated with KH550 using ethanol as the solvent, and (e), (f), and (g), PLLA/lignin treated with KH550, KH560, and KH570, respectively, using water-ethanol as the solvent.



**Fig. 6.** Stress-strain curves of PLLA/lignin bio-composites modified with various silane coupling agents: (a) pure PLLA, (b) PLLA and lignin treated with KH560 using water-ethanol as solvent, (c) PLLA and lignin treated with KH550 using ethanol as solvent, (d) PLLA and lignin treated with KH550 using water as solvent, (e) and (f) PLLA and lignin treated with KH550 and KH570, respectively, using water-ethanol as solvent, and (g) PLLA and original lignin

The PLLA/lignin composites treated with KH560 were strong but brittle (Fig. 6b). KH570 had no obvious effect on the tensile strength of such composites, as shown in Fig. 6f. KH550 dissolved in different solvents yielded the same effects on the tensile properties of the composites (Figs. 6c, 6d, and 6e).

According to the above analysis, 2 wt.% KH550 with water as the solvent was adopted for further investigation of the effect of the lignin content on the interfacial properties and tensile strength of the PLLA/treated lignin bio-composites.

### Interfacial Properties and Tensile Strength of PLLA/KH550 Modified Lignin Bio-composites with Various Lignin Contents

SEM images of the tensile fracture surfaces of PLLA/unmodified lignin and PLLA/KH550 treated lignin bio-composites with various lignin contents (10, 20, and 30 wt.%) are shown in Fig. 7. When the lignin content was 10 wt.%, some lignin particles were visible on the tensile fracture surface (Fig. 7a), but the composite became homogeneous when KH550-treated lignin was used, as seen in Fig. 7a: there were nearly no visible lignin particles. When the original lignin loading was raised to 20 or 30 wt.%, the tensile-fractured surfaces (Figs. 7b and 7c) exhibited severe phase separation. However, they were almost homogeneous (Figs. 7b' and 7c') when KH550-treated lignin was applied. KH550 satisfactorily improved the interfacial properties of the PLLA/lignin bio-composite.

Table 3 shows the mechanical properties of the PLLA/lignin bio-composites before and after KH550 modification. Before modification, the tensile strength of the PLLA/lignin bio-composites decreased sharply with increasing lignin content. However, treatment of lignin with KH550 increased the tensile strength of the PLLA/lignin bio-composites. With 5 wt.% lignin, the tensile strength of the modified bio-composites was actually 3.2% higher than that of the pure PLLA. Because of the enhanced interfacial adhesion, an increase in Young's modulus was also detected, regardless of the lignin loading, as shown in Table 3.

As for the elongation at break (Table 3), when the lignin loading was small (5 or 10 wt.%), there was a remarkable improvement in both the unmodified and modified PLLA/lignin bio-composites. It is known that the polymer-matrix plasticity is determined by the flexibility of its constituent polymer chains. When the lignin loading was low, small-sized lignin acted as a plasticizer and increased the elongation at break. For all samples, the elongation at break decreased dramatically after KH550 modification compared to that of the unmodified bio-composites. This was due to enhanced interfacial adhesion, which decreased polymer chain flexibility.

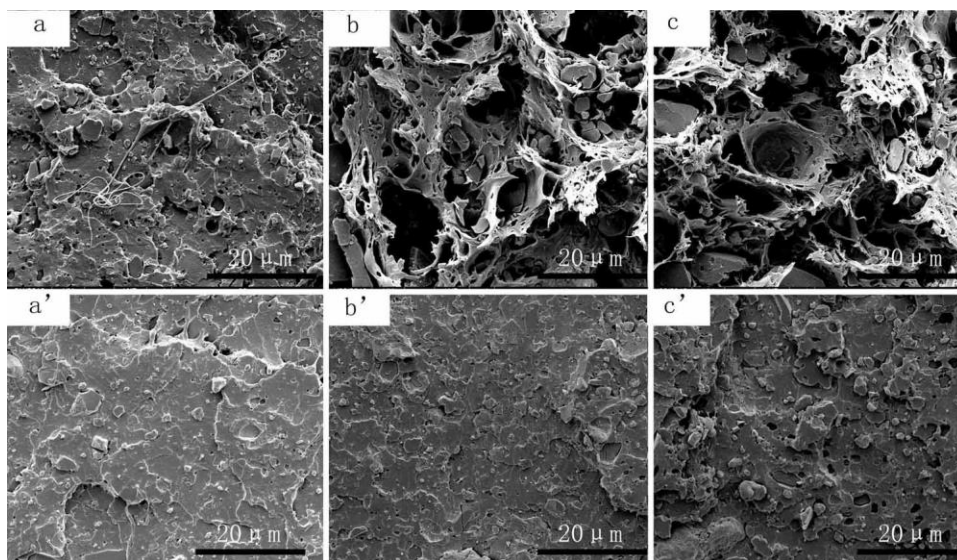
**Table 3.** Tensile Properties of the PLLA/Lignin Bio-Composites With and Without KH550 Modification

Lignin Content <sup>1</sup>	Tensile Strength (MPa)		Young's Modulus (MPa)		Elongation at Break (%)	
	Before	After	Before	After	Before	After
0 wt.%	64.9 ± 0.3	—	1578 ± 15	—	10.3 ± 0.4	—
5 wt.%	55.1 ± 0.2	67.0 ± 0.3	1589 ± 10	1641 ± 9	20.3 ± 0.5	12.4 ± 0.2
10 wt.%	48.6 ± 0.4	60.7 ± 0.2	1586 ± 3	1634 ± 14	17.9 ± 0.5	11.7 ± 0.6
20 wt.%	43.3 ± 0.3	49.7 ± 0.2	1543 ± 19	1629 ± 17	8.0 ± 0.5	7.9 ± 0.2
30 wt.%	38.0 ± 0.1	44.9 ± 0.1	1562 ± 4	1631 ± 3	5.0 ± 0.2	4.7 ± 0.3

<sup>1</sup>based on the weight of the bio-composites



When the lignin content was 10 wt.%, the elongation at break was still 11.7%, higher than that of pure PLLA (10.3%). When the lignin loading was increased to 20 wt.%, the elongation at break decreased to 7.9%, inferior to that of the pure PLLA.



**Fig. 7.** SEM images of tensile-fractured surfaces of PLLA/lignin bio-composites: (a), (b), and (c), PLLA/lignin bio-composites before modification at lignin contents of 10, 20, and 30 wt.%, respectively; (a'), (b'), and (c'), PLLA/lignin bio-composites after modification with KH550 at lignin contents of 10, 20, and 30 wt.%, respectively

## CONCLUSIONS

1. KH550 using water as solvent was shown to be an efficient treatment method for improving the interfacial and mechanical properties of PLLA/lignin bio-composites. With 5 wt.% KH550-modified lignin, the tensile strength, Young's modulus, and elongation at break of the PLLA/lignin bio-composites were increased by 3.2, 4.0, and 20.4%, respectively, compared to those of pure PLLA.
2. KH560 using water-ethanol as solvent can also improve the miscibility of PLLA and lignin, the corresponding composites are strong and brittle.
3. KH570 using water-ethanol as solvent can improve the dispersion of lignin in the PLLA matrix, but had no obvious effect on the tensile strength of such composites.

## ACKNOWLEDGMENTS

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