

Investigation of Novel Thermosetting Copolymer-Based Monomethylolurea–Glyoxal for Wood Manufacturing

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Cite This: *ACS Omega* 2022, 7, 35055–35062



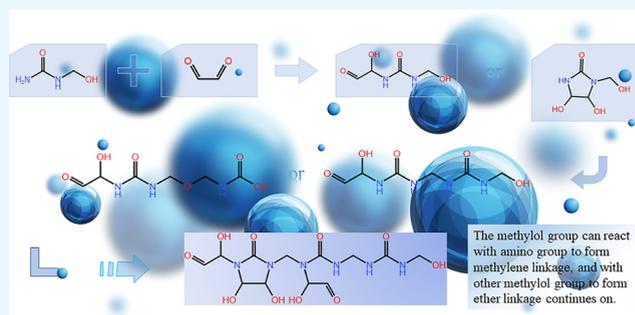
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ABSTRACT: The purpose of this investigation was to design novel alternating copolymers (monomethylolurea–glyoxal, MMU–G) as adhesives for wood manufacturing. MMU–G were synthesized under acid (pH = 5) conditions. After the 120-day storage period, the MMU–G resins were used for plywood production, which exhibited a wet shear strength of about 2.15 MPa, similar to the freshly prepared MMU–G resin. The excellent water resistance and long storage stability showed that MMU–G has particular characteristics and properties all of their own, which, in certain respects, are very different from those of urea-formaldehyde (UF) adhesives. The X-ray diffraction results showed that only a few crystallinities occurred in MMU–G resins, indicating the presence of long side chains in the MMU–G polymer structures, leading to better adhesion strength than UF resins. The structure characteristics of the MMU–G resin were studied by Fourier transform infrared and electrospray ionization mass spectrometry, and a possible molecular structure has been inferred, which is consistent with spectroscopic results.



1. INTRODUCTION

Wood adhesives are a crucial component in the wood products industry because adhesives make the manufacture of wood composite panels from residues and waste wood possible.

Due to their low cost, low cure temperature, resistance to microorganisms, acceptable hardness, excellent thermal properties, and colorlessness of the cured resin, urea-formaldehyde (UF) resins are widely used in the wood industry. However, the major disadvantage of UF adhesives is their bond deterioration caused by water and moisture and relatively low storage stability.^{1–3} These drawbacks limit the application of UF and have attracted more attention to their overcoming.

Some modified UF resins have been studied, such as melamine-modified urea formaldehyde, tannin-modified urea formaldehyde, glyoxal-modified UF, and phenol-UF.^{4–9}

Glyoxal is considered a nontoxic nonvolatile reactive aldehyde and can partly or fully replace formaldehyde as a cross-linker for tannin-, lignin-based adhesives, which are blended with isocyanates [(polymeric 4, 4'-diphenyl methane diisocyanate as adhesives for wood panels.^{10,11} The synthesis of the condensed glyoxal-UF resins with low formaldehyde emission¹² and zero formaldehyde emission urea–glyoxal resin was reported.¹³ To explore the reaction mechanism between glyoxal and the UF resin, monomethylolurea–glyoxal (MMU–G) resins in these abovementioned studies were prepared according to the traditional synthetic route of the UF resin. However, in all

of these studies, only the dry shear strengths of plywood made with the modified UF resin by glyoxal were given and their wet shear strengths were not reported. Therefore, the water resistance of the modified resin adhesive cannot be judged from these reports.

In this work, MMU–G was mixed to develop a novel MMU–G adhesive. The aim of this work was to optimize the synthesis of the resin and to develop a modified UF resin with satisfactory performance, especially water resistance.

2. MATERIALS AND METHODS

2.1. Materials. Rotary-cut veneer sheets of eucalyptus wood were conditioned at 5–7% moisture and had a thickness of 1.6 mm without visible defects.

As a control, a commercial UF resin was from a wood-based panel Co., Ltd. in Kunming with a final F/U molar ratio of 1.05 and 53.8% solid content. The viscosity of the resin was 89 mPa·s, and the condensation time was 56 s. The resin was stored at pH 8.2.

Received: June 23, 2022

Accepted: September 5, 2022

Published: September 21, 2022



Industrial grade glyoxal solution 40 wt %, urea 99 wt %, formaldehyde solution 37 wt %, and monomethylolurea 95 wt % purchased from Tianjin Damao Chemical Reagent Factory (Tianjin, China) were used for the synthesis of resin adhesives. Aqueous solutions of both formic acid (20 wt %) and sodium hydroxide (20 wt %) were used to adjust the pH. An aqueous solution (20 wt %) of ammonium chloride (NH_4Cl) was used as a hardener.

