Simultaneous Enhancement in Strength and Elongation of Waterborne Polyurethane and Role of Star-Like Network with Lignin Core

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ABSTRACT: We have reported that a star-like network structure with lignin as center in polyurethane resulted in the simultaneous enhancement in mechanical strength and elongation. In this study, we aimed to enhance the mechanical properties of waterborne polyurethane by adding nitro-lignin (NL) to form analogical star-like network. It was found that the resultant material has optimal mechanical performances when the NL content is 3.0 wt %, i.e., its apparent mechanical strength and elongation increased by about 80% at one time. Especially, its real mechanical strength reaches 71.3 MPa at this time, which is 3.6-fold over that of neat waterborne polyurethane material. The simultaneous enhancements in strength and elongation are attributed to the forming of star-like network in the com-

posites. The stiffness of lignin improved the mechanical strength, while the entangling and crosslinking in polyurethane component increased the elongation. However, higher NL loading and lower grafting level induced the forming of supramolecular NL aggregates, and hence greatly inhibited star-like network, resulting in lower mechanical strength and elongation. However, the Young's modulus of the material is enhanced with an increase of rigid supramolecular aggregates. © 2008 Wiley Periodicals, Inc. J Appl Polym Sci 109: 56–63, 2008

Key words: waterborne polyurethane; nitro-lignin; network; mechanical properties; structure-properties relationship

INTRODUCTION

Lignin, an abundant renewable resource, shows a great potential as raw substances for chemical industry and material by virtue of the high reactivity and easy-to-derivable characters.[1,2] Especially, industrial lignin derived from by-product of pulping and papering can be commercially available in low-cost.[3] Recently, high reactive lignin with a unique phenylpropane structure has been used to replace petroleum-resources, while environment protection also impulses the research of lignin-based materials due to its biodegradability and nontoxicity.[2,4] Traditionally, lignins have been evolved as polymeric materi-

als via chemical reaction[4,5] or graft polymerization,[2,6,7] and incorporated into polymer matrices as filler.[2,8–12] As the multilevel structures of lignin and its derivatives, such as chemical structure,[13] spherical conformation,[14] and supramolecular aggregate,[8,15] have been gradually identified, the understanding in the role of lignin in polymeric materials has made great progress. Usually, a three-dimensional network structure of lignin,[3] which is built on C—C and C—O linkages of phenylpropane units, is shown as a dense and rigid sphere,[16] and acts as core to derivate star-like[7] or hyperbranched structures.[17] The stretching grafted chains of star-like hydropropyl lignin can be tightly associated with soy protein matrix, and hence facilitate the reinforcing of the lignin core.[10] At the same time, spherical nitro-lignin (NL) was blended into polyurethane to form a great star-like networks with the NL core, resulting in the remarkably enhancement in strength and elongation at one time.[18,19] In addition, the inter- and intramolecular hydrogen bonds based on various polar groups in lignin could induce supramolecular aggregation,[20] and is generally shown as oblate domains in blends. The characters of such supramo-

lecular domains are under control of lignin's structure. For example, the excluded effect of stretching chains on hydropropyl lignin produced a supramolecular domain that permitted polymer matrix penetrating,[10] which is impossible for unmodified lignin. Meanwhile, hydrogen bonding, originated from —COO— in polyester and —OH in alkylated kraft lignin in peripheral regions of supramolecular domains in the blends, should be powerful enough to facilitate the plasticizing effect of polyester, but not so strong as to dismantle these huge associated entities significantly.[8]

Polyurethane shows predominant and controlled mechanical performances depending on the synergistic effect of soft- and hard-segments as well as various optional species.[21–23] Currently, polyurethane has been extensively used as coating, adhesive, elastomer, foam, fiber and so on.[24] As increasing concern on environment-friendliness and human health, organic solvent-free polyurethane (i.e., waterborne polyurethane) has been developed by introducing hydrophilic groups into polyurethane,[25] which almost inherits all applications of solventborne polyurethane. Lignin and its derivatives can alternatively act as the component of soft- and hard-segment in polyurethane depending on molecular weight,[26] resulting in low-cost, high glass transition temperature and rigid composite materials. To reduce the rigidity of lignin-based polyurethane, flexible diisocyanates and linear soft-segments were used,[19,27] while the content and structure of lignin[26,28] as well as NCO/OH molar ratio[18] in polyurethane should also be controlled. If not considering that high lignin loading severely decreases cost, low loading level of lignin (lower than ~9 wt %) can simultaneously enhance strength and elongation.[14,18,19,29]

