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PII: S0143-7496(16)00004-X  
DOI: <http://dx.doi.org/10.1016/j.ijadhadh.2016.01.003>  
Reference: JAAD1783

To appear in: *International Journal of Adhesion and Adhesives*

Received date: 23 April 2014  
Accepted date: 4 January 2016

Cite this article as: Hongyun Duan, Teng Qiu, Longhai Guo, Jun Ye, Yang Yuan and Xiaoyu Li, The aminolysis of styrene-maleic anhydride copolymers for a new modifier used in urea-formaldehyde resins, *International Journal of Adhesion and Adhesives*, <http://dx.doi.org/10.1016/j.ijadhadh.2016.01.003>

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# The aminolysis of styrene-maleic anhydride copolymers for a new modifier used in urea-formaldehyde resins

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**Abstract:** Styrene (St) and maleic anhydride (MA) alternating copolymers with different molecular weights (MW) were synthesized via radical copolymerization. The copolymers were subsequently transferred into water-soluble maleic amic acid derivatives (SMAA) via the aminolysis of anhydride groups using  $(\text{NH}_4)_2\text{CO}_3$  as the ammonia sources. The synthesized polymers were applied as a new kind of macromolecular modifier and added into the reaction system during the synthesis of urea-formaldehyde (UF) resins via the traditional alkaline-acidic-alkaline three-step process. The UF resins modified with SMAA were characterized using Fourier Transform Infrared Spectroscopy (FT-IR),  $^{13}\text{C}$  nuclear magnetic resonance ( $^{13}\text{C}$ -NMR) spectroscopy, and thermal gravimetric analysis (TGA). All the results confirmed the successful incorporation of SMAA chains into the crosslinking network of the UF resins. The modified UF resins were further employed as wood adhesives and the effect of synthesis parameters on their performance was investigated. Meanwhile, the influence of SMAA molecular weight (MW) on the properties of the modified UF resins was also studied. When the UF resins were synthesized with a low molar ratio of formaldehyde/urea (F/U) and a predetermined amount of SMAA added into the reaction system at the second step, plywood bonded using these modified UF resins showed much improved bonding strength (BS) and depressed formaldehyde emission. Moreover, the as-modified UF resins showed good storage characteristics.

**Keywords:** urea-formaldehyde resins; styrene-maleic anhydride alternating copolymers; wood adhesive; crosslinking network; formaldehyde emission; plywood

## 1. Introduction

Urea-formaldehyde (UF) resin is one of the most important wood adhesives, which has been widely used in the manufacture of particle board, medium density fiberboard, and plywood. Nowadays, for the furniture and building decoration industries, more than 80% of wood panels are bonded using UF resins - based adhesives.[1] UF resins show many advantages low price and an abundant supply of raw and processed materials, such as formaldehyde (F) and urea (U) in particular. Besides, the synthesis protocol of UF resin is simple. However, due to formaldehyde emission (FE) issues, the application of UF resins has been restricted,[2-4] this being due to its toxicity to human health and the possibility of triggering cancer and fetal deformities as confirmed by the World Health Organization in 2004. Thus considerable effort has been devoted to the minimization of FE whilst attempting to maintain beneficial resin characteristics [5].

In many studies on the synthesis of UF resins, it has been demonstrated that a low molar ratio of F/U is an effective way to reduce FE. [2-5] In practice FE mainly results from the hydrolytic degradation of the *N*-hydroxymethyl and/or methylene ether groups contained within the UF resin structure. Compared with the traditional synthesis approach with a F/U molar ratio in the range of 0.95-1.80, a UF resin synthesized at a lower F/U molar ratio can result in a decreasing amount of *N*-hydroxymethyl and/or methylene ether groups, which in turn leads to lower FE and the shorter storage period for wood panels prepared using such UF resins as adhesives. However, properties and characteristics such as internal bonding strength (BS) and water resistance are also depressed. [6-9] Therefore, it is important to consider more effective modification methods for UF resins.

In the UF resin synthesis process, melamine, phenol, and alkylamines or amides

have been the most commonly used modifiers.[10-14] These small and reactive molecule modifiers can be introduced into the UF resin during the synthesis process, so as to modify the structure of the UF resin. Moreover, they could also serve as formaldehyde scavengers to reduce FE related problems.

Besides these small molecules, low or middle molecular weight (MW) polymers with reactive multifunctional groups provide another modification choice. In our previous study on the synthesis of glycidyl ether modified UF resins, it was found that the longer molecular chain length of the modifier can lead to a better performing adhesive. [15] However the further prolongation of the MW of glycidyl ether was limited due to its poor water solubility. Studies on the modification of UF resins using polyvinyl alcohol (PVA) [16] and polyacrylamide (PAM) [17] have shown that the incorporation of macromolecular modifiers can effectively modify the network structure of a UF resin, so as to reduce FE. However, with such modification approaches, cost related issues also require serious consideration in terms of their practical utilization as wood adhesives.

Copolymers of poly(styrene-maleic anhydride) (SMA) and their water-soluble amphiphilic derivatives, such as styrene-maleic amic acid resins benefit from relatively inexpensive supply of starting materials such as styrene (St) and maleic anhydride (MA). They are nowadays used in a wide variety of applications. Such resin types have been extensively used due to their high functionality (and hence ability to contribute to high levels of crosslinking), good thermal characteristics, low viscosity a high solids content, good mechanical strength, colorless behavior, and low VOC behavior.[18] One of the applications for SMAs with low to middle MW is as modifiers for adhesives. The modification of epoxy resin by incorporation of SMA has been reported [19], where improvements in toughness, rigidity, initial adhesion,

fluidity, stability in moisture and/or thermal environments of the final cured polymers have been noted. Improvements in interface characteristics demonstrated by using SMAs in resin systems has also been well documented-[20]. However, publications relating to the use of SMA modified UF resin adhesives is still quite limited.

In this work, we explored the modification of UF resin by using SMA as the modifier. We first synthesized the SMA alternating copolymers via solution polymerization in butanone. The synthesis of UF resin was carried out in water with a low molar ratio of F/U. The styrene-maleic amic acid (SMAA) was prepared via the aminolysis of SMA in order to improve water solubility. The obtained SMAA could then be conveniently added into the synthesis system of the UF resin during the traditional three-step (alkaline-acidic-alkaline) reaction process. However, only the synthesis with SMAA added in the second (acidic) step gave obvious evidence for the incorporation of SMAA chains into the crosslinking network of the UF resin. In addition, SMA modified UF adhesive demonstrated a prolonged storage capability with depressed FE characteristics. The performance of the SMA modified UF resin was affected by the MW of the SMAA used in the synthesis, which was also investigated in this work.

## 2. Experiment

### 2.1. Materials

Formaldehyde (F, 37% aqueous solution, Tianjin Fuchen Chemical Reagents Factory), urea (U, nitrogen content  $\geq 46.4\%$ , China Petroleum), styrene (St, industrial grade, Tianjin Fuchen Chemical Reagents Factory), maleic anhydride (MA, industrial grade, Tianjin Guangfu Chemical Reagents Factory), and ammonium carbonate (reagent grade, Beijing Chemical Factory) were directly used as received in this work.

The other reagents used in this work were commercial analytical products purchased from the market. The water used in all reactions was deionized water prepared in our laboratory. The basswood veneers (5% moisture content), with dimensions of 300x300x1.2mm were employed to evaluate the synthesized adhesives.