2.2. Preparation of MMU–G Resins and Their Properties. The glyoxal solution was placed in the reactor, and then the pH value was adjusted to 4–4.5 with a formic acid solution. The mixture temperature was then heated up to 45 °C. Afterward, a certain amount of monomethylolurea was added. Then the temperature was heated to 90 °C under reflux for 1 h. A certain amount of urea was added to the mixing system. Then, the MMU–G resin was cooled to room temperature. The final molar ratio MMU–G was 1:1.

The resin solids content of the final resin MMU–G was 61.2%. The viscosity of the resin was 109 mPa·s, measured using the NDJ-SS digital viscometer provided by Shanghai Jitai Electronic Technology Co., Ltd., Shanghai, China. The gel time of the resin with 3% NH_4Cl (20 wt %) as hardener was 282 s, measured in boiling water.

2.3. Water Contact Angle Tests. The measurement is performed by applying a water droplet on the surface of the cured adhesive to determine the water resistance of the cured adhesives.

The same amount of the liquid resin UF and MMU–G was uniformly coated on the eucalyptus veneers surface and then placed in an oven at 60 °C for 15 min to form a precured resin film. Then, it was pressed under a pressure of 1.6 Mpa for 1 min at 180 °C to form a cured resin film.

The surface contact angles of the cured resin films were measured with an optical contact angle goniometer (JC2000D3R, China). The measurements were performed via the sessile droplet method under standard parameters such as room temperature and drop volume (3 μL). The contact angle (θ) was determined by measuring the tangent angle to the surface of the liquid droplet at 5 s.

All the tested angles were averaged over three individual measurements at different areas of the cured resin film.

2.4. Preparation of Plywood and Its Test. 3-ply plywood was made from eucalyptus veneers with adhesive layers of 120 g/ m^2 per adhesive layer. The plywood was prepared under a pressure of 1.6 Mpa for 4 min (1 min/mm) at 140, 160, and 180 °C.

The bonding strength of plywood panels was determined according to China National Standard GB/T 17657-2013 for Type II plywood (≥ 0.70 Mpa) by a WDS-50KN mechanical testing machine. For the wet shear strength test, plywood specimens were immersed in 63 ± 2 °C water for 3 h prior to the test, and the reported data was then the mean of 6 specimens.

2.5. Fourier Transform Infrared Spectroscopy. A drop of the liquid resins sample was spread on the surface of a polished KBr plate, and then another KBr plate was placed on top of the first plate to get them together. The resulting pallet was then subjected to a Varian 1000 [Fourier Transform Infrared (FT-IR)] spectrometer with a DTGS KBr detector and XT-KBr beam splitter. Single beam spectra of the samples were obtained after averaging 32 scans in the wavenumber range of 4000 to 500 cm^{-1} with a resolution of 4 cm^{-1} and 34 scans. The functional groups of the standard UF resin and MMU–G resins were tested and compared.

2.6. Electrospray Ionization Mass Spectrometry. The samples were dissolved in deionized water (10 $\mu\text{L}/\text{mL}$). Mass spectrometric determinations were carried out on a quadrupole time-of-flight (Q-TOF) high-resolution mass spectrometer (Q-TOF liquid chromatography/mass spectrometry (LC/MS) 6540 series, Agilent Technologies, Santa Clara, CA) coupled with electrospray ionization (ESI). The data were acquired using Mass Hunter Workstation software, and the detection was performed in a positive ESI mode. The MS parameters were optimized as follows: the fragment or voltage was set at 135 V; the capillary was set at 3500 V; the skimmer was set at 65 V; and nitrogen was used as the drying (300 °C, 8 L min^{-1}) and nebulizing (30 psi) gas.

2.8. X-ray Diffraction Analysis. X-ray diffraction analysis (D8 ADVANCE, Bruker, Karlsruhe, Germany) of cured UF and MMU–G resins was investigated. The powdered cured resins were analyzed at ambient temperature using a CuK α -1 X-ray source with a wavelength (λ) of 1.5406 Å. The angle of incidence changed from 10 to 70° by steps of 0.02°/min.

The X-ray diffraction (XRD) diffractogram was analyzed by MDI jade5.0 software. The crystallinity of cured the UF resin was obtained.

