Performances of Larch (*larix gmelini*) Tannin Modified Urea-Formaldehyde (TUF) Resin and Plywood Bonded by TUF Resin

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ABSTRACT: Tannin from larch (*Larix gmelini*) bark extracts, as a natural renewable resource, was used to prepare tannin–urea–formaldehyde (TUF) resin. The chemical structures of larch tannin and TUF resin were characterized by matrix-assisted laser desorption/ionization-time of flight mass spectrometry and ^{13}C nuclear magnetic resonance. The thermal behaviors of TUF resin were evaluated by differential scanning calorimetry (DSC) and thermomechanical analysis (TMA). The performances of TUF resin were investigated by measuring the bond strength and formaldehyde emission of its bonded plywood. It was clearly shown that larch tannin is mainly composed of prodelphinidin repeating units. Phenolic groups were introduced into TUF resin mainly linked by methylene bond. Larch tannin has an adverse effect on the resin curing. However, it promoted the rigidity and flexibility of the glued system and upgraded the properties of plywood. Therefore, larch tannin could be applied in the modification of urea–formaldehyde resin. © 2014 Wiley Periodicals, Inc. J. Appl. Polym. Sci. **2014**, *131*, 41064.

INTRODUCTION

Urea–formaldehyde (UF) resins are still the most commonly used wood adhesives in the manufacture of plywood, medium density fiberboard, particleboard, and other nonstructural wood products. UF resins have advantages of high reactivity, fast curing, water solubility, and low price. However, they have poor water resistance and emit formaldehyde, which have stimulated efforts to develop improved and/or new adhesives based on UF resins. One of the most effective ways is introducing components like melamine to modify it. Melamine has the potential to improve water resistance and reduce formaldehyde emission due to its high functionality, its stable molecular structure in comparison to urea, and its reaction with formaldehyde, which is similar to that of urea.[1–3] However, melamine is much more expensive than urea. Especially in recent years, the rising cost and scarcity of petrochemicals have led researchers to use natural products from renewable resources.

Condensed tannins, as one of the important natural products, are widely distributed in nature and particularly in the wood and bark of various trees. These tannins have been used in many traditional industries, such as leather-making, medicine,

and agriculture. Due to the phenolic natural of tannins, they are also suitable for synthesis of polymeric resins and wood adhesives. Many studies showed that condensed tannins are desirable substitute for phenol in adhesives and resins preparation. Lu and Shi[4] had prepared tannin–phenol–formaldehyde (TPF) resin with 60% of phenol substituted by larch bark tannin. The results showed that the performances of TPF resin are comparable to some synthetic phenol–formaldehyde (PF) resin on the basis of the properties of particleboards. Vázquez et al.[5] had compared the thermal curing of a commercial PF resin and a TPF resin, both of which were suitable for using in the manufacture of exterior-grade plywood boards. The corresponding kinetic calculations predicted that the TPF resin cures faster than the PF resin. This finding implied the possibility that the TPF resin may allow the achievement of higher productivity by permitting the use of shorter press times than with conventional PF resins. Moubarik et al.[6] introduced the cornstarch and quebracho tannin into the classic adhesive formulation to substitute a part of PF resin, and the results showed that plywood bonded by cornstarch–tannin–phenol formaldehyde resin (15 : 5 : 80, w/w/w) exhibited better mechanical properties than plywood bonded by commercial PF. Other studies focused on the

synthesis of tannin-based resins with low or zero formaldehyde emission.[7–10] However, studies of using condensed tannins in the modification of UF resin have been limited.

Larch (*Larix gmelini*) is one of the most important tree species in northern China. Tannin from larch bark extracts, consisting of flavonoid units which could react with formaldehyde, could be a potential modifier for UF resins. Therefore, this study was conducted to modify UF resin with larch tannin and to evaluate the performance of TUF resin by measuring the bond strength and formaldehyde emission of plywood. The thermal behaviors of TUF resin were measured by differential scanning calorimetry (DSC) and thermomechanical analysis (TMA). Matrix-assisted laser desorption/ionization-time of flight mass spectrometry (MALDI-TOF-MS), and ^{13}C nuclear magnetic resonance (NMR) were used to characterize the chemical structures of larch tannin and TUF resin. The results of this investigation are expected to help develop a new, environmentally friendly TUF resin.

EXPERIMENTAL

Materials

Formaldehyde (HCHO, 37 wt % aqueous, AR) and formic acid (HCOOH, AR) were purchased from Xilong, China. Solid urea (CON$_2$H$_4$) was industrial reagents obtained from Lanyi Chemical, China. Larch tannin was obtained from Forest Chemical Laboratory, Beijing Forestry University, China. Sodium hydroxide (NaOH), ammonium chloride (NH$_4$Cl), and all other chemicals used were of AR grade from Beijing Chemical Works, China.

