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Poly(lactic acid)/Lignin Blends Prepared with the Pickering Emulsion Template Method

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Abstract

Lignin has attracted particular interest for the preparation of functional polymers, and the dispersion and compatibility of lignin in a polymer are key parameters determining properties. In this work, the Pickering emulsion template method was used to introduce lignin nanoparticles into poly(lactic acid) (PLA) with improved dispersion. The effect of lignin as the stabilizer of Pickering emulsions was studied in the paper as well as its influence on the thermal, rheological and mechanical properties of the blends prepared. The obtained PLA/lignin films had reduced light transmission in the UV light region, and Young's modulus of PLA/lignin blends increased, while their tensile strength and elongation-at-break decreased as compared to neat PLA film. The introduction of lignin improved crystallinity of PLA from 7.5% to over 15%, and increased its decomposition temperature by about 10 °C. The lignin in the blends prepared by the Pickering emulsion template approach had much larger load bearing capacity than the dispersed lignin particles in the usual melt blended material, because of better dispersion and smaller particles. All the results indicated that the Pickering emulsion template method improves the dispersion of lignin (over 5.0 wt%) in PLA and improve UV protection, crystallinity, decomposition temperature and Young's modulus of PLA, which had an advantage in industrial applications.

Key words: Lignin nanoparticles, Decomposition temperature, Reinforcement, Rheology

Introduction

Lignin, as the second most abundant renewable and biodegradable natural resource next to cellulose, is a complex amorphous polyphenol biopolymer whose structure and properties basically depend on the type and growing conditions of the plant and on the extraction method used [1]. The main precursors of lignin are three monomer phenylpropanoids, i.e. *p*-coumaryl, coniferyl and sinapyl alcohol, linked together by ether or C-C bonds such as β-O-4, 5-5, β-5, 4-O-5, β-1 and β-β [2]. Many functional groups such as carbonyl, carboxyl, phenolic or aliphatic hydroxyls, etc. are found in different proportions in lignin. The abundance of functional groups on its surface is one of the reasons why it is widely studied as an active component for plastics and rubbers [3, 4]. Meanwhile, the low price and abundance of lignin also makes it an attractive feedstock for many researchers to attempt to use lignin in different fields which can give greater value to this natural material [5, 6]. Therefore, several authors have studied the technical feasibility of using lignin as a component for functional polymers [7-9] and as a stabilizer for plastics [10]. Other authors have proved that lignin has considerable influence on the thermal and mechanical behavior of blends prepared from different polymers such as poly(ethylene terephthalate), poly(ethylene oxide), polystyrene and poly(lactic acid) [8, 11-15].

Poly(lactic acid) (PLA) has been widely studied for replacing commodity polymers because it is a material obtained from agricultural waste and have positive features such as: availability, low flammability, renewability, good biodegradability and good mechanical properties [16, 17]. Furthermore, some studies already exist offering information about the effect of the inclusion of lignin into PLA [18, 19]. The dispersion of lignin in PLA plays an important role in the determination of the properties of PLA/lignin blends. Lignin is difficult to disperse in PLA because of its incompatibility with the polymer and the large particle size of commercial lignin. An accepted and easy method is melt mixing, in which lignin powder is added to the molten PLA and homogenized, and subsequently thin films are prepared by compression molding [20]. In order to improve the dispersion of lignin in PLA, a co-rotating twin screw micro-compounding system was used to homogenize lignin and PLA at high temperature [19, 21, 22]. The chemical modification of lignin was claimed to improve dispersion [23]. Another approach to achieve good dispersion is solvent casting in which the solution of the modified lignin and the organic solution of the PLA are mixed with each other at room temperature, and then PLA/lignin films are prepared directly by solvent casting [24, 25]. However, these methods have limitations such as agglomeration and inadequate particle dispersion in the case of both melt mixing and solvent casting of the chemically modified lignin.

Pickering emulsions stabilized by solid particles have attracted considerable attention for the preparation of functional polymer composites. The emulsion droplets can serve as templates guiding the assembly process of the solid particles onto their interface for numerous potential practical applications [26-28]. In our previous work, cellulose nanofibrils and regenerated cellulose were used to reinforce poly(lactic acid) via the Pickering emulsion approach [29, 30]. In this work, a Pickering emulsion template was used for the preparation of PLA/lignin blends in order to improve the dispersion of lignin in PLA, and we focused our attention onto the study of the effect of lignin on the stabilization of the Pickering emulsion and also on the thermal, rheological and mechanical properties of the blends prepared.

