



Lignosulfonate as reinforcement in polyvinyl alcohol film: Mechanical properties and interaction analysis



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ABSTRACT

Recently, there has been a growing research interest on renewable composite due to sustainability concerns. This work demonstrated the possibility of using eucalyptus lignosulfonate calcium (HLS) particles as reinforcement in polyvinyl alcohol (PVA) matrix. 41% and 384.7% improvement of pure PVA tensile strength and Young's modulus were achieved with incorporation of 5 wt% HLS. The above results were ascribed to specific intermolecular interactions between HLS and PVA, suggested by the increasing PVA glass transition and crystalline relaxations temperature, depression of melting point with HLS incorporation. Moreover, this interaction was quantitatively determined by q value of -62.4 ± 10.0 in Kwei equation. Additionally, the remarkable red shift of wavenumber corresponding to hydroxyl group also indicated the formation of strong hydrogen bond in HLS/PVA blend. SEM characterization confirmed that HLS/PVA blends are at least miscible.

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1. Introduction

The lignocellulosic biomass is composed of cellulose (35–83% dry weight basis), hemicellulose (0–30% dry weight basis), lignin (1–43% dry weight basis) and some other compounds [1]. Traditionally, after pulp and paper-making operations, lignins are viewed as a waste material or low value of pulping by-product mainly to generate energy [2]. It has been estimated that only small amount of lignin (approximately 1–2%) is isolated from pulping liquors and utilized as specialty products [3]. With the depletion of oil and the rising environmental awareness, the design of biobased materials has attracted great attention owing to their availability and rather low cost [4]. Therefore, it is desirable to fully utilize these renewable industrial lignins (over 50 million tons annually) [5].

During the last three decades, two main strategies are adopted for developing lignin-based materials. The one approach is tailoring lignin structures by chemical methods because of its abundant groups, such as hydroxyl group, aromatic hydrogen and Methoxyl group [6–9]. The other one is blending lignins with other natural resources or synthetic polymers [10–13] to improve a specific property of materials. For example, considering high thermal stability and radical capturing ability of lignins, they are demonstrated

as promising candidates for functional additives, such as antioxidant, flame retardant, UV stabilizer and thermal stabilizer in polypropylene, polyvinyl chloride and natural rubber et al. [14–18]. Additionally, they also can be utilized to improve the thermal and photochemical stability of polyolefin [19,20]. However, mechanical properties usually deteriorate with lignin proportion because of very low compatibility/miscibility of polar lignin in nonpolar polymer matrix.

PVA, a water-soluble and biodegradable polymer, exhibits excellent chemical resistant, gas barrier properties, biocompatibility and optical properties [21]. PVA and PVA-based composites are used in a wide range of applications including coatings [22], optical films [23], packaging materials [24] and nano-fibers [25]. However, the low mechanical strength of PVA requires the use of reinforcing agents, such as carbon nanotubes [26], cellulose nanofibres [27], nanofibrillated celluloses [28] and cellulose nanocrystals [29]. These nano-fillers show extremely high Young's modulus ranging from 10 GPa to 150 GPa [28,29]. However, the improvement of mechanical properties usually is unsatisfied due to their nano-scale sizes and poor dispersions [30]. In contrast, kraft lignin particles, with a few micrometers and relatively lower Young's modulus (around 4 GPa) [31], can form strong interactions with PVA via hydrogen bonding [32]. Previous studies have demonstrated that strong interfacial interaction is beneficial to obtaining outstanding reinforcement effects [33]. To our best knowledge, the modification effect of industrial lignins on PVA's mechanical properties has not yet been studied. Using pulping waste to reinforce composites

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Nomenclature

HLS	eucalyptus lignosulfonate calcium
PVA	poly(vinyl alcohol)
T_g	glass-transition temperature
T_m	melting temperature
ΔH_m	heat of fusion
ΔC_p	specific-heat increment
T_α	crystalline relaxations
CNCs	cellulose crystals
$X_c\%$	relative crystallinity

structure provides a promising approach for reducing the demand on petroleum-based and non-biodegradable materials [33–36].

The eucalyptus, a fast-growing and typical hardwood, are widely used as raw materials in the pulping and paper industry in the worldwide [37]. In this work, eucalyptus lignosulfonate calcium (HLS)/PVA blends which could be potentially used as eco-friendly packaging film were prepared by water solution casting. Here, we mainly focused on the mechanical and thermal properties of blends which were investigated by DSC, DMA analysis and universal tensile method. Furthermore, the intermolecular interactions of blends were elucidated by calculating q value in Kwei equation. In addition, the crystallinity and compatibility of blends were studied by XRD spectroscopy and SEM microscopy.

