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Preparation and characterization of a melamine-urea-glyoxal resin and its modified soybean adhesive

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A R T I C L E I N F O

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A B S T R A C T

Although polyamidoamine-epichlorohydrin (PAE)-modified soybean meal (SM) adhesives exhibit desired bond properties and technological applicability, their commercial application is still limited by the high cost of PAE resin. In this study, a formaldehyde-free crosslinking agent, melamine-urea-glyoxal (MUG) resin for SM adhesive, was developed based on investigations of the effects of melamine content and storage time on the structure and properties of MUG resin and MUG-modified SM adhesive. The test results confirmed that melamine could effectively copolymerize with glyoxal and urea to form an aldehyde-terminated MUG resin that was crosslinkable to soybean protein. The melamine content in MUG had important effects on the bond properties of the SM adhesive, attributed to the incorporation of aromatic triazine rings into the aliphatic urea-glyoxal chains and the greater reactivity and functionality of melamine than urea. However, the addition of melamine at more than 10% led to a shorter storage time of MUG resin and worse bond properties of MUG-modified SM adhesive. Owing to the further reactions of residual aldehyde and amino groups of MUG resin, the water resistance of the MUG-modified SM adhesive decreased with the storage time of the MUG resin. The allowable storage of the optimal MUG-10 resin was 3 weeks to ensure an acceptable bonding quality. Due to the much lower cost of MUG resin than PAE resin, it is beneficial for the wide commercial applications of formaldehyde-free SM adhesives in wood composites.

1. Introduction

Formaldehyde-based adhesives, including those based upon urea-formaldehyde (UF), phenol-formaldehyde (PF) and melamine-formaldehyde (MF) resins, are extensively used in wood-based composites owing to their low cost, water solubility, high reactivity and allowable adhesion properties [1–3]. However, the utilization of these formaldehyde-based adhesives not only consumes non-renewable petrochemical resources but also leads to hazardous volatile compound emission issues that are detrimental to the human body and negatively impact the living environment [4,5]. Consequently, the development and application of biomass-derived adhesives without formaldehyde addition is an available approach to eliminate formaldehyde contamination of wood-based panels and to replace petroleum-based synthetic adhesives [6].

Soybean meal (SM), an agricultural byproduct of soybean oil production, is considered an ideal raw material for the preparation of bio-based wood adhesives owing to its advantages of low price, abundance, renewability and degradability [7]. However, conventional SM adhesives usually exhibit insufficient water resistance and bonding strength owing to their inherent structure with high hydrophilicity and weak intermolecular interactions [8]. Therefore, various strategies have been proposed in recent years to promote the bonding strength and water resistance of SM adhesives, such as the physical blending method [9,10], chemical cross-linking modification [11,12], and enzymatic treatment technology [13,14]. Among these, cross-linking modification presents an efficient and promising performance enhancement for commercial applications.

Polyamidoamine-epichlorohydrin (PAE) resin is a new-generation crosslinking agent and dispersant that has been commercially applied

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Abbreviations: SM, soybean meal; MUG, melamine-urea-glyoxal; PAE, polyamidoamine-epichlorohydrin.

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for SM adhesives in the past two decades [15,16]. In particular, its active azetidinium groups can efficiently react with the residual amino and carboxyl groups of soybean protein and polysaccharides in SM and form three-dimensional networks [16,17]. Its good crosslinking characteristics results in excellent bond strength and water resistance. For instance, its bondline could not only withstand a 3-h soaking in 63 °C water but also retain a wet strength after soaking beyond the required value for interior use according to the Chinese standard GB/T 9846–2015 [18]. However, the cost of PAE-modified SM adhesive is approximately 40–80% higher than that of UF resin owing to the expensive raw materials for PAE resins such as diethylenetriamine and epichlorohydrin. As a result, its high cost strongly restricts wide commercial applications, and the substitution of crosslinkers with better cost-effectiveness than PAE is desired.

