

Enhanced Mechanical Performances of Waterborne Polyurethane Loaded with Lignosulfonate and its Supramolecular Complexes

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ABSTRACT: The modified waterborne polyurethane (WPU) with enhanced mechanical properties has been prepared after introducing lignosulfonate calcium (LS). Meanwhile, the LS was associated with WPU component by chemical grafting and/or physical attraction and hence produced a star-like network with LS and its supramolecular complexes as center. Especially, when the LS content was 1.5 wt %, the strength and elongation of WPU/LS blends (WLS) simultaneously increased. At this time, the center of network was dominated by the single molecules of spherical LS. Thereafter, with the increase of LS content, the strength of WLS blends increased unceasingly up to 6.0–7.5 wt % of LS loading while the elongation gradually decreased. Because the LS tend to aggregate as supramo-

lecular complexes spontaneously, the center of network was gradually replaced by the LS supramolecular complexes. The structural changes of WLS blends were characterized by FTIR, DSC, and DMA. The results suggested that the LS component was mostly fused with hard-segments of WPU component and hence induced the formation of physical interaction, importantly for hydrogen bonding, depending on the compulsive association of chemical grafting and the impulse of similar hydrophilicity between the hard-segment and LS. © 2007 Wiley Periodicals, Inc. *J Appl Polym Sci* 106: 4257–4263, 2007

Key words: waterborne polyurethane; lignin; star-like network; supramolecular complexes; mechanical properties

INTRODUCTION

Lignin, a by-product of pulping and papering with low cost, has been evaluated as a potential raw substance for the fields of chemical industry and material.^{1,2} Especially, based on its renewable, non-toxic, and biodegradable character, lignin-based materials has been considered to deal with the petroleum-resources crisis and environment pollution. Since lignin has all kinds of functional groups (hydroxyl, carboxyl, phenol, etc.), it can be chemically modified as

a raw material or incorporated into polymer matrix as filler to develop lignin-based materials.³ For example, lignin as precursor has been used to synthesize many kinds of polymer materials, such as phenol-formaldehyde resin,^{4,5} polyurethane,^{6,7} polyester,⁸ and so on. Meanwhile, lignin was also blended with rubber,^{9,10} polyolefin,^{11,12} polyester,^{13–15} polyether,^{16,17} starch,¹⁸ and soy protein^{19–21} to enhance the strength, water resistance, thermal stability, and other properties. On the basis of the understanding into the supramolecular aggregation of lignin induced by inter- and intramolecular hydrogen bonding of various polar groups in lignin,¹³ it has been realized that the lignin in the blends also aggregated as supramolecular complexes and even located into nano-scale.^{20,21} This finding opened a way to optimize the properties of blends by controlling the lignin structure and the character of formed supramolecular complexes thereon. At the same time, the nano-scale dispersion of lignin was also the key to fully perform the function of reinforcing and fire-retardance.

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The reactivity between —OH in lignin and isocyanate has caused an increased interest in developing the lignin-based polyurethane. Especially, the concern on lowering cost impelled many research groups to endeavor to synthesize the polyurethane loaded with high lignin content. However, high lignin loading (higher than 30 wt % as usual) not only led to the great loss of toughness, but went against the reinforcing function.⁷ Recently, the effect of simultaneous enhancement of strength and elongation by filling a small amount of lignin was discovered,^{22–25} attributing to the formation of star-like network centered by spherical lignin molecules with high rigidity.²⁶ To improve the mechanical properties of the environment-friendly waterborne polyurethane (WPU), such star-like network has been attempted to migrate into WPU. As expected, adding a small amount of nitro-lignin (NL)²⁷ in the stage of chain-extending produced the optimal star-like network structure and still showed the simultaneous enhancement of strength and elongation (1.8-fold over the pure WPU). Although adding NL at the stages of as-emulsification and emulsification thereafter can not obviously improve the mechanical properties, it put forward an approach to compound the hydrophilic industrial lignin, such as lignosulfonate, into WPU.

