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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 macro-molecular 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.

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## 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 based on 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] mainly because of 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

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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 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 cross-linking), good thermal characteristics, low viscosity in 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 related to the use of SMA modified UF resin adhesives are 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  $300 \times 300 \times 1.2 \text{ mm}^3$  were employed to evaluate the synthesized adhesives.

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

#### 2.2.1. 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.

#### 2.2.2. Synthesis of SMAA

The synthesized SMA copolymers (50 g) and ammonium carbonate (35 g) were respectively ground into 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  $\text{NH}_3$  gas judged by wet litmus paper. The reaction time for this step was about 5 h.

#### 2.2.3. 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 to 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.

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