Glyoxal is the simplest aliphatic dialdehyde and is less toxic and volatile than formaldehyde [19]. As a result, glyoxal is not only universally applied as an ideal green environmental agent in the paper and textile industries but is also partially or totally substituted for formaldehyde to prepare wood adhesives [20,21]. A urea-glyoxal (UG) resin, with a much lower cost than PAE resin, has been synthesized and used as a crosslinker of SM adhesives, which resulted in good bonding strength [22]. However, the wet strength after soaking at 63 °C for 3 h of UG-modified SM adhesive still needs to be improved, which is marginally higher than the required value according to the commercial standard.

Melamine is a low-cost triazine compound that is highly reactive to aldehyde groups and is frequently used to modify urea-formaldehyde resins to improve water resistance by incorporating aromatic heterocyclic rings into the aliphatic chains [23]. Similarly, melamine can be used to copolymerize with urea and glyoxal to obtain a melamine-urea-glyoxal (MUG) resin, which can economically enhance the water resistance of an SM adhesive due to the much lower cost of MUG resin (~165 USD/ton) than PAE resin (~380 USD/ton) at the same concentration of 12 wt%. As a result, this study focuses on the effects of melamine content and storage time on the structure and properties of a MUG resin and a MUG-modified SM adhesive based on FTIR, ^{13}C NMR, TGA, sol-gel tests, and plywood evaluations to develop a cost-effective crosslinking agent for SM adhesives.

2. Experimental

2.1. Materials

Glyoxal solution ($C_2H_2O_2$, 40% concentration in water) was obtained from Shanghai Macklin Biochemical Technology Co., Ltd., China. Analytical grade urea (CH_4N_2O) and melamine ($C_3H_6N_6$) were provided by Tianjin Fuyu Chemical Co., Ltd., China. A sodium hydroxide standard solution (NaOH, 0.5001 mol/L) was supplied by Tianjin Fuchen Chemical Reagent Co., Ltd., China. Hydrochloric acid and hydroxylamine hydrochloride were of analytical grade and supplied by Tianjin Kemiou Chemical Reagent Co., Ltd., China. Soybean meal (SM) with an average soy protein content of 51.4% was obtained from Harbin Hi-Tech Soybean Food Co., Ltd. Poplar veneers with 5–7% moisture content and dimensions of 350 mm × 350 mm × 1.6 mm (thickness) were purchased from Weihe Fulin Wood Factory, China.

2.2. Syntheses of MUG resins with various melamine content

In a 500-mL three-necked flask, 145 g of 40 wt% glyoxal solution and 265 g of distilled water were charged, and the pH value was adjusted to 9.3–9.5 with 30% NaOH solution. Then, 30 g of urea was added at 20–25 °C with stirring, and the reactant mixture was heated to 60 ± 1 °C within 30 min. When the temperature reached 60 °C, different amounts of melamine (0, 5, 10, 15, and 20 wt%, on the mass basis of urea) were introduced into the urea-glyoxal mixture for condensation polymerization at 60–65 °C for another 150 min. Finally, the reactant mixture was cooled to room temperature to obtain MUG resins, and additional distilled water (0–25 g) was added to produce a similar solid concentration (approximately 20 wt%) of each MUG resin. According to the melamine dosage used, the MUG resins were labeled as MUG-0 (UG), MUG-5, MUG-10, MUG-15, and MUG-20.

Approximately 25 g of each MUG resin was sampled and placed in an oven at 120 ± 2 °C for 4 h to obtain a thermally cured MUG sample. Meanwhile, another batch of each MUG resin (approximately 25 g) was immersed in liquid nitrogen and then freeze-dried at −30 °C and −10 kPa for 5 days to obtain freeze-dried MUG samples for an FTIR analysis.