In this work, based on simultaneous reinforcing and toughening of the great star-like network with lignin core,[14,18,19] high mechanical performances of NL modified waterborne polyurethanes are expected. Besides the effects of NL content, the network structures in NL modified waterborne polyurethane might be regulated by adding NL at given stage in the synthetic process of waterborne polyurethane, such as chain-extending (Method I), in the midst of emulsification (Method II) and mixing with WPU latex post of emulsification (Method III). In such three stages, the numbers of reactive isocyanate groups are obviously different. Moreover, Method I gave network structure similar to previous report[18]; in the midst of emulsification, —OH in NL could compete with H_2O to react with reactive isocyanate groups to produce a network structure of low grafting level; when mixing with WPU latex post of emulsification, the NL mainly dispersed into polyurethane matrix. As a result, the role of star-like networks with spherical NL core will be fully understood by comparing the structures and properties of composites prepared by three methods, which were characterized by Fourier transform infrared spectroscopy (FTIR), differential scanning calorimetry (DSC), dynamic mechanical analysis (DMA), and tensile tests.

EXPERIMENTAL

Materials

Polyoxypropylene glycol with a number-average molecular weight (M_n) of 2000 (PPG_{2000}) and dimethylol propionic acid (DMPA) were, respectively, donated by Nanjing Zhongshan Co. Ltd. (Nanjing, China) and Huzhou changsheng Co. Ltd. (Zhejiang, China) while toluene diisocyanate (TDI) and triethylamine (TEA) were purchased from Sinopharm Chemical Reagent Co. Ltd. (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.

The preparation and structural character of NL was detailedly described in our previous publication.[14] The hydroxyl number in NL was determined as 57 —OH per 100 C_9 units according to previous report.[30] The weight-average molecular weight (M_w) of NL was determined by multiangle laser light scattering instrument (MALLS, DAWN® DSP, Wyatt Technology Co., USA) equipped with a He-Ne laser (λ = 632.8 nm) to be 20.6×10^4 while its intrinsic viscosity [η] in THF at 25°C was determined by Ubbelohde viscometer to be 4.42 mL g^{-1}. The structure similar to Einstein sphere of NL has been deduced by noting that the [η] value is much lower than those for normal polymers with the same M_w, which is attributed to its dense network structure.[14]

Preparation of NL modified waterborne polyurethane films

The synthesis of waterborne polyurethane (WPU) is depicted as follows. PPG_{2000} and TDI were firstly placed into a three-necked round-bottomed flask equipped with a mechanical stirrer and a reflux condenser. Subsequently, the reactant was heated up to ~ 65°C, and then kept mechanical stirring under a nitrogen atmosphere for 2 h. After DMPA as chain-extender was dissolved into acetone and then dropwise added, the reaction temperature was elevated up to 75°C followed by continuing the reaction for 1 h. In this period, acetone was supplied to lower the viscidity of reactant. Afterward, the resultant product with NCO/OH molar ratio of 1.5 was cooled down to lower than 40°C, and then —COOH was neutralized by adding TEA. At last, the emulsification was carried out by adding icy water under severer shearing to produce waterborne polyur-

ethane latex with a solid content of 20 wt %. After removing acetone under vacuum, the latex was caste in the Teflon mold and then cured at 50°C by evaporating water to obtain WPU film.

In such process, NL was added at three stages, such as chain-extending (Method I), in the midst of emulsification (Method II) and mixing with WPU latex post of emulsification (Method III), and finally produced the films of NL modified waterborne polyurethane (WUL). At the stage of adding DMPA, NL of given content was dissolved into acetone together with DMPA and then added (Method I). The resultant WUL films were coded as WUL-1.5, WUL-3.0, and WUL-4.5, respectively, where the numbers represent the content of NL in whole solid films. In addition, NL was dissolved into water, and then incorporated in the midst of emulsification (Method II) or mixed with WPU latex post of emulsification (Method III). The resultant WUL films containing 3 wt % NL was coded as WUL-3.0-II and WUL-3.0-III, respectively. The preparation of all the WUL films as well as WPU film is depicted in Scheme 1.

Characterization

Fourier transform infrared (FTIR) spectra of all the films were recoded on a FTIR 5700 spectrometer (Nicolet, USA) by using Smart OMNT reflect accessories in the range of 4000–700 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°C min^{-1}. The films were scanned in the range of −100 to 150°C after a pretreatment of eliminating thermal history (heating from 20 to 100°C and then cooling down to −100°C).

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 $30 \times 10 \times \sim 0.7$ mm^3.