## 2.2. Synthesis and characterization of SMAA copolymers and modified UF resins

### *Synthesis of SMA copolymers*

The SMA copolymers were synthesized as described previously [21-25]. A typical example of the synthesis procedure was as follows: MA (35.35 g) and dodecyl mercaptan (0.5 g) were dissolved in butanone (200 mL). Subsequently, the solution was transferred into a four-neck round-bottom flask equipped with a mechanical stirrer, a thermometer, a condenser pipe, and a nitrogen inlet and outlet. The reaction system was degassed with nitrogen for 20 min and then heated to 70 °C in a water bath.

After the dropwise addition of benzoyl peroxide (BPO, 0.28 g) solution into St (33.26 g) over a period of 45 min, temperature was increased to 80 °C and maintained at this temperature for 5 h before cooling to room temperature. The nitrogen atmosphere was maintained during the whole polymerization process. Finally, petroleum ether was added to the butanone solution so as to obtain a white solid deposition of SMA, which was further filtered and dried in a vacuum oven at 50 °C for 24 h. The MW of the as-prepared SMA could be adjusted via changing the amount of dodecyl mercaptan (DM) during the reaction process.

### *Synthesis of SMAA*

The synthesized SMA copolymers (50 g) and ammonium carbonate (35 g) were respectively ground into a fine powder [26-28] and subsequently added into a 250 mL three-necked round-bottom flask equipped with a mechanical stirrer and a condenser.

The mixture was heated to 90 °C in a thermostatic water bath under continuous stirring at 800 rpm. The aminolysis reaction was stopped when there was no released NH<sub>3</sub> gas judged by wet litmus paper. The reaction time for this step was about 5 h.

### *Synthesis of UF resins*

The UF resins were synthesized by a three-step alkaline-acidic-alkaline process with an F/U molar ratio of 1.05. The typical synthesis protocols were as described below.

**Step 1: Addition reaction.** The aqueous solution of formaldehyde (170 g) was added into a 500 mL four-necked round-bottom flask equipped with a mechanical stirrer and condenser. The pH of the solution was adjusted in the range from 8.8 to 9.0 by using sodium hydroxide aqueous solution (20 wt%), which was carried out with the temperature of the solution at 30-35 °C. Subsequently, the first quantitative amount of urea (72 g) was added into the flask and the solution was heated to 90 °C in a thermostatic water bath. The addition reaction was carried out for about 45 min.

**Step 2: Condensation reaction.** By using the formic acid aqueous solution (30 wt%), the pH of the mixture was further adjusted in the range from 4.8-5.0 after the addition reaction in step 1, with the temperature maintained at 90 °C. After 15 min, the second quantitative amount of urea (30 g) was added to the mixture. Then, the temperature of the reactor was decreased to 85 °C, and the reaction was stopped when the viscosity of the mixture reached 300-350 cp.

**Step 3: Post treatment.** By using the sodium hydroxide aqueous solution (20 wt%), the pH value of the mixture was adjusted to 7.5-8.0. The third quantitative amount of urea (18 g) was then added into the flask. The temperature of reactor was then decreased to 80 °C, and the reaction stopped after 15 min. The final UF resin with F/U = 1.05 was obtained after cooling to room temperature.



The as-synthesized SMAA was employed as the macromolecular modifier for the UF resin. In this work, the SMAA was added into the reaction by different protocols as listed in Table 1. Different amounts of SMAA were added from 2.5 to 10 wt%, based on the total solid content of UF resin. For the sake of convenience, the UF resin modified by SMAA is designated hereafter as “UF-SMAA<sub>M</sub>(X-Y)”, where  $M \times 10^4$  stands for the molecular weight of SMAA, X stands for the addition method as listed in Table 1, and Y stands for the percentage of added SMAA. For example, UF-SMAA<sub>0.98</sub>(II-5) means that SMAA modifier with a MW of  $0.98 \times 10^4$  was added in Step 2 during the synthesis of UF resin and the addition amount was 5 wt% of the total solid content. Meanwhile, the pure UF resin without the addition of SMAA was defined as the blank UF resin for comparison.

#### *Plywood preparation*

The wood veneers were layered up in cross-banded plies and glued by using the synthesized UF-SMAA resins or blank UF resin, as appropriate. The adhesive was firstly mixed with ammonium chloride solution (5 g, 20 wt%, aq.) and then spread onto the faces of each veneer piece. The resin consumption of prepared plywood was about 150 g/m<sup>2</sup>. The wood plies were hot-pressed at 120 °C and 10<sup>5</sup> kg/m<sup>2</sup> pressure. The hot-press time was determined by the thickness of veneer at 1.0 min/mm.

#### *FTIR and <sup>13</sup>C-NMR*

The UF samples (0.5 g) dried in an air blowing thermostatic oven at 60 °C for 8 h were rinsed 3 times with deionized water, and then further dried in a vacuum oven at 80 °C for 5 h. The samples thus prepared were held in the vacuum oven at room temperature until the FT-IR and <sup>13</sup>C-NMR measurements. The transmission FTIR spectra were recorded at room temperature for the as-prepared UF sample by using a Bruker Tensor 37 Fourier transform IR spectrometer via the KBr pellet method. A

total of 32 scans were accumulated with a resolution of  $4 \text{ cm}^{-1}$ . The  $^{13}\text{C}$ -NMR spectra were recorded at 400 MHz at ambient temperature by using a Bruker Fourier Transform AVANCE 400. The deuterated reagents of  $\text{DMSO-}d_6$  and  $\text{D}_2\text{O}$  were employed as the solvent for SMA and SMAA, respectively.

#### *TGA analysis*

For the TGA measurement, the synthesized UF resin (10 g) was mixed with ammonium chloride solution (0.7 g, 20 wt%, aq.) and then cured at  $120 \text{ }^\circ\text{C}$  for 10 min. The cured resin samples were further rinsed 3 times using deionized water. Finally, the samples were dried in a vacuum oven at  $80 \text{ }^\circ\text{C}$  for 5 h. The TGA characterization was carried out on PerkinElmer TGA-4000 in the temperature range  $30 \text{ }^\circ\text{C}$  to  $300 \text{ }^\circ\text{C}$  with a heating rate of  $10 \text{ }^\circ\text{C}/\text{min}$  under a nitrogen flow of  $20 \text{ mL}/\text{min}$ .

#### *GPC measurement*

GPC was employed to determine the MW of synthesized SMA by using a GPC515-2410 from Waters Corporation (Milford, MA) that consists of a HPLC Pimp and Refractive Index Detector. THF was employed as the mobile phase at a flow rate of  $1 \text{ mL}/\text{min}$ . The THF solution of the SMA sample was injected at a concentration of  $3 \text{ mg}/\text{mL}$  after filtration through a  $0.45 \text{ }\mu\text{m}$  microporous membrane. Columns and detectors were maintained at  $30 \text{ }^\circ\text{C}$ . The MW of specimens was calculated with a calibration curve based on narrow polystyrene standards

#### *MA content and conversion of SMA*

The MA content [29] of SMA was carried out as follows: a  $0.5 \text{ g}$  SMA sample was dissolved in  $10 \text{ mL}$  of acetone in a conical flask, followed by the addition of  $0.2 \text{ g}$  sodium hydroxide standard solution. The mixture was refluxed at  $60 \text{ }^\circ\text{C}$  for 12 h. After the solution was cooled to room temperature, the residual sodium hydroxide was titrated by using  $0.1 \text{ mol}/\text{L}$  hydrochloric acid standard solution. The MA molar

percentage content in SMA noted by  $F_{MA}$  was calculated using eq 1.

$$F_{MA} = \frac{104 \times (m - 40cV)}{40G + 6 \times (m - 40cV)} \times 100\% \quad (1)$$

where  $m$  stands for the weight of sodium hydroxide,  $c$  the molarity of hydrochloric acid standard solution,  $V$  for the consumed volume of hydrochloric acid standard solution and  $G$  for the SMA weight. The conversion of SMA was determined by gravimetry based on raw materials.

