

EFFECTS OF COMPATIBILIZERS ON THE MECHANICAL PROPERTIES OF LOW DENSITY POLYETHYLENE/LIGNIN BLENDS*

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Abstract Low density polyethylene (LDPE)/lignin blends were prepared using melt blending. Two kinds of compatibilizers, ethylene-vinylacetate (EVA) which is softer than LDPE and polyethylene grafted with maleic anhydride (PE-g-MA) which is harder than LDPE were used to improve the interfacial adhesion. Scanning electron microscope (SEM) was used to investigate the dispersion of lignin in LDPE matrix. The results showed that both of the compatibilizers could improve the interaction between the low density polyethylene and lignin. However, the effects of the two compatibilizers on the mechanical properties of LDPE/lignin blends were different. The elongation at break of the blends was obviously increased by adding EVA, while significant improvement of tensile strength was observed by adding PE-g-MA. Several theoretical models have been used to further analyze the experimental data, combined with the morphological observation of tensile fractured surfaces by SEM.

Keywords: Low density polyethylene (LDPE); Lignin; Compatibilizers; Mechanical properties; Blends.

INTRODUCTION

Lignin, a natural polymer found in wood, is a polyaromatic polyol that is readily available and relatively inexpensive. It exists in plant cell walls, and its amount is only less than that of cellulose in overall natural abundance. Enormous amounts of industrial lignin are produced as byproducts of papermaking. The structure of lignin is dependent on wood species and processing conditions^[1]. Ordinarily, its macromolecular structure is chemically complex and the main monomer units constituting lignin molecules are 2-methoxy-4-propylphenol (guaiacol) in softwood and a mixture of guaiacol and 3,5-dimethoxy-4-propylphenol (syringol) in hardwood. There was effective utilization in lignin by blending with compatible polymers: polyvinyl chloride^[2], polyesters^[3, 4] and polyethers^[5–7]. For example, a novel series of 85% kraft lignin-based thermoplastics has been fabricated for the first time by Li *et al.*^[3].

Because of the different structures between polyolefin and lignin, it will be difficult to blend polyolefin with lignin. As reported by Toriz *et al.*^[8], the blending of polypropylene with unmodified lignin resulted in materials with almost all of mechanical properties reduced. Blending of LDPE with lignin has been studied by Rusu *et al.*^[9] and Alexy *et al.*^[10], whose results also showed a drastic decrease in mechanical properties as compared with those of virgin LDPE. Lignin catalytically grafted to LDPE showed improved mechanical properties^[11]. Kharade and Kale^[12] observed the improved mechanical properties *via* addition of poly(ethylene-co-(acrylic acid)) and a titanate coupling agent. Various polyolefin/lignin blends with acceptable properties were

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achieved by adding copolymers as compatibilizers, which were studied by many researchers^[13–15]. Glasser and co-workers^[16–18] carried out chemical modification of lignin and showed that through the manipulation of the network structure and substituents in lignin, the physical properties of lignin-based materials could be manipulated. Although a lot of work has been done to develop polyolefin/lignin blends, the influence of different compatibilizers on polyolefin and lignin blends is seldom reported.

To better understand the role of compatibilizers and obtain LDPE/lignin blends with various properties for different applications, in this work, two kinds of compatibilizers were chosen, ethylene-vinylacetate (EVA) and polyethylene grafted with maleic anhydride (PE-g-MA), of them EVA is softer than LDPE and PE-g-MA is harder than LDPE. Different interfacial interactions between filler and matrix were investigated through SEM and mechanical properties. Several theoretical models have been used to further analyze the experimental data, combined with the morphological observation of tensile fractured surfaces by SEM. Our work is important for full using of lignin and developing eco-friendly products.

EXPERIMENTAL

Materials

The materials used in this study are shown in Table 1. Two kinds of compatibilizers were used, EVA with 33 wt% VA content and PE-g-MA grafted with 1.2 wt% maleic anhydride.

