Improving Aging Resistance and Mechanical Properties of Waterborne Polyurethanes Modified by Lignin Amines

Jun Liu,[1,2] Hai-Feng Liu,[1,2] Li Deng,[1] Bing Liao,[1] Qing-Xiang Guo[3]

[1]Key Laboratory of Cellulose and Lignocellulosics Chemistry, Guangzhou Institute of Chemistry, Chinese Academy of Sciences, Guangzhou 510650, China
[2]University of Chinese Academy of Sciences, Beijing 100039, China
[3]Department of Chemistry, University of Science and Technology of China, Hefei 230026, China
Correspondence to: L. Deng (E-mail: dengli@gic.ac.cn) or Q.-X. Guo (E-mail: qxguo@ustc.edu.cn)

ABSTRACT: In this article, we report the enhanced anti-aging and mechanical properties of waterborne polyurethanes (WPUs) modified by lignin amines, which were prepared from lignins, formaldehyde, and diethylenetriamine via a Mannich reaction. When we introduced amino groups into the lignin, its solubility in water and reactivity with isocyanate was obviously improved. Consequently, the interaction between WPU and the lignin additive were promoted; this provided a higher mechanical performance, that is, a higher tensile strength and elongation at break. More importantly, the intrinsic antioxidative activity of lignin also benefitted the modified WPU in terms of aging resistance. According to artificial accelerated aging tests, mechanical measurement, attenuated total reflectance–Fourier transform infrared spectroscopy, and scanning electron microscopy analysis, the lignin amine modified WPU did not show any evidence of degradation after 2 months of artificial accelerated aging, whereas the pure WPU was obviously degraded.
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INTRODUCTION

Polymer degradation is a common phenomenon, which leads to changes in the chemical, physical, and mechanical properties of the polymer.[1] Particularly in outdoor use, where polymers are exposed to weathering, uncontrolled aging or oxidation due to the effect of UV radiation, rain, oxygen, and variation in temperature can easily induce degradation of polymers. To prevent or retard this aging or oxidation, various antioxidants can be added to these polymers, such as derivatives of phenols, amines, organosulfurs, and organophosphorous compounds. However, some of these traditional antioxidants volatilize, migrate, or are extracted under severe conditions because of their relatively low molecular weight. Therefore, the concentration of the antioxidant in the polymer matrix decreased, which affects its age-resistant behavior.[2] In recent years, polymeric antioxidants[3–5] especially natural polymeric antioxidants such as lignin, have received a great deal of attention.[6–8]

Lignin, a natural irregular macromolecule comprised of phenolic units, is the second most abundant plant biomass component after cellulose. In industry, lignins are usually obtained as byproducts or waste from papermaking and emerging cellulosic ethanol production. With the aim of economic and environmental sustainability, the large-scale application of lignin should be urgently realized in various ways. Recently, the use of lignin as a polymeric material additive and feedstock has been commonly accepted as an effective and economically practical method.[9] The rigid structure of lignin allows its utilization as a low-cost reinforce filler for several materials. Sulfur-free lignin was proven to enhance the mechanical properties of styrene–butadiene rubber, even when the lignin content was up to 50 wt %, because of the good miscibility of the blend.[10] In blended complexes containing lignin and waterborne polyurethane (WPU), lignin formed a starlike network, which rendered a WPU with enhanced tensile strength (σ_b) and elasticity.[11] On the other hand, lignin exhibited excellent stability (as an antioxidant) in both natural and manmade complexes under UV radiation,[12] heat,[13] and oxidation[14] because of its phenolic structures. A polyhydroxybutyrate modified by lignin showed significant improvement in its thermal stability.[15]

Additional Supporting Information may be found in the online version of this article.
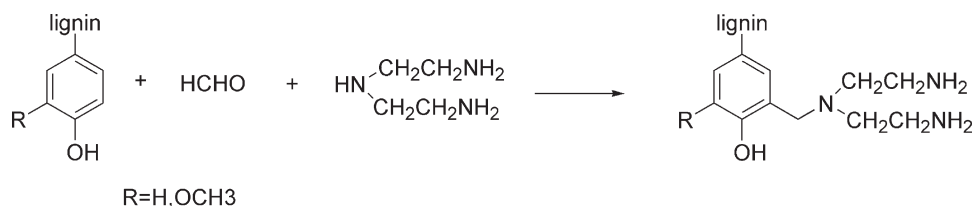
Scheme 1. Synthesis of the lignin amine by a Mannich reaction.