#### ***Aminolysis degree of SMAA***

The aminolysis degree of SMAA copolymers were determined as amine value according to previous literature [30, 31]. 0.5 g of SMAA was placed into a 250 mL conical flask. Then, 20 mL of glacial acetic acid/dioxane (volume ratio at 2:1) mixed solvent was added into the conical flask to dissolve the sample completely. The solution was titrated using 0.1 mol/L of perchloric acid-glacial acetic acid standard solution with methyl violet as the indicator. Thereafter, the weight of consumed standard acid was transformed into stoichiometric equivalent of the weight of KOH (mg KOH/g). The weight of KOH (mg KOH/g) was defined as the amine value.

#### ***Solid content***

Solid content was measured by gravimetry. About 1.0 g of resin sample was poured into an aluminum dish and then dried in the oven at 100 °C until a constant weight was achieved. The nonvolatile solids content was weighed after drying. Three replications were conducted and the average result was taken.

#### ***Viscosity of UF resin***

The viscosity of modified UF resins were measured at 25 °C by a cone-plate viscometer (NDJ-5S, Shanghai Changji Geological Instrument Co., Ltd.) with No. 2 spindle rotating at 60 rpm.

***Storage period***

The storage stability of the resin was evaluated by its storage period at room temperature. An approximately 100 g resin sample was placed into a 200 mL conical flask equipped with a plug. The storage period was defined as the duration time until the resin sample lost its fluidity.

***Plywood bonding strength (BS)***

Three-layered plywood was used for measuring BS according to National Standard of People's Republic of China GB/T 17657-1999. In the measurement, the prepared three-layer plywood was cut into  $25 \times 100$  mm specimens each with two notches of  $20 \times 25$  mm. These specimens were soaked in water at  $63 \pm 2^\circ\text{C}$  for 3 h. Following this the specimens were cooled to ambient temperature for 10 min before testing. A universal material testing equipment (CMT 4304 from Shenzhen, Xinsansi Material Testing) operated in tension mode was used with a test loading speed of  $10 \text{ N/mm}^2$ . Thirty specimens were measured for each sample and the average result was calculated.

***Plywood formaldehyde emission (FE)***

According to National Standard of People's Republic of China GB/T 17657-1999, 7-layer boards were cut into ten specimens having dimensions of  $10 \times 50 \times 150$  mm as soon as the produced plywood had cooled down to room temperature. These samples were put into a 10 L covered glass desiccator together with a Petri dish filled with 300 mL of DI water within 30 min after the production of the plywood. FE was evaluated by the formaldehyde concentration in the water after 24 h of absorption of emitted formaldehyde under  $20^\circ\text{C}$ , which was determined with acetylacetone by using a UV-3150 SHIMZDZU UV-vis-NIR spectrometer. [32]

### 3. Results and discussion

#### 3.1. Synthesis of SMA and SMAA

The experimental protocol of the synthesis of SMA and SMAA is sketched in Scheme 1. By using BPO as initiator, the copolymerization of St and MA monomers was first carried out via radical polymerization, where the molar ratio of St/MA was controlled at 1/1. It has been reported that when the reaction temperature is below 60 °C, both of the reactivity ratios of St and MA monomers are approximately equal to 0 and the St and MA monomers tend to form the alternating copolymer [17-21]. However, random copolymers can be obtained, if the reaction temperature is above 90 °C. In this work, in order to carry out the polymerization at a desirable rate, the reaction temperature was controlled at 80 °C. Through adjustment of the molar ratio of MA and St monomers during the reaction process, the content of MA in the copolymer was controlled at 49.4%, which was determined by the titration method. And the final monomer conversion of this polymerization was at 96.8%. A predetermined amount of DM was employed during the copolymerization process with the purpose to depress the propagation rate of the SMA monomer. Based on the GPC results, the  $M_n$  of SMA (and the following SMAA) synthesized at this condition was in the range from  $0.5 \times 10^4$  to  $2 \times 10^4$  with the MW of the SMA changing with the concentration of DM employed, as listed in Table 2. From these results it can be seen that the  $M_n$  increased from  $0.53 \times 10^4$  to  $1.98 \times 10^4$  when the amount of DM was decreased from 0.97 to 0.81 g. The distribution of MW was correspondingly broadened with the decreasing amount of DM as indicated by the increasing value of PDI. Moreover, for the reactions with different parameters, the monomer conversion and MA molar percentage in the copolymer chain were stable at 95-96% and 49.3-49.6%, respectively. Amine value decreased with increasing MW of SMA in the

range of 120.6-128.5 mg KOH/g, which was due to increased amounts of entangled macromolecular chains preventing reactive  $\text{NH}_3$  from permeating into the interior matrix. As the SMAA originated from the aminolysis of SMA, the MW of SMAA was assumed to be similar to that observed for the precursor SMA.

The IR spectrum of the  $\text{SMA}_{0.98}$  is shown in Figure 1. The characteristic bands due to PS segment can be obtained around 3033 (stretching vibration of C-H in benzene ring), 1452, 1496, 1597 (the skeletal vibration of benzene ring), 702, 760  $\text{cm}^{-1}$  (out-of-plane bending vibration of C-H in benzene ring). The bands around 1780 and 1855  $\text{cm}^{-1}$  were due to the symmetrical and asymmetrical stretching vibration of C=O groups in maleic anhydride units, respectively. The band around 2931  $\text{cm}^{-1}$  was attributed to the stretching vibration of C-H in alkane groups, which were induced by the copolymerization from the unsaturated bonds in St and MA.

The IR spectrum of  $\text{SMAA}_{0.98}$  is also shown in Figure 1. The bands around 3343 and 3194  $\text{cm}^{-1}$  were due to the asymmetrical and symmetrical stretching vibration of N-H bond of the primary amide groups, respectively. The evidently broad band from 2944 to 3456  $\text{cm}^{-1}$  confirmed the existence of large amounts of -COOH groups. The stretching vibration bond of C=O groups in SMAA was affected by the formation of amide groups, whose intensity became weak and the peak position red-shifted from 1855 to 1715  $\text{cm}^{-1}$  and from 1780 to 1662  $\text{cm}^{-1}$ , respectively. In addition, the band around 1560  $\text{cm}^{-1}$  was corresponded to the in-plane bending vibration of N-H in primary amide groups. The band around 1405  $\text{cm}^{-1}$  was due to the stretching vibration of C-N bond. All of these bands confirmed the transformation of anhydride groups to amic acid structures.