Table 1. Characteristics of the studied materials

	Trade name	MFI ^a (g/10 min)	Density (g/cm ³)		Producer
LDPE	2426K	4.0	0.92		Lanzhou Petrochemical Corporation
EVA	MB11	45	0.96	$\alpha(\text{VA}) = 33\%$	Sumitomo Chemical Co. Ltd
PE-g-MA		1.3	0.97	$\alpha(\text{MA}) = 1.2\%$	Chenguangzhongyi Technology Co., Ltd
Lignin			1.35		Xuemei paper industry Co. Ltd

MFI^a = Melt flow index (190°C, 2.16 kg)

Samples Preparation

Lignin was first dried in a vacuum oven at 65°C for 24 h before mixing. LDPE/lignin blends were melt-mixed in various proportions using a TSSJ-25 co-rotating twin-screw extruder with a barrel temperature of 130–170°C and the screw speed was 50 r/min. The proportions are summarized in Table 2. For example, 40L+EVA means lignin:EVA:LDPE is 40:20:40. The amount was all based on weight fraction of the whole blends throughout the study. After being pelletized and dried for 12 h at 60°C, dumbbell shaped specimens were prepared by an SZ 100-g injection-molding machine at 180°C with a pressure of 900 kg/cm².

Table 2. The proportions of various blends

Sample	LDPE (wt%)	Lignin (wt%)	EVA (wt%)	PE-g-MA (wt%)
LDPE (pure)	100	0	0	0
10L	90	10	0	0
20L	80	20	0	0
30L	70	30	0	0
40L	60	40	0	0
0L+EVA	80	0	20	0
10L+EVA	70	10	20	0
20L+EVA	60	20	20	0
30L+EVA	50	30	20	0
40L+EVA	40	40	20	0
0L+PE-g-MA	80	0	0	20
10L+PE-g-MA	70	10	0	20
20L+PE-g-MA	60	20	0	20
30L+PE-g-MA	50	30	0	20
40L+PE-g-MA	40	40	0	20

Scanning Electron Microscopy (SEM) Observations

The morphologies of cryogenically fractured specimens and tensile fractured surfaces were examined under an acceleration voltage of 20 kV with a JEOL JSM-5900 LV scanning electron microscope. Before being examined, the specimens of LDPE/lignin blends were cryogenically fractured perpendicular to the flow direction in liquid nitrogen (-170°C), then the fractured surface was coated with a thin layer of gold. The pure lignin was dispersed in solvent and dried before SEM observation.

Mechanical Properties Measurements

Standard tensile tests were performed using an Instron universal tensile testing machine with a cross-head speed of 50 mm/min at room temperature (23°C). The width and the thickness of the dumbbell shaped specimens were about 10.20 mm and 4.24 mm, respectively. The tensile strength at yield was determined according to GB/T 1040-92 standard. Pure LDPE samples were also tested under the same conditions to serve as a reference. At least five samples were measured, and the average values were reported.

RESULTS AND DISCUSSION

Morphology of Lignin and LDPE/Lignin Blends

The SEM micrograph, as shown in Fig. 1, reveals the spherical morphology of lignin. Many agglomerates and some spherical particles can be seen. The diameter ranges from 0.1 μm to 1.5 μm . However, it is difficult to determine the primary size of lignin precisely due to aggregation of lignin.