TUF Resin Synthesis and Measurement

TUF resin was synthesized in the laboratory based on a weak acidic-alkaline procedure. Larch tannin was added in the first stage, and the amount of it was 10% by weight of urea (about 3.8% by weight of the resin mixture). Formaldehyde (535.2 g) was poured into a three-necked flask, followed by larch tannin (36 g). The reaction mixture was blended using a stirrer. The pH value was adjusted to 3.2–3.4 with formic acid (10 wt %). The first urea (123.8) was added slowly and kept the temperature under 60°C for 30 min. After that, the pH value was adjusted to 5.0 for condensation. The second urea (77.1 g) was added and the temperature was gradually increased to 90°C and maintained at this temperature until the end point was reached. The end point was determined by the cloudy appearance when dropping the solution mixture into a beaker of water at 20°C. After the end point, the pH value was adjusted to 7.5–8.0 with sodium hydroxide (30 wt %). The third urea (50.5 g) was added and the temperature was decreased to 70–80°C and maintained for 40 min. Then, the temperature was decreased to 60–70°C and the fourth urea (114.8g) was added, with a final F/U ratio of 1.1. The reaction mixture was maintained at 60–70°C for 30 min. At the end, the pH value was adjusted to 8.0, and the mixture was cooled to ambient temperature.

Unmodified UF resin was synthesized as a control. The synthesis of UF resin was reported previously.[11] Characteristics of the resins were determined. The free formaldehyde content of the resins was measured using the ammonium chloride method. 5.0 g of resin was dissolved in 50 mL of distilled water in a 250 mL Erlenmeyer flask. Eight drops of bromocresol green-methyl red mix indicator were added, and the mixture was carefully neutralized by titration with hydrochloric acid. Then 10 mL of 10% ammonium chloride solution and 10 mL of 1 mol/L sodium hydroxide solution were added to the mixture quickly. The mixture was sealed and stirred and then kept at 20–25°C for 30 min. The resulting mixture was slowly titrated with the 1N hydrochloric acid. The solids content was determined by evaporation of volatiles in 2 g of resin for 3 h at 120°C. The curing time was determined at 100°C after the addition of curing agent. Viscosity was measured with a NDJ-5S rotational viscometer at a constant temperature of 20°C. As a curing agent, 1% ammonium chloride was used in all of the resins.

DSC Measurement

DSC analysis with a TA Instruments model Q2000 was used to evaluate the curing behaviors of TUF resin and UF resin at a heating of 10°C/min. Resin curing was catalyzed with 1% ammonium chloride (20 wt %). For each scan, about 3–5 mg of sample was added to an aluminum pan. The pan was sealed and then heated from 30°C to 160°C in a 50-mL/min flow of N$_2$. The onset temperature, peak temperature, and heat of reaction were recorded, and an average value from at least two replications is presented.

TMA Measurement

TMA analysis was conducted by using Mettler TMA SDTA 840 thermomechanical analyzer with STARe software for data treatment. All experiments were tested under the same conditions: 25 mg of resin, heating rate 10°C/min in the temperature range 25–250°C. Deflection curves, which allow determining the modulus of elasticity (MOE), have been obtained in three point flexion mode on two beech wood veneers of dimensions 17 mm × 5 mm × 0.5 mm for each specimen while the liquid resin layer was spread between the two specimens. The measurements of the thermomechanical properties were made in triplicates on three similar specimens and the average value was taken.

Solid Phase ^{13}C-NMR Analysis

A Bruker AVANCE-400 spectrometer, with a CP-MAS probe for 4-mm diameter rotors at rotational speed of 12 kHz, was used for recording the NMR spectra of cured TUF resin. The cured TUF resin sample was grinded into powder and washed by distilled water to make sure that there were no unreacted small molecules left in the sample. The pulse duration at 90° was 3.9 μs and the contact time was 1 ms (using cpramp100) while the recycle time was 5 s. Decoupling was used in CW mode. The chemical shifts of ^{13}C spectrum were reported in ppm relative to tetramethylsilane by taking the methine carbon of solid adamantane (29.50 ppm) as an external reference standard.