Experimental

Materials

Poly (lactic acid) (PLA, Ingeo 2003D, D-lactic acid: 1.4%, L-lactic acid: 98.6%, granules, density: 1.2 g/cm^3) with the number average molecular weight (M_n) of ~150000

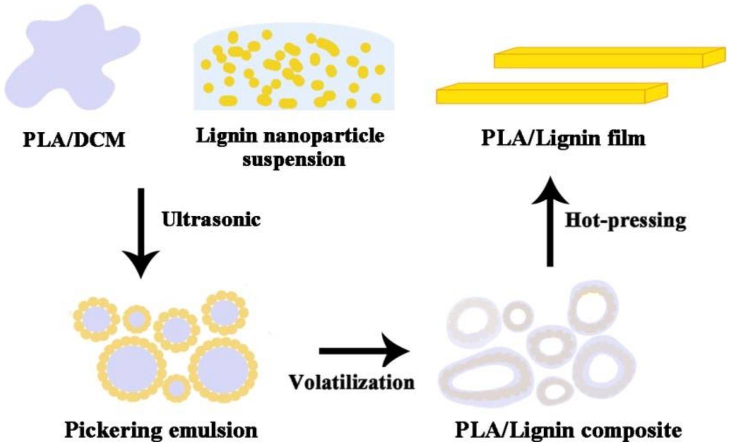
Da and weight-average (M_w) of ~200000 Da, respectively) was supplied by Natureworks, USA. Lignin, extracted from corn stalk, was bought from Yanghai Environmental Protection Materials Co., Ltd. Ethylene glycol was obtained from Shanghai Lingfeng Chemical Reagent Co., Ltd. Phosphoric acid (85% in water) was purchased from Shanghai Titan scientific Co., Ltd. Dichloromethane (DCM) was supplied by Sinopharm Chemical Reagent CO., Ltd.

Preparation of lignin nanoparticle suspension

The lignin nanoparticle suspension was prepared as previously reported by Yang et al. [31]. In detail, a solution of 4.0 wt% of lignin in ethylene glycol was prepared and stirred for 3 h at 35 °C. The impurities of lignin were removed by filtration. Subsequently, 800 mL deionized water was added quickly to the filtered solution. H_3PO_4 was added dropwise to the lignin solution with continuous stirring until the pH value of 2.0 was reached. The lignin nanoparticle suspension (pH = 6.6) was obtained after centrifugation and washing with water. The solid content of the lignin suspension was 1.2 wt%.

Preparation of PLA/lignin composite film

The Pickering emulsions were formed from the lignin nanoparticle suspension as the aqueous and the PLA/DCM solution as the oil phase by ultrasonication (JY 92-IIDN, Scientz, China) with 720 W power for 3 min. The amount of each component is listed in **Table 1**. The emulsion was stored at ambient temperature for 24 h to evaporate DCM completely and the resulting mixture was vacuum-filtered to yield the PLA/lignin blend. The blend was collected from the filter and vacuum-dried at 40 °C for 24 h. Finally, the PLA/lignin blend films were compression molded with 20 MPa pressure at 180 °C for 5 min. The procedure of film preparation is illustrated in **Scheme 1**.



Scheme 1 Schematic illustration of the preparation of PLA/lignin film via the Pickering emulsion template

Microscopy

Cryo-transmission electron microscopy (Cryo-TEM) was performed on FEI Tecnai 20. A drop of lignin suspension (8 mg/mL) was dropped onto a copper grid coated with holey carbon support film. The copper grid was immersed into liquid C_2H_6 immediately and then transferred into liquid nitrogen for further observation.

The morphology of the particles obtained was studied also by scanning electron microscopy (SEM). A drop of the lignin nanoparticle suspension was placed onto an aluminum foil. The PLA/lignin blends were coated directly on the conductive adhesive tape. Subsequently, all the samples were coated with a gold-palladium alloy for the thickness of 5 nm. Micrographs were taken from the lignin nanoparticles by using a field emission scanning electron microscope (FE-SEM) (S-4800, Hitachi, Japan), while those on PLA/lignin blends were recorded with a scanning electron microscope (SEM) (TM3030, Hitachi, Japan).

Optical microscopy was used for the study of the emulsion prepared. The Pickering emulsion samples were diluted with deionized water and uniformly mixed by hand shaking. The emulsion droplets were observed using an optical microscope (Eclipse 80i, Nikon, Japan) at room temperature.

Ultraviolet-visible spectroscopy

The light transmittance of neat PLA and PLA/lignin films was measured using a varian ultraviolet–visible (UV-Vis) spectrophotometer (TU-1901, Persee, China). The scan was carried out from 250 nm to 800 nm with a rate of 120 nm/min. The thickness of all the films was 30 μm.