The lignosulfonate, derived from the process of cellulose manufacture by the sulfite method from wood and other plant raw materials,²⁸ is a water-soluble polydisperse polyelectrolyte with high rigidity and contains metal ion (Ca^{2+} , Mg^{2+} , or Na^+), hydrophilic sulfate and hydroxyl as well as hydrophobic phenol groups. Compared with the NL obtained by further derivation, the lignosulfonate has prominent advantage to easy-to-availability and low cost as well as many kinds of active groups. In this work, we had used water-soluble lignosulfonate calcium (LS) to add into the WPU in the midst of emulsification or mix with WPU latex post of emulsification. Although the chemical grafting between LS and polyurethane chain was inhibited, the LS components can be closely associated with polyurethane chains by strong physical interactions and hence induced the formation of star-like network. Meanwhile, due to inter- and intramolecular hydrogen bonding of various polar groups in LS, the center of star-like network might be dominated by the LS single molecule and the supramolecular LS complex with increasing LS content.²⁰ Furthermore, the structures of WPU/LS blends were characterized by Fourier transform infrared spectroscopy (FTIR), differential scanning calorimetry (DSC), dynamic mechanical analysis (DMA), and tensile tests. The role of LS in WPU will be understood while the relationship of structure–mechanical property was discussed.

EXPERIMENTAL

Materials

Polyoxypropylene glycol with a number-average molecular weight (M_n) of 2000 (PPG₂₀₀₀) and dimethylol propionic acid (DMPA) was respectively donated by Nanjing Zhongshan Co. (Nanjing, China) and Huzhou Changsheng Co. (Zhejiang, China), while toluene diisocyanate (TDI) and triethylamine (TEA) were purchased from Sinopharm Chemical Reagent Co. (Shanghai, China). All the reagents are dehydrated under vacuum at 80°C for 12 h before use. Acetone of analytical grade was used as reaction solvent. Lignosulfonate calcium (LS) was donated by the key laboratory of cellulose and lignocellulosics chemistry (Guangzhou Institute of Chemistry, Chinese Academy of Sciences, China), and its weight-average molecular weight (M_w) was 26,630 while the polydispersity ($d = M_w/M_n$) was 2.98.

Preparation of lignosulfonate/waterborne polyurethane blend films

The synthesis of waterborne polyurethane (WPU) was depicted as follows. PPG₂₀₀₀ and TDI were first placed into a three-necked round-bottomed flask equipped with a mechanical stirrer and a reflux condenser. Subsequently, the reactant was heated up to ca. 65°C, and then kept mechanical stirring under a nitrogen atmosphere for 2 h. Thereafter, DMPA as chain-extender was dissolved into acetone and then dropwise added with elevating temperature up to 75°C followed by reaction for 1 h. In this course, acetone was supplied to lower the viscosity of reactant. Afterward, the resultant product with NCO/OH molar ratio of 1.8 was cooled down to lower than 40°C followed by neutralizing carboxylic acid groups of DMPA in polyurethane chain by TEA. At last, the emulsification was carried out by adding iced water under vigorous stirring to produce WPU latex with solid content of 20 wt %. After removing acetone, the latex was cast on the Teflon mold and then cured at 50°C by evaporating water to obtain WPU film.

In the process of synthesizing WPU, LS was introduced at two stages, that is in the midst of emulsification (Method I) and mixing with WPU latex post of emulsification (Method II), namely the LS aqueous solution was used as emulsification (Method I) or mixed with WPU latex (Method II). According to the LS content and compounding method, the resultant LS modified waterborne polyurethane (WLS) were respectively coded as WLS-1.5-I, WLS-3.0-I, WLS-4.5-I, WLS-6.0-I, WLS-7.5-I, WLS-9.0-I for Method I as well as WLS-1.5-II, WLS-3.0-II, WLS-4.5-II, WLS-6.0-II, WLS-7.5-II, WLS-9.0-II for method II, where the numbers represent the LS content in whole solid films.

