

## Synthesis, Structure, and Characterization of Glyoxal-Urea-Formaldehyde Cocondensed Resins

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**ABSTRACT:** To decrease the formaldehyde emission of urea-formaldehyde (UF) bonded products at source, monomethylol urea (MMU) was chosen to react with glyoxal (G), a nonvolatile and nontoxic aldehyde, to prepare a novel glyoxal-urea-formaldehyde (GUF) cocondensed resin. The GUF resins were synthesized with different MMU/G molar ratios, and the basic properties were tested. The GUF resins were characterized by ultraviolet-visible spectroscopy, Fourier transform infrared spectroscopy, carbon-13 nuclear magnetic resonance spectroscopy and matrix assisted laser desorption ionization time of flight mass spectrometry (MALDI-TOF-MS). The results show that the synthesized GUF resins remain stable for at least 10 days at ambient temperature. Conjugated structures, and large amounts of —OH, —NH—, C—N, and C=O groups with different levels of substitution exist in the GUF resin. There are two repeating motives in the MALDI-TOF-MS spectrum of the GUF resin, one of  $175 \pm 1$  Da and a second one of  $161 \pm 1$  Da. Moreover, the peaks due to the dehydration condensation reaction of MMU also appear in the spectra. © 2014 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* **2014**, *131*, 41009.

**KEYWORDS:** adhesives; resins; spectroscopy

Received 3 February 2014; accepted 12 May 2014

DOI: 10.1002/app.41009

### INTRODUCTION

Urea-formaldehyde (UF) resins are currently the major wood adhesive for the manufacture of interior-use wood composite boards such as particleboards, medium-density fibreboards and plywood owing to their low cost, fast curing, and good performance.<sup>1–3</sup> However, they present the major disadvantage of toxic formaldehyde emission from UF-bonded products. Formaldehyde (LD50 rat  $\geq 100$  mg/kg; LD50 mouse  $\geq 42$  mg/kg)<sup>4</sup> is found to cause cancer and to cause irreversible health effect. Due to this drawback, research on decreasing formaldehyde emission from UF resins has attracted increasing worldwide attention. Thus, to decrease F emission, many approaches have been tried during the last decades and much progress has been achieved.<sup>5–8</sup>

The main drawback of UF resin is on one hand, the unreacted F which remains in the final resin. On the other hand, F is emitted because both methylation and condensation reactions in UF resins are reversible. Moreover, the methylene ether linkages (—CH<sub>2</sub>—O—CH<sub>2</sub>—) in the condensed resins are unstable

at high temperature and under acid conditions.<sup>9</sup> Thus, F emission from UF resins can be minimized but will be an inevitable problem. The increasingly strict standard regulations on F emission have induced considerable research. This has focused on decreasing F emission of UF resins but also on developing alternative resins to substitute UF resin such as cornstarch and tannin wood adhesive, lignins and tannins wood adhesive, soy-based adhesive, and so forth.<sup>10–17</sup> One relatively unexplored approach is the use of alternative, nontoxic, nonvolatile aldehydes to produce urea-based resins for wood adhesive. Up to now, the reported alternative aldehydes are dimethoxyethanal,<sup>13,18</sup> propionaldehyde,<sup>19</sup> succinaldehyde,<sup>20</sup> glutaraldehyde,<sup>21,22</sup> and isobutyraldehyde.<sup>23</sup> However, these aldehydes still have problems: either they are toxic to some extent or they are volatile; or they present other problems such as low reactivity, solubility, or high cost. These problems restrict their application. Thus, choosing an alternative aldehyde for these resins is a determining step directly related to their industrial application.

As the simplest aliphatic dicarbonyl compound, glyoxal is nontoxic (LD50 rat  $\geq 2960$  mg/kg; LD50 mouse  $\geq 1280$  mg/kg) and

nonvolatile.<sup>4,24</sup> Because of its advantages such as mature production technology, low cost, and easy biodegradation, G has been widely used as an ideal green environment-friendly agent in the papermaking and textile industries.<sup>25,26</sup> In wood adhesive, it is mainly used to substitute partially or totally F as the crosslinker and hardener of natural wood adhesives such as tannin-based adhesives,<sup>27</sup> lignin-based adhesives,<sup>28</sup> and protein-based adhesives.<sup>29</sup> Nonetheless, the literature about glyoxal-based resins' application in wood adhesive is rather scarce so far. Therefore, the study of the reactivity and chemical structure of glyoxal-urea (UG) resins or glyoxal-methylol urea (G-MMU) resins is of interest to provide a theoretical basis for the synthesis of urea-based resins modified by G for wood adhesives applications.

In our laboratory, much work has been conducted to study environment-friendly aminoresins by choosing G to substitute partially or totally F. This was done to eliminate or markedly decrease formaldehyde (F) emission. Recently, a UG resin has been successfully synthesized under weak acid conditions (pH = 4–5),<sup>30</sup> and could be directly used as wood adhesive for interior decoration and furniture material. In continuation of our previous study, the present work first reports the synthesis of a novel glyoxal-urea-formaldehyde (GUF) cocondensed resin using G reacting with MMU. MMU was mainly chosen for direct reaction with G to prepare a novel GUF co-condensed resin, mainly for the following considerations: (i) to avoid GUF resin's preparation by just empirical trial and error, thus helping to design specific, workable synthetic routes to prepare GUF resins. (ii) The reaction among G, U, F in water solution is rather complicated. MMU was chosen to directly react with G to prepare GUF co-condensed resins to reduce the complexity of the reaction, and then render easier to study the reaction mechanism of GUF resins. (iii) G is less reactive than F in nucleophilic addition reactions.<sup>31,32</sup> As a major UF resin intermediate, especially at F/U molar ratios lower than 1, MMU can further participate in addition and condensation reaction owing to the active amino ( $-\text{NH}_2$ ) and hydroxymethyl ( $-\text{CH}_2\text{OH}$ ) groups in its structure. MMU could be deemed as a potentially suitable reactant to produce aminoplastic resins, thus solving the lower reactivity of G. (iv) The synthesis of GUF resin using G, U, and F as raw materials is still unclear, hence the study of reactivity of G with MMU and the structure of the novel GUF resin is significant in designing a suitable synthesis route and co-condensation method of such resins.