Thermal analysis

The decomposition of neat PLA and PLA/lignin blends were studied by thermogravimetric analysis (TGA) (209F1, Netzsch, Germany). The samples were heated from 30 to 600 °C at the heating rate of 10 °C/min.

The relaxation transition as well as the melting and crystallization of PLA and the PLA/lignin blends were analyzed using differential scanning calorimetry (DSC) (DSC 4000, Perkin Elmer, USA). The samples were heated from 25 to 200 °C, held at 200 °C for 5 min to eliminate thermal history, cooled down to 25 °C, held at 25 °C for 5 min and heated again to 200 °C under nitrogen atmosphere. The heating rate was 10 °C/min, while the cooling rate 5 °C/min. Crystallization temperature (T_c) and crystallization enthalpy (ΔH_c) were determined from the cooling scan. The glass transition temperature (T_g), cold crystallization temperature (T_{cc}), melting temperature (T_m), cold crystallization enthalpy (ΔH_{cc}) and melting enthalpy (ΔH_m) were determined from the second heating scan. The crystallinity (χ) of PLA and lignin/PLA composites was calculated by:

$$\chi\,(\%)=\left(\frac{\Delta H_{m}+\Delta H_{cc}}{\Delta H_{m}^{0}\times\left(1-\frac{c}{100}\right)}\right)\times 100 \qquad (1)$$

where ΔH is the melting enthalpy of a 100% crystalline polymer matrix (93.0 J/g [20]) for PLA, and *c* is the weight percentage of lignin in the blend.

Rheological properties

Rheological analysis was performed using a rheometer (Haake-Mars 60, Thermo Fisher Scientific, USA) equipped with parallel plates of 35 mm in diameter. A frequency sweep from 0.01 to 100 rad/s was used to study the viscoelastic parameters with strain fixed at 1%. The rheological measurements were performed at 200 °C.

Mechanical characteristics

The mechanical properties of the neat PLA and PLA/lignin blend films were determined using a universal mechanical testing machine (UH6502, Youhong, China). The gauge length was 50 mm and the testing speed was set to be 10 mm/min. Three parallel measurements were done for each sample.

Results and discussion

Preparation and morphology

According to Cryo-TEM and FE-SEM micrographs (**Fig. 1**), lignin nanoparticles were prepared successfully. The size of lignin nanoparticles was 55 ± 9 nm.

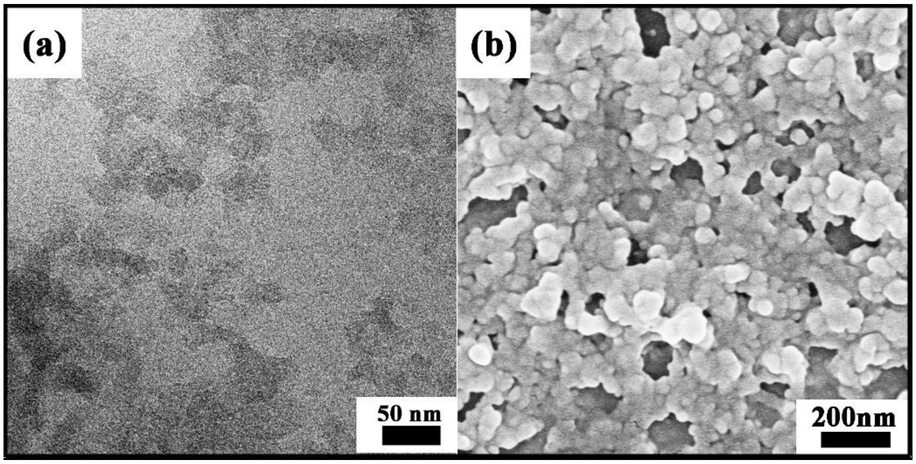


Fig. 1 Cryo-TEM **(a)** and FE-SEM **(b)** micrographs recorded on of lignin nanoparticles

As shown in **Table 1**, Pickering emulsion did not form when lignin content was 2.5 wt% in PLA, maybe because the amount of lignin was not sufficient to stabilize the Pickering emulsion. When lignin content increased above 5.0 wt%, the formed Pickering emulsions were stable. The size of the Pickering emulsion droplets obviously decreased with increasing lignin content (**Fig. 2**). The PLA/lignin blend formed upon the evaporation of DCM. The procedure of blend formation is illustrated in **Scheme 1**. All the blends showed shriveled microsphere and fragment morphology after the evaporation of DCM as shown in **Fig. 3**. P1-5.0% blends consisted of less shriveled microsphere particles and more fragments than P1-10%, because larger droplets tend to break up the DCM oil phase inside the droplets, and more fragments were obtained as a consequence. Although regular microspheres were not formed, lignin was incorporated into PLA and the blends were obtained as powder.