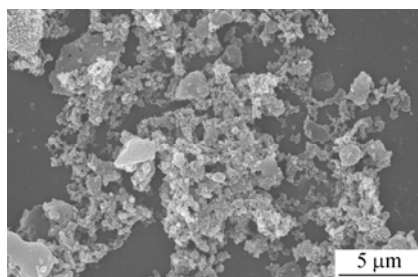


Fig. 1 SEM photo for morphology of lignin

It is well-known that the dispersion of filler in the polymer matrix and the interfacial interactions between filler and matrix both are key factors for the enhancement of mechanical properties of polymer composites^[19]. In this work, the lignin is seen to be well-dispersed in LDPE matrix both with and without compatibilizers. Even at a high lignin content of 40 wt%, homogeneous dispersion is achieved as shown in Fig. 2. But it is apparent that the dispersion size of lignin is different among the three kinds of blends. The dispersion size of lignin in LDPE is about 1 μm (Fig. 2a), which is larger than that in the compatibilized blends (Figs. 2b, 2c). It also can be found that there is an obvious interface between lignin and LDPE in uncompatibilized blends (Fig. 2a), which indicates typical immiscibility of the two phases. By adding compatibilizers, the dispersion size of lignin becomes smaller, and the interface becomes blurring. For EVA compatibilized blend, the interface of lignin and matrix is blurrier, and a little lignin can be seen. However, by adding PE-g-MA, the dispersion of lignin in matrix becomes more uniform, and the size of lignin phase declines. Furthermore, good interfacial interaction between lignin and LDPE can be achieved, as shown in Fig. 2(c). The reasons of those results are as follows: (1) For uncompatibilized blends, lignin has a great number of hydroxyl groups and LDPE is an entirely hydrophobic polymer, consisting nearly completely methylene groups, which will lead to low chemical adhesion between the lignin and LDPE. (2) By adding compatibilizers, both EVA and PE-g-MA have the hydrophobic segment and the hydroxyl segment, which will result in strong physical interaction and hydrogen bonding between LDPE and lignin on the interface. In a word, SEM results indicate that both EVA and PE-g-MA can improve the compatibility of LDPE/lignin blends.

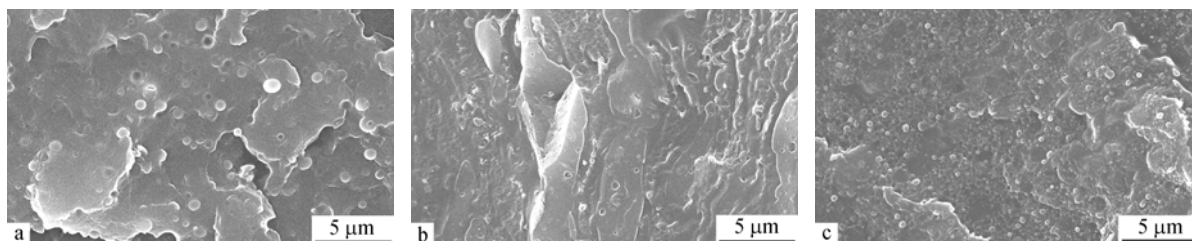


Fig. 2 SEM photos for LDPE/lignin blends

a) Uncompatibilized LDPE/lignin blends with 40 wt% lignin content; b) EVA compatibilized LDPE/lignin blends with 40 wt% lignin content; c) PE-g-MA compatibilized LDPE/lignin blends with 40 wt% lignin content

Stress-Strain Curves

In order to investigate the influence of compatibilizers on mechanical properties of LDPE/lignin blends, tensile tests have been performed. Figure 3 shows the stress-strain curves for uncompatibilized and compatibilized blends with 10 wt% to 40 wt% lignin content. The stress-strain curve for pure LDPE is also given in the plot for comparison. The test data obtained from stress-strain curves are shown in Fig. 4. It is interesting to find that EVA and PE-g-MA show different influence on tensile properties of LDPE/lignin blends.

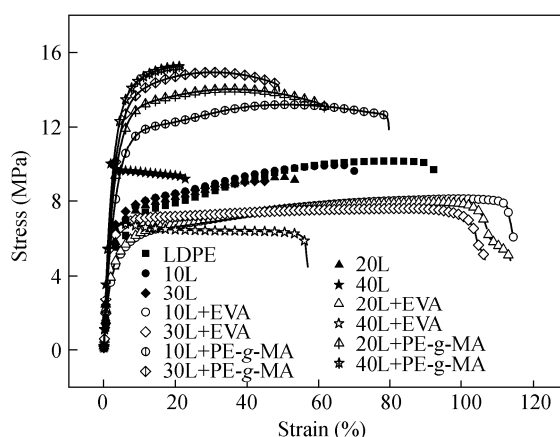


Fig. 3 Stress-strain curves for uncompatibilized and compatibilized blends with 10 wt% to 40 wt% lignin content