Moreover, for many polyolefin materials, such as polypropylene[14,16] and polyethylene, lignin was employed as an antioxidant, whereas it was also used as a UV stabilizer for poly(vinyl alcohol),[17] polyethylene,[12] and acrylic polyurethane coatings.[18]

In this study, a lignin modified via a Mannich reaction, lignin amine, was tested in a blend with WPU with the aim of enhancing both the mechanical properties and aging resistance of the WPU. To our knowledge, lignin derived from a pulp process has poor compatibility with polyurethane, so diethylenetriamine (DETA) and formaldehyde were used to functionalize lignin (Scheme 1). There were at least three advantages of this modification with the regard to blending, including the following:

1. A high solubility in water caused by the hydrophilic amino groups made the emulsion system containing the polyurethane and lignin amine homogeneous and stable under neutral conditions with a long storage period over 6 months. Thus, the water-insoluble lignin could be blended with WPU adequately according to this method.
2. The amino groups introduced into lignin were much more reactive in the nucleophilic reaction with isocyanates than the intrinsic hydroxyl and phenolic hydroxyl groups of lignin; this resulted in greater interactions between the lignin amine and polyurethane via chemical bonding and cross-linked hydrogen bonding.
3. With the radical scavenging capability of the lignin compounds, lignin amine was a good polymer antioxidant, which would not volatilize, migrate, or be extracted easily compared to some traditional antioxidants, because of its high molecular weight and great interaction with the WPU.

Therefore, an artificial accelerated aging test and subsequent mechanical measurement, attenuated total reflectance (ATR)–Fourier transform infrared (FTIR) spectroscopy, and scanning electron microscopy (SEM) analysis were also carried out. On the basis of the experimental results, we proved that lignin amine was not only a low-cost reinforce filler but could also be used as anti-aging additive for WPU materials.

EXPERIMENTAL

Materials

All of the chemical reagents were commercially available. Kraft lignin (KL) and alkali lignin (AL) were purchased from Sigma-Aldrich. The poly(propylene glycol) [PPG; number-average (M_n) = 1000], toluene diisocyanate, dimethyol propionic acid, triethylamine, and DETA were obtained from Aladdin Reagent Co., Ltd. The PPG was dried at 110°C under 20 mmHg for 2 h before use.

Preparation of Lignin Amine

The lignin amine was synthesized according to the modified method of Yue et al.[19] Briefly, 10 g of lignin and 15 g of DETA were dissolved in 100 mL of distilled water. The pH of the mixture was adjusted to 10–10.5 with a 0.1M NaOH solution and an HCl solution. The mixture was added to a three-necked flask, and 10 g of formaldehyde solution (37 wt %) was added stepwise with stirring at room temperature. Next, the mixture solution was heated to 50°C for 4 h. After that, the solution was added to about 500 mL of isopropyl alcohol to precipitate the lignin amine. The resulting brown precipitate was recovered by suction filtration, washed with isopropyl alcohol three times, and then dried in a vacuum oven at 40°C.