2. Experimental

2.1. Materials

Eucalyptus lignosulfonate calcium (HLS, ~96%) was purchased from Aladdin Chemical Company. PVA (polymerization degree, 1700; 99% hydrolyzed) was obtained from Sichuan Vinylon Factory, SINOPEC (China) in granule form.

2.2. Preparation of blends by casting method

Predetermined weights of PVA and HLS were dissolved in 100 ml distill water under stir at 95 °C for 3 h. HLS/PVA solution was then casted in Petri dishes and evaporated at 70 °C at vacuum oven. Finally, films obtained from various components of HLS to PVA (0/100, 5/95, 15/85, 25/75, 35/65, 50/50 and 60/40, wt/wt) were recorded as PVA, 5LPVA, 15LPVA, 25LPVA, 35LPVA, 50LPVA and 60LPVA, respectively.

2.3. Characterizations

Prior to characterizations except for mechanical test, all films were dried under vacuum ($P < 0.3$ MPa) at 105 °C for 5 h to remove water (proved by TG results, only about 0.5% weight loss between 25 °C and 150 °C after vacuum dry).

2.3.1. Differential scanning calorimetry (DSC)

Glass-transition temperature (T_g) and melting temperature (T_m) of blends were determined on a TA instrument (Mettler Toledo DSC 1 Star system) with a scan rate of 10 °C/min over the temperature ranged from –40 °C to 300 °C. All samples were preheated to 125 °C for further removing water. The flow rate of nitrogen atmosphere was maintained at 50 ml/min during processes. T_g , T_m and heat of fusion (ΔH_m) were obtained from the minimum value of curve first derivative, the minimum of peak and area of the melting peak,

respectively [38]. In addition, relative crystallinity ($X_c\%$) of PVA in blends was calculated as the following equation:

$$X_c\% = 100\% \times \frac{\Delta H_m}{\Delta H_m^0 \times w_t}$$

ΔH_m of 100% crystalline PVA is 161 J g⁻¹ [31].

2.3.2. Dynamic mechanical analysis (DMA)

The mechanical loss tangent ($\tan\delta$) was measured with DMTA Q800 (TA instruments, DE, USA) at 1 Hz oscillatory frequency in the nitrogen atmosphere. Temperature was raised from 0 °C to 200 °C at the rate of 3 °C/min.

2.3.3. Infrared spectroscopy (FTIR)

FTIR spectra of samples were recorded on the Nicolet 560 FTIR spectrometer using Attenuated Total Reflection method. Each spectrum was obtained with 32 scans in the frequency range of 4000–600 cm⁻¹ with 2 cm⁻¹ resolution.

2.3.4. X-ray diffractograms (XRD)

The crystallinity of the various blends was determined by using an X'Pert MPD diffractometer with Ni-filtered. Scan was performed in the 2θ range of 3–50° with speed of $2\theta = 0.06^\circ \text{ s}^{-1}$.

2.3.5. Scanning electron microscope (SEM)

The fracture surfaces were analyzed by SEM (JSM-5900LV) in order to identify the compatibility of blends. Prior to characterizations, blends were immersed in the liquid nitrogen for 3 h to obtain freeze-fractured surfaces which were then covered with a layer of gold.

2.3.6. Mechanical properties

The tensile strength, Young's modulus and elongation at break of composites were determined by using an Instron 5567 Universal Testing machine at a speed of 20 mm/min. Prior to tensile testing, the test specimens were equilibrated in an ambient environment for 7 days at a relative humidity of 54% (saturated Mg(NO₃)₂ solution). The thickness average values were measured with a micrometer five times. Five species were performed for each composite.

3. Results and discussion

3.1. DSC analysis

DSC has been extensively used to assess the extent of miscibility for polymer blends. Generally, a single T_g is considered as a decisive evidence of the single-phase system and homogeneous miscibility [39]. Here, the results of DSC analysis for HLS/PVA blends were shown in Fig. 1 and Table 1. As for pure PVA, the former platform ($T_g = 74.9^\circ\text{C}$) in the lower temperature (0–120 °C) region is apparently attributed to PVA chain movement in the amorphous region [40]; the latter one (β_c , locating at 132.8 °C) in the higher temperature region (120–180 °C) is associated with crystalline relaxations (T_α) of PVA [34]. Amorphous HLS exhibits one T_g at 149.2 °C which is obviously higher than that of PVA [38].

HLS/PVA blends show a single compositional dependent T_g over the entire blend ratio, which obviously rise gradually from 74.9 °C to 103.5 °C. This single T_g strongly indicates that HLS/PVA blends show miscibility on a dimensional scale between 5 and 15 nm. The dependence of a single T_g on the proportion of individual components was illustrated in Fig. 2. It is demonstrated that this T_g versus composition do not obey either Fox, Couchman or Gordon–Taylor relationships, but it could be well fitted by Kwei

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