The tensile strength (σ_b), elongation at break (ε_b) and Young's modulus (E) were measured on a CMT6503 universal testing machine (Shenzhen SANS Test Machine Co. Ltd., Shenzhen, China) with a crosshead 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. During the stressing, the films occur greatly elongated, so we regulate the data as follows: the nominal strain (ε_{nom}) and the nominal stress (σ_{nom}) were calculated by $\varepsilon_{nom} = e/L_0$ and $\sigma_{nom} = F/S_0$, respectively, where S_0 is the initial cross section. The true strain (ε_{true}) can be determined by $\varepsilon_{true} = \ln(L/L_0)$,
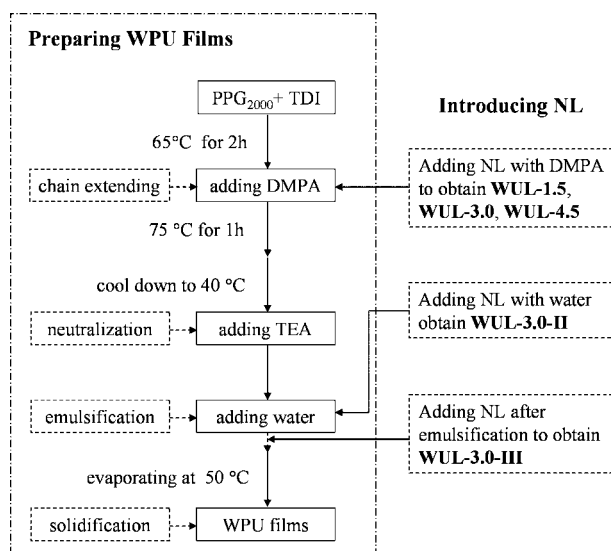
Scheme 1 Schematic illustration for synthesizing WPU and WUL films with different compounding methods.

where L is the length of the sample during the test ($L = L_0 + e$). The true stress (σ_{true}) can be calculated by $\sigma_{true} = F/S$, where S is the area of cross section. S was determined assuming that the total volume of the sample remained constant during the test, so that $S = S_0 L_0/L$.

RESULTS

Mechanical properties of NL modified waterborne polyurethane films

Table I depicts the effects of the NL content and the preparation method on mechanical properties of WUL films, including the nominal and true values of tensile strength ($\sigma_{b,nom}$ and $\sigma_{b,true}$), the nominal and true values of elongation at break ($\varepsilon_{b,nom}$ and $\varepsilon_{b,true}$), and Young's modulus (E_{nom}). The true values can more factually reflect the mechanical performances in service. Although there are distinct difference between regulated true values and nominal data, similar changing trends happened depending on NL content and preparation methods, except that WUL-3.0-II with the lowest $\sigma_{b,nom}$ in all the WUL films containing 3.0 wt % NL showed higher $\sigma_{b,true}$ than WUL-3.0-III due to greater elongation.

As expected, the tensile strength and elongation of the WUL films prepared by Method I were enhanced at one time. With an increase of NL content, the elongation gradually increased up to an almost constant value, while the strength firstly increased until adding 3 wt % NL and thereafter decreased. Meanwhile, the E decreased after introducing NL, and then increased up to WUL-4.5, which had higher E than WPU. Thus it can be seen that the optimal loading of NL was 3.0 wt %, resulting in the $\sigma_{b,nom}$ and $\varepsilon_{b,nom}$ values as $\sim$ 1.8-fold over those of neat

TABLE I
Mechanical Properties of WUL and WPU Films

Sample	E (MPa)		σ_b (MPa)		ε_b (%)	
	nominal	$E_{100\%}$	nominal	true	nominal	true
WUL-1.5	7.1	3.4	6.04	53.60	787	218
WUL-3.0	15.4	2.9	7.38	71.30	866	227
WUL-3.0-II	4.7	2.2	3.73	35.21	844	224
WUL-3.0-III	6.8	3.0	4.39	14.49	330	119
WUL-4.5	39.5	3.3	5.12	46.08	900	230
WPU	15.9	3.3	3.89	19.41	499	161

WPU film. It is worth of noting that the $\sigma_{b,\text{true}}$ of 71.3 MPa for WUL-3.0 was enhanced by over 3.6 times at this time.