Preparation of the WPU Modified by Lignin Amine

WPU was synthesized as follows: PPG (100 g, 0.1 mol) and toluene diisocyanate (34.8 g, 0.2 mol) were added to a four-necked flask equipped with a thermometer, stirrer, dropping funnel, and condenser. Subsequently, the resulting mixture was stirred, heated to about 65°C, and mechanically stirred under a nitrogen atmosphere for 2 h. Then, dimethyol propionic acid (4.72 g, 35 mmol) was dissolved in acetone and added dropwise. The reaction was performed at 80°C until the ─NCO content reached a desired value, which was determined with a standard dibutylamine titration method. After the reaction was cooled to 40–50°C, acetone was added to lower the viscosity of the reaction mixture, and the carboxylic acid groups were neutralized with triethylamine (3.54 g, 35 mmol). Then, the emulsification was carried out by the addition of an iced lignin amine water solution under vigorous stirring to produce a WPU latex with a solid content of 20 wt %. After acetone was removed, the latex was cast onto a Teflon mold and then cured at room temperature by the evaporation of water; this gave WPU films with a thickness of about 0.6 mm. Finally, the WPU films were dried further in a vacuum oven at 50°C for 10 h. The resulting WPU films modified by kraft lignin amine (KLA) or alkali lignin amine (ALA) were defined as WPU–KLA–X and WPU–ALA–X, where the X represents the percentage of lignin amine in the whole solid film.

Artificial Accelerated Aging Test

The accelerated aging test was conducted in an Atlas xenon weatherometer with UVA-340 fluorescent lamps and operated under wet-cycle conditions: 102 min of UV irradiation and 18 min of water spraying at 50°C. All of the samples were exposed to UV light for 1500 h.

Determination of the Total Phenolic Content (TPC)

TPC was estimated by the Folin–Ciocalteu colorimetric method with gallic acid as a standard phenolic compound. Each sample

Table I. Structural Properties of the Lignin Amines

Entry	Sample	N (%)	M_w	M_n	M_w/M_n
1	KL	0	1356	1163	1.16
2	AL	0.6	2049	1602	1.28
3	KLA	2.97	1502	1288	1.17
4	ALA	4.67	2027	1773	1.14

M_w, weight-average molecular weight.

solution in 1 mL of dioxane–water (9:1) was added to 0.2N Folin–Ciocalteu reagent solution (5.0 mL), and the mixture was shaken for 5 min. After this procedure, Na_2CO_3 (75 g/L, 4 mL) was added, and the mixture was shaken for another 1.5 h at 30°C. The absorbance was measured at 760 nm (UV-2550, Shimadzu, Japan). A linear calibration curve of gallic acid in the range of 50–400 mg/L was achieved ($A = 0.000890\ c$, $r^2 = 0.998$; A is the slope and r refers to the correlation coefficient).

Determination of the Lignin and Lignin Amine Radical Scavenging Activity

The radical scavenging activity of the lignin samples and standard tert-butyl-4-methoxyphenol (BHA) was determined with 2,2-diphenyl-1-picrylhydrazyl (DPPH) as a radical precursor.[20,21] A lignin sample solution in 0.1 mL of dioxane–water (9:1 v/v) was added to 3.9 mL of a DPPH solution (32 mg/L in ethanol) as the free-radical source and kept for 90 min at room temperature. After a 90-min incubation period in the dark, the absorbance was measured at 517 nm (UV-2550, Shimadzu). The DPPH radical scavenging activity (I) was calculated according to the following formula:

$$I(\%) = [(\text{Abs}_0\text{-Abs}_1)/\text{Abs}_0]\times100\% \qquad (1)$$

where Abs_0 is the absorbance of the blank and Abs_1 was the absorbance in the presence of the test sample at different concentrations. The concentration providing 50% inhibition (IC_{50}) was calculated graphically with a calibration curve within the

linear range by the plotting of the sample concentration versus the corresponding scavenging effect. The antioxidant activity was expressed as the antioxidant activity index (AAI; the final concentration of DPPH divided by IC_{50}).

Characterization

The FTIR spectra of the lignins and lignin amines were recorded with a Bruker TENSOR 27 type FTIR spectrophotometer equipped with an ATR accessory. Each sample was scanned 64 times at a resolution of 4 cm. All of the spectra were scanned within the range 400–4000 cm^{-1}. To ensure the reproducibility of the results, each sample was scanned at three different locations.

Thermogravimetric analysis was performed on a Netzsch TG209F3 thermogravimetric analyzer to investigate the thermal stability of the lignin amine modified WPU films. Approximately 6 mg of the composite was placed in a platinum pan and heated from room temperature to 600 at 10°C/min under a 20 mL/min air flow.