Table 1 Composition of PLA/lignin blends prepared *via* the Pickering emulsion template approach

Materials	Lignin/PLA (wt%)	Oil phase (g)	PLA/DCM (wt%)	Aqueous phase (g)	Lignin/oil phase (wt%)	Pickering emulsion
P1-2.5%	2.5	30	10	60	0.25	No
P1-5.0%	5.0	30	10	60	0.50	Yes
P1-7.5%	7.5	30	10	60	0.75	Yes
P1-10%	10	30	10	60	1.00	Yes

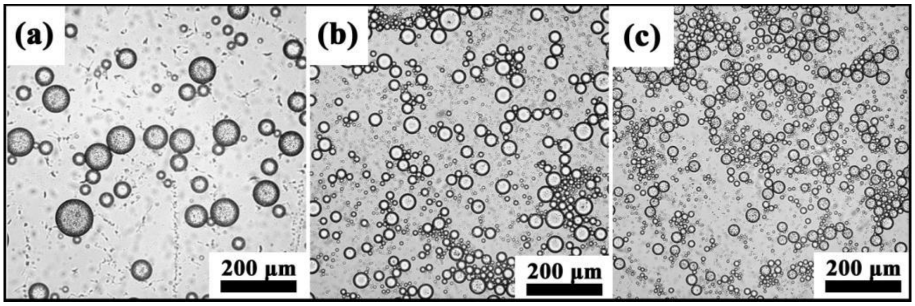


Fig. 2 Optical micrographs taken on the Pickering emulsions prepared; **a)** P1-5.0%, **b**) P1-7.5%, **c**) P1-10%**.**

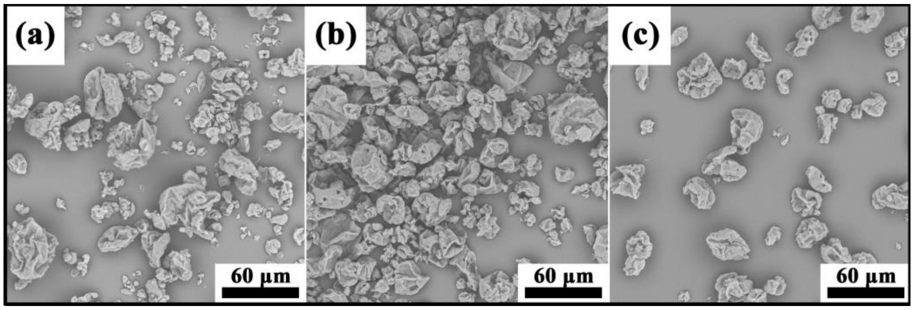


Fig. 3 SEM micrographs recorded on the PLA/lignin blends obtained; **a**) P1-5.0%, **b**) P1-7.5%, **c**) P1-10%**.**

Optical properties

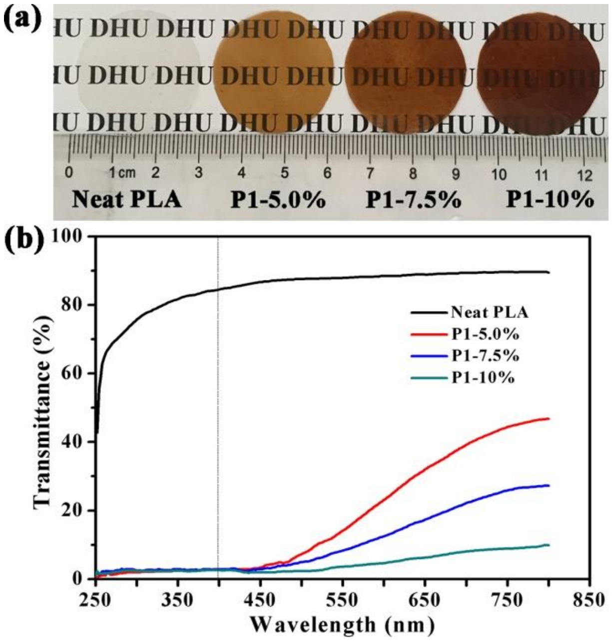


Fig. 4 Visual appearance **(a)** and UV-Vis spectra **(b)** of neat PLA and PLA/lignin films.