MALDI-TOF-MS Analysis

The spectra were recorded on a MALDI-TOF instrument (AXIMA Performance, Shimadzu). The irradiation source was a pulsed nitrogen laser with a wavelength of 337 nm. The duration of a single laser pulse was 3 ns. The measurements were carried out using the following conditions: polarity-positive, flight path-linear, mass-high (20 kV acceleration voltage), and 100–150 pulses per spectrum. The delayed extraction technique
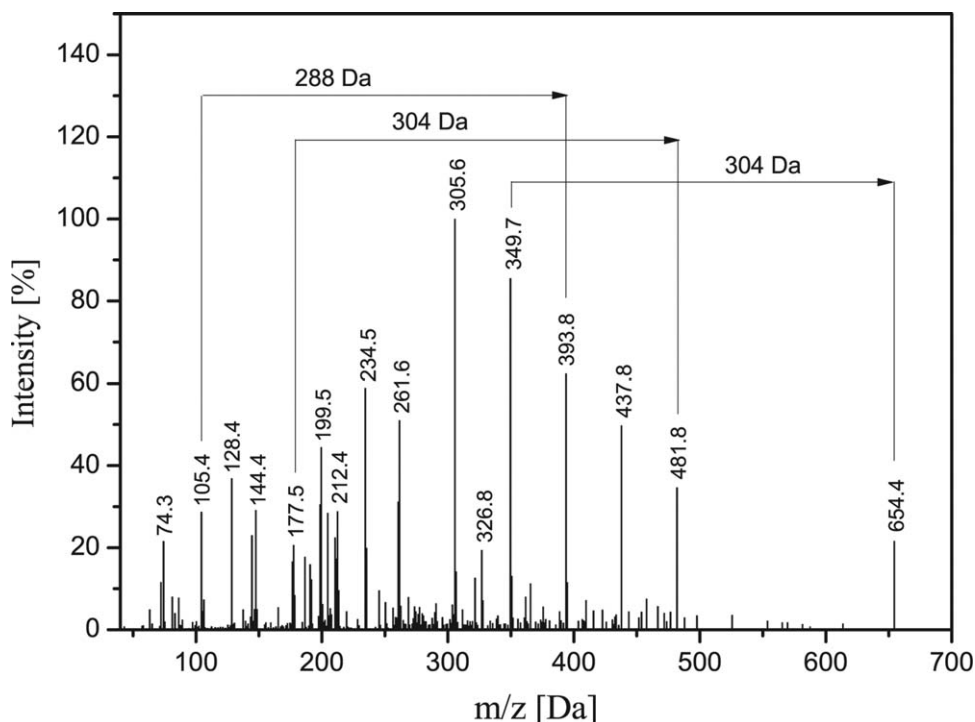
Figure 1. The MALDI-TOF spectrum of larch tannin.

was used by applying delay times of 200–800 ns. The samples were dissolved in acetone (5 mg/mL). As the matrix, 2,5-dihydroxy benzoic acid (DHB) was used. For the enhancement of ion formation, $0.1M$ NaCl was added to the matrix. The solutions of the sample and matrix were mixed in equal amounts, and 1.5 μL of the resulting solution was placed on the MALDI target. After evaporation of the solvent, the MALDI target was introduced into the spectrometer.

Preparation and Performance Measurement of Plywood

Three-ply plywood was manufactured from poplar veneers with dimensions of 410 mm × 410 mm × 1.5 mm on a laboratory hot press under the following conditions: the adhesive formulation was 100 parts resin, 1 part ammonium chloride, and 20 parts wheat flour, the glue spread amount was approximately 280–300 g/m^2 (double glue line), the hot press temperature was 120°C, the hot press pressure was 1.1 MPa, and the hot press time was 6 min. The bond strength (soaked in 63°C water for 3 h) and formaldehyde emission of plywood were tested according to Chinese National Standard GB/T 17657-1999. The formaldehyde emission of plywood was determined using the desiccator method. Ten specimens (150 mm × 50 mm) per panel were placed in a 9–11 L sealed desiccator which contains a crystallizing dish (12 cm × 6 cm) holding 300 mL distilled water. After being closed, the desiccator was kept at 20 ± 2°C for 24 h. The dish was then removed and the water was analyzed for formaldehyde content. The results were expressed as mg/L of formaldehyde in the air.