The surface morphology of the WPU films were studied by SEM (JSM-6360LV, Japan) at 20 kV. After tensile testing, the films' surfaces were sputtered with gold and then photographed.

The tensile measurement was carried out on a universal testing machine (LR 10 KPLUS, Fareham, United Kingdom) with a load cell of 10 kN in accordance with ASTM D 412 at room temperature with a crosshead speed of 500 mm/min.

RESULTS AND DISCUSSION

Synthesis and Characterization of the Lignin Amine

KL and AL from the pulping process could not be dissolved adequately in water under neutral conditions (lignin precipitation was observed), so it was hard to generate a homogeneous emulsion by their blending with WPU. Consequently, it was necessary to increase the solubility of lignin in water through the introduction of hydrophilic functional groups. To our knowledge, the Mannich reaction is a powerful tool for grafting alkyl amino groups onto the aromatic ring of lignin (Scheme 1). On the basis of this method, the resulting lignin amines
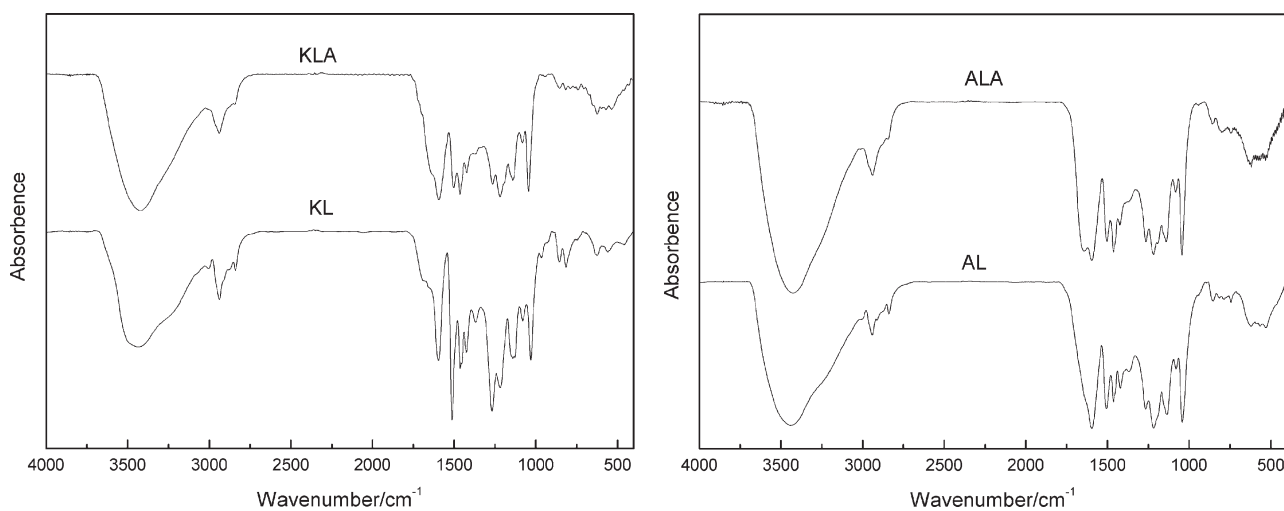
Figure 1. FTIR spectroscopy of the lignins and lignin amines.

Table II. TPC and Radical Scavenging Performance of the Lignins and Lignin Amines

Entry	Sample	TPC (mg of GAE/g of dry material)	IC$_{50}$	AAI
1	KL	330	5.32 ± 0.9	5.98 ± 0.05
2	KLA	260	6.94 ± 0.05	4.61 ± 0.04
3	AL	240	7.40 ± 0.06	4.32 ± 0.03
4	ALA	250	5.85 ± 0.04	5.47 ± 0.05
5	BHA		3.21 ± 0.05	9.96 ± 0.11

(KLA and ALA) could be readily dissolved in water under neutral and even weakly acidic conditions.