The SMA copolymers with alternating structure provided enough reactive maleic anhydride groups for the following aminolysis reaction.[26-28] The reactive  $\text{NH}_3$  was

generated from the thermal decomposition of ammonium carbonate. Then, the anhydride ring would experience a ring-opening reaction with  $\text{NH}_3$  for the quantitative transformation into of the maleic amic acid structure, i.e. one carboxylic acid and one amide group. For the maximum degree of aminolysis of SMA, the molar ratio of ammonium carbonate over anhydride groups was adjusted to 1.5, where the amount of ammonium carbonate was in excess. The final degrees of aminolysis obtained are indicated in Table 2 where it can be seen that the increasing MW of the SMA results in a lower amine value for the corresponding SMAA. This can be attributed to the MA units enhancing MW and thus polymer chain entanglement. The amine value (126.8 mg KOH/g) of the synthesized SMAA was obtained via chemical titration. The high aminolysis degree guaranteed good solubility in water of the SMA derivate. The aqueous solution of SMAA was transparent with a slight faint yellow coloration and the pH value was about 5.0-5.3 due to the amic acid moieties.

### 3.2. Characterization of UF-SMAA resins

Due to the good solubility of SMAA in water, it is potentially advantageous to add SMAA resin into UF resins during the synthesis process in order to improve the adhesive's performance. The possible reactions are shown in Scheme 2. The amide groups in SMAA could react with formaldehyde to allow the formation of SMAA-CO-NH- $\text{CH}_2\text{OH}$  structures. This structure would rapidly condense under acidic conditions with amide and *N*-hydroxymethyl groups in urea, SMAA, methylolurea, dimethylolurea and/or UF prepolymers for the formation of *N*-methylene linkages.

The  $^{13}\text{C}$ -NMR spectrum of UF-SMAA<sub>0.98</sub>(II-10) is shown in Figure 2 together with that of blank UF. The assignment of each peak is listed in Table 3. The chemical shift at 45.9 ppm was attributed to the carbon of methylene linkages. The chemical shift at

49.1 ppm was assigned to the carbon of residual methanol in formaldehyde. The chemical shift at 52.7 ppm was assigned to the carbon of methylene groups linked to tertiary amine. The chemical shift at 63.9 ppm was assigned to the *N*-hydroxymethyl carbon in UF resins. The chemical shifts at 69.2 and 69.8 ppm were attributed to the carbons of various methylene ether linkages. The chemical shift at 82.3 ppm was assigned to the carbon of formaldehyde hydrate. The chemical shifts at 158.8, 160.1 and 161.5 ppm were assigned to the carbonyl carbons of urea derivatives in the UF resin structure. These peaks were all typical of UF resin synthesized under a low F/U molar ratio and emerged in both of the two spectra shown in Figure 2. However, some new peaks could be found in the  $^{13}\text{C}$ -NMR spectrum of SMAA modified resin.

The chemical shifts at 54.7 and 56.3 ppm were designated to the two alkyl carbons of maleic amic acid monomer segments and the chemical shifts at 59.1 and 59.4 ppm were attributed to the two alkyl carbons of styrene units in SMAA. The peaks at 74.6 and 77.9 ppm were assigned to the carbons of SMAA- $\text{CON}(\text{CH}_2)\text{CH}_2\text{NH}$ - and SMAA- $\text{CON}(\text{CH}_2)\text{CH}_2\text{N}(\text{CH}_2)$ - structure, respectively, indicating the addition and condensation of the amides in SMAA with *N*-hydroxymethyl as shown in Scheme 2. The chemical shifts at 129.1 and 137.3 ppm were assigned to the carbons of the benzene ring. The chemical shift at 176.1 ppm was attributed to the carbon of the SMAA- $\text{CON}(\text{CH}_2)\text{CH}_2\text{NH}$ - structure. The peaks at 179.3 and 180.2 ppm were assigned to the carbons of amide and carboxylic acid groups in maleic amic acid structures, which indicated the residual of unreacted amide groups in the resin system.

The IR spectra of UF resins modified by the addition of SMAA (SMAA<sub>0.98</sub>) at different reaction steps are displayed in Figure 3, as well as that of blank UF. For the blank UF, the wide band around  $3337\text{ cm}^{-1}$  was assigned to the stretching vibration of N-H and O-H. The band at  $2960\text{ cm}^{-1}$  was assigned to the stretching vibration of C-H



bonds in  $-\text{CH}_2-$  groups. The peak at  $1650\text{ cm}^{-1}$  was designated to the  $\text{C}=\text{O}$  stretching vibration of amide. The peak at  $1570\text{ cm}^{-1}$  was designated to the  $\text{N-H}$  stretching vibration of secondary amide. The peak at  $1390\text{ cm}^{-1}$  was attributed to the out-of-plane bending vibration of  $-\text{CH}_2-$  in the UF resin structure. The peak at  $1245\text{ cm}^{-1}$  was ascribed to the  $\text{C-N}$  bending vibration of secondary amide. The peak at  $1135\text{ cm}^{-1}$  was ascribed to the  $\text{C-O}$  stretching vibration of alkyl ethers contained within secondary amide groups. All these peaks mentioned above were observed not only in the FTIR spectrum of the blank UF resin but also in that of the SMAA modified UF resins with small variances on their positions and relative intensities influenced by addition and condensation reactions during the synthesis process.

However, two new peaks could be found in the spectra of UF-SMAA resins at  $1450$  and  $702\text{ cm}^{-1}$  by comparing the FTIR spectra in Figure 3. The emerging of the two peaks were especially obvious in the FTIR spectra of UF-SMAA<sub>0.98</sub>(I-10) and (II-10). These two peaks were attributed to the skeletal vibration of benzene rings and out-of-plane bending vibration of  $\text{C-H}$  in benzene rings, respectively. The new appearance of IR bond due to benzene provided the positive evidence for the successful modification reaction of SMAA on UF resins. Compared with these three FTIR spectra of SMAA modified UF resins, the strongest intensity of the two peaks was observed in the spectrum of (II-10) sample, which meant that the maximum amount of SMAA could incorporate into the UF skeleton by chemical bonding if it was added in the second step, i.e. under the acidic condition together with the second batch of urea in comparison with other addition methods. SMAA could also be introduced into the UF network but with decreasing amount when SMAA was added in the first step under alkaline conditions based on the weaker intensity of the peaks of benzene in the spectrum of (I-10). The incorporation efficiency of SMAA into the UF

network should be the lowest when SMAA was added with the third batch of urea after the condensation as nearly no peaks could be distinguished at either 1450 or 702  $\text{cm}^{-1}$  in the spectrum of (III-10). In addition, the reaction of amide groups in SMAA with the UF resin system would also alter the network structure. The relative intensity of the bending vibration peak of C-N within the secondary amide at 1245  $\text{cm}^{-1}$  in the spectra of (I-10) and (II-10) was weaker than that of (III-10) or the blank UF. The peak at 1135  $\text{cm}^{-1}$  for the C-O stretching vibration of alkyl ether in secondary amide became weak in the spectrum of (I-10) and even disappeared in that of (II-10). These phenomena suggested that the condensation of SMAA with the *N*-hydroxymethyl groups in the UF resin should lessen the probability of the formation of unstable bis(hydroxymethyl)urea or *N*-alkyl ether linkages which have been deemed responsible for FE in many applications employing UF resins.