2.9. Dynamic Thermomechanical Analysis. Dynamic thermomechanical analysis (DMA) of MMU–G and UF resins was performed by using the NETZSCH DMA-242 equipment. The samples were prepared by applying each adhesive between two poplar wood plies, with dimensions of 50 mm \times 10 mm \times 3 mm. These poplar-resin-poplar sandwiches were tested in nonisothermal three-point bending mode at between 30, and 250 °C with a heating rate of 10 °C/min, frequency of 10 Hz, strain amplitude of 60 μm , and dynamic force of 1.5 N. The tested results were analyzed by NETZSCH Proteus software.

3. RESULTS AND DISCUSSION

3.1. Water Contact Angle Analysis. Contact angle measurement is a qualitative way to characterize the solid–



Figure 1. Water contact angles of UF and MMU–G.

liquid interaction. If the water contact angle of the cured resin is larger, the cured resin glue will have better hydrophobicity and better water resistance, which will also improve the wet shear strength of the plywood.

The contact angle test results of the cured UF and MMU–G resin film were presented in Figure 1. The water contact angles of the UF resin and MMU–G resin were, respectively, 75 and 102°.

It is generally believed that if the contact angle is greater than 90°, the surface is hydrophobic, and if the contact angle is less than 90°, the surface is considered hydrophilic. It means that the hardened MMU–G network surface was sufficiently hydrophobic to prevent the moisture-induced break of methylene ether bridges ($-\text{CH}_2-\text{O}-\text{CH}_2-$) in the MMU–G network. The cured MMU–G resin showed better water resistance than UF resin.

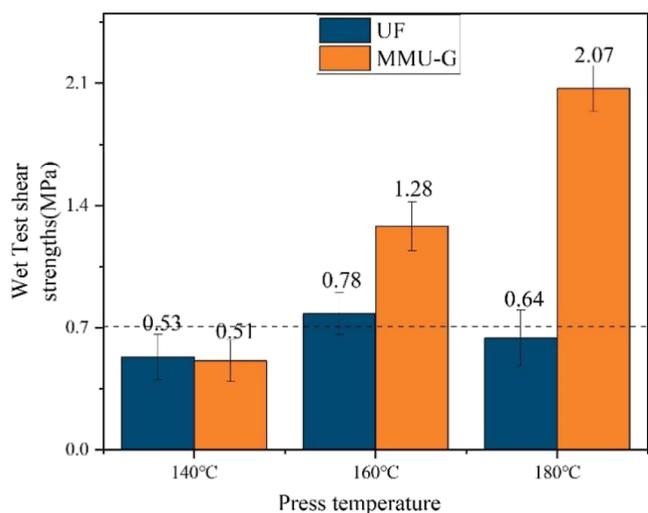


Figure 2. Wet tensile shear strength of MMU-G resin-based plywood with specifically 140, 160, and 180 °C press temperature.

3.2. Bonding Performance of Resins. Figure 2 shows the 63 ± 2 °C wet shear strength of MMU-G resin-based plywood pressed at press temperatures of 140, 160, and 180 °C.

It is well-known that the unmodified UF resin showed poor water resistance. As seen in Figure 2, almost all of the wet shear strength of the UF resin was not satisfied the requirement of GB/T 17657-2013 (0.7 MPa) pressed at 140, 160, and 180 °C. However, for MMU-G resin, although the wet shear strength of plywood pressed at 140 °C was not acceptable, the strengths pressed at 160 and 180 °C were good enough to meet the requirement of the relative standard.

The plywood prepared at press temperature 180 °C exhibited the highest wet shear strength. It was 390 and 162% higher than those at press temperatures of 140 and 160 °C, respectively. The wet shear strength analysis showed that the plywood prepared by the MMU-G resin had the optimal wet tensile shear strength, indicating that the hydrophobic property of cured MMU-G was better than the UF resin.

3.3. Shelf Life of Resins. The shelf life refers to the period in which adhesive systems retain an ideal bond and is essential to the user. The wet tensile shear strength of MMU-G resin-based

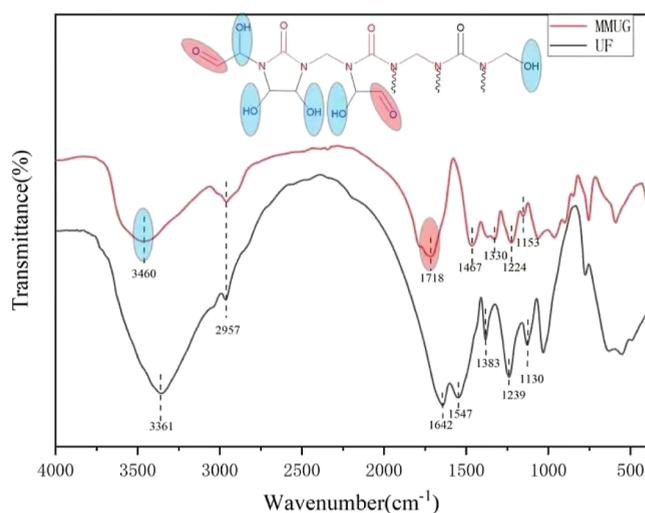


Figure 4. FTIR spectra of liquid UF resins and liquid MMU-G resins.