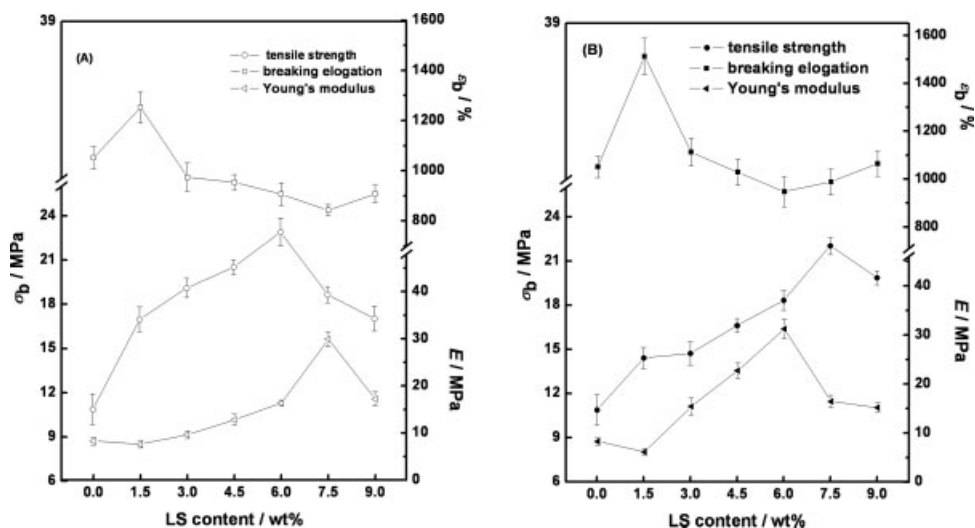


Figure 1 Effects of LS content on the mechanical properties of the WLS films prepared by Method I (A) and Method II (B) as well as the pure WPU film.

Characterization

Fourier transform infrared (FTIR) spectra of all the films were recorded on a FTIR 5700 spectrometer (Nicolet, USA) by using Smart OMNT reflect accessories in the range of $4000\text{--}700\text{ cm}^{-1}$.

Differential scanning calorimetry (DSC) was carried out on a DSC-204 instrument (Netzsch, Germany) under nitrogen atmosphere at a heating or cooling rate of $20^\circ\text{C min}^{-1}$. The films were scanned in the range of -100 to 150°C after a pretreatment (heating from 20 to 100°C and then cooling down to -100°C) of eliminating the thermal history.

Dynamic mechanical analysis (DMA) was carried out on a DMA 242C dynamic mechanical analyzer (Netzsch, Germany) at a frequency of 1 Hz . The temperature ranged from -150 to 100°C with a heating rate of 3°C min^{-1} . Measurements were performed using a dual cantilever device and the size of the testing samples was $30 \times 10 \times 0.7\text{ mm}$.

The tensile strength (σ_b), elongation at break (ϵ_b), and Young's modulus (E) of the films were measured on a CMT6503 universal testing machine (Shenzhen SANS Test Machine Co., Shenzhen, China) with a tensile rate of 200 mm min^{-1} according to GB13022-91. The tested samples were cut into the quadrate strips with the width of 10 mm while the distance between testing marks was 30 mm . An average value of five replicates of each sample was taken.

RESULTS

Mechanical properties of lignosulfonate/waterborne polyurethane blends

Figure 1 showed the effects of LS content on the mechanical properties of blends prepared by two meth-

ods, including tensile strength (σ_b), elongation at break (ϵ_b), and Young's modulus (E). The reinforcing effect of LS was obvious, resulting in the gradual increase of σ_b up to the LS content of $6.0\text{ wt}\%$ (Method I) and $7.5\text{ wt}\%$ (Method II). The Method I might favor more the higher strength. Meanwhile, after the initial enhancement at $1.5\text{ wt}\%$ LS the lower ϵ_b , in contrast to that of pure WPU, gradually decreased until the LS content of $7.5\text{ wt}\%$ (Method I) and $6.0\text{ wt}\%$ (Method II) followed by a slight increase. The changes of E functioned as LS content were very opposite to those of ϵ_b . It was worth noting that the addition of $1.5\text{ wt}\%$ resulted in the simultaneous enhancement of σ_b and ϵ_b . The ϵ_b of WLS-1.5-II was slightly higher than that of WLS-1.5-I.