RESULTS AND DISCUSSION
Structure of Larch Tannin

Tannin from larch bark extracts is a kind of condensed tannins. They are mostly composed of flavan-3-ols repeating units, such as profisetinidin, prorobinetinidin, procyanidin, prodelphinidin, smaller fractions of simple sugars, and other polysaccharides. Figure 1 shows the MALDI-TOF spectrum of larch tannin. It gives information about the structural units of larch tannin. The major peak observed in this spectrum was at 305 Da, which was identified as prodelphinidin [Figure 2(a)]. This may indicate that prodelphinidins were the main constituents of this natural polymer. The major peak-to-peak mass increments observed were 304 Da and 288 Da. These masses corresponded to prodelphinidin [Figure 2(a)] and procyanidin [Figure 2(b)] repeating units, respectively. The peaks at 177 Da and 481 Da can be identified as galloyl group [Figure 2(c)] + Na$^+$, gallocatechin gallate/epigallocatechin gallate [Figure 2(d)] + Na$^+$, respectively. Studies have shown that the flavonoid repeating units in procyanidins (phloroglucinol A-ring; catechol B-ring) and prodelphinidins (phloroglucinol A-ring; pyrogallol B-ring) are mainly linked to each other at C4–C8.[12] Therefore, the structure of the fundamental unit or monomer of larch tannin may be represented as in Figure 3. It must be pointed out that tannins have complex chemical structures made of flavan-3-ols repeating units, with variations on the number of repeating units and on the sites at which the flavan bonds are created.

Structure of TUF Resin

The A-rings of flavan-3-ols units in condensed tannins have a strong nucleophilicity. They can react with formaldehyde rapidly and irreversibly and generate the network of adhesives.[13] Under the acid/base catalytic action, condensed tannins will react with formaldehyde and produce hydroxymethyl adducts, which can continue to participate in further condensation and cure reaction. The reaction mechanism between condensed tannins and formaldehyde is essentially the same as the reaction of phenol–
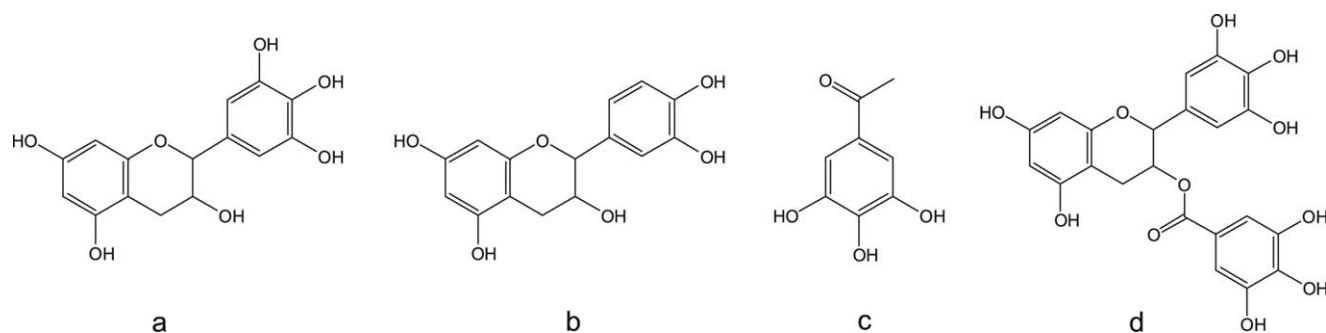
Figure 2. A typical polymer structure of larch tannin repeating units.

formaldehyde resin. In this study, larch tannin was used as a modifier in the synthesis of UF resin. It can act as a powerful free formaldehyde scavenger, and the reaction of formaldehyde and larch tannin will promote the polymerization through methylene bridge linkages at reactive positions on the nucleophilicity A-rings of larch tannin.

Figure 4 shows the MALDI-TOF spectrum of TUF resin. Generally speaking, polymers with electronegative elements like oxygen or nitrogen can be cationized by H^+, Li^+, or Na^+. Despite the use of NaCl as an ionizing agent, we cannot eliminate the interference of H^+ and Li^+ completely. The major peaks observed in this spectrum were 137 Da and 155 Da. They represented the matrix in the form of DHB-H_2O+H^+ and DHB+H^+ respectively. The MALDI-TOF mass spectrum showed clear repetitive patterns of peaks that allow for the identification of specific oligomer series present in TUF resin. The main peak-to-peak mass increment observed was 72 Da, which is representative of the following repeating unit I: —NH—CO—NH—CH_2—.

It indicate that the structures of modified TUF resin were very similar to UF resin, which was composed of a large number of oligomers mainly bonded by methylene and methylene-ether bond, methylolureas, unreacted urea, and free formaldehyde. With the incorporation of larch tannin, the fundamental unit of

larch tannin (Figure 3) could react with formaldehyde as phenol did and form some methylene and methylene-ether bonds during the polymerization of TUF resin. The assignments of the main fundamental chemical structures of TUF resin are given in Table I.

The molecular weight in the MALDI-TOF spectrum (m/z, Da) can be calculated by using this expression: M + H^+/Li^+/Na^+ = 1 (H)/7 (Li)/23 (Na) + 72 m+ 304 n+2 × endgroups (17 for —OH/59 for —NH—CO—NH_2), where m, n is the number of repeating unit I and prodelphinidin, respectively; and m is far greater than n because of the low levels addition of larch tannin in TUF resin. It should be noted that some dimethylene ethers structures exist with the same molecular weight as some methylene-linked structures. For instance, the following two structures have the same value of molecular weight but have different structural compositions.