2.3. Preparation of SM adhesives and cured samples

Each MUG resin (42 g) was mechanically mixed for approximately 3 min with distilled water (28 g) and SM (24.5 g) using a rotating mixer at 800 rpm at room temperature to form a homogeneous modified soybean adhesive without obvious particle clusters. An adhesive prepared with SM without a crosslinker was used as a control. The obtained adhesives were labeled as SM, SM/UG, SM/MUG-5, SM/MUG-10, SM/MUG-15, and SM/MUG-20, according to the MUG resin used.

Adhesive samples were spread on a polytetrafluoroethylene container and thermally cured at 120 ± 2 °C for 4 h to obtain the cured SM adhesive. After cooling to room temperature, the cured samples were crushed into a fine powder that passed through a 160-mesh sieve for subsequent characterization.

2.4. Characterization of UG, MUG resin and SM adhesive samples

2.4.1. Determination of the aldehyde value of the MUG resin

The aldehyde value of the MUG resin was determined by hydroxylamine hydrochloride titration using the following procedure. Approximately 1.5 g (m_0, accurate to 0.0001 g) MUG resin was dispersed in 100 mL distilled water in a 250-mL beaker under magnetic stirring, and the pH was adjusted to 4.0 with 0.1 mol/L HCl. Subsequently, 25.00 mL of hydroxylamine hydrochloride solution with a concentration of 10 wt% was transferred into the mixture, and the beaker was sealed with PE film. After magnetic stirring for 5 min, the pH value of the above system was titrated to 4.0 with NaOH standard solution (c_0, 0.5001 mol/L). The consumed volume (V_0, accurate to 0.01 mL) of the NaOH standard solution was recorded. The aldehyde value was defined as the mass percentage of the free aldehyde group (-CHO) in the MUG resin and calculated as $[c_0 \times V_0 \times M/(m_0 \times 1000)] \times 100\%$, where M represents the molar mass (29.03 g/mol) of the –CHO group.

2.5. Viscosity measurement

The viscosities of the MUG resin and SM adhesive samples were measured using a Brookfield DV-II Pro viscometer (USA) at 25 °C according to the Chinese standard GB/T 14074–2017. Spindle S61 at a rotating speed of 100 rpm was selected for the low-viscosity MUG resin, while spindle S64 at a rotating speed of 1 rpm was selected for the highly viscous SM adhesive.

2.6. Fourier transform infrared (FTIR) spectroscopy

FTIR analyses of both the synthesized MUG resins and cured adhesive samples were recorded in the range of 4000 to 400 cm^{-1} with a 4 cm^{-1} resolution and 32 scans on a Spectrum One FTIR spectroscope (Nicolet Co., USA). The IR peak at approximately 2930 cm^{-1}, which represents the C–H vibration, was selected as an internal standard, and a baseline calibration was carried out using the software OMNIC E.S.P. (Nicolet Co., USA).

2.6.1. ^{1}H nuclear magnetic resonance (NMR) and solid-state ^{13}C-CP/MAS NMR analyses

The MUG solution was dissolved in D_2O for ^{1}H NMR analysis using a

500 M ^{1}H nuclear magnetic resonance spectrometer (Bruker AVANCE-III, Germany) with a 2.5 μs 90° pulse width and 3 s relaxation delay, and the water peak was suppressed during the examination process to obtain a high signal-to-noise ratio. The cured SM adhesive powder was subjected to solid-state ^{13}C NMR analysis with a CP/MAS probe on a Bruker 400 MHz spectrometer (Bruker AVANCE NEO 400WB, Germany) using a 3.84 μs 90° pulse width and 3 s relaxation delay.

2.6.2. Thermogravimetric analysis (TGA)

The thermal stabilities of the cured SM adhesives were measured using a Netzsch 209 F3 TGA instrument and scanned from 20 °C to 600 °C at a heating rate of 10 °C/min under a nitrogen atmosphere.