For all these reasons, MMU was chosen to directly react with G to prepare novel co-condensed resins. To gain further insight into the reaction of G with MMU and the structure of GUF resins, modern laboratory analysis techniques were used, including ultraviolet-visible spectroscopy (UV-vis), Fourier transform infrared spectroscopy (FTIR), carbon-13 nuclear magnetic resonance spectroscopy (<sup>13</sup>C NMR), and matrix assisted laser desorption ionization time of flight mass spectrometry (MALDI-TOF-MS). It was thus hoped to accumulate useful experimental data and provide theoretical insight for the synthesis of GUF cocondensed resins for wood adhesives.

## EXPERIMENTAL

### Materials and Instruments

The G ( $\text{C}_2\text{H}_2\text{O}_2$ , 40% water solution) and MMU ( $\text{C}_2\text{H}_6\text{N}_2\text{O}_2$ ) used are analytical grade (AR), obtained from the China

National Pharmaceutical Group Corporation. The cassava starch was purchased from Guangzhou Jinguang Chemical Plant, China. Poplar veneer with moisture content of 8%–10% was obtained from Wen'an veneer factory of Hebei Province, China. The equipment used was: a MALDI-TOF instrument (AXIMA Performance, Kratos, Shimadzu, UK); a Brüker Advance III 400M NMR spectrometer, Buchi, Switzerland; an AVATAR-FTIR-360 infrared spectrometer, Thermo Nicolet; an UV-2401PC ultraviolet-visible spectrophotometer, SHIMADZU, Japan.

### Preparation of GUF Resin and Determination of Its Basic Properties

GUF resins were prepared at different G/MMU molar ratio, namely 0.8:1, 1:1 and 1.2:1. G (40% water solution) was placed in the reactor equipped of reflux condenser. The pH was adjusted to 3–4 using 30% NaOH. MMU was then added, and the mixture heated to 75–80°C for 3 h under continuous mechanical stirring. The pH was then adjusted to pH 7–8 and the resin cooled to room temperature.

The resin nonvolatile solid content was determined by pouring 1 g GUF resin into a disposable aluminum dish and measuring its weight before and after drying at  $120 \pm 1^\circ\text{C}$  for 2 h. The test was done in triplicate. The viscosity of the GUF resin was measured using a NDJ-1 rotary viscometer at 25°C.

The stability of synthesized GUF resins was evaluated mainly by their change in viscosity and appearance over a period of time. The GUF resins were stored at room temperature and their viscosity measured and their appearance assessed every 5 days. If the viscosity and appearance before and after storage had not changed, the resin was considered as stable.

The GUF resins free formaldehyde was measured according to the China National Standard GB/T 14074-2006 on testing methods for wood adhesives and their resins.

### Three-Layer Plywood Preparation

The performance of the GUF resin was tested by preparing laboratory plywood and evaluating its dry shear strength. Duplicate three-layer laboratory plywood panels of  $300 \times 220 \times 4.5 \text{ mm}^3$  were prepared using the G-MMU resins and poplar veneers. To all glue mixes were added 2% by weight  $\text{NH}_4\text{Cl}$  hardener on resin solids,  $\text{NH}_4\text{Cl}$  being predissolved to a 25% water solution, 15% by weight Cassava starch filler was added on total resin weight. The glue spread used was  $250 \text{ g/m}^2$  (single side), hot pressing time was 5 min at  $160^\circ\text{C}$  and 1.5 MPa pressure. After hot pressing, the plywood was stored for 48 h under ambient conditions ( $20^\circ\text{C}$  and 12% relative humidity) before testing. Triplicate plywood panels were made for each adhesive formulation.

### Measurement of Dry Shear Strength

After 48 h conditioning at room temperature, the plywood panels were cut into 12 specimens according to China National Standard GB/T 17657-1999 test methods for evaluating the properties of wood-based panels and surface decorated wood-based panels. All specimens were chosen randomly for testing for dry shear strength by compression loading on a WDS-50KN mechanical testing machine. The values of the dry shear strength were calculated by the following equation and the

**Table I.** Properties of GUF Resin

| MMU/G | Appearance          | Viscosity (mPa s) | Nonvolatile solid content (%) | Dry Shear strength (MPa) | Curing time | Free F (%) | F emission (mg/L) |
|-------|---------------------|-------------------|-------------------------------|--------------------------|-------------|------------|-------------------|
| 0.8:1 | Light yellow liquid | 81                | 58.4                          | 0.96                     |             | 0.04       | 0.86              |
| 1.0:1 | Light yellow liquid | 100               | 60.9                          | 0.91                     |             | 0.05       | 1.09              |
| 1.2:1 | Light yellow liquid | 130               | 64.7                          | 0.73                     |             | 0.04       | 1.23              |

average strength was calculated for 18 test specimens from three panels.