Hydrogen bonding in lignosulfonate/waterborne polyurethane blends

The FTIR spectra of the WPU and WLS films prepared by two methods were shown in Figure 2, respectively, and the absorptions of urethane --C=O was specifically amplified. As well-known, --NH of WPU can be hydrogen bonded with the urethane --C=O of hard-segments and the ether- or ester-oxygens of soft-segments. As a result, the changes of --NH absorption can be associated with the hydrogen bonding of hard-hard-segment and hard-soft-segment while the absorption of --C=O can reflect the extent of hydrogen bonding of hard-hard-segment. Herein, the stretching vibration of --NH consisted of two bands, that is, hydrogen-bonded --NH (the peak at 3310 cm^{-1}) and free --NH (the peak at 3485 cm^{-1}).²⁹ Correspondingly, the absorption of urethane --C=O also included the bands of hydrogen-bonded --C=O at 1710 cm^{-1}

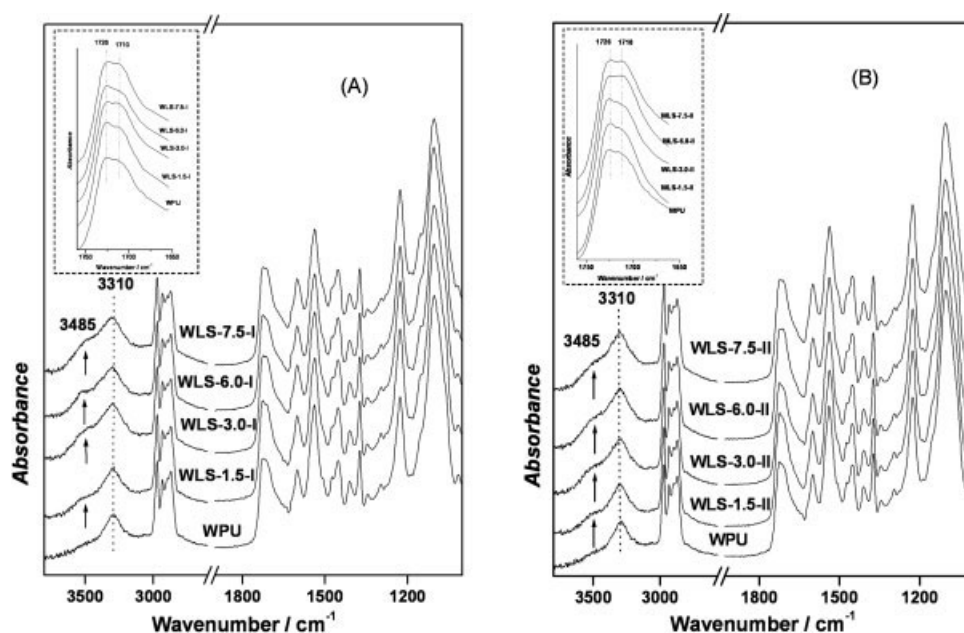


Figure 2 FTIR spectra for the WLS films with various LS content prepared by Method I (A) and Method II (B) as well as the pure WPU film.