2.6.3. Determination of boiling-water-insoluble content of cured SM adhesive by a sol-gel test

Approximately 0.5 g of cured adhesive powder (W_1, accurate to 0.0001 g) and 50 g of distilled water were added to a 250-mL Erlenmeyer flask and boiled for 4 h. The obtained boiling-water-insoluble product was cooled to room temperature and filtered with pre-dried and weighted quantitative filter paper (W_2, accurate to 0.0001 g). The filtered residue was washed three times with 50 mL of distilled water and dried in an oven at 120 °C to a constant weight (W_3, accurate to 0.0001 g). The boiling-water-insoluble content was defined as the mass percentage of the obtained insoluble residue after boiling in water to the untreated cured adhesive powder, which reflects the gel content or crosslinking degree of the cured soybean adhesive and was calculated as $[W_3–W_2/W_1] \times 100\%$.

2.6.4. Bond strength and water resistance evaluation by three-layer plywood

Plywood panels were fabricated by evenly spreading both faces of the cored veneer (poplar) with 200 g/m^2 of adhesive (single glue line). The glued veneer (poplar) was sandwiched between two uncoated face veneers with their horizontal wood grains perpendicular to each other. The adhesive-coated veneer was cold-pressed at 0.9 MPa at room temperature for 30 min and then hot-pressed at 120 °C and 0.9 MPa for 5 min. The prepared three-layer plywood panels were cut as specimens according to ASTM D906-2017 to evaluate the bond properties. The bond strength and wet strength for interior use (Type II plywood) were determined according to the GB/T 9846-2015 standard using a tensile testing machine with a crosshead speed of 5 mm/min. The specimens (10 pieces) for the wet strength test were soaked in water at 63 ± 2 °C for 3 h and then cooled to room temperature before the strength test. The specimens for the dry shear strength tests were directly measured.

2.7. Statistical analysis

Data are reported as the mean ± standard deviation. A single-factor analysis of variance was conducted to determine the significant differences among the mean values. Statistical significance was set at $P < 0.05$.

3. Results and discussion

Due to the absence of aromatic rings in the aliphatic main chains of the synthesized UG or MUG-0 resin, its modified SM adhesive had undesired water resistance in terms of a wet strength of 0.76 MPa (after soaking in 63 °C water for 3 h) that was slightly higher than the required value for indoor-use plywood and had an insufficient strength surplus for controlling the panel quality in commercial manufacturing. To improve the water resistance of the UG-modified SM adhesive economically, melamine was introduced into copolymerization with urea and glyoxal, by which aromatic triazine rings were incorporated into the aliphatic chains of the UG resin, which increased the