Table 1. Assignment of FT-IR Signals of UF and MMU-G

absorption (cm ⁻¹)	UF (cm ⁻¹)	MMU-G (cm ⁻¹)	functional group
3500–3100	3361	3460	O–H stretching and free NH groups
3000–2930	2957	2957	C–H stretching in –CH ₂ and –CH ₃
1738–1709		1718	C=O stretch in nonconjugate carbonyl groups
1680–1630	1642		C=O stretching (amid I)
1600–1550	1550		C=O stretching (amid II)
1470–1370	1383	1467	C–H stretching in –CH ₂ – and –CH ₃
1230–1210	1239	1224	–OH deformation of CH ₂ OH
1150–1130	1130	1153	asymmetric stretching of –N–CH ₂ –N group

plywood and the MMU-G resin viscosity change was tested in order to reflect the MMU-G shelf life (see Figure 3).

Based on the test results, including MMU-G viscosity and wet tensile shear strength of MMU-G resin-based plywood, it was observed that the MMU-G resin has over a 120-day shelf-

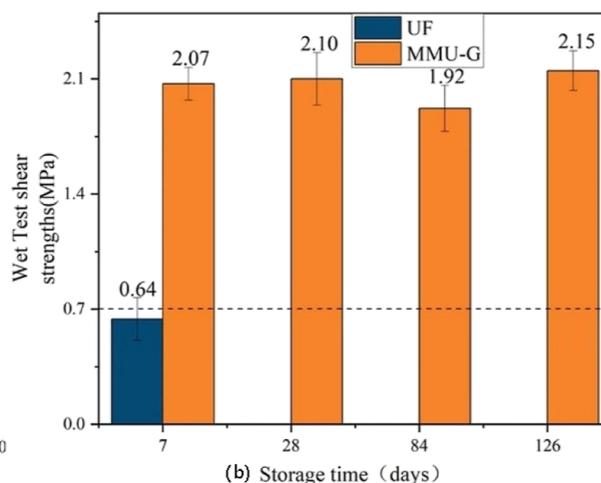
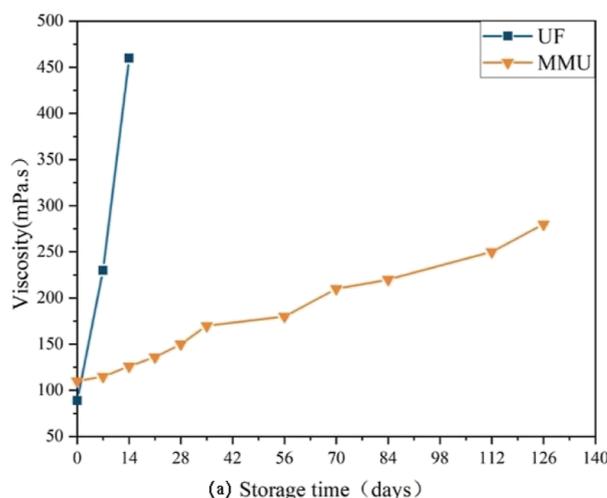


Figure 3. (a) Viscosity and (b) wet tensile shear strength of resin-based plywood with 180 °C press temperature as a function of storage time at room temperature for the UF and MMU-G resins.