(Ref. 29) and the band of free —C=O at 1726 cm^{-1} .^{30,31} Obviously, the free —NH band of the WLS films prepared by two methods became stronger after adding LS, and even its intensity increased with increasing LS content. It suggested that the added LS destroyed the original hydrogen bonds in pure WPU component while high LS content might boost the damage extent. Meanwhile, the intensity of hydrogen-bonded —C=O , in contrast to that of free —C=O , was firstly decreased for WLS-1.5-I and WLS-1.5-II, and then increased with the unceasing increase of LS content. It indicated that adding least LS (1.5 wt %) resulted in the damage of hydrogen bonds between hard- and hard-segments originally existed in pure WPU component. However, the increased intensity of absorption associated with hydrogen bonded —C=O might resulted from the hydrogen bonding between the polar groups in LS and urethane —C=O . On the whole, the FTIR analysis depicted that the introduction of LS destroyed the original hydrogen bonds associated with hard-segment (—NH and —C=O) in WPU component while the LS component might be close to the hard-segment and hence formed new hydrogen bonds between the polar groups in LS and urethane —C=O .

Thermal analysis of lignosulfonate/waterborne polyurethane blends

DSC thermograms of the WPU and WLS films prepared by two methods were shown in Figure 3, and the effect of LS content on the data of glass and

melting transitions, such as glass transition temperature ($T_{g,\text{mid}}$) and heat-capacity increment (ΔC_p) as well as melting temperature (T_m) and enthalpy (ΔH_m), were summarized in Table I. As well-known, the glass transition temperature can be used to reflect the mobility of soft-segment and hence evaluate microphase separation between hard- and soft-segments in polyurethane. For two series of WLS films, the T_g s were firstly increased for WLS-1.5-I and WLS-1.5-II, and then decreased followed by a slight increase. However, the variance of T_g s was not obvious as a whole, that is, the difference was lower than ca. 1.1°C . It suggested that the soft-segment do-

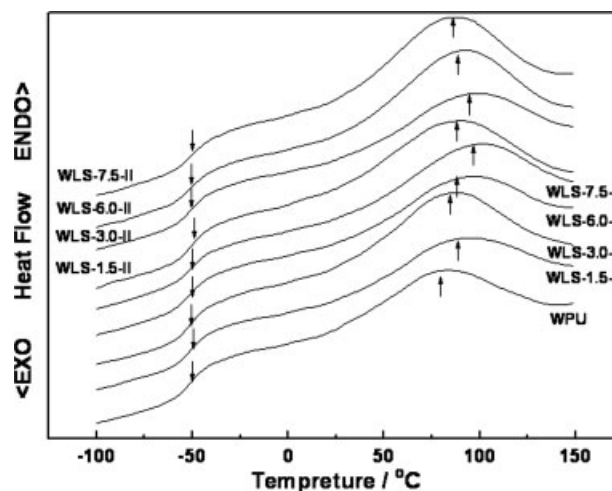


Figure 3 DSC curves as a function of temperature for the WLS films prepared by two methods as well as the pure WPU film.

TABLE I
DSC and DMA Data of the WLS and WPU Films

Sample	DSC data				DMA data	
	$T_{g,mid}$ (°C)	ΔC_p (J g ⁻¹ K ⁻¹)	T_m (°C)	ΔH_m (J g ⁻¹)	$T_{\alpha,max}$ (°C)	Height of loss peak
WLS-1.5-I	-49.9	0.455	88.9	35.29	-36.1	0.442
WLS-3.0-I	-51.0	0.536	84.6	50.07	-37.1	0.389
WLS-6.0-I	-50.3	0.458	88.6	30.51	-35.3	0.371
WLS-7.5-I	-50.2	0.453	96.7	41.32	-39.4	0.294
WLS-1.5-II	-49.8	0.505	87.4	48.79	-37.2	0.447
WLS-3.0-II	-50.6	0.475	94.3	37.71	-36.4	0.309
WLS-6.0-II	-50.5	0.495	89.7	53.51	-37.6	0.323
WLS-7.5-II	-49.7	0.485	84.3	53.28	-39.2	0.372
WPU	-50.6	0.525	79.6	37.47	-32.6	0.437

main was not almost affected by the added LS. In contrast to no obvious changes of T_g s, the T_m s of hard-segment obviously increased after adding LS. It suggested that the LS restricted the motion of hard-segments by virtue of the chemical grafting and newly formed hydrogen bonds between the polar groups in LS and urethane —C=O, which proved by the FTIR results. Meanwhile, except for the effect of hydrogen bonding mentioned above, the increase of ΔH_m after adding LS also attributed to better molecular orientation in the hard-segment domains.