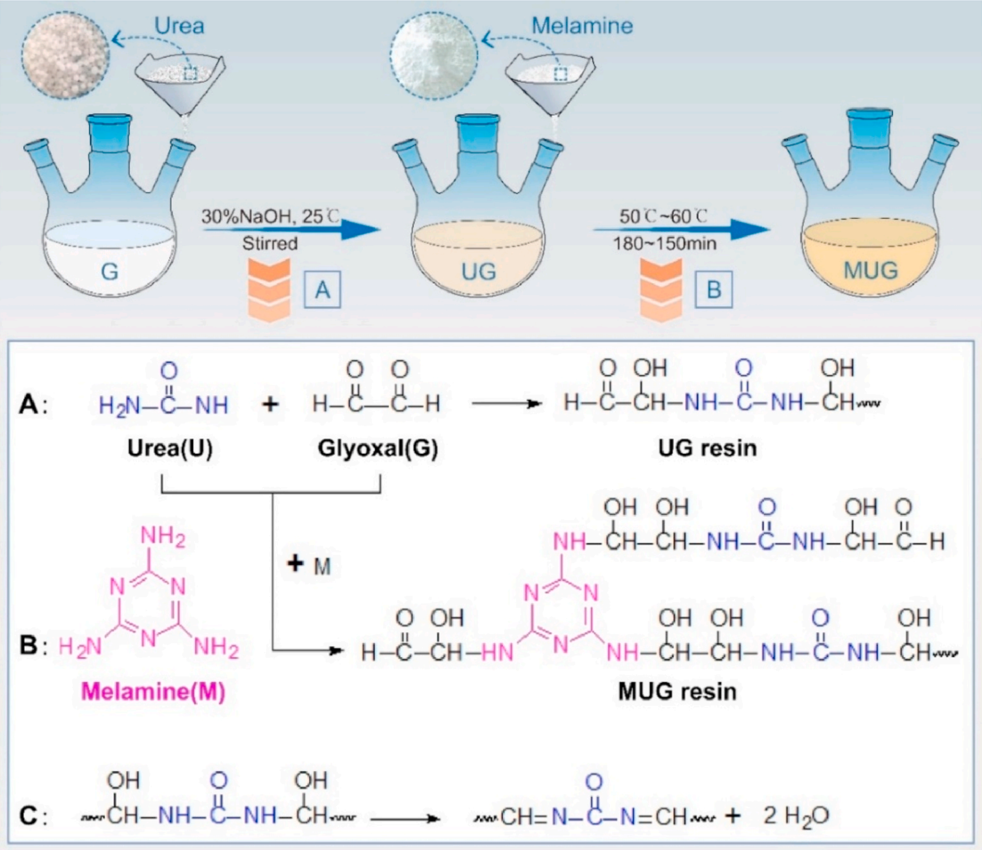

Fig. 1. Reaction schemes of UG and MUG resin.

crosslinking density of the cured adhesive. The main copolymerizing reactions of the MUG resin are illustrated in Fig. 1.

3.1. Physical properties and structure of MUG resin with various melamine contents

Because of the higher reactivity and increased reactive sites of melamine over urea, MUG resins prepared with higher melamine contents but the same synthetic conditions had lower aldehyde values, as shown in Table 1, indicating that melamine could effectively copolymerize with glyoxal and urea. The increased dark color and solid content of the MUG resin with higher melamine content was attributed to the incorporation of more aromatic triazine rings into the aliphatic UG chains, as shown in Fig. 1. However, the viscosity of the MUG solution did not increase with the melamine content but passed a maximum (8.90 mPa s) when the melamine content was 10%, implying that not all the melamine linearly copolymerized with UG resin to increase the molecular weights of polymer matrices; some turned into a branched structure because each melamine has three amino groups reactive to glyoxal without obvious steric hindrance.

The FTIR spectra of the freeze-dried MUG-0 resin (yellow line in Fig. 2A) showed a broad IR absorption peak at 3286 cm^{-1}, attributed to the stretching modes of N–H bonds in the amino group and O–H bonds in the hydroxyl group. Compared with the spectrum of pure urea in Fig. 2B, the intensity of the IR peak of UG resin at 3200–3500 cm^{-1} was obviously weakened, and the absorption peak of the amino group in urea at 1590 cm^{-1} disappeared, indicating that glyoxal effectively reacted with the amino group of urea [24].

After melamine was introduced, a new IR absorption peak at 1552 cm^{-1} was detected in the MUG resin (colored lines in Fig. 2A), which was assigned to the typical stretching vibration peak of the triazine ring in melamine [25]. With increasing melamine content, the IR absorptions of the C–O bond at 1031 cm^{-1} and the C–N bond at 1236 cm^{-1} increased, indicating that melamine successfully copolymerized with UG resin. The C–N absorption peak at 1236 cm^{-1} split into double peaks for the cured MUG resins (black lines in Fig. 2A). Moreover, thermal curing led to an obvious decrease in the IR absorption intensity of the N–H/O–H bonds and C–O bonds in the MUG resin, while their peak positions shifted from 3296 cm^{-1} to 3256 cm^{-1} and from 1031 cm^{-1} to 1078 cm^{-1}, respectively, suggesting that a more stable structure in the resin was formed by hydroxyl dehydration during the thermal curing process, as illustrated in Fig. 1C.