The difference in the mechanical properties of WUL films, prepared by three methods, verified the key role of the chemical reaction between NL and polyurethane prepolymer on the simultaneous enhancement in strength and elongation. The WUL-3.0-II and WUL-3.0-III films, prepared by Method II and III, respectively, showed the decreasing $\sigma_{b,\text{nom}}$ and $\varepsilon_{b,\text{nom}}$ in contrast with WUL-3.0. WUL-3.0-II had higher $\sigma_{b,\text{true}}$ than WUL-3.0-III in spite of the lowest $\sigma_{b,\text{nom}}$, which was attributed to a elongation close to WUL-3.0. In addition, the E of WUL-3.0-III was intervenient between WUL-3.0 and WUL-3.0-II with the lowest E.

Hydrogen bonding after introducing NL

The FTIR spectra of the WUL and WPU films are shown in Figure 1. As well-known, —NH in waterborne polyurethane could be hydrogen-bonded with the urethane —C=O of hard-segments and the ether-oxygen of the PPG$_{2000}$ soft-segments. As a result, the hydrogen-bonded —C=O represents the extent of hard-segment aggregation. The FTIR spectrum of the WPU film showed two predominant absorption at 1710 and 1726 cm^{-1}, assigned to hydrogen-bonded and free —C=O in urethane, respectively.[31,32] With an increase of NL content, the intensity of hydrogen-bonded —C=O, in contrast with that of free —C=O, was firstly almost kept for WUL-1.5, and then decreased for WUL-3.0 followed by a slight increase once more for WUL-4.5. Meanwhile, the relatively intensities of hydrogen-bonded —C=O for WUL-3.0 and WUL-4.5 were lower than that of WPU. It suggested that adding NL hindered the hydrogen bonding between hard-segments except for the lowest loading of NL (1.5 wt %). At the same time, with a decrease of reaction between —NCO and —OH in NL, the intensity of hydrogen-bonded —C=O, in contrast with that of free —C=O, slightly increased for WUL-3.0-II and decreased for WUL-3.0-III. Similar to WUL-4.5, the increasing intensity of hydrogen-bonded —C=O for WUL-3.0-II was attributed to the cooperative effects
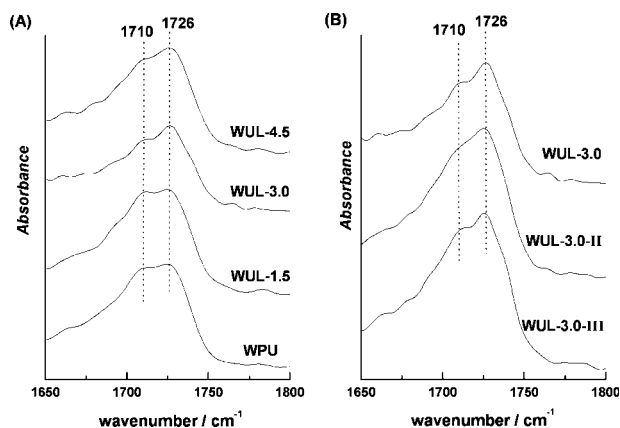

Figure 1 FTIR spectra in the range of 1650–1800 cm^{-1} for WUL and WPU films prepared from various NL contents (A) and compounding methods (B).

of the NL aggregation and star-like network, which inhibited the cleavage of ordered hard-segment structure. However, excess dispersed ungrafted NL in WUL-3.0-III destroyed the aggregation of hard-segments.

Thermal properties of NL modified waterborne polyurethane films

DSC thermograms of the WUL and WPU films are depicted in Figure 2, and the data of glass and melt-
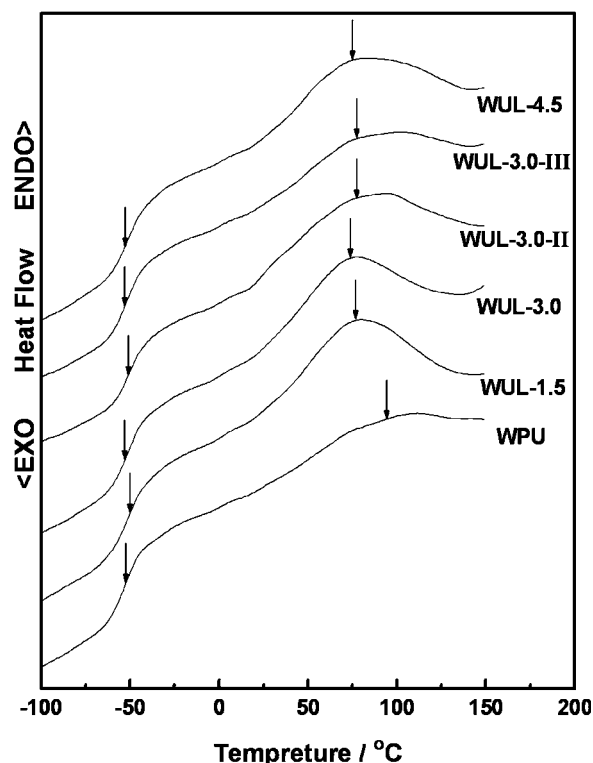
Figure 2 DSC curves as a function of temperature for the WUL and WPU films.