Table I shows that the nitrogen content rose from 0 and 0.6 wt % to 2.97 and 4.67 wt % for KLA and ALA, respectively. These results suggest that about 0.2 and 0.3 mol of DETA on average was grafted onto each mole of lignin units (C9 unit) of KL and AL. Moreover, compared with the lignin feedstock, the molecular weight of the lignin amine increased slightly, maybe because of the grafting and because no decomposition occurred, according to the GPC analysis.

After the Mannich reaction, the FTIR spectra of KAL and ALA (Figure 1) showed that the relative intensity of the broad peak at 3480 cm^{-1} increased (relative to the benzene skeleton vibrations at 1450, 1570, and 1600 cm^{-1}); this was attributed to the introduction of amino groups.[19] Moreover, the greatly weakened band of aromatic C—H stretching vibrations at 817 and 856 cm^{-1} confirmed that the benzene ring of lignin was functionalized via the Mannich reaction.

The antioxidation activity of the lignins and lignin amines was measured by the 2,2-diphenyl-1-picrylhyhydazyl (DPPH) method. As shown in Table II, the TPC values of KL, AL, KLA, and ALA were 330, 260, 240, and 250 mg of gallic acid equivalents (GAEs)/g, respectively. Their radical scavenging activity was closely related to the value of TPC. Specifically, the AAI value of the lignins increased in the same order as TPC, whereas IC$_{50}$ did so in the reverse order. Note that the value of AAI was all above 4 and was 40–60% of that of the common radical scavenger BHA; this was indicative of a good radical scavenging activity in lignin and lignin amine[22] and a potential capability of aging resistance
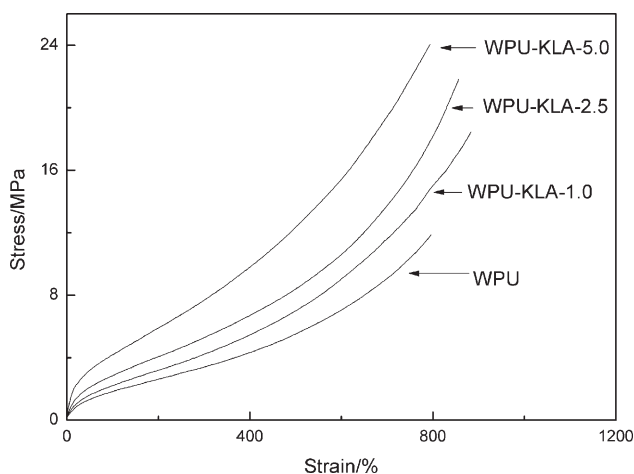
Lignin Amine Modified WPU Material

To our knowledge, there are two methods for blending lignin additives with WPU.[11] One is the addition of lignin to emulsified polyurethane, and the other is the mixture of lignin and polyurethane during emulsification. According to the literature,[11] the later method provides better compatibility between lignin and polyurethane; thus, this method was used to prepare the lignin amine modified WPU in which the lignin amine could act as a chain extender because of its high reactivity to —NCO. The prepared emulsion of WPU with a lignin amine content below 7.5 wt % was stable after even 6 months of storage. On the basis of laser diffraction analysis, the emulsion had a mean particle size of 0.3 μm. When the KLA loading was 10.0

wt %, the particle size increased sharply to 30–100 μm (see Figure S1 in the Supporting Information) and the emulsion precipitated after only 2 days. Thus, the content of KLA could be carefully controlled below 10.0 wt %. Figure 2 shows the stress–strain curves of the WPU modified by 1–5 wt % KLA. σ_b of polyurethane increased with the content of lignin amine from 12 MPa (pure polyurethane) to 18 MPa (with 1 wt % KLA) and 24 MPa (with 5 wt % KLA). To our delight, the elasticity of the modified WPU did not decrease with the increase in σ_b. The elongation at break (ε_b) values were 770 and 800–880% for the pure WPU and the WPUs modified by KLA, respectively. A similar result was observed for the ALA-modified WPU (Table III). The previous results revealed that the interaction between lignin amine and polyurethane enhanced the strength of the hard microdomains rather than that of the soft microdomains; this gave an improved σ_b and a stable elasticity simultaneously.[23] Furthermore, SEM analysis (Figure 3) proved the good compatibility between WPU and lignin amine because no aggregate was observed; this was in agreement with the enhanced mechanical properties.