$$\text{Shear strength (MPa)} = \frac{\text{Maximum force (N)}}{\text{Effective gluing area (m}^2\text{)}}$$

**Formaldehyde Emission Measurement.** The plywood formaldehyde emission was determined by the desiccator method in accordance with the procedure described in China National Standard GB/T17657-1999. After 48 h conditioning at room temperature, 50 by 150 mm plywood specimens were prepared. Ten specimens per panel were placed into a 9- to 11-L sealed desiccator at  $20 \pm 2^\circ\text{C}$  for 24 h. The emitted formaldehyde was absorbed on 300 mL of deionized water in a container. The formaldehyde content in the water was measured by visible light spectrophotometry to obtain the value of the formaldehyde emissions. The average value of formaldehyde emissions was calculated from three panels.

#### FTIR and UV-Vis

FTIR spectra were recorded on an AVATAR-FTIR-360 spectrophotometer (Thermo Nicolet Company). For the solid MMU, the KBr disk technique was used. For the liquid GUF resin and G solution, their spectra were recorded with the OMNI Sampler accessory.

A UV-2401PC spectrophotometer (Shimadzu Company, Japan) was used for UV-vis spectral measurements. A series of tested solutions were prepared and added to quartz cuvettes. The absorption spectra of these solutions were determined with distilled water as reference.

#### $^{13}\text{C}$ NMR

The  $^{13}\text{C}$  NMR spectra of the samples were obtained on a Brüker Avance III 400M NMR spectrometer (Buchi, Switzerland) with a relaxation delay of 5 s. G was mixed with the equal amount of deuterium oxide ( $\text{D}_2\text{O}$ ) by adding tetramethylsilane (TMS) as internal standard. MMU and GUF resin were dissolved in dimethyl sulfoxide.

#### MALDI-TOF-MS Analysis

According to the literature,<sup>33</sup> the samples were dissolved in acetone (5 mg/mL). 2,5-Dihydroxy benzoic acid ( $\text{C}_7\text{H}_6\text{O}_4$ ) was used as the matrix. 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  $\mu\text{L}$  of the resulting solution was placed on the MALDI target. After evaporation of the solvent, the MALDI target was introduced into the spectrometer.

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 performed 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 was used by applying delay times of 200–800 ns.

## RESULTS AND DISCUSSION

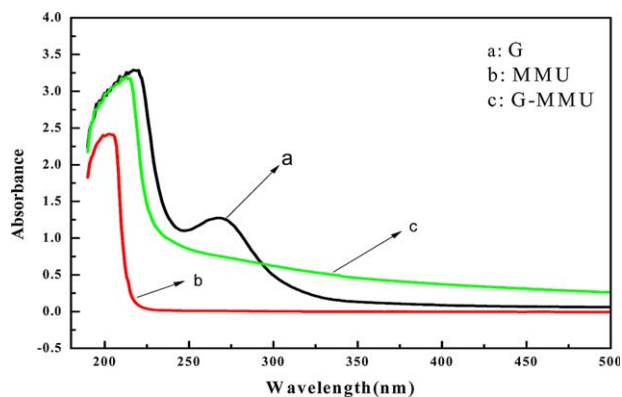
### Properties of the Novel GUF Resins

GUF resins with different MMU/G molar ratio were synthesized under acid condition at pH 3–4 and their properties are summarized in Table I. The synthesized resins can remain stable for at least 10 days or more at ambient temperature. Table I shows that the viscosity and nonvolatile solids content of the GUF resins increase with the MMU/G molar ratio. This is probably because the molar proportion of MMU increases. Thus, either more glyoxal has reacted with MMU or a greater level of self-condensation among MMU molecules has occurred, or both.

From Table I, the free formaldehyde of the GUF resin is so small that it can be said that the resins do not contain free formaldehyde. The dry shear strength of the plywoods bonded with the GUF resins appears clearly to decrease with the MMU/G molar ratio. It is however, always higher than 0.70 MPa, thus meeting the requirements of the type III grade plywood of China national standard GB/T 9846.3–2004. The formaldehyde emission increases with the MMU/G molar ratio, but it is always lower than the 1.5 mg/L required by the  $\text{E}_1$  level in China National Standard GB/T 9846.3–2004. In conclusion, the plywoods bonded with the GUF resins could be directly used as interior decoration and furniture material under dry conditions.

### UV-Vis of the Reaction System

To investigate the reactivity of MMU with G in aqueous solution and the structure of the synthesized GUF resin, the UV-vis absorption spectra of G, MMU and the GUF resins are shown in Figure 1. In Figure 1(a), the absorption spectra shows two peaks at 221 and 266 nm, respectively, this being consistent with our previous reports.<sup>30</sup> The strong peak at 221 nm is attributed to the  $\pi \rightarrow \pi^*$  transition of the two conjugated carbonyl group in the G molecule. The weak peak at 266 nm is caused by the  $n \rightarrow \pi^*$  transition of the carbonyl group.<sup>34</sup> In the spectrum of MMU in aqueous solution shown in Figure 1(b), there is just one absorption peak at 203 nm, which is due to the  $n \rightarrow \sigma^*$  transition in the amino ( $-\text{NH}_2$ ) and hydroxymethyl ( $-\text{CH}_2\text{OH}$ ) groups in the MMU molecule. In order to get more information on the reaction system, the absorption curve of GUF resin is shown in Figure 1(c). Noticeably, there is a new peak at 213 nm caused by the  $\pi \rightarrow \pi^*$  transition, which implies that MMU completely reacts with G in the system to