TABLE II
DSC and DMA Data of the WUL and WPU Films

Sample	DSC data for glass and melting transition				DMA data for α-transition	
	$T_{g,\text{mid}}$ (°C)	ΔC_p (J g^{-1} K^{-1})	T_m (°C)	ΔH_m (J g^{-1})	$T_{\alpha,\text{max}}$ (°C)	Height of loss peak
WUL-1.5	−50.8	0.516	76.9	30.70	−34.6	0.487
WUL-3.0	−51.2	0.515	73.8	25.78	−38.2	0.427
WUL-3.0-II	−50.1	0.451	77.5	27.79	−32.6	0.467
WUL-3.0-III	−51.6	0.520	77.3	18.20	−52.4	0.306
WUL-4.5	−50.9	0.496	75.5	25.95	−34.7	0.422
WPU	−52.6	0.516	94.1	14.14	−34.3	0.501

ing transitions, such as glass transition temperature at midpoint ($T_{g,\text{mid}}$)and heat-capacity increment (ΔC_p) as well as melting temperature (T_m) and enthalpy (ΔH_m), are summarized in Table II. Usually, the glass transition temperature is used to evaluate the mobility of soft-segment and the extent of microphase separation between hard- and soft-segment in polyurethane. Independent upon the NL content and the synthesis method, there is nearly no difference observed on the values of $T_{g,\text{mid}}$ and ΔC_p between the WPU film and the composite films. As a result, the forming of star-like network and/or the aggregation of NL did not obviously affect the motion of soft-segments on the domain scale. However, the T_ms assigned to ordered hard-segment aggregates in waterborne polyurethane matrix showed obvious changes. After adding NL, the T_ms of the WUL films shifted to lower temperature of ∼ 75°C in contrast with the T_m of 94.1°C for WPU. However, the whole transition range did not change. Meanwhile, the ΔH_ms of the WUL films increased, and especially the WUL-1.5 with no change of hydrogen bonding associated with —C=O showed the highest T_m. As regards to the WUL-3.0-III, the NL only dispersed into waterborne polyurethane matrix. At this time, the absence of star-like network resulted in the low-

est T_m of WUL-3.0-III, which was close to that of WPU. The position of melting transition and corresponding ΔH_m can be generally proportional to the scale and number of ordered hard-segment domains, respectively.[33] The analogical range of melting transition proved that the WUL films inherited all the scale of ordered hard-segment domains in neat WPU. Meanwhile, the decrease of T_ms suggested that long-range ordered structure in hard-segment domains was destroyed to some extent. In addition, the higher ΔH_ms of the WUL films indicated that the ordered structure in shorter range might be improved.