The ^{1}H NMR spectrum in Fig. 2C shows a weak peak at approximately 8.35 ppm attributed to residual aldehyde groups, demonstrating that the synthetic resin was terminated with aldehyde groups [26]. The signals at 5.15–5.18 ppm were assigned to the proton peaks of hydroxyl attached to the adjacent carbon of the aldehyde group. Peaks 2 ($\delta =$ 5.10–5.12 ppm) and 3 ($\delta = 5.01$–5.07 ppm) corresponded to the protons of methylene and free hydroxyl from the G-U long chain, respectively. The strong signal or large area of peaks 1 and 3 in Table 2 indicate that the MUG resins were rich in hydroxyl groups. Notably, the peaks in the 3.9–4.0 ppm region (ascribed to –NH–) moved to the high-magnetic-field area, and the integrated area of peak 1 decreased when urea was partially substituted by melamine. These facts, in combination with less aldehyde remaining with more melamine, further evidenced that melamine was sufficiently polymerized with glyoxal. However, the decrease in the relative integrated area of peak 4 or group N–H concentration when the melamine content was more than 10% indicated that some amino groups in melamine were consumed to form a branched structure, as evidenced by the decreased viscosity in Table 1.

Table 1
Physical properties of MUG resins with different melamine contents.

Resin ID	Melamine content (%)	Color	Aldehyde value (%)	**Viscosity (mPa·s)**	Solid content (%)
MUG-0 (UG)	0	Light yellow	3.21 ± 0.02	5.72 ± 0.01	18.55 ± 0.02
MUG-5	5	Light yellow	2.85 ± 0.01	6.23 ± 0.04	18.64 ± 0.02
MUG-10	10	Middle yellow	2.66 ± 0.03	8.90 ± 0.06	18.64 ± 0.04
MUG-15	15	Yellow	2.57 ± 0.01	8.36 ± 0.06	18.60 ± 0.05
MUG-20	20	Light brown	2.47 ± 0.02	8.24 ± 0.02	18.62 ± 0.04

3.2. Structure and property of SM adhesive modified with fresh MUG resin

The remaining aldehyde groups in the MUG resin are cross-linkable to the amino groups of the soybean protein, contributing to the crosslinking of the SM adhesive and formation of a three-dimensional network to withstand hot water soaking, as illustrated in Fig. 3. Meanwhile, as confirmed by FTIR and NMR (Fig. 2), MUG resin is rich in groups that can physically crosslink to soybean meal and wood via hydrogen bonding. The combination of aldehyde crosslinking and hydrogen bonding can improve the bond strength and water resistance of the MUG-modified SM adhesive.

When the SM slurry created by dispersing SM flour in distilled water at room temperature was used as an adhesive, its bonded plywood had a low dry shear strength of 1.32 MPa and very poor water resistance that could not withstand hot water (63 ± 2 °C) soaking, as shown in Table 3. The adhesion of the SM slurry was attributed to molecular entanglement, surface absorption, and mechanical interlock, all of which are easily destroyed by hot water owing to the absence of chemical crosslinking between SM molecules. As a result, the cured SM slurry had a very low crosslinking density in terms of 29.34% boiling-water-insoluble content (Table 3), and its bondlines were all delaminated during the 60-min soaking in 63 °C hot water and had no wet strength.

When MUG-0(UG) resin was used as the crosslinking agent and disperser of SM flour, the bond strength of the UG-modified SM adhesive was increased by 20.5% compared with the SM slurry without the crosslinking agent. The bondline could not only withstand a 3-h hot water soaking but also retained a wet strength of 0.76 MPa, which reaches the required value (≥0.7 MPa) for interior use (poplar veneer) according to the Chinese National Standard (GB/T 9846–2015), indicating the obvious improvement of water resistance due to the crosslinking via the retained aldehyde of MUG-0 with soybean protein as illustrated in Fig. 3. However, its wet strength is marginally higher than the required value. As a result, melamine was introduced to copolymerize with urea and glyoxal to further improve the bond properties.