Neat PLA has poor UV barrier characteristics (**Fig. 4**) which must be improved to expand its application into areas such as medicine bottles or food packaging. **Fig. 4a** shows the visual appearance of the neat PLA film and the films prepared from PLA and lignin with different lignin contents. The thicknesses of all films were 30 μm. The color of the PLA/lignin films became brown because of their absorption in the blue to violet region of the visible spectrum [32], and the brown color deepened with increasing lignin content. UV-Vis spectra of the neat PLA and the PLA/lignin films are presented in **Fig. 4b**. Neat PLA was transparent in both the visible (400-800 nm) and the UV region (250-400 nm) of the spectrum. Compared to neat PLA, all the PLA/lignin films had small light transmission in the UV light region. It can be clearly seen that the ultraviolet-visible light transmittance of the films decreased with increasing lignin content. This phenomenon may have two reasons. The films had a strong absorption in the blue to violet region, on the one hand, [32, 33]; and lignin has a good blocking effect in the UV light region in PLA/lignin blends, on the other hand, because of larger refraction and reflection, as reported by Yang et al [34].

Differential scanning calorimetry

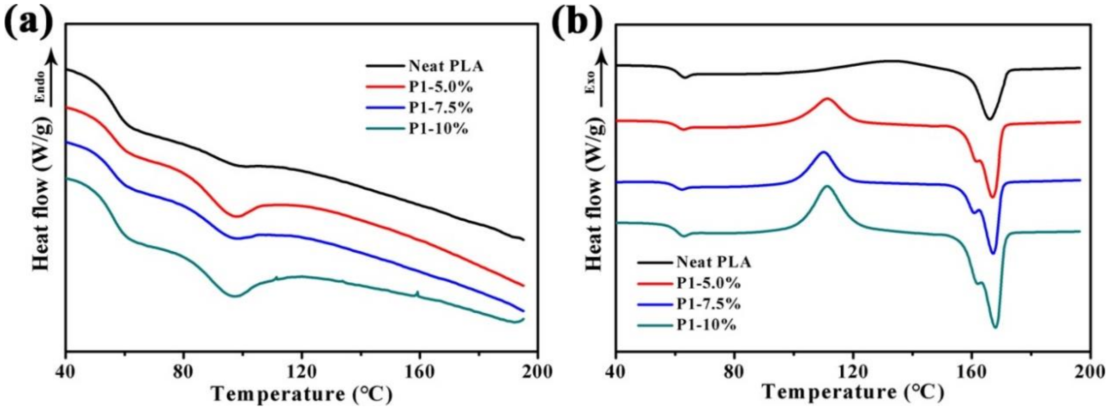


Fig. 5 DSC traces recorded in the cooling scan **(a)** and during the second heating scan **(b)** on PLA and PLA/lignin films.

Table 2 DSC analysis of PLA and PLA/lignin films in the second heating scan

Materials	T_g (°C)	T_{cc} (°C)	T_m (°C)	ΔH_{cc} (J/g)	ΔH_m (J/g)	χ (%)
Neat PLA	60.6	132.7	165.9	-23.5	30.5	7.5
P1-5.0%	60.6	111.4	167.1	-25.8	40.5	15.5
P1-7.5%	60.2	110.4	168.0	-26.1	41.2	16.3
P1-10%	60.3	111.2	168.0	-20.0	37.7	19.6

The cooling scan is shown in **Fig. 5a**. Neat PLA exhibits an exothermic peak with low intensity indicating rather limited crystallization capability. In the case of the blends, P1-5.0%, P1-7.5% and P1-10%, the crystallization peaks are more intense as a result of enhanced tendency for crystallization, which may be due to the homogeneous distribution of nanoparticles in PLA leading to the increased mobility of the matrix polymer [35, 36]. The glass transition (T_g), cold crystallization (T_{cc}) and melting temperatures (T_m) as well as crystallinity (χ) derived from the DSC traces (**Fig. 5b**) from the second heating scan are reported in **Table 2** for all samples. The T_g and T_m temperatures of PLA/lignin films measured did not differ significantly from that of neat PLA (60.6 °C and 165.9 °C), respectively, in the first run and the tendency was similar also in the second heating scan. Thus, the introduction of lignin had little effect on the glass transition and the melting temperature. The rate and degree of cold crystallization increased for the PLA/lignin films shown by the decrease of T_{cc} and a sharper peak as compared to neat PLA (132.7 °C). This behavior can also result from the larger mobility of the polymer molecules leading to faster crystallization and larger crystallinity [36]. The crystallinity (χ) of neat PLA and the PLA/lignin blends was calculated from the second heating scan (see **Table 2**). Crystallinity values increased considerably from 7.5% for the neat PLA to over 15 % of the PLA/lignin blends because of the increased cold crystallization due to the presence the lignin particles.