DMA is a powerful technique to study initial motion of frozen polymer segments through α-relaxation at molecular-level for which the specific heat increment of glass transition at domain-scale measured from DSC is generally ill-defined. Herein, the tan δ curves functioned as temperature and corresponding data assigned to α-relaxation of the WUL and WPU films, such as $T_{\alpha,\text{max}}$ and height of loss peak, are shown in Figure 3 and Table II, respectively. As usual, the $T_{\alpha,\text{max}}$ provided by DMA generally is higher than corresponding T_g obtained by DSC (up to 10°C higher) due to the dynamic nature of DMA test.[34] The $T_{\alpha,\text{max}}$s of the WUL films were
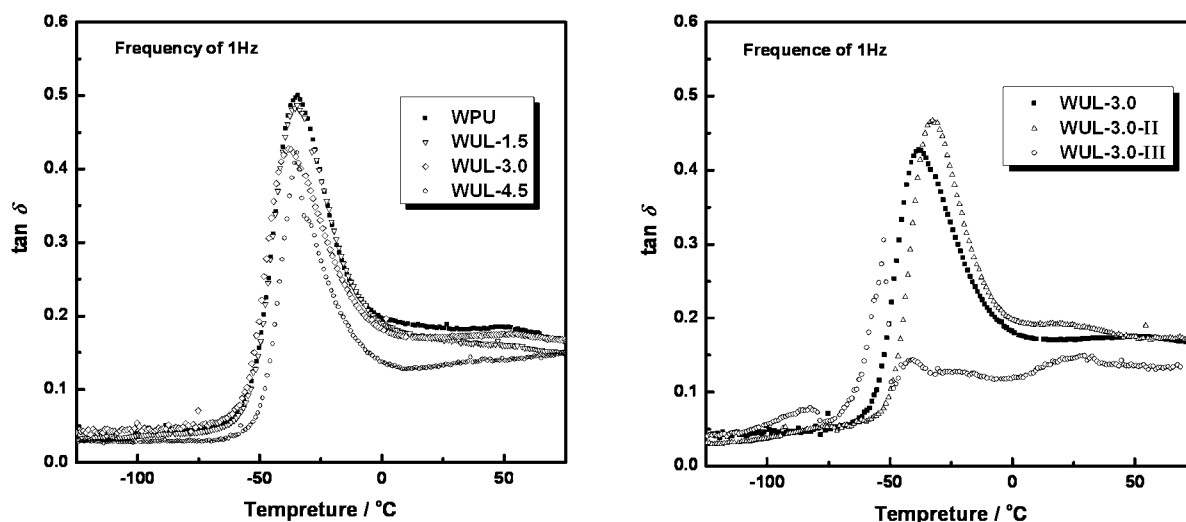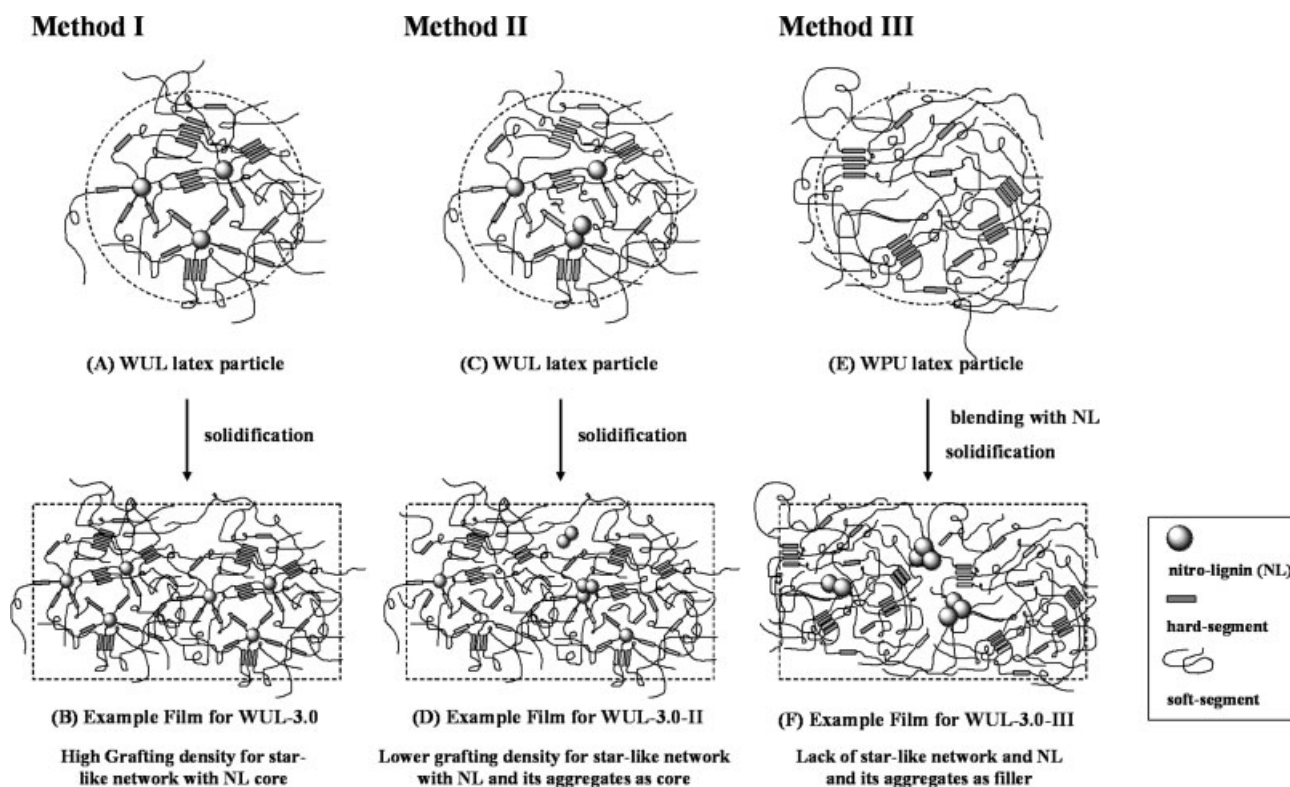

Figure 3 Mechanical loss (tan δ) as functions of temperature for the WUL and WPU films.