The different extents of SMAA incorporation into the UF crosslinked network for (I-10), (II-10) and (III-10) can be explained by the different reaction characteristics of the UF resin during the different synthesis steps. SMAA would be expected to react with formaldehyde in either alkaline or acidic conditions. However, the main product would be the carboxylic salt of multi *N*-hydroxymethyl substituted SMAA when SMAA was added in the first alkaline step of UF resin dominated by the addition reaction. The direct addition of low molecular weight substances like HCHO to the water soluble SMAA will lead to different low molecular weight *N*-substituted products which would be inclined to remain in the aqueous phase rather than participate in further condensation reactions with the UF resin. As a result, the effective incorporation of SMAA into the resin should be decreased. Moreover the addition of formaldehyde to the numerous amide groups of the SMAA under alkaline condition would consume a considerable amount of formaldehyde, which would make

the actual F/U molar ratio lower than the designed one. The lowered F/U ratio would have an important influence on both the structure and the properties of the prepared UF resins as reported<sup>4</sup>. However, the formation of water soluble addition products could be avoided to some extent if the SMAA was added during the acidic stage, where the addition would be rapidly followed by condensation reactions thus contributing to the development of the crosslinked structure. The viscosity of the mixture was correspondingly increased. As a weak acid, the conformation of SMAA should be twisted under acidic conditions. The rapid condensation, the large viscosity rise and the twisted molecular conformation suggest that the SMAA should only be partially hydroxymethylated and condensed into the UF crosslinked network with amide groups buried instead of the formation of water soluble by-products. The influence on the molar ratio of reagents also decreased to a minimum. The third possibility for the difference of modified resins using different addition protocols was due to the influence of the pH of the SMAA. As a weak acid, SMAA would not be expected to change significantly the pH of the system as a whole when added in acidic conditions in the second step. But if it was added in the first alkaline stage, the exact pH of the reaction would slightly deviate from the designed one. The produced  $\text{COO-Na}^+$  species would also act as a pH buffer after the first reaction step, which would mean more organic acid would be needed to adjust the pH to acid range for condensation. The departure on pH also influenced the network structure of the synthesized UF resin. Based on the three reasons above, the sample of (II-10) showed a higher incorporation efficiency of SMAA on UF than that of (I-10). For the case when SMAA modifier was added into the UF resin in step 3, the amide groups in the SMAA structure would not be expected to react with the UF resin because of the much elevated viscosity and the moderate reaction conditions of the system. Moreover,

the acidity of the SMAA copolymers would also have had a negative impact on the storage stability of the synthesized UF system. Therefore, it can be concluded that method II is the preferred way for the incorporation of SMAA into UF resin for a modified crosslinking network.

The synthesized UF-SMAA and blank UF resins were cured and the TGA curves of the cured resins are shown in Figure 4. The weight loss of 7% from 50-250 °C can be considered due to the evaporation of water and the elimination of formaldehyde from the UF resin; the latter coming from the disintegration of weak bonds like methylene ether linkages and *N*-hydroxymethyl groups. A weight loss of 70% from 250-350 °C corresponds to the decomposition of main chains in the UF resin structure and the final weight loss of 15% from 350-600 °C corresponding to the decomposition of residual short chains. TGA curves specific to the temperature region of 50 to 250°C are shown in Figure 4(2). Analysis of this data reveals the following thermal stability (i.e. weight loss over this temperature region) trend: UF-SMAA<sub>0.98</sub>(II-10) < (I-10) < (III-10) < blank UF. At 250 °C, the weight loss of the blank UF reached 6.89%, which was much higher than that of the SMAA modified samples at 3.36% (II-10), 3.82% (I-10), and 4.07% (III-10), respectively. The reduced weight loss of the modified resins implied the better thermal stability over this moderate temperature range. However, the best thermal stability was shown by the sample of (II-10) when the modifier was added in the second step of the resin synthesis process with the highest incorporation efficiency of SMAA into the UF crosslinked network as suggested by the IR spectrum. The discussed results further indicate that the incorporation of SMAA can improve the crosslinking efficiency of the modified UF resin.

### 3.3. *BS of plywood bonded by UF-SMAA resins*

The existence of an improved crosslinked network can be further substantiated by

the improved performance of the SMAA-modified UF resin when employed as a wood adhesive. The BS of plywood bonded by UF-SMAA resins with different addition amounts of SMAA was tested in this work and the results are displayed in Figure 5. For comparison, the blank UF resin was employed as reference and the BS results of plywood using blank UF as adhesive is also shown by a dotted line equating to 0.54 MPa in Figure 5. For all UF-SMAA<sub>0.98</sub> resins prepared via the different SMAA addition methods, the BS increased with SMAA content with the exception of the 10% concentration system. Significantly, an improvement in BS could be obtained when the amount of SMAA increased above 5%. Plywood bonded by UF-SMAA resins at 7.5% SMAA showed the best BS of 0.80 MPa. However, a slight decrease of BS was found as the SMAA amount was increased to 10%.

Comparing all the columns shown in Figure 5, the UF-SMAA<sub>0.98</sub> system prepared via method II showed the highest BS values, which can be attributed to the highest incorporation efficiency of SMAA into the UF crosslinking network. The modification effect became more apparent with increasing concentration of SMAA until an optimum value of 7.5% was reached. A further increase in SMAA concentration was not encouraged based on the experimental results obtained. Actually, the superfluous introduction of SMAA with abundant hydrophilic –COOH and unreacted –CONH<sub>2</sub> groups would, in all likelihood, decrease the water resistance of the adhesive. Moreover, SMAA dissociating in the water phase would also act as thickeners for the system, which may benefit initial adhesion as well as the storage stability. However, too high a viscosity would be inclined to decrease the reaction possibility of SMAA with the different intermediates of UF. Considering the structure and properties of SMAA and the production process of UF resin, SMAA should be added in step 2 with an optimum concentration of 7.5%.

### 3.4. FE of plywood bonded by UF-SMAA resins

For the plywood bonded by UF-SMAA resins, the decrease of FE was lower than that for plywood bonded with blank UF resin (2.00 mg/L) (Figure 6). For the resin with an SMA content of only 2.5 %, the FE was 1.65 mg/L, which was a 17.5% decrease in comparison with the FE of the blank UF resin, even though the BS of the plywood bonded using it as adhesive was only slightly improved (Figure 5). Moreover, the values of FE also decreased gradually with increasing amount of SMAA from 2.5% to 7.5% although there was a slight increase on going to 10% SMAA addition. It can also be found that when the SMAA was added via method II, the lowest FE of plywood was obtained, which was consistent with the TGA results which indicated that the incorporation of SMAA could improve the crosslinking efficiency of the modified UF resin with a more stable chemical structure. The residual  $-\text{CONH}_2$  groups also contributed to the decreased FE due to their ability to react with formaldehyde, thus acting as a formaldehyde scavenger. However, the best FE results were obtained from the UF-SMAA<sub>0.98</sub>-II resins thus indicating the most effective incorporation approach for SMAA into the resin structures. The veneers bonded by UF-SMAA<sub>0.98</sub>(II-7.5) exhibited the lowest FE value of 1.20 mg/L, with an increased SMAA concentration of 10% not resulting in any further decrease in FE.