Scheme 1. Hypothetical Reaction between MMU–Glyoxal

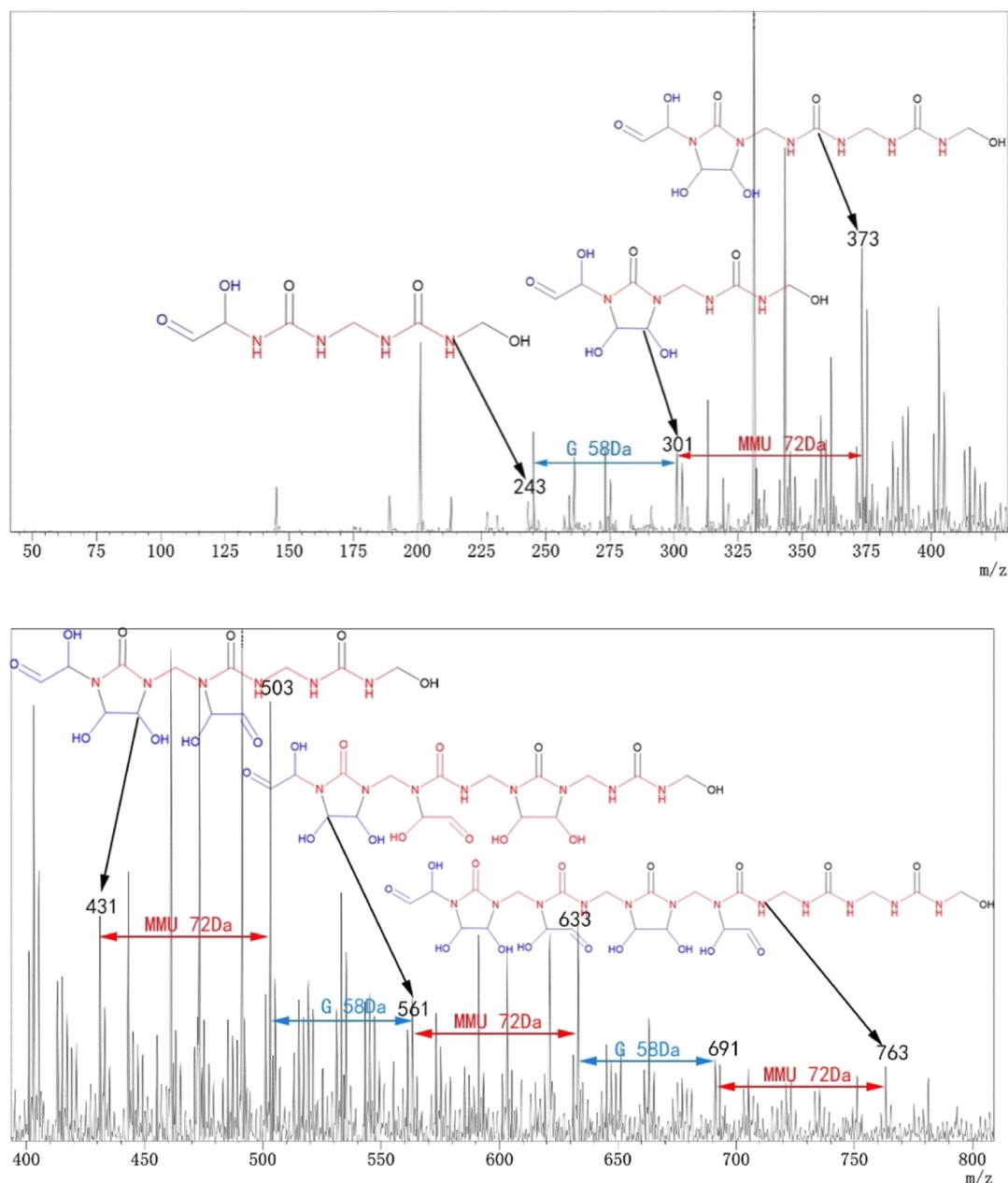
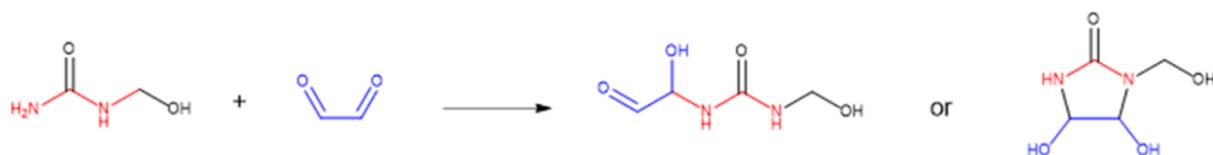


Figure 5. ESI mass spectrum of MMU–G resin.