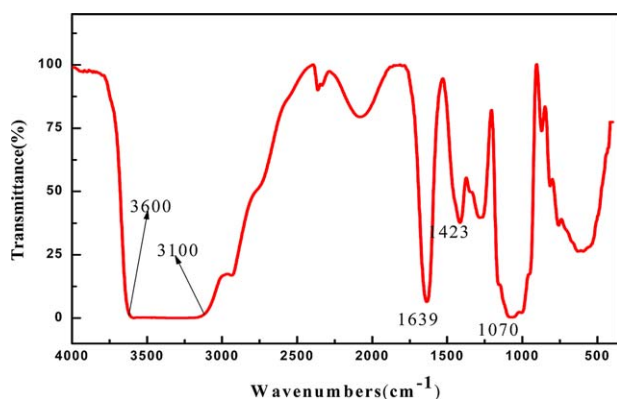
**Figure 1.** UV-vis adsorption spectra of G, MMU, and GUF resin. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

produce a GUF resin with a conjugation structure under the synthesis conditions used.

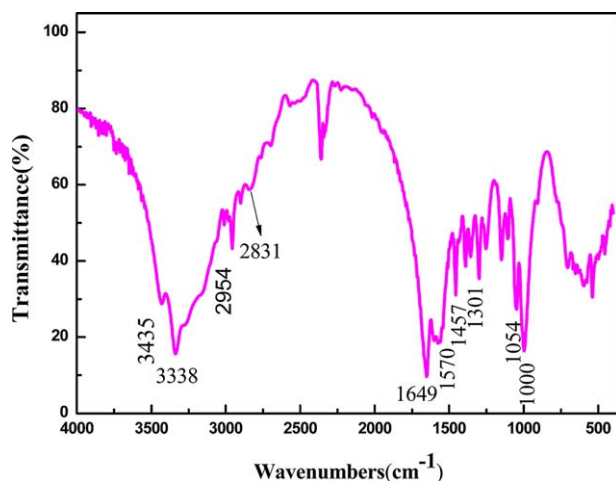
### FTIR of G, MMU, and GUF Resin

FTIR is widely used to characterize the structures of UF wood adhesive resins and other macromolecule compounds.<sup>35–40</sup> To obtain the information about the reaction of G with MMU and the chemical structure of the GUF resin, the FTIR spectra of G, MMU, and GUF resin were done and are shown in Figures 2–4. Their corresponding main assignments are listed in Table II. The strong and wide absorption band at 3100–3600  $\text{cm}^{-1}$  in Figure 2 is attributed to the O–H stretching vibration in the hydroxyl groups. This indicates that G exists mainly in the hydrated form in aqueous solution. This result is in line with our previous reports about the form G is present in aqueous solution.<sup>30</sup> The band at 1639  $\text{cm}^{-1}$  is related to the C=O stretching vibration. Owing to the influence of hydrogen bonding, the adsorption peak of C=O shifts to lower wavenumber.<sup>41</sup> The peaks at 1423 and 1070  $\text{cm}^{-1}$  are attributed, respectively, to the saturated C–H deformation and C–O stretching vibrations.

The weak absorption peak at 3435  $\text{cm}^{-1}$  in Figure 3 is attributed to the hydroxyl groups O–H stretching vibration. The sharp, stronger absorption peak at 3338  $\text{cm}^{-1}$  belongs to the amino groups N–H stretching vibration. This shows clearly



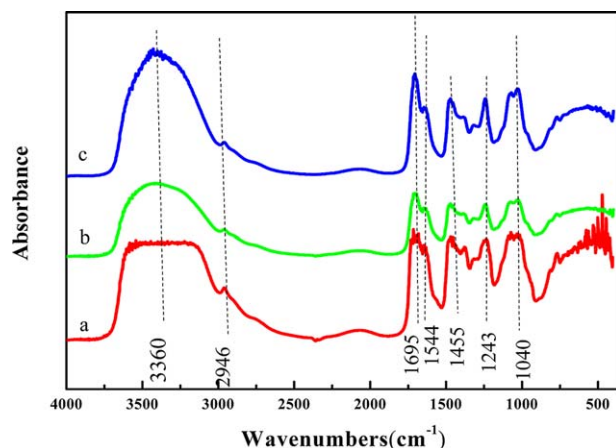
**Figure 2.** FTIR of glyoxal (G). [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]



**Figure 3.** FTIR of MMU. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

that the content of O–H groups is lower than that of N–H groups as shown in its molecular structure. Owing to the  $p$ - $\pi$  conjugation effect between  $-\text{NH}_2$  and C=O in MMU, the C=O peak shifts to a lower wavelength of 1649  $\text{cm}^{-1}$ .