For uncompatibilized blends, the tensile strength reduces slightly as the content of lignin increases from 10 wt% to 30 wt% but it shows a little increase by the presence of 40 wt% lignin. As we know that two factors will influence the tensile strength of the blends, one concerns the interfacial interaction between lignin and LDPE, and the other concerns the reinforcing effect of lignin on LDPE. Because of the weak interfacial adhesion, the tensile strength of the blends shows a little decrease with the addition of lignin. However, as the content of lignin increasing to 40 wt%, the tensile strength can slightly increase due to the higher strength of lignin than that of LDPE. The tensile modulus increases and the elongation at break of blends decreases as shown in Fig. 4, which indicates that the addition of lignin will reduce the elongation at break of LDPE/lignin blends, although the modulus of the blends can be increased. Compared with LDPE/lignin blends, the addition of 20 wt% EVA can effectively increase the toughness (as observed by the area under the stress-strain curves) of blends. The elongations at break of all blends are above 100% when lignin content increases from 10 wt% to 30 wt%. The reason may be that EVA can act as good compatibilizer to improve interface interaction between LDPE and lignin. But tensile modulus of the blends shows no obvious changes with the addition of EVA at

lower lignin content, and then it decreases when lignin content is higher than 30 wt% as shown in Fig. 4(b). This may be attributed to the lower modulus of EVA than LDPE (the tensile modulus of pure EVA is only 3 MPa and that of LDPE is 144 MPa obtained from our measurements). Since PE-g-MA is another kind of compatibilizer with higher modulus than EVA (the tensile modulus of pure PE-g-MA is 465 MPa), there must be different influence of PE-g-MA on the mechanical properties of LDPE/lignin blends. As shown in Fig. 4, both tensile strength and tensile modulus of blends increases with the addition of 20 wt% PE-g-MA (Figs. 4a, 4b). By adding PE-g-MA, blends with 40 wt% lignin are significantly improved in tensile strength increasing by 146% as compared with virgin LDPE. The tensile modulus of blends also shows obvious increase with increasing lignin content until lignin content reaches 30 wt%. Since PE-g-MA has good compatibilization effect, it can improve the strength of the blends and meanwhile keep a relative large elongation at break. It should be noticed that the mechanical properties of these blends are the comprehensive performance of all the components. When the lignin content is above 30 wt%, the lignin can easily aggregate and this results in a decrease of the tensile properties of the blends.