### 3.5. Viscosity and storage stability of UF-SMAA resins

The viscosity and storage stability properties of the synthesized UF-SMAA resins were evaluated in this work as listed in Table 4. The viscosity of the UF-SMAA resins was higher than that of the blank UF resin, thus indicating a thickening effect of SMAA on the UF resin adhesive. The viscosity of the synthesized UF resin increased following the sequence: blank UF < UF-SMAA<sub>0.98</sub>(I-7.5) < (II-7.5) < (III-7.5), which was the reverse to the amount of amide groups of SMAA that could participate

in the reaction with resins by using different addition methods. The dissociated SMAA could act as a water soluble protective colloid which could increase viscosity as well as colloidal stability. As a result, the storage period of the UF resins was also enhanced along with increased levels of viscosity.

### 3.6. Effect of MW on UF- SMAA properties

During the synthesis process of the UF-SMAA resins discussed above, all effort was devoted to the SMAA<sub>0.98</sub> system. It was however recognized that the MW of SMAA could also affect the properties of the UF-SMAA resins. Thus, other SMAA modifiers with different MW of 5300, 14200, and 19800, respectively were studied. The results are listed in Table 5, where it can be seen that the viscosity of the synthesized UF-SMAA resins increased with increasing SMAA MW. For the storage time, an optimum result of 35 d was obtained with an SMAA MW of 9800, with further increases in MW resulting in a decrease in storage time. All of these results were consistent with our prediction that a small amount of SMAA could act as a protective colloid. With the synthesized MW below 9800, the SMAA was easy to be accepted as a water soluble polymer working for such purpose performed with the increase of the viscosity with MW and the correspondingly improved storage period for the UF-SMAA resins. The decreased stability of polymer dispersion was also common when the MW of the protective polymer was too large for the associated flocculation. [33] Besides the longer storage period, at a MW of 9800 improvements in BS and FE were also obtained in comparison to the modified UF resins. Specifically the BS of plywood bonded by UF-SMAA resins increased with the MW ( $M_n$ ) of SMAA up to 9800, with further increases in MW resulting in a decline in strength. With FE, the addition of SMAA with increasing MW initially resulted in a reduction in this important property followed by increases in FE with MWs in excess

of 9800. It might be deduced that changes in MW in excess of 9800 would alter the distribution of the grafting and crosslinking points caused by the chemical incorporation of SMAA into the UF resin. As clearly indicated in Table 5, the optimum MW of SMAA for modification of the UF resin was approximately 10000.

#### 4. Conclusions

Alternating copolymers of SMA were synthesized via radical copolymerization and subsequently subjected to aminolysis to produce a water soluble derivate SMAA, using  $(\text{NH}_4)_2\text{CO}_3$  as an ammonia source. The synthesized polymers were used as a new macromolecular modifier for UF resins with amide groups acting as active points for incorporation of SMAA into the crosslinked network of the UF-based adhesive. This was confirmed by  $^{13}\text{C}$ -NMR, FTIR, and TGA characterization. The improved crosslinked network structure was further demonstrated by the improved performance of the modified UF resins synthesized under low molar ratios of F/U in comparison with that of the unmodified UF resin used as a plywood adhesive. The adhesive performance of the liquid resins was affected by the SMAA addition methods, together with the amount and MW of SMAA employed. The modification results indicated that SMAA added during step 2 under acidic conditions could react with the UF resin resulting in the most effective way of conducting the modification process. The optimum result was shown with resin samples using 7.5% of SMAA modifier added by method II with a MW of 9800, the corresponding FE and bonding strength values were 1.20 mg/L and 0.80 MPa, respectively i.e. much improved in comparison to the 2.00 mg/L and 0.54 MPa obtained for the blank UF resin. The available storage period for the modified UF resins was also enhanced from 25 d for the unmodified system to 35 d for the resin synthesised under the optimum modification conditions.



**Acknowledgment**

This work has been financially supported by the National Science and Technology Support Program during the twelfth five-year plan (grant number 2011BAE19B01) and Fundamental Research Funds for the Central University at Beijing University of Chemical Technology.

Accepted manuscript

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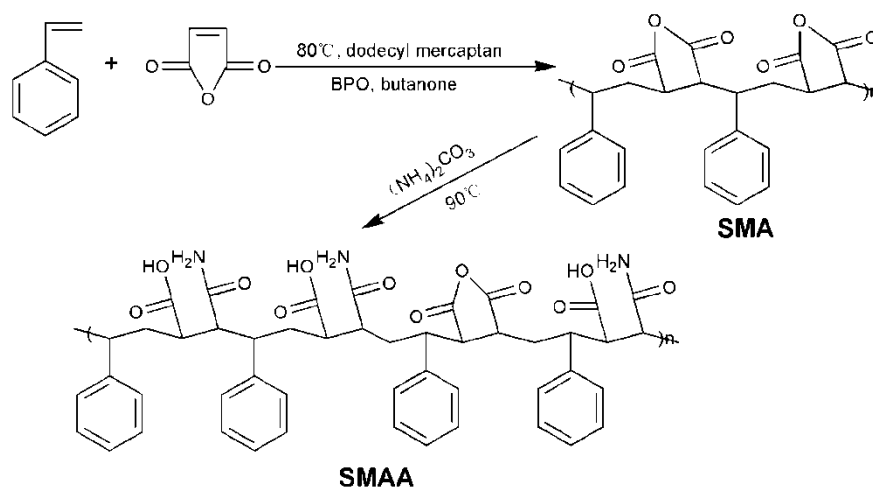
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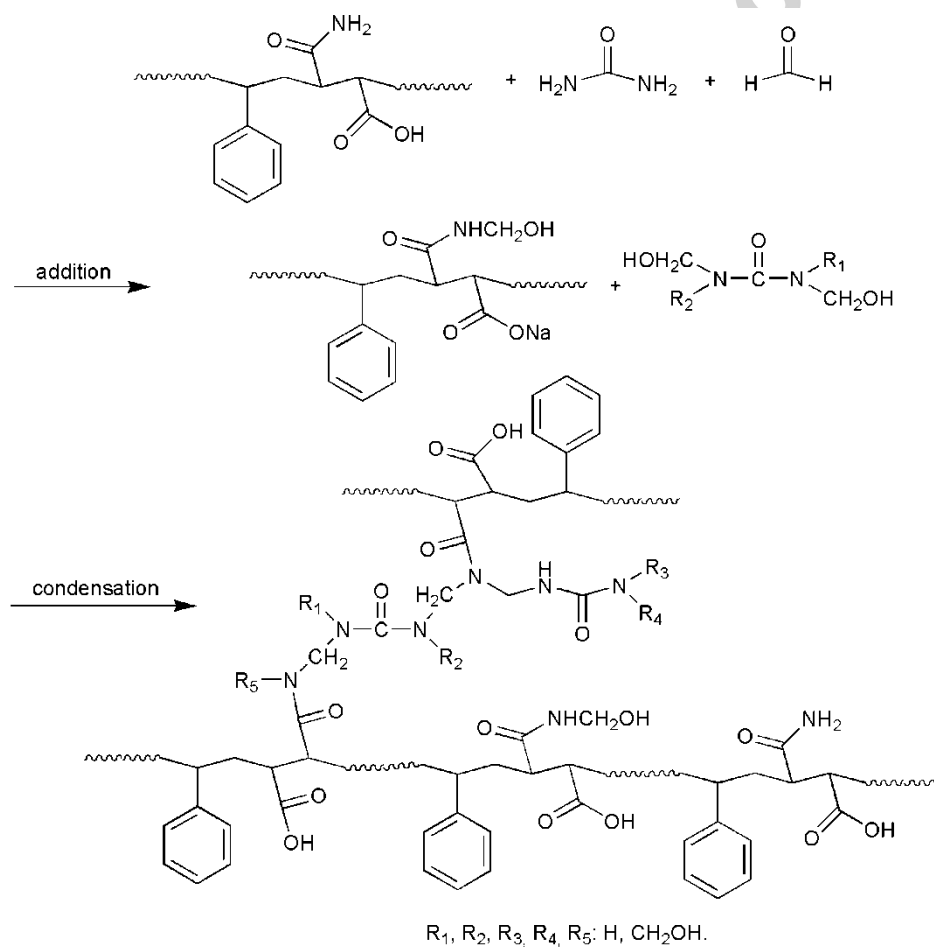
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Captions for schemes, figures and tables.