Thermal decomposition, stability

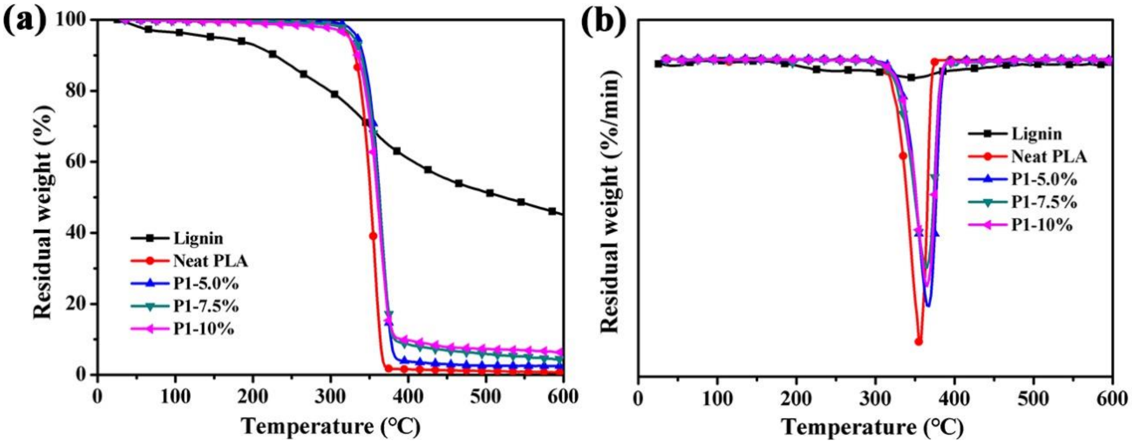


Fig. 6 TGA **(a)** and DTG **(b)** traces of lignin, neat PLA and PLA/lignin blends.

Table 3 Thermal parameters (T_{end}, T_{max}) and residual mass (%) for neat PLA and PLA/lignin blends

Materials	T_{end}(°C)	T_{max}(°C)	Residual mass (%)at 600 °C
Neat PLA	373	356	0.66
P1-5.0%	385	366	2.48
P1-7.5%	383	365	4.37
P1-10%	383	365	6.24

The thermal decomposition of neat PLA and lignin/PLA blends was studied by TGA measurements, by following the weight loss as a function of temperature. The results are summarized in **Fig. 6a**. Lignin loses water first and then it starts to degrade slowly at about 200 °C. It loses weight at a relatively slow rate over a wide temperature range up to about 450 °C and then continues to lose mass, but at an even slower rate. Neat PLA decomposes completely at 373 °C losing almost all of its mass. PLA/lignin blends decompose completely at about 383 °C at somewhat higher temperature than neat PLA. It should be noted here that the introduction of lignin resulted in an increase in the decomposition temperature of neat PLA. Moreover, the yield of char obtained at 600 °C increases with increasing lignin content (**Table 3**) due to the strong tendency of lignin to char and its limited heat release during burning. The derivative traces (DTG) indicate that the maximum degradation temperature (T_{max}) of neat PLA is 356 °C and that of the PLA/lignin blends is higher, around 365 °C (**Fig. 6b & Table 3**). Upon the introduction of lignin into PLA, the decomposition of lignin cannot be observed separately, it occurs simultaneously with that of PLA, probably because of the homogeneous dispersion of lignin in the PLA matrix.

Rheological properties

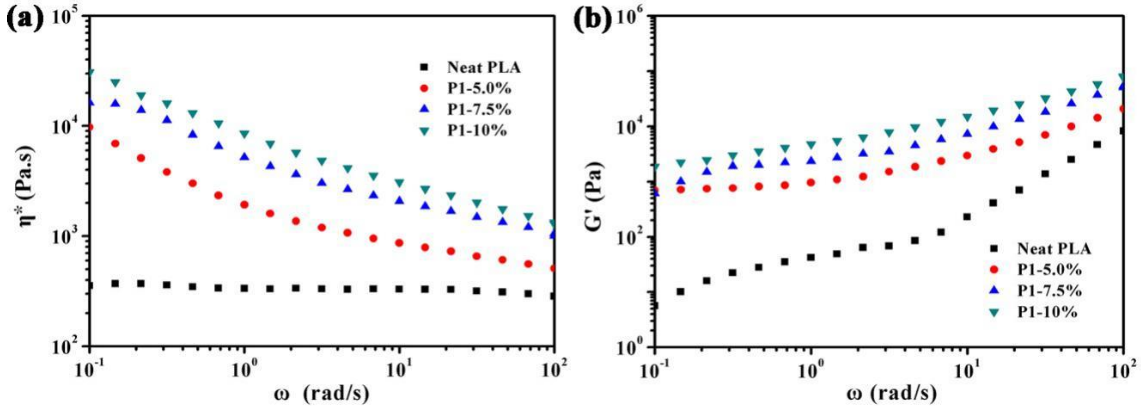


Fig. 7 Complex viscosity, η* (**a**) and storage modulus, G' (**b**) plotted against frequency, ω for the PLA and the PLA/lignin blends at the stain of 1 %.