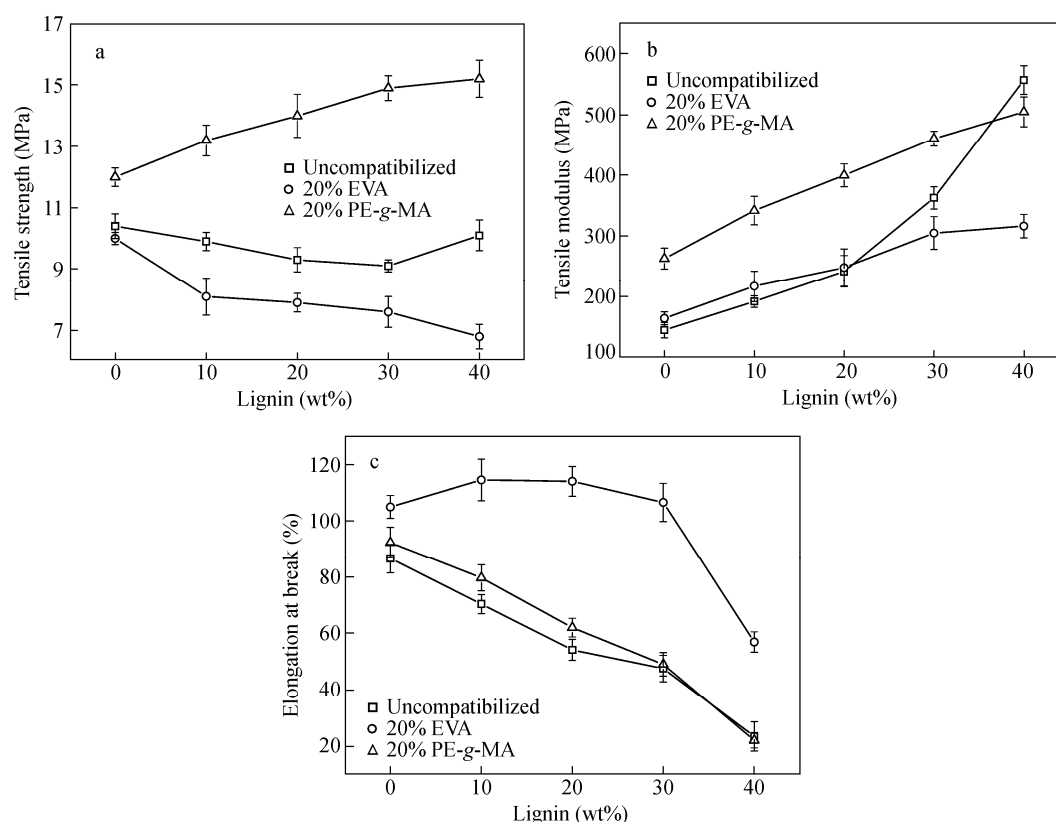


Fig. 4 Mechanical properties curves for LDPE/lignin blends
a) Tensile strength; b) Tensile modulus; c) Elongation at break

From above discussion, it is apparent that EVA and PE-g-MA show different effects on the mechanical properties of LDPE/lignin blends although they all act as a compatibilizer between LDPE and lignin. The most probability of this result may originate from the different structure and properties of these two raw materials. Both EVA and PE-g-MA act as compatibilizer to improve the interface adhesion. EVA may also act as toughness modifier to absorb energy, and PE-g-MA may also act as reinforcement agent to transfer energy from matrix to filler.

Relative Tensile Strength

To better investigate the change law of mechanical properties of LDPE/lignin blends, relative tensile strength, relative tensile modulus and relative elongation at break will be analyzed as follows.

Figure 5 shows the relative tensile strength (RTS) (*i.e.* the ratio of tensile strength of the blend to that of the matrix) of the blends from 10 wt% to 40 wt% lignin content. When adding EVA or PE-g-MA to LDPE, LDPE/EVA and LDPE/PE-g-MA act as the matrix, respectively. As shown in Fig. 5, the tensile strength reduces as the content of lignin increases owing to poor stress transfer from the uncompatibilized matrix to the filler. Similar results have been obtained by Rusu *et al.*^[9] and Alexy *et al.*^[10] for unmodified lignin. For EVA compatibilized blends, the RTS values reduce as the lignin content increases. However, for PE-g-MA compatibilized blends, the RTS values increase as the lignin content increases. For blends with 40 wt% lignin content, the RTS value increases by 27% (as compared with matrix LDPE/PE-g-MA) with the addition of PE-g-MA.

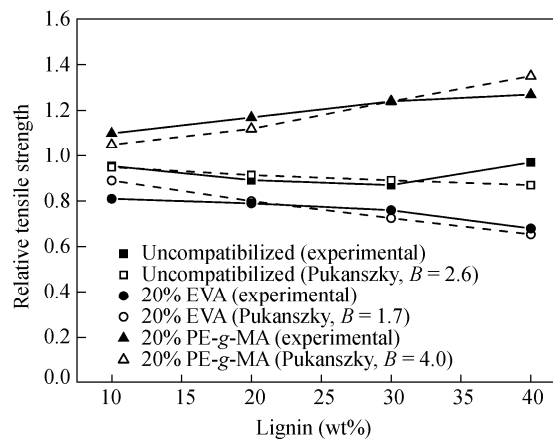


Fig. 5 Relative tensile strength (RTS) of LDPE/lignin blends with 10 wt% to 40 wt% lignin content, showing both experimental and theoretical (Pukanszky) values