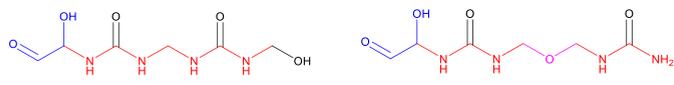
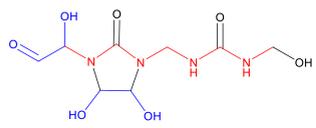
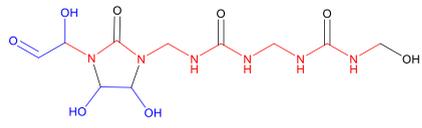
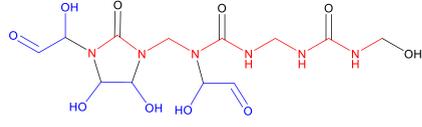
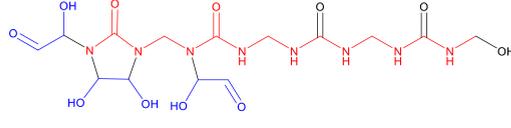
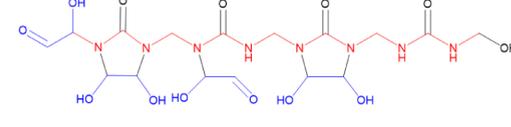
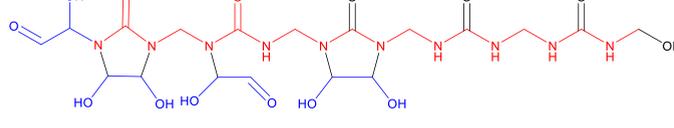
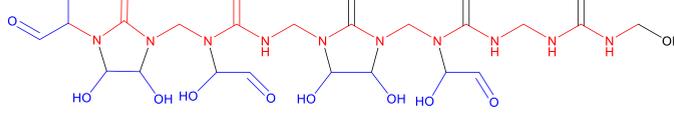
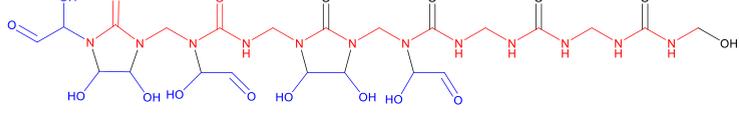
life at room temperature. It indicated that the storage stability of the MMU–G resin is better than that of UF resin.

The press temperature of 160°–180 °C is quite high relative to today's industrial practice, but it is believed that with the study of MMUG, a suitable catalyst can be found to reduce the curing temperature.

3.4. IR Results. The IR spectra of MMU–G and UF are shown in Figure 4, and their assignments can be seen in Table 1. There are some differences in absorbance bands relating to

specific chemical groups. In Figure 4, it can be noted that a broad absorption band was observed in the range of 3700–3000 cm^{-1} , which can be assigned to the stretching vibration of N–H and O–H bonds in the amides and hydroxyl groups. The shift of N–H and O–H bonds in MMU–G is 59 cm^{-1} compared with UF. It is reasonable to conclude that the concentration of the –OH group representing the main chain in the MMU–G is higher than in the UF.

Table 2. Oligomers Identified by the ESI Mass Spectrum of the MMU–G Resin

$M \pm H^+$	Da	possible structure + Na^+
243		 MMUGMMU
301		 MMUG MMUG
373		 MMUG MMUG MMU
431		 MMUG MMUG MMUG
503		 MMUG MMUG MMUGMMU
561		 MMUG MMUG MMUG MMUG
633		 MMUG MMUG MMUG MMUGMMU
691		 MMUG MMUG MMUG MMUG MMUG
763		 MMUG MMUG MMUG MMUG MMUG MMU