Scheme 2 Model of WUL latex particle containing star-like network structure with NL as core (A) and/or with NL and its aggregate as core (C) and the resultant film (B from A; D from C) as well as WPU latex particle (E) and the solidified film after blending NL (F).

lower than that of WPU except for WUL-3.0-II with higher $T_{\alpha,max}$. It suggested that the motion freedom of some soft-segments was enhanced, in spite that the soft-segment motion might be hindered by star-like network. The $T_{\alpha,max}$s of the WUL films containing 1.5 wt % and 4.5 wt % NL were close to that of WPU, while the WUL film with moderate NL content (3.0 wt %) had lower $T_{\alpha,max}$. At the same time, with an increase of NL content, the height of loss-peaks gradually decreased. The distinct lower $T_{\alpha,max}$ of WUL-3.0 suggested that the freedom of soft-segment motion increased when the star-like network structure perfectly formed as well as the absence of great NL aggregates. The loss-peak height represents the loss energy required by the motion of frozen segments, which is associated with the number of segments located in various chemical environments except for the freedom of segment motion. As a result, although the soft-segments in WUL-3.0 had higher freedom of motion (lower $T_{\alpha,max}$), more soft-segments, which located in confined chemical environment, resulted in higher loss-peak in contrast with WUL-4.5. In addition, with a decrease of reaction between —NCO and —OH in NL, the $T_{\alpha,max}$ firstly increased for WUL-3.0-II, and then sharply decreased for WUL-3.0-III. The height of loss-peaks showed a tendency of changes similar to the $T_{\alpha,max}$. Consequently, the coexistence of star-like network

and NL aggregates farthest restricted the soft-segment motion and then produced the highest $T_{\alpha,max}$ for WUL-3.0-II, while the absence of star-like network provided the highest motion freedom for soft-segments in WUL-3.0-III.

DISCUSSION

Proposed structure model of star-like network

In our previous work,[18] the NL was added into polyurethane prepolymer solution at the stage of chain-extending to produce a great star-like network with NL as core mediated with the reaction between —NCO in polyurethane prepolymer and —OH in NL. Similarly, in the process of synthesizing waterborne polyurethane, the NL was also added at the stage of chain-extending (Method I). Consequently, the resultant latex particles contained star-like network with NL as core [Scheme 2(A)], and thereafter the solidified films [Scheme 2(B)] inherited such structure in latex particles. However, when adding NL with the water in the midst of emulsification (Method II), —OH in NL might compete with water to react with —NCO, while the NL tended to self-aggregate as supramolecular complexes. In the latex particles, the grafting between NL and polyurethane prepolymer decreased. At the same time, the NL

and its aggregate acted as the core of star-like network as well as a little isolated NL aggregates [Scheme 2(C)], which was also existed in the solidified films [Scheme 2 (D)]. When mixing NL with the latex particles of waterborne polyurethane [Scheme 2(E)] post of emulsification (Method III), the self-aggregated supramolecular NL complexes cannot played the core to form star-like network and only dispersed into the solidified film [Scheme 2(F)] due to the lack of active —NCO in polyurethane component.

In addition, the NL loading also affected the micro-structure in spite of applying the same Method I. Compared with the schematic structure for WUL-3.0 in Scheme 2(A,B), the WUL-1.5 with lower NL loading had lower network density in the latex particles and solidified films. However, when the NL loading was higher (4.5 wt %), excess NL might self-aggregate as supramolecular complexes and then dispersed into the latex particle and solidified film. As a result, WUL-4.5 had a similar structure to WUL-3.0-II prepared by Method II in Scheme 2(C,D), but the grafting degree and resultant network density were higher.