**Scheme 1.** The copolymerization of St and MA and the aminolysis of the copolymers.



**Scheme 2.** The modification reactions of SMAA on UF resins.

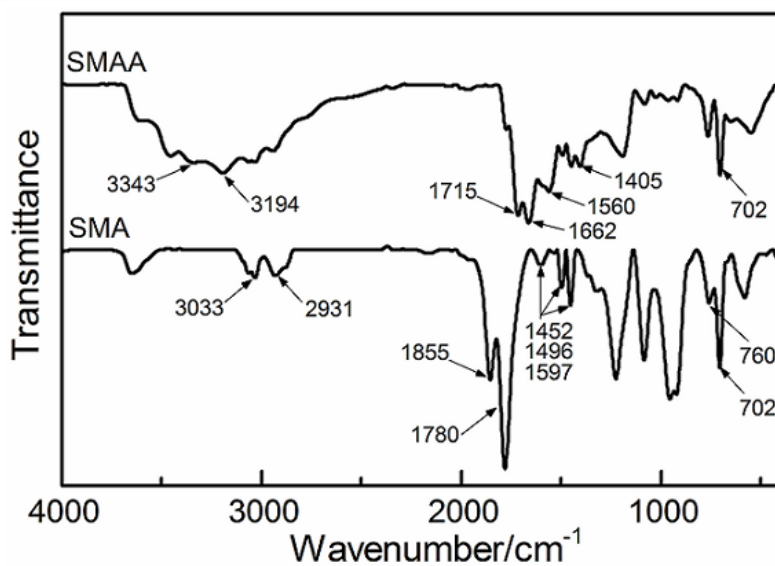


Figure 1. FTIR spectra of SMA<sub>0.98</sub> and SMAA<sub>0.98</sub>.

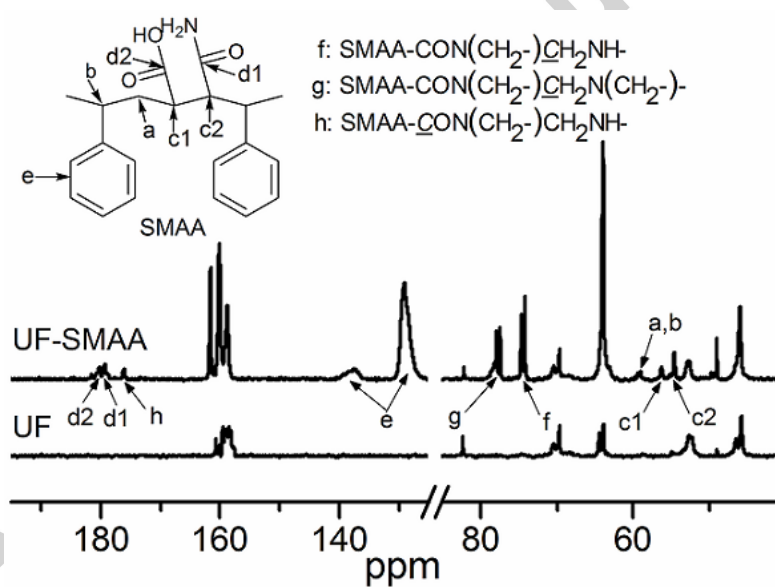
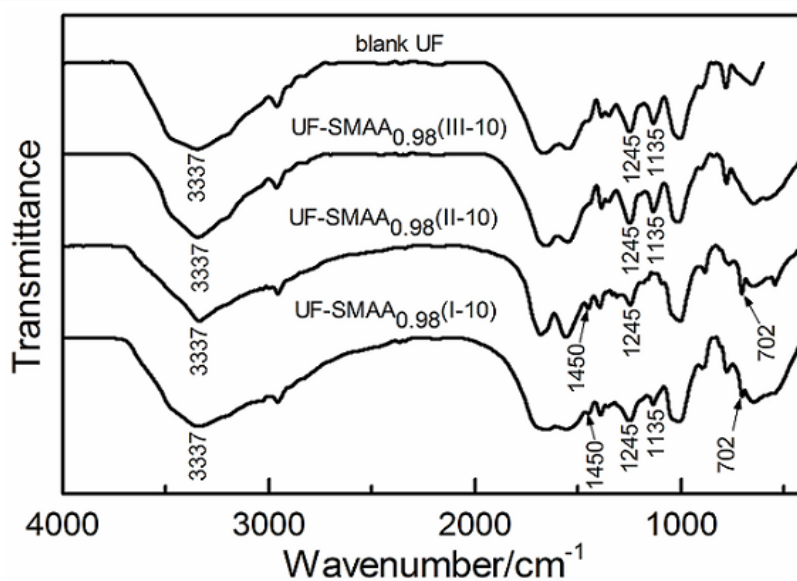
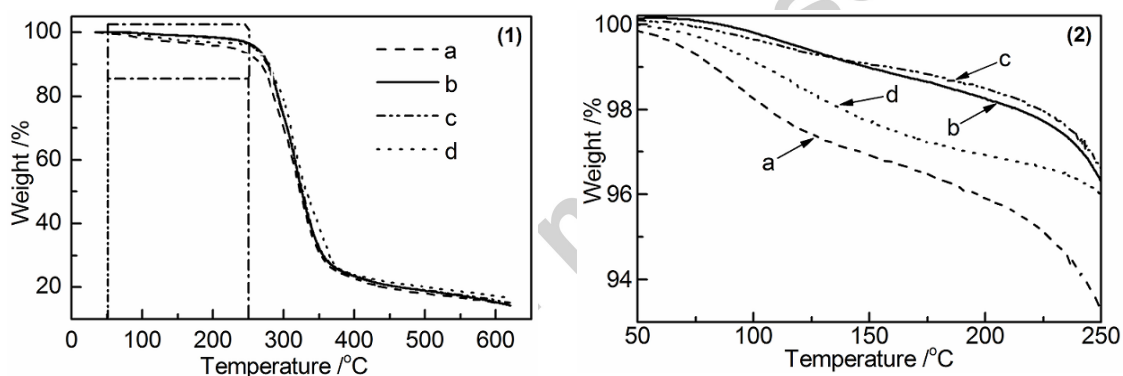


Figure 2. <sup>13</sup>C-NMR spectra of blank UF and UF-SMAA<sub>0.98</sub>(II-10) resins.