Scheme 2. Hypothetical Reaction Mechanism in the Formation of the MMU-G

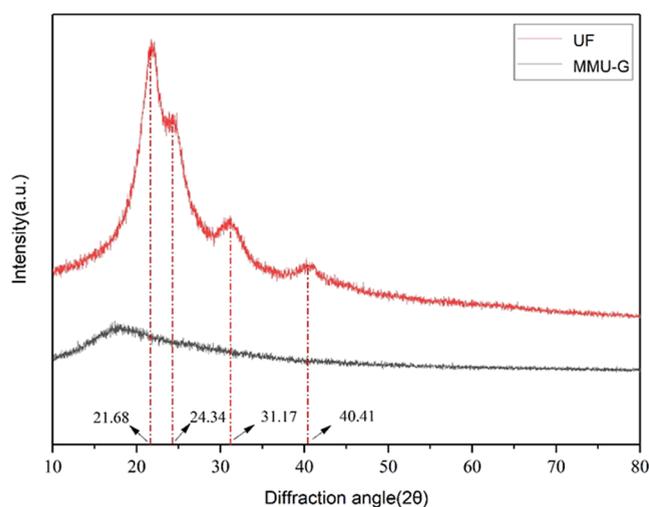
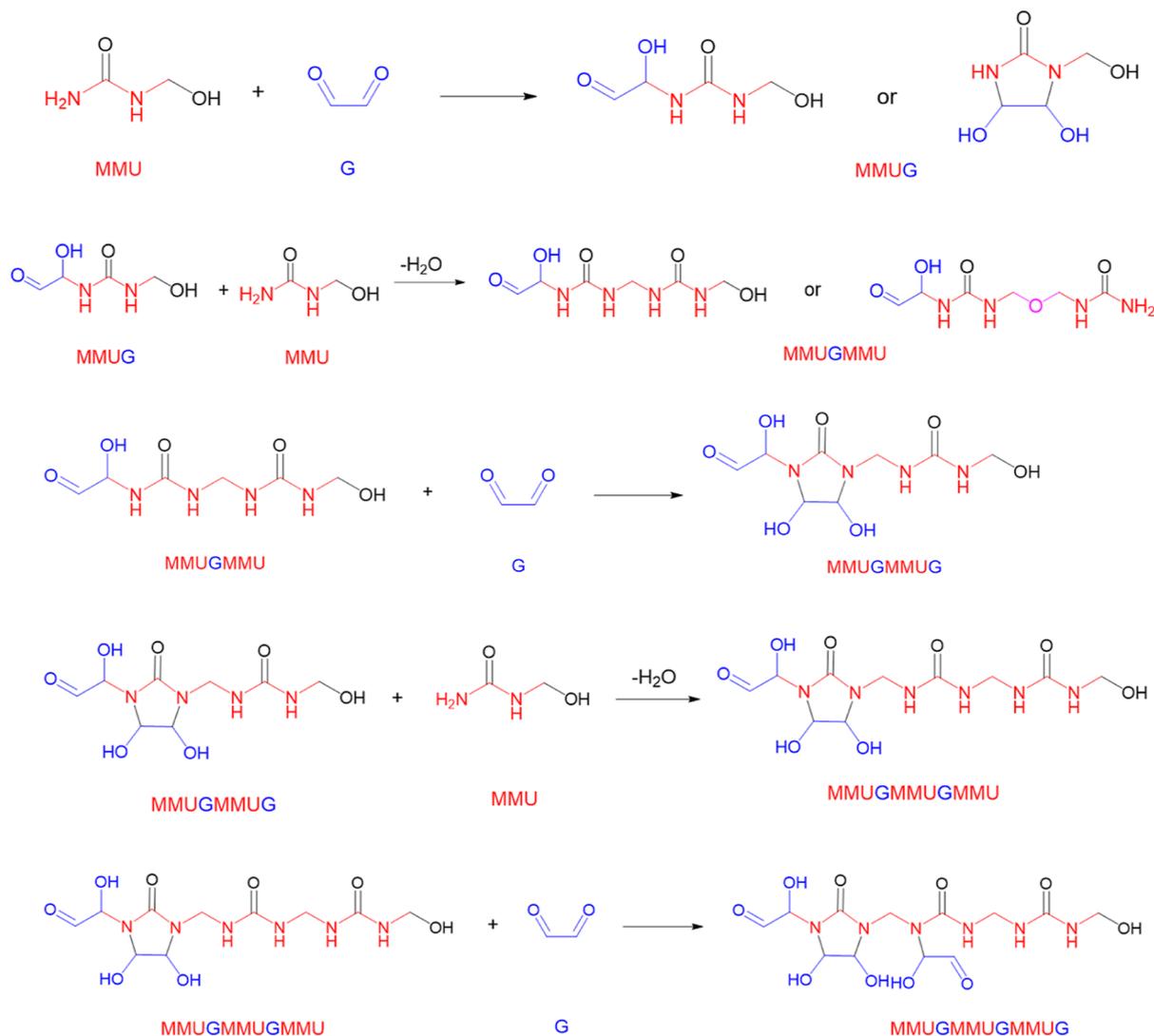


Figure 6. X-ray diffractograms of UF resins and MMU-G resins.

The MMU-G showed similar absorption bands with UF, except for one signal at 1718 cm^{-1} assigned to the C=O stretch in unconjugated carbonyl groups. Due to the reaction between

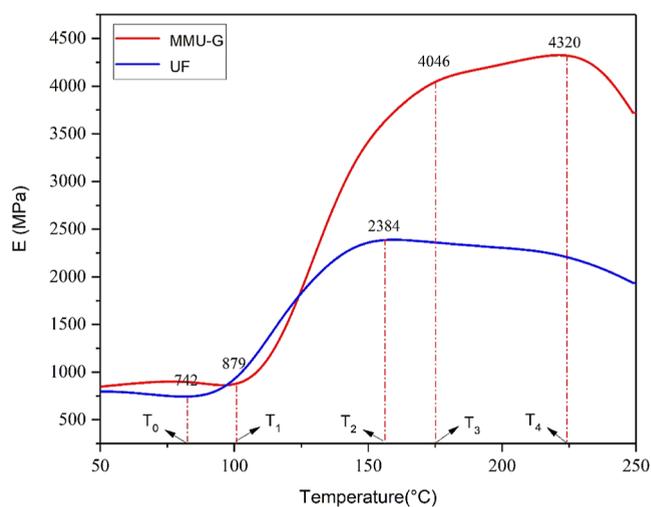


Figure 7. Storage modulus E of UF resins and MMU-G resins as a function of temperature.

glyoxal and the -NH₂ group of MMU, the carbonyl group was successfully introduced into the MMU-G molecular structure.