As mentioned previously, via the Mannich reaction, lignin was grafted with amino groups, and this allowed a high solubility in water and the reaction with isocyanate. Consequently, the compatibility of the lignin amine/WPU blends was improved. All of the lignin amine modified WPU films possessed good compatibility with WPU, and this led to a transparent character, whereas the lignin/WPU blends showed an opaque character (see Figure S2 in the Supporting Information). According to the ATR–FTIR analysis (Figure 4), the strong and broad absorption peak of N—H stretching vibrations at 3400 cm^{-1} disappeared when ALA was added to polyurethane. This was strong evidence that most of the free amino groups in lignin amine reacted with isocyanate and formed a crosslinked structure by hydrogen bonding.

Thermogravimetric analysis (see Figure S3 in the Supporting Information) showed that the addition of lignin amine did not change the thermal stability obviously. The intensity of the differential thermogravimetry peaks declined with increasing content of lignin amine, and the corresponding temperature was around 320°C.

Figure 2. Stress–strain curves of the WPU materials modified by difference lignin amine contents.
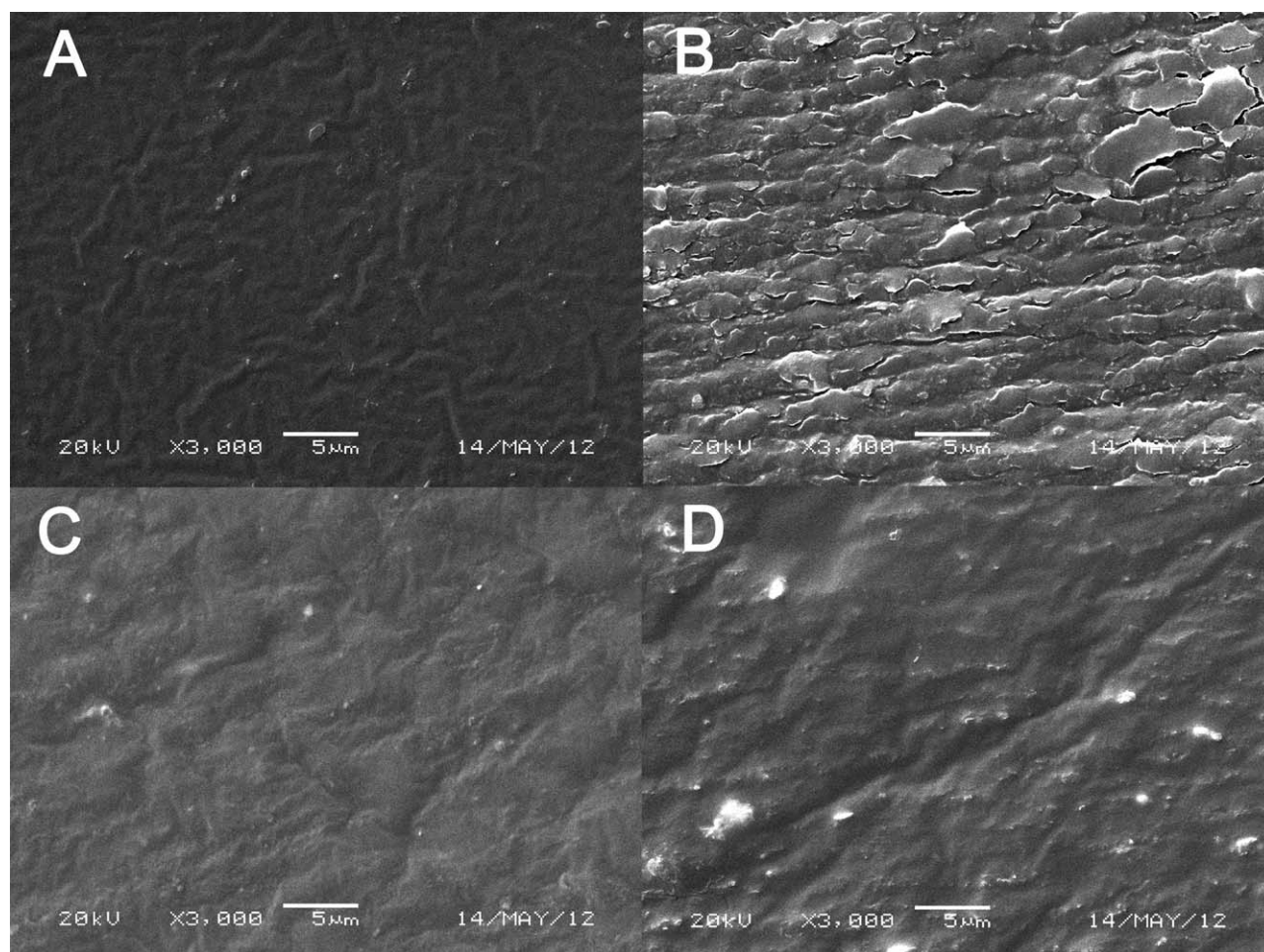
Figure 3. SEM images of the (A) fresh pure WPU film, (B) aged pure WPU film, (C) fresh WPU–ALA-2.5 film, and (D) aged WPU–ALA-2.5 film after the tension tests.