The test results in Table 3 show that the introduction of 5–10% melamine for copolymerization could effectively improve the bond strength and water resistance. Notably, the dry strength and soaked shear strength of the MUG-modified SM adhesive with 10% melamine addition were significantly increased by 32.1% (to 2.10 MPa) and 21.1% (to 0.92 MPa), respectively, compared with those modified by MUG-0. This was mainly attributed to the introduction of aromatic triazine rings with strong cohesive strength into the aliphatic UG chains and the greater number of reactive sites available for the melamine ring (3 cites) than urea (2 cites), which improved the crosslinking density, as shown in Fig. 1B. However, further increasing the melamine content would consume more aldehyde groups during the copolymerization of melamine with urea and glyoxal, as evidenced by the aldehyde value in Table 1, leading to a decrease in the bonding property of the MUG-modified SM adhesive because of insufficient aldehyde groups available to crosslink the soybean protein into good networks.

The gel content, in terms of the boiling-water-insoluble content in Table 3, did not increase with increasing melamine content, further demonstrating that the crosslinking density of the MUG-modified SM adhesive was not only defined by the functionalities of melamine and melamine content but also by the residual aldehyde value of the MUG

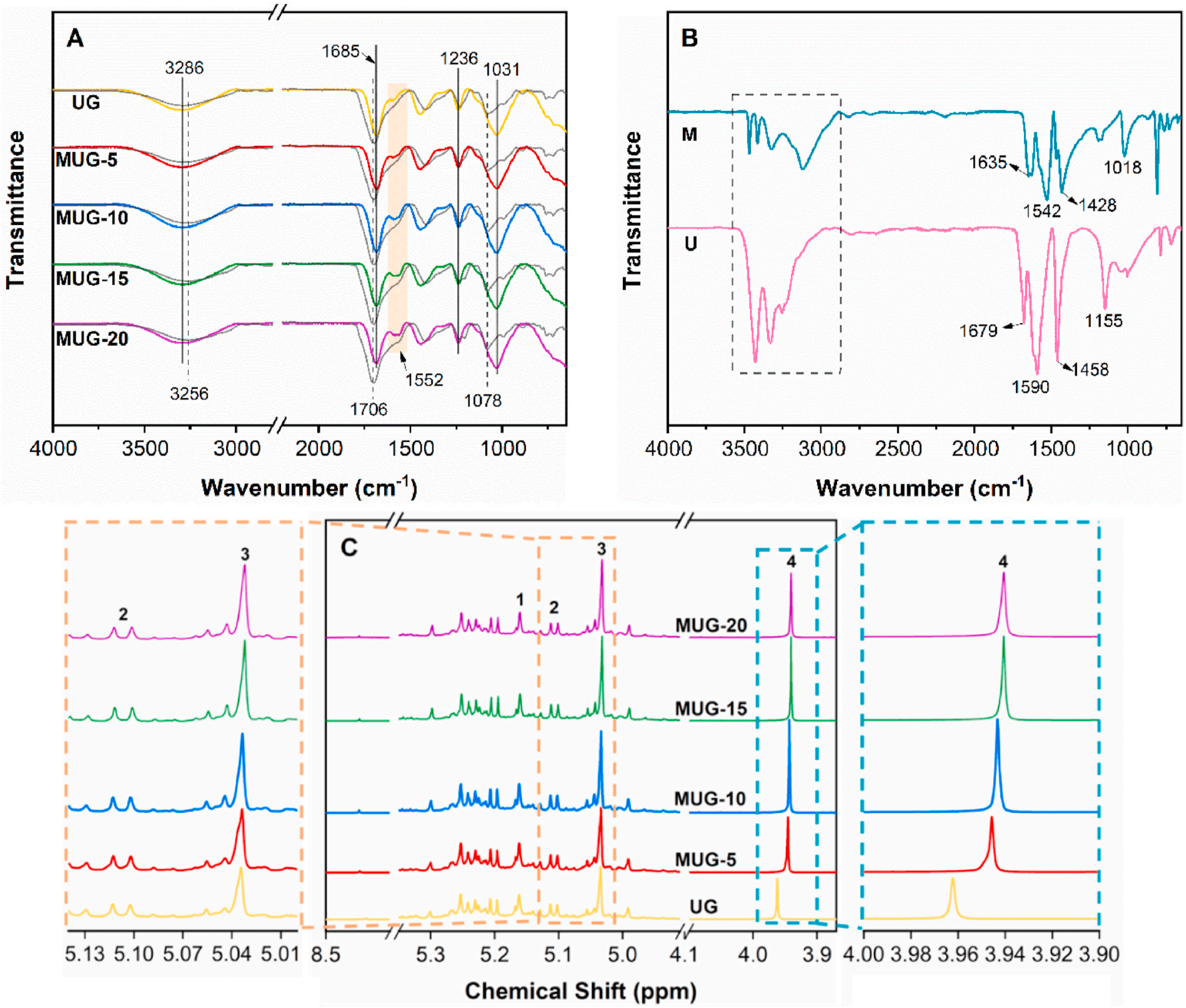

Fig. 2. FTIR spectra of (A) Freeze-dried and cured MUG resins, (B) Melamine and urea, and (C) ^{1}H NMR spectra of MUG solutions.

Table 2

^{1}H- relative integral area of MUG resins with different melamine contents.

Peak ID	Chemical shifts (ppm)	Peak assignments	Relative integral area (%)				
			MUG-0	MUG-5	MUG-10	MUG-15	MUG-20
1	5.15–5.18	(CHO)CH–O**H**	7.2	7.1	6.4	6.2	6.0
2	5.10–5.12	-C**H**-	3.8	3.9	3.9	3.9	3.8
3	5.01–5.07	-CH-O**H**	12.5	14.6	15.6	15.9	16.1
4	3.90–4.00	-N**H**-	3.6	4.3	6.0	5.8	5.7