Structural changes in NL modified waterborne polyurethane

For the WUL composites, there are four factors to determine the mechanical performances of materials cooperatively, such as (i) the grafting degree, (ii) network density in star-like network, (iii) the distribution of ungrafted NL (iv) and the structural changes of waterborne polyurethane matrix. When the grafting degree between NL and polyurethane prepolymer was lower (i.e., WUL-1.5), the hydrogen bonding associated with —C=O between hard-segments was almost kept. Although the star-like network might restrict the motion of soft-segment, the lower $T_{\alpha,max}$ suggested that some soft-segments had higher motion freedom because they escaped from the binding of hard-segments. In addition, lower T_m and higher ΔH_m indicated that the long-range ordered structure based on hard-segments was destroyed while more short-range ordered structure formed. When the NL loading increased up to 3.0 wt %, the density of star-like network increased, which augmented the extent of destroying hard-segment domains and gave higher motion freedom of soft-segments. At this time, the $T_{\alpha,max}$ decreased as well as less hydrogen bonds associated with —C=O. In contrast with WUL-1.5, the decreasing T_m and ΔH_m indicated the cleavage of ordered hard-segment structure. As regards to WUL-4.5 with highest loading, the formed supramolecular NL complexes inhibited the motion of soft-segments, shown as an increasing $T_{\alpha,max}$ once more, in spite that the increasing microphase separation between soft- and hard-segments, proved by more hydrogen

bonds associated with —C=O in hard-segments, facilitated the motion of soft-segment. On the other hand, a slight increase of T_m and ΔH_m suggested that the scale and number ordered structure of hard-segment increased at one time.

When applying Method II, the grafting degree between NL and polyurethane prepolymer as well as the density of star-like network in WUL-3.0-II decreased. The complex structures of star-like network with NL and its aggregates as core and isolated NL aggregates restricted the motion of soft-segments, resulting in an obvious increase of $T_{\alpha,max}$ and loss-peak height. In addition, the increasing T_m and ΔH_m indicated that the ordered hard-segment structure was improved due to increasing hydrogen bonding associated with —C=O. However, when the NL absolutely dispersed as supramolecular aggregates in WUL-3.0-III, the $T_{\alpha,max}$ and loss-peak height severely decreased due to the lack of the restriction of star-like network. At the same time, a sharp decrease of ΔH_m suggested that ordered hard-segment structure was severely destroyed, accompanied with the cleavage of hydrogen bonds associated with —C=O in hard-segments.

Role of NL to enhance mechanical performances

Herein, the star-like network with NL as core resulted in a simultaneous enhancement in strength and elongation at the expense of modulus. Although the supramolecular nano-aggregates of lignin can generally enhance strength and modulus of materials,[10] the forming of the NL aggregates in this case only enhanced the modulus as well as lowering the strength. For example, the E of WUL-4.5 containing star-like network and dispersed NL aggregates was higher than that of WUL-3.0, while WUL-3.0-III only containing dispersed NL aggregates had higher E in contrast to WUL-3.0-II containing star-like network and NL aggregates. Although the increasing modulus verified the reinforcing function of the NL aggregates, the absence of star-like network decreased strength and elongation.

As for the star-like network with NL core, the mechanism of simultaneous enhancement in strength and elongation was described as follows: (i) the spherical NL acted as the core of star-like network and can endure higher stress transferred along polymer chains by virtue of its three-dimensional highly crosslinking structure; (ii) the grafting between NL and polyurethane prepolymers as well as the entangling and crosslinking in polyurethane matrix provided a chance for the stress transferring; (iii) the curling and entangling polyurethane segments would stretch to produce higher elongating based on the ability of NL to endure higher stress. Consequently, depending on enough grafting degree and

the moderate number of NL core, the role of star-like network in enhancing strength and elongation can be fully played, such as WUL-3.0 containing 3.0 wt % NL prepared by Method I. When the NL content was lower (1.5 wt %), the number of NL core was not enough to give the optimal strength and elongation. However, other methods (Method II and III) and high loading (4.5 wt %) cannot provide enough grafting degree and even destroy star-like network to some extent, resulting in lower mechanical performances.

CONCLUSIONS

The simultaneous enhancement in strength and elongation of star-like network for solventborne polyurethane was successfully transplanted into the waterborne polyurethane system. The mechanical performances were optimal when adding 3.0 wt % NL to react with polyurethane prepolymer, resulting in the nominal strength and elongation as ∼ 1.8-fold over those of neat waterborne polyurethane. At this time, the true strength of such composite reached 71.3 MPa, which was enhanced by over 3.6 times. The simultaneous enhancements in strength and elongation were attributed to the forming of star-like network with NL core, in which the NL can endure higher stress by virtue of its densely three-dimensional network while the associations among polyurethane segments improved elongation. However, excess NL loading and lower grafting chance between NL and polyurethane segments led to the damage and/or absence of star-like network, and hence formed the rigid supramolecular NL aggregates in the composites. Although the strength and elongation decreased at this time, the rigid supramolecular NL aggregates contributed to higher modulus.

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