The infrared spectra in Figure 4 of the GUF resins at different molar ratios exhibit similar characteristics in shape and absorption position of the main absorption peaks. This indicates that the MMU/G molar ratio has very little effect on the main functional groups of the GUF resins. Comparing Figures 2, 3 with Figure 4, the strong and wide absorption band near 3360  $\text{cm}^{-1}$  is attributed to the superposition of the stretching vibration of the amino groups N–H and of the stretching vibration of the hydroxyl groups O–H. In the GUF resin, the C=O peak is observed at 1695  $\text{cm}^{-1}$  due to the structural difference of the GUF resin and MMU. Similarly, other absorption bands such as the N–H deformation vibration and the C–O stretching vibration also occur at the corresponding shifts. It is worth noting that the disappearance of the absorption band at 1301  $\text{cm}^{-1}$  and the appearance of the absorption band at 1243  $\text{cm}^{-1}$  in



**Figure 4.** FTIR of the GUF resins with different molar ratios. (a) MMU/G = 0.8; (b) MMU/G = 1.0; (c): MMU/G = 1.2. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]



**Table II.** FTIR Assignments of G, MMU and GUF Resin

| Species   | Absorption band (cm <sup>-1</sup> ) | Chemical structure assignments                          |
|-----------|-------------------------------------|---|
| G         | 3100–3600                           | O–H stretching vibration                                |
|           | 1639                                | C=O stretching vibration                                |
|           | 1423                                | Saturated C–H deformation vibration                     |
|           | 1070                                | C–O stretching vibration                                |
| MMU       | 3435                                | O–H stretching vibration                                |
|           | 3338                                | N–H stretching vibration                                |
|           | 2954                                | C–H asymmetric stretching vibration in –CH <sub>2</sub> |
|           | 2831                                | C–H symmetric stretching vibration of secondary amide   |
|           | 1649                                | C=O stretching vibration                                |
|           | 1570                                | N–H deformation vibration of secondary amide            |
|           | 1457                                | C–H deformation vibration of –CH <sub>2</sub> –         |
|           | 1301                                | Composite absorption of C–N and N–H in secondary amide  |
|           | 1054                                | C–N stretching vibration                                |
|           | 1000                                | C–O stretching vibration of methylol groups             |
| GUF resin | 3360                                | stretching vibration of O–H and N–H                     |
|           | 2946                                | C–H asymmetric stretching vibration in –CH <sub>2</sub> |
|           | 1695                                | C=O stretching vibration                                |
|           | 1544                                | N–H deformation vibration of secondary amide            |
|           | 1455                                | C–H deformation vibration of –CH <sub>2</sub> –         |
|           | 1243                                | C–O–C stretching vibration in ester                     |
| 1040      | C–N stretching vibration            |   |

GUF resins indicates the existence of C–O–C bonds in the GUF resin.<sup>37,40</sup> Besides these, there are absorption bands at 1243 and 1040 cm<sup>-1</sup>, which can be ascribed, respectively, to the C–N and C–O stretching vibrations.

### <sup>13</sup>C NMR of G, MMU, and GUF Resin

The structure and property of the resins vary as the synthesis conditions change. Investigation of the structures formed under different conditions can provide the theoretical basis for the control and optimization of the resins structure. Nuclear magnetic resonance spectroscopy (NMR) is one of the most effective method to study resins structure. In particular, <sup>13</sup>C NMR has been successfully used to characterize the structures of wood adhesive resins such as UF resin,<sup>42–45</sup> PF resin,<sup>46</sup> PUF resin,<sup>47–49</sup> and MUF resin.<sup>50</sup>

To study the structural change of the GUF resin before and after the reaction, the <sup>13</sup>C NMR spectra of G, MMU, and the GUF resin were examined (Figures 5–7). Shifts were assigned on the

basis of the <sup>13</sup>C NMR analysis of amino resins, especially of UF resins,<sup>42–45</sup> as well as fully considering the chemical shifts of <sup>13</sup>C NMR spectra of G, MMU, and GUF resin.

The technology of distortionless enhancement by polarization transfer (DEPT) was used in this study. In the DEPT 90 spectrum, only the –CH– group appears as a positive peak and other groups do not appear. In the DEPT 135 spectrum, the –CH– and –CH<sub>3</sub> groups appear as positive peaks, while the –CH<sub>2</sub>– group appears as a negative peak and other groups do not appear at all.

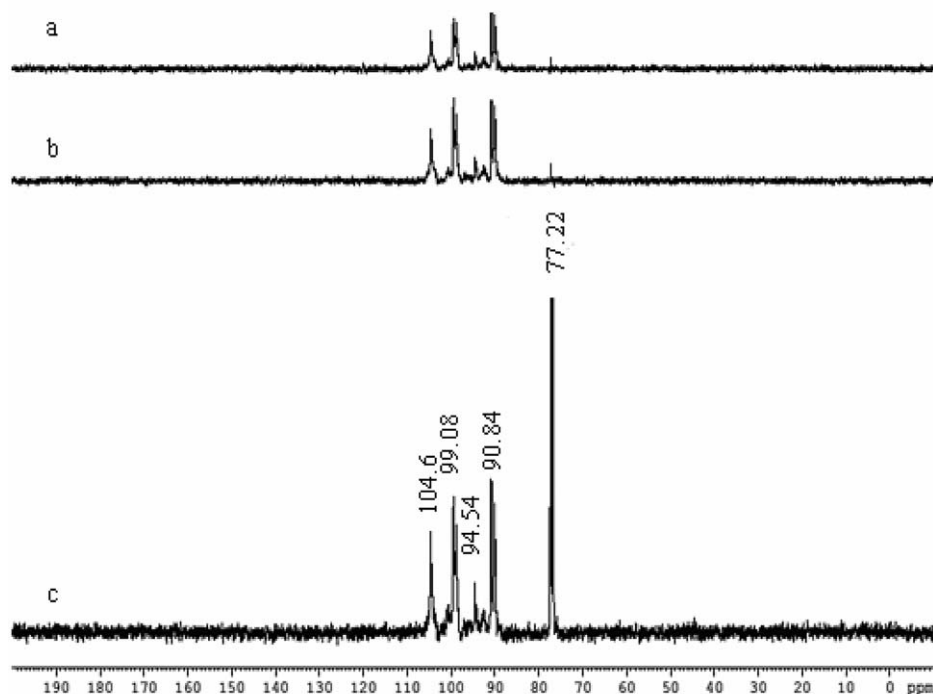
From the <sup>13</sup>C NMR spectrum of G (Figure 5), it appears that there are no bands in the low magnetic field areas higher than 110 ppm and in the high magnetic field areas lower than 80 ppm. Comparing the DEPT90 (a) and DEPT135 (b) spectra with the proton broadband decoupling spectrum (c), it can be seen that the peaks in Figure 5(c) appear also in the same position as in the DEPT90 (a) and DEPT135 (b) spectra. This could be ascribed to the signals of –CH in the structures of the protonated and hydrated glyoxal, and there is no negative peak in DEPT135 spectrum (b). This confirms that there is no –CH<sub>2</sub>– group in the structures of the protonated and hydrated glyoxal, these results being relevant for further studies of the existing form of glyoxal in aqueous solution.