Strength of particulate-polymer blends relies on the parameters of particle loading, interface adhesion and particle size, which has been reviewed in detail by Fu *et al.*^[19]. Whilst many phenomenological and semi-empirical models have been proposed, there is no single equation that can be applied to all particulate composites under all conditions. However, these models can predict the changing tendency of the strength against any specific parameter. For very strong particle-matrix interfacial bonding, the empirical model has been given by Pukanszky *et al.*^[20] and is calculated as:

$$\text{RTS} = \frac{\sigma_b}{\sigma_m} = \left[\frac{1 - \phi_f}{1 + 2.5\phi_f} \right] \exp(B\phi_f) \quad (1)$$

where σ_b and σ_m are the tensile strengths of the blend and matrix, respectively, ϕ_f is the volume fraction of the filler. The volume fraction is calculated as suggested by Willett^[21]:

$$\phi_i = \frac{(w_i / \rho_i)}{\sum (w_i / \rho_i)} \quad (2)$$

where ρ_i and w_i are the density and weight fraction of component i in the blends.

B is an empirical constant, which depends on the surface area of particles, particle density and interfacial bonding energy. In the validity domain the polymer/filler pairs are characterized essentially by the value of the parameter B , which is obviously connected with the interfacial properties of the given system and also depends on the yield stress of the matrix. For poor interfacial bonding, the particles do not carry any load, so $B = 0$ ^[20, 22]. In this work, the B values of uncompatibilized blends, EVA compatibilized blends and PE-g-MA compatibilized

blends are calculated to match the experimental data and are found to be 2.6, 1.7 and 4.0, respectively, as shown in Fig. 5. Although B has no obvious physical meaning, it is still clear to analyze the interaction between polymer/filler interface^[20]. So it is obviously that PE-g-MA enhances the interfacial bonding between LDPE and lignin, thus the interfacial layer can transfer stress and debonding after deformation. However, soft EVA makes weak stress transfer from the matrix to filler although there is still some interfacial adhesion.

More evidence can be obtained from observing the fracture surface after tensile deformation. Figure 6 shows the SEM micrographs for the tensile fracture surfaces of uncompatibilized and compatibilized blends with 40 wt% lignin content. For uncompatibilized blends, the fracture surface shows ductile fracture and plastic deformation. It suggests that the matrix is able to withstand the load, but the adhesion between lignin particles and LDPE is weak, and lignin is a little deformed along with the matrix as shown in Figs. 6(a), 6(b). For EVA compatibilized blends, highly drawn fibrils with pulled-out regions cover the entire surface. The EVA becomes columniform particles standing with the matrix as shown in Figs. 6(c), 6(d). This large plastic deformation absorbs a large amount of energy for crack initiation and propagation. This is reflected in high ductility and toughness values which are much higher than those of virgin LDPE. For PE-g-MA compatibilized blends, the fracture surface appears a cleavage and dimpled rupture morphology. There is strong interface adhesion between the lignin particles and the adjacent matrix by adding PE-g-MA as shown in Figs. 6(e), 6(f). This suggests that PE-g-MA can help improve adhesion and thereby promote efficient stress transfer from the matrix to the filler. That is why the strength value of blends with 40 wt% lignin content can be about 46% higher than that of virgin LDPE.