Dynamic mechanical analysis of lignosulfonate/waterborne polyurethane blends

DMA is a powerful technique to study initial motion of frozen polymer segments through α -relaxation at molecular scale for which the specific heat increment of glass transition at domain scale measured from DSC is generally ill defined. Thus, the $\tan \delta$ curves

functioned as temperature and corresponding data assigned to α -relaxation, such as $T_{\alpha,max}$ and height of loss peak for the WLS and WPU films were shown in the Figure 4 and Table I, respectively. Although the DSC results showed that the soft-segment domains was not almost affected by the added LS, the obvious decrease of $T_{\alpha,max}$ s for the WLS films, in contrast to that of pure WPU, suggested that the mobility of soft-segment was improved. Combined with the increasing intensity of free —NH in FTIR spectra, it resulted from the cleavage of hydrogen bonds between —NH in hard-segment and ether-oxygen in soft-segment. Except for the WLS films containing 1.5 wt % LS prepared by two methods, the height of loss peak for the other blend films was lower than that of pure WPU. The higher damping for the WLS films containing 1.5 wt % LS was in consistent with the enhanced elongation and decreased Young's modulus, that is, higher toughness.

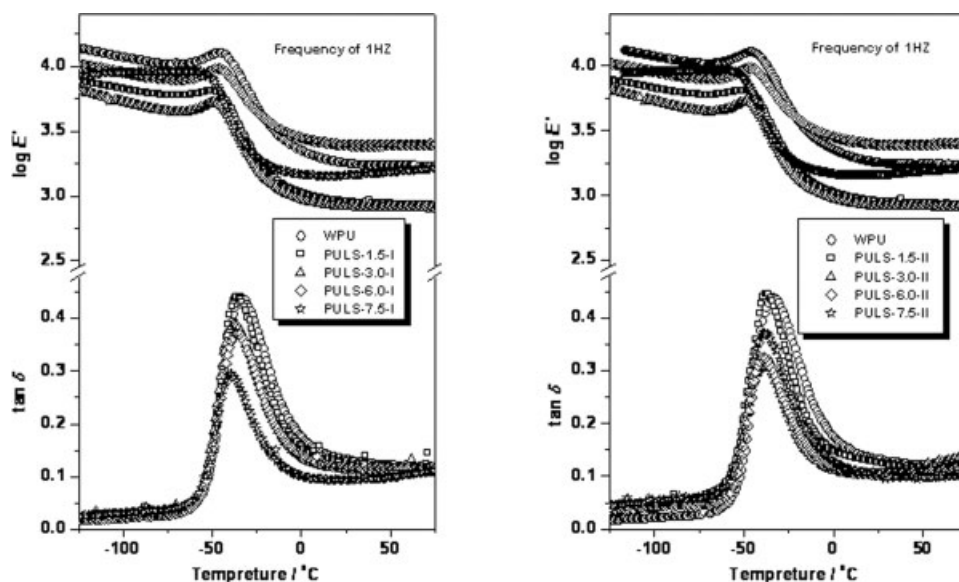


Figure 4 Storage modulus ($\log E'$) and $\tan \delta$ as functions of temperature for the WLS films with various LS content prepared by Method I (A) and Method II (B) as well as the pure WPU film.

DISCUSSION

Proposed structure in lignosulfonate/waterborne polyurethane blends

In this work, only two preparation methods had been applied, that is, adding LS in the midst of emulsification (Method I) and mixing LS with WPU latex post of emulsification (Method II), because of the water-solubility of LS. According to the previous report,²⁷ when adding the LS aqueous solution for emulsification (Method I), —OH in LS might compete with H₂O to react with —NCO. At this time, the LS component as the center of star-like network was associated with polyurethane chains by the chemical grafting of low extent as well as physical interaction, where the hydrogen bonding was the most important physical interaction. The Method II, that is blending LS with the latex particles of WPU, almost eliminated the chemical grafting due to lack of polyurethane prepolymer containing active —NCO after emulsification. As a result, only physical attraction existed between LS and WPU components. Meanwhile, the LS with multifunctional groups played a center of physical crosslinking and also produced a star-like network.