Aging Resistance of Lignin Amine Modified WPU

Because of the radical scavenging capability of the lignin amine, we expected that the modified lignin could extend the lifetime of the WPU materials. After 2 months of artificial accelerated aging, the pure WPU film became dark and rough, whereas the modified WPU films did not change much in terms of color (see Figure S4 in the Supporting Information) and surface roughness. Table III summarizes the mechanical properties of the pure and modified WPU before and after 2 months of aging. It is clear that the mechanical properties of the pure WPU decreased obviously. However, the WPU modified by lignin amine maintained the mechanical properties; some of them exhibited even better mechanical performance (Table III, entries 2–8); this might have resulted from the formation of more crosslinked hydrogen bonding between lignin amine and WPU after 2 months of aging. Despite that, the lignin amines

Table III. Mechanical Properties of the WPUs before and after 2 Months of Artificial Accelerated Aging

Entry	Sample	Fresh σ_b (MPa)	Aged σ_b (MPa)	Fresh ε_b (%)	Aged ε_b (%)
1	WPU	12.5 ± 0.5	11.2 ± 0.6	865.3 ± 75.4	744.0 ± 65.3
2	WPU–ALA-0.5	15.0 ± 0.7	20.7 ± 1.1	957.5 ± 57.2	750.1 ± 25.3
3	WPU–ALA-1.0	25.5 ± 1.2	30.1 ± 3.2	836.2 ± 45.6	861.6 ± 44.3
4	WPU–ALA-2.5	20.5 ± 1.6	21.3 ± 1.4	822.6 ± 53.2	830.3 ± 36.5
5	WPU–ALA-7.5	20.7 ± 1.4	21.4 ± 1.8	520.8 ± 35.3	875.5 ± 61.2
6	WPU–KLA-0.5	14.5 ± 0.7	16.0 ± 0.8	818.5 ± 34.5	972.5 ± 67.3
7	WPU–KLA-1.0	18.5 ± 0.9	18.7 ± 1.0	853.6 ± 65.6	765.5 ± 37.6
8	WPU–KLA-7.5	23.4 ± 1.3	24.3 ± 1.5	804.5 ± 44.3	687.3 ± 30.1
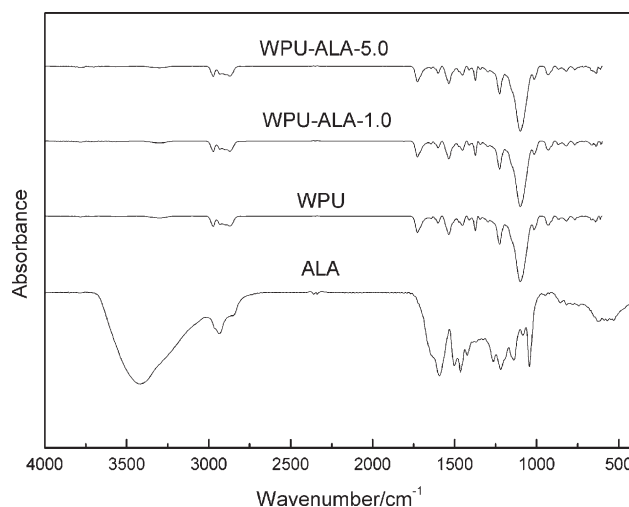
Figure 4. ATR–FTIR spectroscopy of the ALA, pure WPU, and modified WPUs.