Type A: —NHCONH—CH_2—NHCONH—CH_2OH
Type B: —NHCONH—CH_2—O—CH_2—$NHCONH_2$
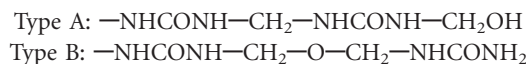
Therefore, a proposed scheme for the synthesis of TUF resin is represented in Figure 5 based on the above analyses.

Figure 6 shows the ^{13}C-NMR spectrum of cured TUF resin. In addition, the assignments of chemical shifts are tabulated in Table II according to the literatures.[14–19] The sharp and high peak at 159 ppm is typical of the presence of carbonyl carbon. These weak peaks at 116 ppm, 130 ppm, and 145 ppm were assigned to larch tannin. The proportional intensity for these peaks is extremely low due to the low levels addition of larch tannin in TUF resin. The chemical shift at 47.5 ppm was assigned to the methylene bonds in the cured TUF resin, indicating that the structures of cured TUF resin were mainly cross-linked by methylene bond.

Thermal Behaviors of TUF Resin

Figure 7 shows typical DSC curves of the UF resin and TUF resin at a heating rate of 10°C/min in the temperature range of 50–160°C. As thermosetting polymers, the curing of UF resin and TUF resin was an exothermal reaction. An obviously exothermic peak was observed during the curing process. The exothermic peak could be attributed to the heat released from the polycondensation reaction of primary amino groups of free urea with hydroxymethyl groups[20] (—CH_2OH) and the cross-linking of oligomers. In addition, the onset temperature increased from 81.46°C to 86.23°C with the addition of larch

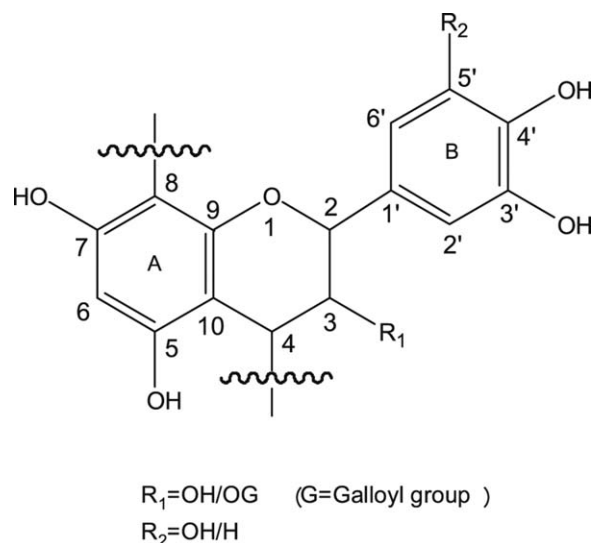R_1=OH/OG   (G=Galloyl group)
R_2=OH/H

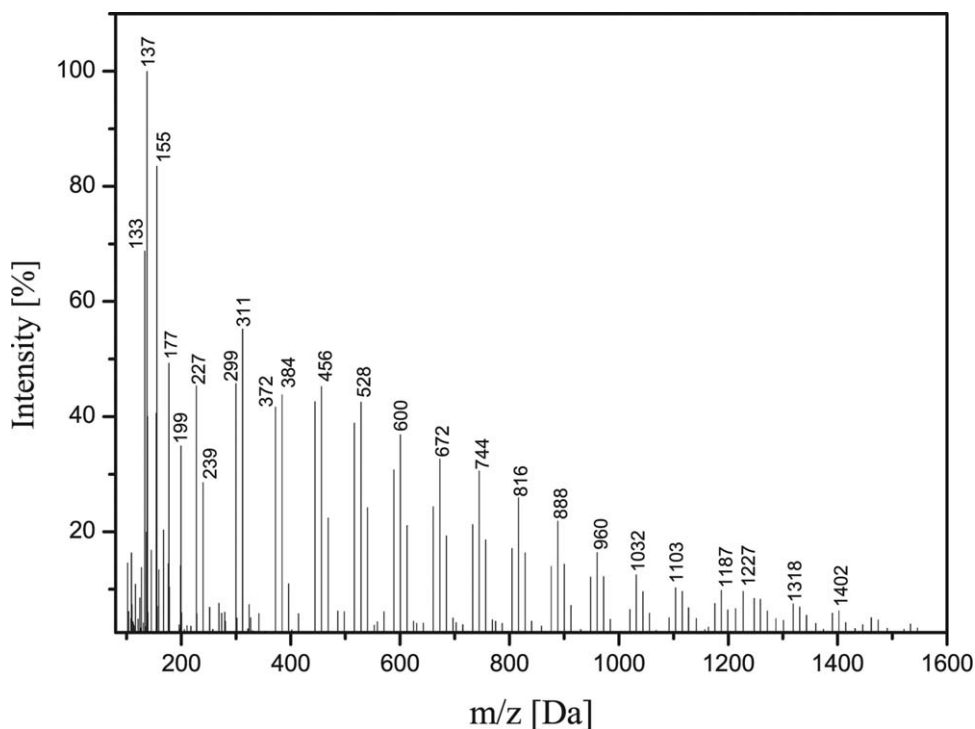Figure 3. The fundamental chemical structure of larch tannin.