As shown in Figure 6, there are two main groups of peaks due to the MMU molecular structure containing only two carbons under different chemical environments. The peaks at 157.94 ppm and 159.74 ppm are definitely the signal of the –C=O, and the peak at 63.63 ppm could be ascribed to the signals of the –CH<sub>2</sub>.

Comparing the <sup>13</sup>C NMR spectrum of the GUF resin (Figure 7) with those of G and MMU, there are many new absorption peaks not appearing in Figures 5 and 6. This indicates that the reaction of MMU with G is rather complex. Based on the absorption position of the peaks and analyzing the factors influencing the chemical shifts of <sup>13</sup>C, the <sup>13</sup>C NMR main assignments of GUF resin are listed in Table III. The peaks in 45–101 ppm regions could be due to the signals of the sp<sup>3</sup> hybridized carbon with different substitution degree in the GUF resin. Furthermore, their <sup>13</sup>C signals move to low magnetic field area because of the influence of the oxygen atom's (O) electronegativity.<sup>41</sup> Clearly, the <sup>13</sup>C absorption in the –C=O group appear at 160.56 and 161.32 ppm, respectively. Compared with the <sup>13</sup>C NMR spectrum of MMU (Fig. 6), the signals are slightly moved to the lower magnetic field area owing to the change of its chemical environment through reaction. This indicates that no free MMU is present in the reaction system. This means that the reaction between MMU and G or the dehydration condensation reaction of MMU change the <sup>13</sup>C chemical shifts in the –C=O group by sensibly changing their chemical environment.

### MALDI-ToF-MS of the GUF Resins with Different MMU/G Molar Ratios

In recent years, MALDI-TOF-MS has been widely used to analyze the structure of biological macromolecules and polymers owing to its advantages such as rapidity, accuracy, high sensitivity, high resolution, and wide mass range measurement

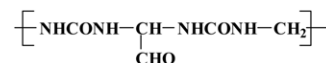


**Figure 5.**  $^{13}\text{C}$ NMR spectrum of G: (a) DEPT90; (b) DEPT135; (c) proton broadband decoupling spectrum.

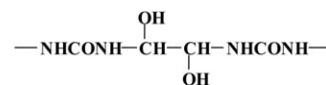
capability. In comparison with the commonly used method of gel permeation chromatography, MALDI-TOF-MS can provide such information as polymers/oligomers molecular weight and their mass distribution range, copolymer composition, and to deduce the most probable reaction mechanism from the species obtained.<sup>51–53</sup>

To further study the molecular weight and oligomers distribution of the GUF resin and to deduce the reaction mechanism of MMU with G, the MALDI-TOF-MS spectra of the GUF resins with MMU/G molar ratio of 1.0 is shown in Figure 8.

There are two repeating motives in the spectrum, one of  $175 \pm 1$  Da and a second one of  $161 \pm 1$  Da, and the representative of the two repeating units are listed as follows:

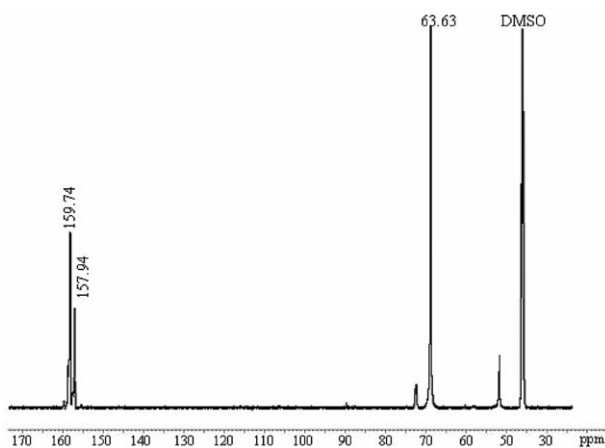


or

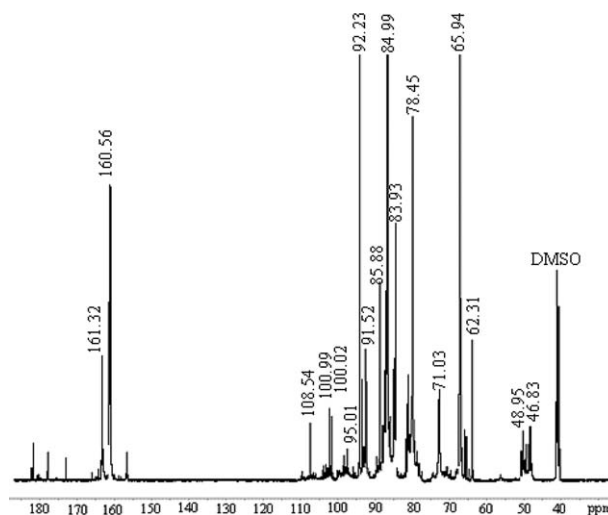


at 174–176 Da

And the second one at 160–162 Da is one of the two which follows



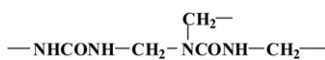
**Figure 6.**  $^{13}\text{C}$ NMR spectrum of MMU.



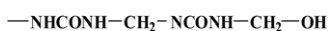
**Figure 7.**  $^{13}\text{C}$ NMR spectrum of the glyoxal-monomethylol urea (GUF) resin with MMU/G molar ratio of 1.0.

**Table III.**  $^{13}\text{C}$  NMR Assignments of GUF Resin

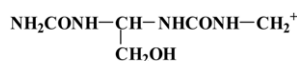
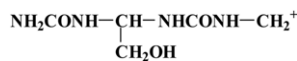
| Chemical shifts (ppm) | Group assignment* |
|-----------------------|-------------------|
| 46.95–48.83           |                   |
| 62.14–65.63           |                   |
| 70.96                 |                   |
| 78.36                 |                   |
| 83.06–86.99           |                   |
| 90.97–92.08           |                   |
| 95.77                 |                   |
| 100.03–100.81         |                   |
| 160.04–160.89         |                   |
| 46.95–48.83           |                   |



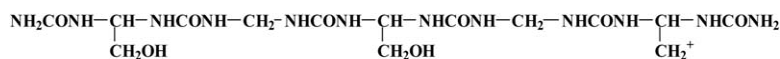
or



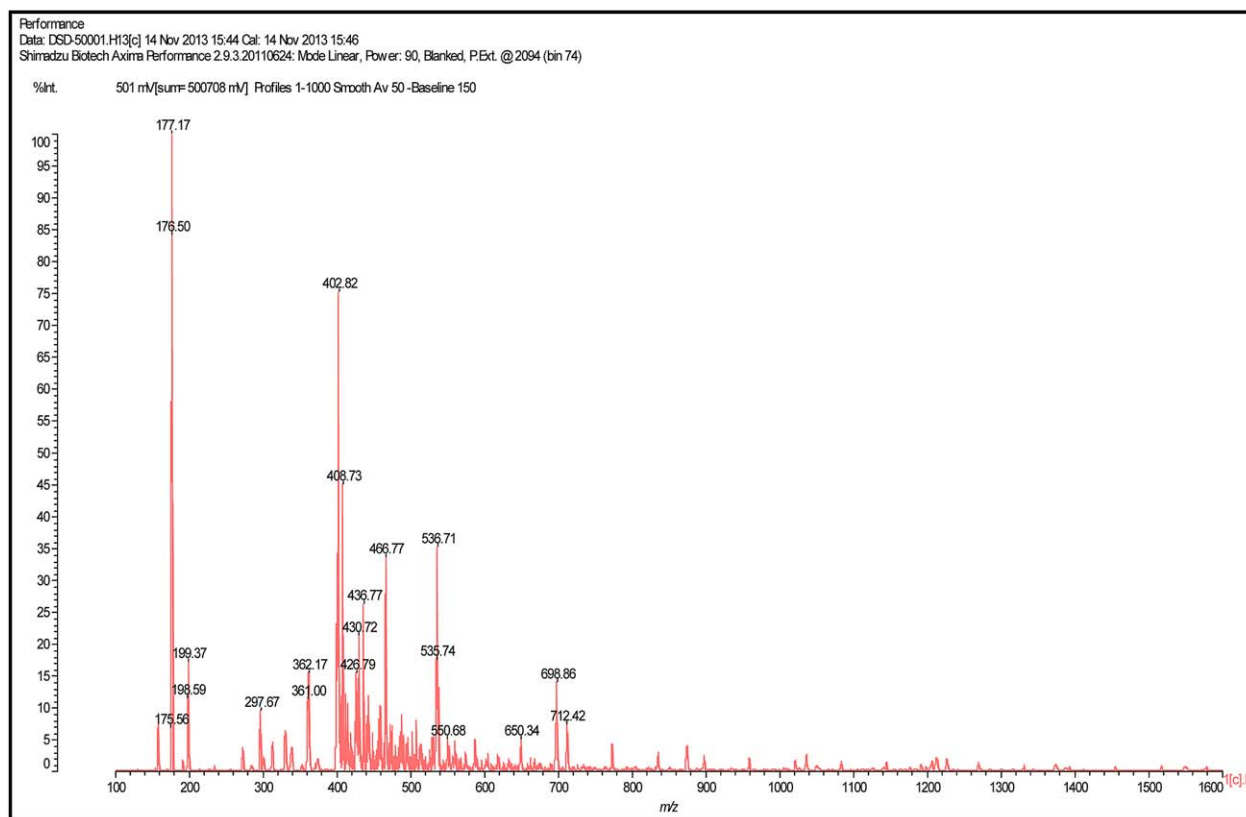
175 Da

175 + 23 Da (Na<sup>+</sup>) = 198 DaFor all the higher oligomer the 23 Da of the Na<sup>+</sup> is taken into account.