prepared via the Mannich reaction were proven to be effective anti-aging reagents for WPU.

Further study based on ATR–FTIR spectroscopy gave more detailed information on the aging effects on the structure of the WPU materials. After 2 months of aging, the FTIR spectrum of pure WPU gave a sharp absorption peak at 1730 cm^{-1}, which could be assigned to the carbonyl groups. The newly generated carbonyl groups were attributed to the direct chain scission or radical-induced process upon exposure to the artificial weathering environments.[24] However, the intensity of this characteristic peak in the spectroscopy of the modified WPU did not increase. Moreover, the bands at 1162 and 1100 cm^{-1} corresponded to the branched ether created by the crosslinking polyether soft segment and the original ether in the polyether soft segment, respectively.[25] The newly generated peak at 1162 cm^{-1} in the spectroscopy of aged pure WPU indicated the oxidation of the soft-segment ethers and the resulting chain scission. By sharp

contrast, the modified WPU did not deteriorate in that way after exposure to the accelerated aging environment, as shown by the ATR–FTIR analysis (Figure 5).

To confirm the effect of the lignin amine on the aging process of WPU, the morphology of the polyurethane exposed surface after tensile testing was investigated with SEM. Figure 3 shows the surface morphologies of the WPU films. Compared with pure WPU, the modified WPU had a smoother surface without much change in the exposed face of samples because of the good anti-aging properties of the lignin amine. After it was subjected to light, moisture, and a high temperature, the pure WPU showed a microcracked, rough surface. The formation of microcracks was due to excessive embrittlement of the aged pure WPU surface, which resulted from the main-chain scission and generation of crosslinked molecules. This result was in good agreement with those of Boubakri et al.[26] in a study of the UV aging of thermoplastic polyurethane materials.

CONCLUSIONS

In summary, lignin amines prepared via a Mannich reaction were successfully blended with WPU at the emulsion stage. Because of the good compatibility of the lignin amine and poly-urethane and the crosslinked hydrogen bonding of amino groups within the hard microdomain, the mechanical properties of the modified WPU were significantly improved. Importantly, in view of the inherent radical scavenging properties of lignin, the WPU modified by lignin amine showed an excellent anti-aging performance. On the basis of the previous results, we demonstrated that lignin amines can be used as dual-function additives for WPU materials to simultaneously enhance their mechanical and anti-aging properties.

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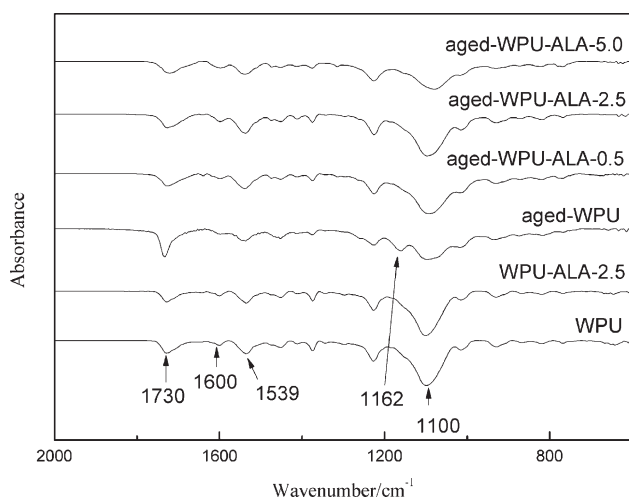
Figure 5. ATR–FTIR analysis of the WPU films before and after 2 months of artificial accelerated aging.

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