Figure 4. The MALDI-TOF spectrum of the TUF resin.

tannin, indicating that the polymerization of TUF resin started at higher temperature. The peak temperature of TUF resin also shifted to higher temperature, that is, 92.86°C, while that of UF was 87.04°C. This suggested that the temperature at which the polymerization of TUF resin reached the maximum conversion rate was higher than that of UF resin. The heat of curing reaction (ΔH) was determined as the area under the exothermic thermogram of a DSC curve. The ΔH values at a heating rate of 10°C/min were 81.93 J/g and 62.60 J/g for UF resin and TUF resin, respectively. The ΔH decreased with the addition of larch tannin. These results indicated that the reactivity of TUF resin decreased with the addition of larch tannin, and more energy was required to complete the curing of TUF resin due to the steric hindrance of tannin itself and the hinder effect of nontannin fractions.

Table I. Group Assignments for TUF Resin in the MALDI-TOF Spectrum[a]

m/z (Da)	Chemical structure assignment
133	$U—CH_2—U + H^+$
199	$HOCH_2—[U—CH_2]_2—OH + Li^+$
227	$[U—CH_2]_2—U + Na^+$
239	$[U—CH_2]_3 + Na^+$
299	$[U—CH_2]_3—U + Na^+$
372	$(HOCH_2)_2— [U—CH_2]_4—OH + Li^+$
384	$[U—CH_2]_5—OH + Li^+$ or $P—CH_2—U + Li^+$
456	$[U—CH_2]_6—OH + Li^+$ or $P— [CH_2—U]_2 + Li^+$
…	……

[a] The letters U and P represent urea and prodelphinidin, respectively.

Figure 8 shows the related TMA curves of the UF resin and TUF resin at a heating rate of 10°C/min. The MOE of a wood–resin system could give a good indication of the end rigidity, which is enough to predict the final application of the glued system. The maximum value of MOE of UF resin and TUF resin were 1777 MPa and 2344 MPa, respectively. It is obvious that with the incorporation of larch tannin, the peak of maximum strength (MOE) was elevated significantly. Maybe it is corresponding to the enhanced load bearing capability of the wood joints glued with TUF resin. First of all, the rigidity of phenolic compounds in tannin is much higher than urea. In the second place, the incorporation of larch tannin within the network skeleton of the resin endowed the network structure with more flexibility, which can relieve of the imposed stress easier and faster.

Performance of TUF Resin and Plywood

Some technical characteristics of the UF resin and TUF resin are presented in Table III. In addition, the bond strength and formaldehyde emission of plywood bonded by these resins are shown in Figure 9.

As it can be seen in the table, the free formaldehyde content of TUF resin was decreased by 34.2% comparing to UF resin. This can be explained by the phenolic natural of tannins, which could react with formaldehyde. The solids content was a little lower than that of UF resin. Because there were some nontannin fractions in larch tannin, consisting mainly of simple sugars and high molecular weight hydrocolloid gums. It was those sugars that have an effect of diluting the adhesive resin solids. The curing time of TUF resin was longer than that of UF resin. One reason is that the nontannin fraction, which cannot participate in the resin formation with formaldehyde, hindered the cure reaction of resin. Besides that, the steric hindrance of tannin itself will also cause
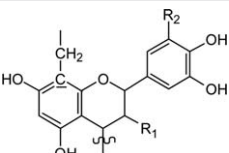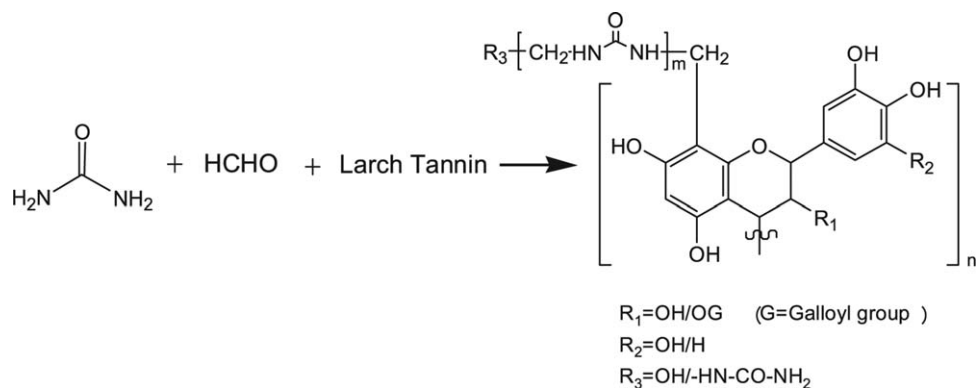
Figure 5. A proposed scheme for the synthesis of TUF resin (*m*, *n* are positive integers, and *m* ≫ *n*).