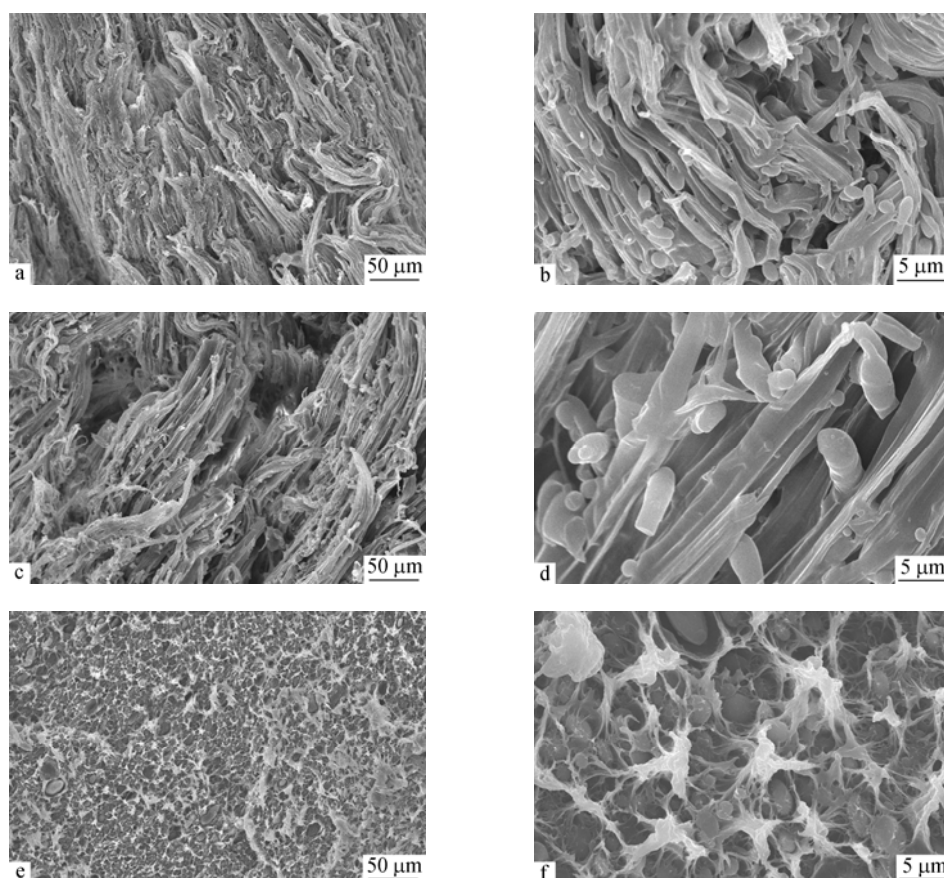


Fig. 6 SEM micrographs for the tensile fracture surfaces of uncompatibilized and compatibilized blends with 40 wt% lignin content
a, b) Uncompatibilized blends; c, d) EVA compatibilized blends; e, f) PE-g-MA compatibilized blends

Relative Tensile Modulus

Figure 7 shows the relative tensile modulus (RYM) of the blends. The tensile modulus increases with increasing Lignin content owing to the stiffness of the lignin particles. This trend was also observed by Rusu *et al.*^[9] and Sailaja^[13]. For uncompatibilized blends, the RYM is found to increase sharply from 1.33 to 3.87 with lignin content from 10 wt% to 40 wt%, while for the same loading of lignin with the addition of EVA or PE-g-MA, the corresponding values are lower, *i.e.* from 1.3 to 1.93, as shown in Fig. 7. This must be due to the improved adhesion between the two phases and the migration of compatibilizers to the interface. The RYM values of compatibilized blends are close to that of LDPE, *i.e.* 1.0.

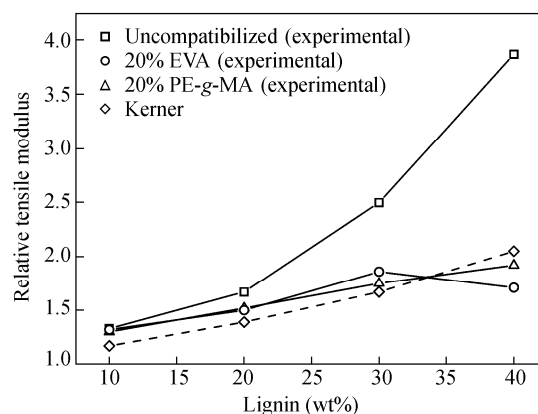


Fig. 7 Relative tensile modulus (RTM) of LDPE/lignin with 10 wt% to 40 wt% lignin content, showing both experimental and theoretical (Kerner) values

Many empirical or semi-empirical equations have been proposed to predict the modulus of particulate-polymer composites^[19]. In this work, the modulus data is compared using Kerner's model^[23] for composites that contains spherical particles in a matrix, in which the filler is more rigid than the matrix. The Kerner equation is given as:

$$\text{RYM} = \frac{E_b}{E_m} = 1 + \left(\frac{\phi_f}{1 - \phi_f} \right) \left(\frac{15(1 - \nu)}{8 - 10\nu} \right) \quad (3)$$

where E_b and E_m are the tensile modulus of the blend and matrix, respectively. ν is Poisson ratio of LDPE, taken to be 0.43^[21]. As shown in Fig. 7, the theoretical values calculated agree well with the observed data for EVA and PE-g-MA compatibilized blends but deviate from those of the uncompatibilized blends. This result agrees well with the above analysis.