The dependence of complex viscosity (η*) and storage modulus (G') on frequency (ω) is presented in **Fig. 7** for the neat PLA and the PLA/lignin blends. In oscillatory shear, η* is the ratio of the amplitude of shear stress and strain rate, which is conventionally divided into a real an imaginary part [37]. G' is related to the imaginary part of complex viscosity and it measures the energy stored in the material during half a cycle. As shown in **Fig. 7**, the η* function of neat PLA shows a long plateau with a slight shear-thinning behavior at high frequencies. The G' function measured for PLA shows the typical behavior of molten polymers with a terminal zone, which, at high frequencies (ω > 10 rad/s), has a slope of 2 on the log-log plot of G' vs. ω function. η* and G' increases considerably with increasing lignin content for the PLA/lignin blends (**Fig. 7**). All blends exhibit a shear-thinning behavior for η* without any plateau region at low frequencies (ω < 10 rad/s), which differs from the behavior of neat PLA (**Fig. 7a**). The slopes of the G' vs. ω correlations of the blends was smaller than that of the neat PLA at all compositions independently of frequency (**Fig. 7b**). These results indicate a transition from liquid-like to solid-like behavior, which is attributed to the good dispersion of lignin nanoparticles in PLA. The large number of lignin nanoparticles in PLA with 10 wt% lignin content might further contribute to the solid like behavior through their contact and possible aggregation. Similar rheological behavior was reported for PLA composites containing cellulose nanocrystals (CNC) in which a good dispersion was achieved [38].

Mechanical properties

The mechanical properties of materials are very important for their selection for a specific application. The properties of the blends prepared by the Pickering emulsion technique such as Young's modulus, tensile strength and elongation-at-break have reasonable values, which do not show strong composition dependence (**Fig. 8**). Young's modules increased from 3.5 to 4.0 GPa (**Fig.8a**). Stiffness increases with increasing lignin content, probably because of the increase of crystallinity of PLA in the composite and the stiffness of the lignin phase [15]. The difference in the composition dependence of melt blended materials and those prepared by the Pickering emulsion technique must be in the dispersion of the lignin phase. Poorly dispersed large lignin particles cannot carry load because of the weak interaction developing between lignin and the matrix polymer and also because of the small specific surface area [20, 21, 23]. In our work, the introduction of more than 5.0 wt% of lignin results in a slight decrease of tensile strength from 64 to 60 MPa (**Fig. 8b**) and elongation-at-break decreases from 2.4 to 1.5% (**Fig. 8b**). These results were similar with that of previous report [39]. The slight decrease of properties results from the large stiffness of the matrix and the existence of lignin particles which prevented the formation of a long range continuous phase of PLA; it has been shown many times that reinforcement depends also on matrix properties, it is smaller in stiff and larger in soft matrices because of the different relative load bearing capacity of the components [40].

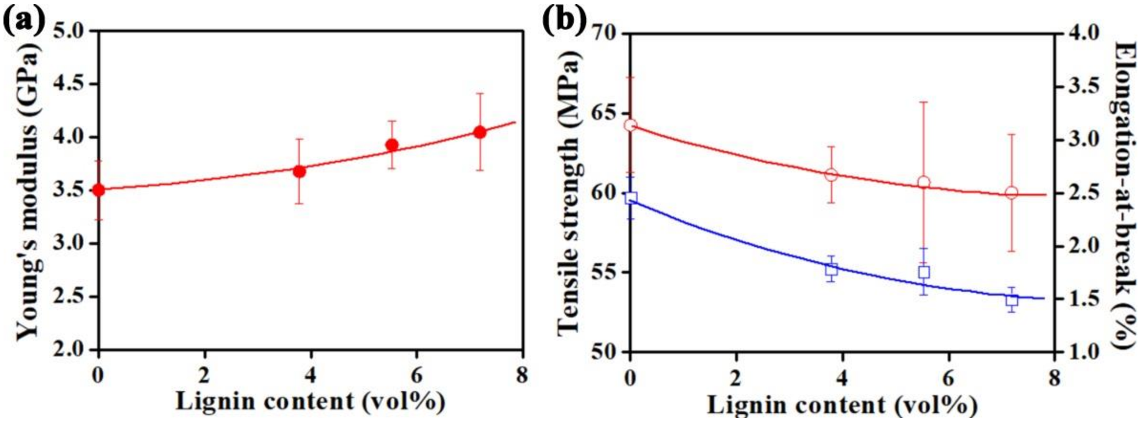


Fig. 8 Effect of lignin content on the tensile properties of PLA/lignin blends; a) (●) stiffness, b) (○) tensile strength (left axis), (□) elongation-at-break (right axis).