the extension of curing time. This was consistent with the DSC data and it suggested that a higher temperature or longer time was needed to cure TUF resin. The viscosity of TUF resin was higher than that of UF resin due to the high molecular weight hydrocolloid gums in larch tannin. The density was increased after we introduced larch tannin into UF resin.

As shown in Figure 9, the bond strengths of plywood bonded by UF resin and TUF resin after soaking in 63°C water for 3 h were 0.81 MPa and 1.01 MPa, respectively. The addition of larch tannin to UF resin endowed plywood with higher bond strength than UF resin did. This result was in parallel to the increased rigidity of TUF resin in the TMA data. The formaldehyde emissions of plywood were 1.56 mg/L and 1.16 mg/L for UF resin and TUF resin, respectively. Compared to UF resin, the formaldehyde emission of TUF bonded plywood decreased approximately 25%. One of the reasons is that the addition of larch tannin reduced the free formaldehyde content of resin. The other possible reason is that the bonds of methylene to nitrogen from urea are quite susceptible to hydrolysis and can release formaldehyde due to a reverse methylolation reaction, while the bonds to phenolic group are more stable than that to urea. According to Chinese National Standard GB/T 9846.3–2004, the formaldehyde emission of plywood manufactured with TUF

Table II. ^{13}C-NMR Shifts and Group Assignments for TUF Resin

Chemical structure assignment	Chemical shift (ppm)	
	Reference	Experimental
—NH$\underline{C}$H$_2$NH—	44–49	47.47
—N($\underline{C}$H$_2$)CH$_2$NH—	53–55	53.95
—NH$\underline{C}$H$_2$OH	63–65	64.74
—NH(CH$_2$)$\underline{C}$H$_2$OH or —NH—$\underline{C}$H$_2$OCH$_3$	71–73	72.29
C2′, C5′	116–120	115.99
	129–131	130.02
C3′, C4′	145–148	145.12
–NH–$\underline{C}$O–N–	159–160	159.69

resin can reach E1 grade (0.5 mg/L < E1 ≤ 1.5 mg/L), while UF resin is E2 grade (1.5 mg/L < E2 ≤ 5.0 mg/L). Overall, the addition of larch tannin to UF resin for bonding plywood enhanced

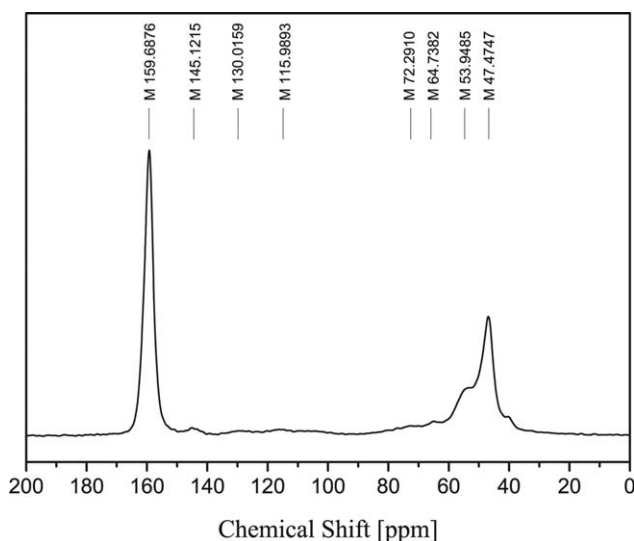**Figure 6.** The ^{13}C-NMR spectrum of cured TUF resin.