Relative Elongation at Break

The relative elongations at break (REB) of lignin/LDPE blends are shown in Fig. 8. Because lignin is a kind of lower ultimate elongation filler, Rusu *et al.*^[15] observed a drastic decrease in relative elongation at break with increasing Lignin content. The similar trend is observed in this work. The REB is only 27.1% for uncompatibilized blends with 40 wt% lignin content (the percentage elongation at break for virgin LDPE is 86.6%). However, for EVA compatibilized blends, the REB values show much higher, *i.e.* 109%, 109%, 101% and 54% of that of the matrix, from 10 wt% to 40 wt% lignin content, respectively, as shown in Fig. 8. From Figs. 6(c), 6(d), it can be observed that EVA strongly bonds with the matrix and leads to plastic deformation. This is because EVA has quite good ductility and toughness which can load large plastic deformation before fracturing. So EVA improves the ductility and toughness of blends significantly. Compared with EVA, PE-g-MA can improve the interface adhesion but can not support large deformation. So, PE-g-MA has a little influence on the elongation at break for the blends.

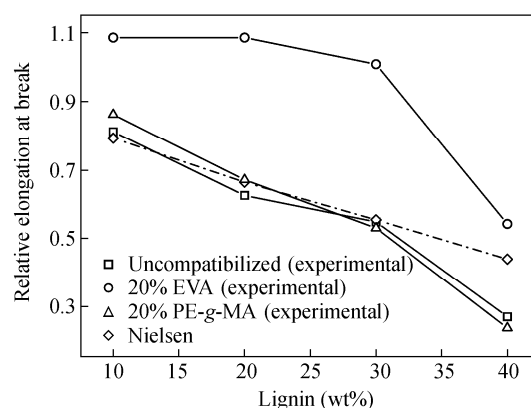


Fig. 8 Relative elongation at break (REB) of LDPE/lignin blends with 10 wt% to 40 wt% lignin content, showing both experimental and theoretical (Nielsen) values

The modified Nielsen model is often used to predict the theoretical values of REB for the adhesion, in the case of spherical particles with good adhesion to matrix, and is given as^[24, 25]:

$$REB = \frac{\varepsilon_b}{\varepsilon_m} = 1 - k\phi_f^{2/3} \quad (4)$$

where ε_b and ε_m are the percentage elongations at break for the blend and matrix, respectively, and k is an adjustable parameter that depends on filler geometry and has been adjusted to a value of 1.2. The predicted theoretical values agree well with the observed data except for EVA compatibilized blends, as shown in Fig. 8.

CONCLUSIONS

LDPE/Lignin blends were prepared using melt blending with different lignin contents. PE-g-MA and EVA were used as compatibilizers to improve the interface interactions between LDPE and lignin, respectively. SEM results show that both EVA and PE-g-MA can improve the compatibility of LDPE/lignin blends. But their influence on mechanical properties is totally different. Because the soft compatibilizer EVA absorbs a large amount of energy and the hard compatibilizer PE-g-MA transfers stress well, compatibilizer EVA increases the toughness obviously and compatibilizer PE-g-MA is effective to improve the tensile strength. Several theoretical models have been used to further analyze the relative tensile strength, relative tensile modulus and relative elongation at break of the experimental data, combined with the morphological observation of tensile fractured surfaces by SEM. Experimental results suggest that the addition of different compatibilizers can result in different surface adhesion and morphology which will lead to different mechanical properties of final products. In this way, lignin can be used in the development of eco-friendly products by choosing different compatibilizers depending on different usages.

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