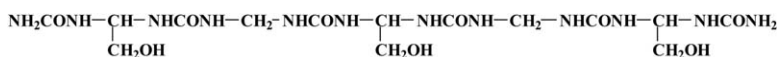
520 Da:



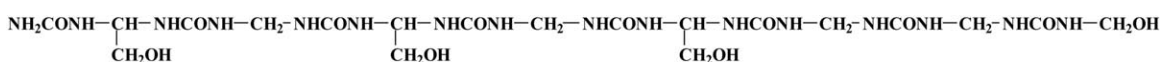
534–536 Da:



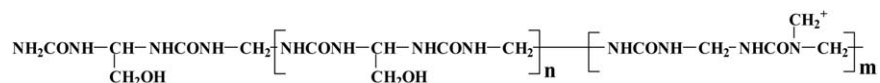
**Figure 8.** MALDI-TOF spectra of GUF resin with a MMU/G molar ratio of 1.0. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]



696–698 Da:



For all the other peaks the general formula is



Thus for

696 Da,  $n = 2$  and  $m = 1$

874 Da,  $n = 3$  and  $m = 1$

1036 Da,  $n = 3$  and  $m = 2$

Etc.

It must be pointed out that rather than to have a series of block polymers alternating in which the two main motives above alternates it is also possible that two series of polymers occur, separate and independent from each other, one based on the 176 Da repeating motive only and one based on the 162 Da motive only.

In this scenario then we would have a repeating motive of 176 Da  $\times 2 = 352$  Da and one with a repeating motive of 162 Da  $\times 2 = 324$  Da.

In this case the main pattern would be



Where What We Have is Then

536 Da,  $n = 2$  minus one —OH

874 Da,  $n = 3$  minus one —OH

1212 Da,  $n = 4$  minus one —OH

Etc.

This implies one series of urea-glyoxal polymers only, parallel to one series of UF polymers only. Considering the differences in



reactivity of formaldehyde and glyoxal, and considering the manner in which the resins have been made, the first explanation is far more probable, thus a single series of mixed urea-glyoxal-formaldehyde block copolymers.

It is worth noticing that there are some peaks of 402, 467, 530, 551, 604 Da in MALDI-TOF spectra, which are due to the self-condensation reaction among MMU molecules. Their assignments are listed as follows:

402 Da:  $\text{NH}_2\text{CONH}-\text{CH}_2-[-\text{NHCONH}-\text{CH}_2-]_4-\text{OH}$

474 Da:  $\text{NH}_2\text{CONH}-\text{CH}_2-[-\text{NHCONH}-\text{CH}_2-]_5-\text{OH}$

530 Da:  $\text{NH}_2\text{CONH}-\text{CH}_2-[\text{NHCONH}-\text{CH}_2-]_5-\text{NHCONH}_2$

551 Da:  $\text{NH}_2\text{CONH}-\text{CH}_2-[-\text{NHCONH}-\text{CH}_2-]_4-\text{NHCONH}-\text{CH}-\text{CH}-\text{NHCONH}_2$

604 (602) Da:  $\text{NH}_2\text{CONH}-\text{CH}_2-[-\text{NHCONH}-\text{CH}_2-]_6-\text{NHCONH}_2$

Etc.

## CONCLUSIONS

- Using MMU and G as raw materials, novel GUF resins with different MMU/G molar ratios could be synthesized successfully under acid conditions. These resins remain stable for at least 10 days or more at ambient temperature. Their viscosity and nonvolatile solids content increased with the MMU/G molar ratio.
- Comparing the UV-vis spectrum of the GUF resin with those of G and MMU, there is just a new peak at 213 nm caused by the  $\pi \rightarrow \pi^*$  transition, which implies that MMU completely reacts with G to produce GUF resin with a conjugated structure.
- FTIR shows that there are mainly such functional groups as  $-\text{OH}$ ,  $-\text{NH}-$ ,  $\text{C}-\text{N}$ ,  $\text{C}=\text{O}$ , and so forth in the GUF resins. Furthermore, the absorption positions and strengths of the  $-\text{OH}$  groups in FTIR spectrum indicate that the GUF resins contain many hydroxyl groups.
- Comparing the  $^{13}\text{C}$  NMR spectra of the GUF resins, there are many new peaks not appearing in the  $^{13}\text{C}$  NMR spectra of G and MMU, indicating that the reaction of MMU with G is very complex. The peaks in the 45–101 ppm range could be due to the signals of the  $\text{sp}^3$  hybridized carbon with different substitution degree in the GUF resin. The signals of the  $-\text{C}=\text{O}$  group slightly moved to the lower magnetic field area.
- There are two repeating motives in the MALDI-TOF-MS spectrum of GUF resin, one of  $175 \pm 1$  Da and a second one of  $161 \pm 1$  Da. Moreover, the peaks due to the dehydration condensation reaction of MMU also appear in the spectra.

## ACKNOWLEDGMENTS

This work was performed in the frame of research projects supported by the National Natural Science Foundation of China (No. 31260160), State Forestry Administration 948 Project (2014-4-40), and Key program of Science Foundation of Educational Department of Yunnan Province (No. 2013Z087). The second author

thanks the research funds of King Abdulaziz University (KAU), under grant No. (6-130-1434-HiCi).

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