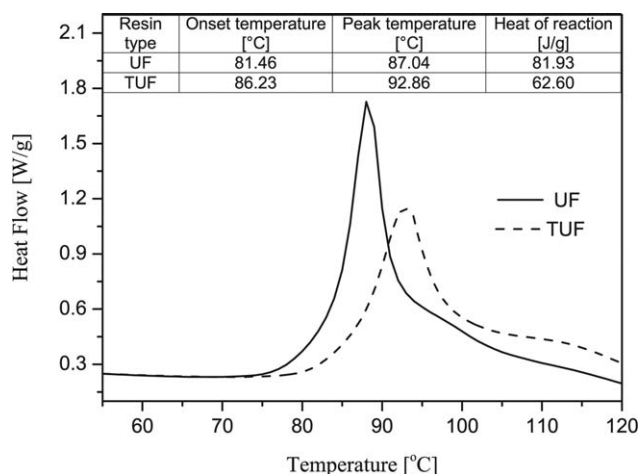| Resin type	Onset temperature [°C]	Peak temperature [°C]	Heat of reaction [J/g]
UF	81.46	87.04	81.93
TUF	86.23	92.86	62.60

Figure 7. DSC curves of the UF resin and TUF resin at a heating rate of 10°C/min.

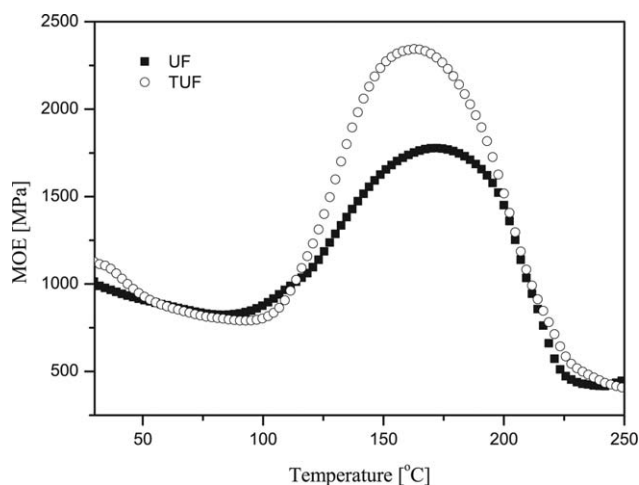**Figure 8.** TMA curves of the UF resin and TUF resin at a heating rate of 10°C/min.

Table III. Characteristics of the UF Resin and TUF Resin

Parameters	UF resin	TUF resin
Free formaldehyde content (%)	0.38 ± 0.04	0.25 ± 0.02
Solids content (%)	56.86 ± 0.28	55.32 ± 0.19
Curing time (s)	96 ± 3	115 ± 3
Viscosity (mPa s)	235 ± 10	380 ± 10
Density (g/cm^3)	1.213 ± 0.002	1.322 ± 0.002
Appearance	Milky white	Reddish brown

the bond strength and reduced the formaldehyde emission. Therefore, larch tannin is a desirable modifier for UF resin.

CONCLUSIONS

i. According to the spectra of MALDI-TOF and 13C-NMR, tannin from larch bark extracts is mainly composed of prodelphinidin repeating units. The structures of TUF re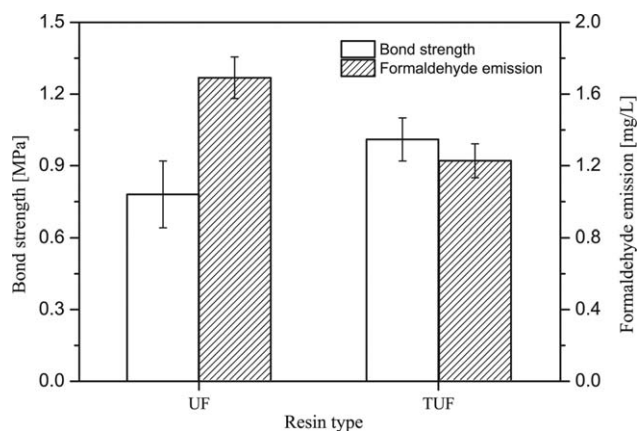sin were very similar to UF resin with the incorporation of phenolic groups. The cure reaction of TUF resin generated crosslinked networking structure mainly linked by methylene bond.

ii. The addition of larch tannin prolonged the curing time and caused an adverse effect on the resin curing. However, it promoted the rigidity and flexibility of the glued system, which was in parallel to the upgraded bond strength of plywood.

iii. Urea–formaldehyde resin modified with larch tannin endowed plywood with higher bond strength and lower formaldehyde emission than UF resin. It proved that larch tannin is a desirable modifier for UF resin and the modified TUF resin can upgrade the properties of plywood.

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Figure 9. Bond strengths and formaldehyde emissions of plywood bonded by UF resin and TUF resin.