Although the LS can disperse as isolated molecule in the blend, the formation of self-aggregated supramolecular complexes was inevitable with increasing LS content. Thus, in the WLS blends with higher LS loading, the center of star-like network might be partly dominated by the supramolecular LS complexes. The FTIR and DSC results showed that the added LS mainly contributed to the structural changes of hard-segment due to the chemical reaction between —OH of LS and —NCO of polyurethane prepolymer to provide compulsive associations as well as the hydrophilicity of DMPA in hard-segment similar to LS to induce the fusion. Once the LS component enriched around the hard-segment, the physical interaction, such as hydrogen bond, consequentially formed. As a result, it can be concluded that the LS component as isolated molecule (low LS content, i.e. 1.5 wt %) and/or aggregated supramolecular complexes (increasing LS content) became the center of star-like network and strongly adhered hard-segments depending on the chemical grafting and physical interaction, which proved by the obvious increased T_m of hard-segment and the formation of newly hydrogen bonding between the —OH in LS and the urethane —C=O.

Structure–mechanical properties relationship

The highlights that adding LS improved mechanical performances was simultaneous reinforcing and toughening for WLS-1.5 only containing 1.5 wt % LS prepared by two methods as well as the further enhancement of strength and modulus with no

obvious expense of elongation up to the LS loading of 6.0 wt % (Method I) and 7.5 wt % (Method II). It mainly attributed to the formation of star-like network with the rigid LS and its supramolecular complexes as center constructed by chemical grafting and physical interaction between LS and WPU components, which profitably put up the reinforcing function of the LS rigidity and preserved high elongation caused by the entanglement of WPU component. Obviously, the covalent bonds of chemical grafting can produce higher strength for the WLS blends prepared by Method I. However, the steric hindrance, derived from chemical grafting, might reduce the associations between the LS component as center and polyurethane chains, resulting in lower elongation. The least loading of LS (1.5 wt %) might produce the star-like network with the isolated LS molecules as center and then provided the increased strength and elongation at one time. Thereafter, the increased LS and its supramolecular complex produced higher crosslinking density with increasing the LS content, which enhanced the strength and dimensional stability of materials. As a result, the elongation decreased. However, too high LS loading might produce the large-scale aggregates of supramolecular complex, resulting in the slight decrease of strength and modulus. Correspondingly, the decrease of the LS component as center led to the slight increase of elongation once more.

CONCLUSION

A series of lignosulfonate modified waterborne polyurethane (WLS) were synthesized by adding LS at two stages, that is, in the midst of emulsification (Method I) and mixing with WPU latex post of emulsification (Method II). The formation of star-like network with the rigid LS and its supramolecular complexes as center by the fusion of LS component and hard-segment via chemical grafting and physical interaction fully showed the reinforcing function of the LS rigidity and preserved high elongation caused by the entanglement of WPU component. It was worth of note that adding only 1.5 wt % LS resulted in the simultaneous enhancement of strength and elongation. At this time, the center of star-like network was dominated by the isolated LS molecules. Thereafter, with the increase of LS content, the center of formed supramolecular LS complexes and the increased crosslinking density resulted in the continuous increase of strength and the decrease of elongation. When the LS loading were too high, the large-scale aggregates of supramolecular LS complexes formed while the network center decreased thereon resulting in the decrease of strength and modulus as well as the increase of elongation.

Since the dispersion state and scale of LS component as well as the interaction between LS center and WPU component in star-like network had a great influence on the mechanical properties of resultant materials, this work submitted a way to control the mechanical performances of the lignin modified WPU by changing the adding content of LS and applying various synthesis methods.

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