The relative load bearing capacity of the dispersed component can be determined quantitatively with the help of appropriate models. The composition dependence of tensile strength can be described in the following way [41, 42] (**Eq. 2**).

$$\sigma_T = \sigma_{T0}\, \lambda^n \, \frac{1 - \varphi}{1 + 1.5\, \varphi} \, \exp(B\, \varphi) \tag{2}$$

where σ_T and σ_{T0} are the true tensile strength of the blend and the matrix, respectively, φ is the volume fraction of the dispersed phase (lignin) in the blend, B expresses the load bearing capacity of lignin and it depends on interfacial adhesion, but also on the specific surface area of the dispersed particles, i.e. on particle size. In the equation true tensile strength ($\sigma_T = \sigma\lambda$, $\lambda = L/L_0$, relative elongation) accounts for the change in specimen cross-section and λ^n for strain hardening occurring with increasing elongation. n characterizes the strain hardening tendency of the polymer and can be determined from matrix properties. The rearrangement of the equation leads to reduced tensile strength

$$\sigma_{Tred} = \frac{\sigma_T}{\lambda^n} \frac{1 + 2.5\,\varphi}{1 - \varphi} = \sigma_{T0} \exp(B\,\varphi) \tag{3}$$

and if we plot its natural logarithm against composition, we should obtain straight lines, the slope of which expresses the reinforcing effect of the fibers quantitatively.

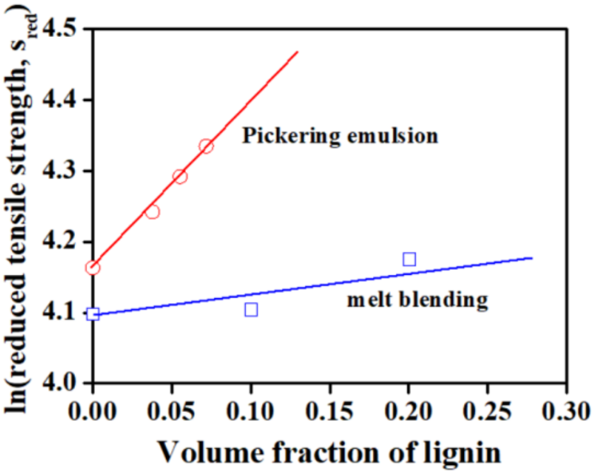


Fig. 9 Relative load bearing capacity (reinforcement) of lignin in PLA/lignin blends prepared by the Pickering emulsion technique (○) and by melt blending (☐).

The tensile strength of the blends prepared by the Pickering emulsion technique is plotted in the way dictated by **Eq. 3** in **Fig. 9**. The strength of a blend prepared by the usual melt blending method is also shown as reference. The striking difference between the two homogenization methods is clear, the slopes of the two lines differ considerably. The B value obtained for the Pickering blend is 2.38 that is relatively large taking into consideration the stiffness of the matrix. Similar values were obtained for wood flour reinforced PLA earlier [43]. On the other hand, reinforcement calculated for the melt blend is very small, 0.43, i.e. the poorly dispersed large lignin particles cannot carry practically any load, or at least their load bearing capacity is very small. The results clearly show that the introduction of lignin into PLA via the Pickering emulsion template method did not significantly deteriorate the mechanical properties of PLA, but reduced its cost, which has an advantage in industrial applications.

Conclusions

PLA/lignin blends containing 5.0, 7.5 and 10 wt% of lignin were produced successfully *via* the Pickering emulsion template approach and then PLA/lignin films were prepared by compression molding. The obtained PLA/lignin films had reduced light transmission in the UV light region as compared to neat PLA. DSC analysis showed that the introduction of lignin enhanced the mobility of the polymer resulting in larger crystallinity, which increased, from 7.5% to over 15 %. Lignin improved the stability of PLA, its decomposition temperature increased by about 10 °C. η^* and G' increased with increasing lignin content, and all the blends exhibited shear-thinning behavior without any plateau region at low frequencies. G' traces also indicated a transition from liquid-like to solid-like behavior, which was attributed to the good dispersion of lignin nanoparticles in PLA. The Young's modulus of PLA/lignin blends increased, while their tensile strength and elongation-at-break decreased as compared to neat PLA film. The lignin in the blends prepared by the Pickering emulsion template approach had much larger load bearing capacity than the dispersed lignin particles in the usual melt blended material, because of better dispersion and smaller particles. Generally, all the results indicated that the Pickering emulsion template method improves the dispersion of lignin (over 5.0 wt%) in PLA and improve several properties, which had an advantage in industrial applications.

Acknowledgements

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