1° and 2°-amides in UF also exhibit 2 strong bending absorptions in the range of 1500 to 1700 cm⁻¹, but the corresponding band from MMU–G is not seen.

The two possible reasons are:

- (1) The cyclization reaction between glyoxal and the amides group of MMU might take place, as illustrated in [Scheme 1](#).^{15–17}
- (2) The absorption peak of C=O is too strong to cover up most of the region of 1500–1700 cm⁻¹.

3.5. ESI-Mass Spectrometry Results. [Figure 5](#) is the ESI-Mass Spectrometry (MS) spectrum of MMU–G resin. Mass spectrometry can provide structure or even molecular mass information on molecules after molecular ionization and ion separation. Combining the results of MS and FT-IR spectra of MMU–G resin, the possible molecular structure of the MMU–G resin could be inferred. The formation of several possible intermediates can be deduced, as shown in [Table 2](#).

Combining the FTIR results, the possible reaction path between glyoxal and MMU is given in [Scheme 2](#).

[Scheme 2](#) shows the reaction of MMU with glyoxal to form a methylene linkage or an ether linkage. The methylol group can react with the amino group to form a methylene linkage and with other methylol groups to form an ether linkage that is continuous.

The introduction of glyoxal into the reaction system markedly increases the number of aldehyde and hydroxyl groups in the polymer network, indicating that it is easy to form highly branched molecules or a cross-linked structure during the curing process.

3.6. XRD Characterization. [Figure 6](#) shows the results of X-ray diffractograms of cured UF resins and cured MMU–G resins. As it is shown, the UF resins also possess crystalline regions. The peaks of the UF crystalline region are located at 21.68, 24.34, 31.17, and 40.41°. In the case of cured MMU–G, the sharpness and intensity of the crystalline reflections were not observed, indicating almost amorphous structures of the MMU–G. These results indicate that the MMU–G resin contains more branches; however, in a low F/U mole ratio, UF resins predominate with linear chains.

This can be explained because the introduction of glyoxal into the reaction system markedly increases the chance of branch formation, thereby hindering the growth of crystalline domains.

In a previous study, it was considered that crystallines do harm bond strength because the greater crystallinity of cured UF resins resulted in a less amount of tridimensional network structure in the bond line.¹⁴

This could be one of the reasons for the better adhesive strength of MMU–G resins compared with UF.

3.7. DMA Results. [Figure 7](#) shows the storage modulus E of UF resins and MMU–G resins. The modulus of the MMU–G resins shows significantly higher values, 4046 MPa at 175 °C. This is consistent with previous results from [Figure 2](#) ([Section 3.2](#)).

The value of E increased gradually in oven temperature up to 104 °C (T₁), which was regarded as the gelation point of MMU–G. Then, it increased dramatically to 175 °C (T₃). 175 °C was considered as the stop point, where the cure rate slows down because the curing reaction has stopped.

4. CONCLUSIONS

In this work, MMU–G was used as material for the preparation of a novel MMU–G wood adhesive. Some conclusions can be drawn:

- (1) It has now been found that the products MMU–G of the reaction of glyoxal and MMU are excellent crosslinking resins for plywood, with stability over 120 days of storage. Better stability against hydrolyzing and more extended storage stability are the main advantages of the MMU–G resin in comparison to UF.
- (2) MS and FT-IR spectra demonstrated that the MMU–G resin is rich in carbon and hydroxyl groups relative to UF resins. The existence of these active groups is beneficial to the polymerization of MMU–G molecules during curing and the formation of covalent bonds between MMU–G and wood. These results may be beneficial to improving the water resistance and strength properties of the cured MMU–G resin.
- (3) The results of XRD of cured MMU–G resins showed that the MMU–G resin has a highly branched structure instead of a linear structure compared with the UF resin.

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Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

This work was supported by the National Natural Science Foundation of China (32160346 and 31870546), the Yunnan Provincial Natural Science Foundation (2019FA012), and the 111 project (D21027).

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