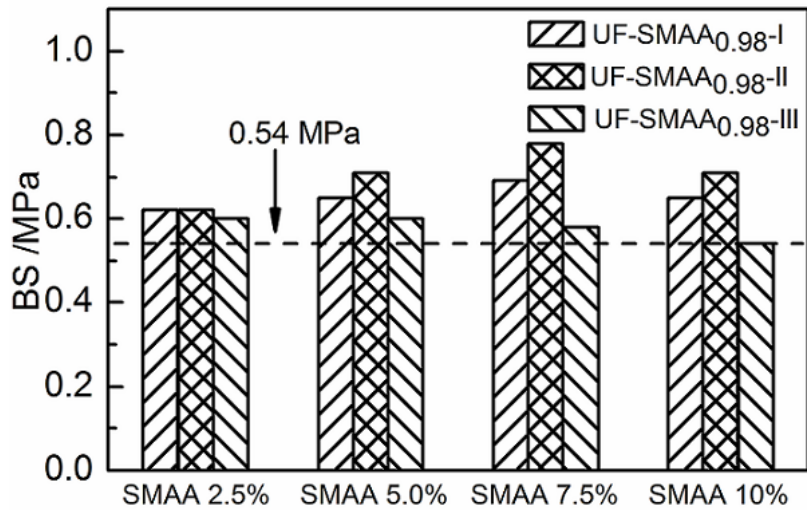


**Figure 3.** FTIR spectra of UF-SMAA<sub>0.98</sub> (I-10), (II-10) (III-10) and blank UF resins.

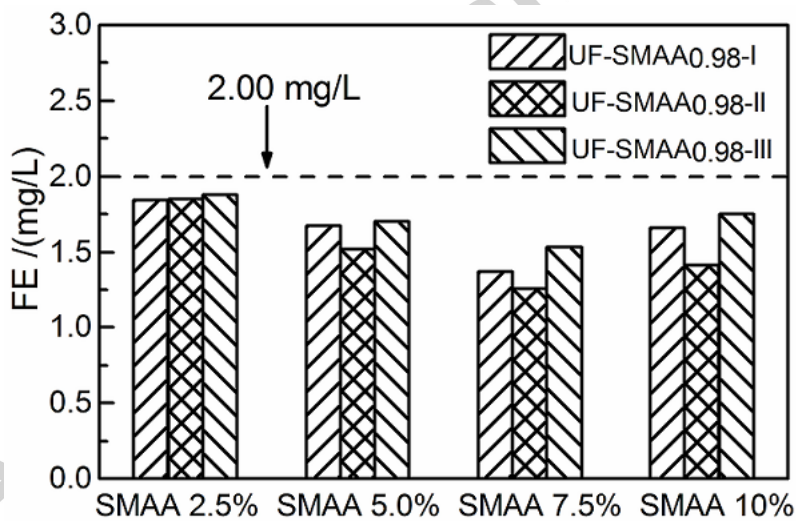


**Figure 4.** (1) TGA curves of cured blank resin and UF-SMAA resins; (2) Zoom-in graph of (1) in the temperature range from 50 to 250°C; a, b, c and d refer to blank UF resin cured, UF-SMAA<sub>0.98</sub>(I-10) cured, UF-SMAA<sub>0.98</sub>(II-10) cured and UF-SMAA<sub>0.98</sub>(III-10) cured, respectively.





**Figure 5.** BS of plywood bonded by UF-SMAA<sub>0.98</sub> resins synthesized via different addition methods (I, II, III) and amounts (2.5, 5.0, 7.5 and 10 in weight percentage).



**Figure 6.** FE of plywood bonded by UF-SMAA<sub>0.98</sub> resins synthesized via different addition methods (I, II, III) and amounts (2.5, 5.0, 7.5 and 10 in weight percentage).

**Table 1.** SMAA addition methods during the UF resin synthesis.

Symbol	Meaning
I	SMAA added at 60°C in Step 1
II	SMAA added together with the second batch of urea in Step 2
III	SMAA added together with the third batch of urea in Step 3

**Table 2.** The synthesis of SMA and SMAA with different MW.

Sample	DM (g)	$M_n$ ( $10^4$ )	PDI	Conv <sub>SMA</sub> (%)	MA (molar percentage, %)	Amine value (mg KOH/g)
SMAA <sub>0.53</sub>	0.97	0.53	1.86	95.1	49.6	128.5
SMAA <sub>0.98</sub>	0.89	0.98	2.05	96.8	49.4	126.8
SMAA <sub>1.42</sub>	0.84	1.42	2.38	96.3	49.4	124.1
SMAA <sub>1.98</sub>	0.81	1.98	2.91	95.6	49.3	120.6

**Table 3.** Assignment of the  $^{13}\text{C}$ -NMR spectra in Figure 2.

Blank UF	UF-SMAA <sub>0.98</sub> (II-10)
45.9 -NH $\underline{\text{C}}\text{H}_2\text{NH}$ -, 49.1 $\underline{\text{C}}\text{H}_3\text{OH}$ , 52.7 -N( $\underline{\text{C}}\text{H}_2$ -)CH $_2\text{NH}$ -	45.7 -NH $\underline{\text{C}}\text{H}_2\text{NH}$ -, 49.1 $\underline{\text{C}}\text{H}_3\text{OH}$ , 52.7 -N( $\underline{\text{C}}\text{H}_2$ -)CH $_2\text{NH}$ -
/	54.7 c2, 56.3 c1, 59.1 a, 59.4 b
63.9 -NH $\underline{\text{C}}\text{H}_2\text{OH}$ , 69.2 -NH $\underline{\text{C}}\text{H}_2\text{OCH}_2\text{NH}$ -,	63.9 -NH $\underline{\text{C}}\text{H}_2\text{OH}$ , 69.3 -NH $\underline{\text{C}}\text{H}_2\text{OCH}_2\text{NH}$ -,
69.8 -NH $\underline{\text{C}}\text{H}_2\text{OCH}_2\text{OH}$	69.8 -NH $\underline{\text{C}}\text{H}_2\text{OCH}_2\text{OH}$
/	74.6 f, 77.9 g
82.3 HO $\underline{\text{C}}\text{H}_2\text{OH}$	82.1 HO $\underline{\text{C}}\text{H}_2\text{OH}$
/	129.1, 137.3 e
158.8, 160.1, 161.5 -(-R1)N $\underline{\text{C}}\text{ON}$ (R2)-, R1,R2: H or CH $_2$ -	158.8, 160.1, 161.5 -(-R1)N $\underline{\text{C}}\text{ON}$ (R2)-, R1,R2: H or CH $_2$ -
/	176.1 h, 179.3 d1, 180.2 d2

**Table 4.** Viscosity and storage stability of UF-SMAA<sub>0.98</sub> resins synthesized by using 7.5% SMAA addition amount.

UF-SMAA <sub>0.98</sub>	Blank UF	(I-7.5)	(II-7.5)	(III-7.5)
Viscosity (mPa·s)	272	293	300	305
Storage Period (Day)	25	31	35	37

**Table 5.** The Properties of UF-SMAA resins by using SMAA as the modifier with different MW.

UF-SMAA-(II-7.5)	Blank UF	SMAA <sub>0.53</sub>	SMAA <sub>0.98</sub>	SMAA <sub>1.42</sub>	SMAA <sub>1.98</sub>
Viscosity (mPa·s)	272	275	298	320	356
Storage period (Day)	25	30	35	29	26
BS (MPa)	0.54	0.73	0.80	0.78	0.74
FE (mg·L <sup>-1</sup> )	2.00	1.54	1.20	1.26	1.41