resin. Theoretically, the introduction of more melamine with higher functionalities into the UG resin could result in a higher crosslinking density. However, in the formulation with more melamine substituted for urea, a greater number of aldehyde groups were consumed and fewer crosslinking reactions occurred between the MUG resin and SM.

The thermal degradation process of SM-based adhesives by TGA (Fig. 4A) is divided into three stages [27]. The first stage (I) with a degraded temperature less than 150 °C is assigned to the evaporation of residual moisture with a rather small weight loss of approximately 3–6%. The second stage (II) with a degraded temperature range of 150–260 °C corresponds to the degradation of oligomeric components, metastable structures, and intermolecular hydrogen bonds with a weight loss of approximately 23–27%. Thermo-degradation in stage (III) with degraded temperatures greater than 260 °C is mainly associated with the degradation of the skeleton structure of SM adhesives with a loss rate of more than 55%. Due to the absence of a crosslinking agent, the SM slurry had both a low degradation temperature and low mass residue (Table 4). The addition of UG(MUG-0) resin as a crosslinking agent resulted in a greater amount of mass residue of cured SM adhesive in thermal degradation due to the good crosslinking reaction between the UG resin and SM but a lower thermal degradation temperature due to the aliphatic structure of the UG resin. The copolymerization of melamine with UG led to an improvement in the thermal degradation temperature up to 309.2 °C owing to the introduction of aromatic triazine rings with the desired heat resistance. However, the addition of melamine to MUG resin did not result in sufficient crosslinking density owing to the over-consumption of crosslinkable aldehyde groups during copolymerization.

In the FTIR spectra of the cured SM adhesive in Fig. 4B and C, the peak absorptions at approximately 3286 cm^{-1} and 2932 cm^{-1} were

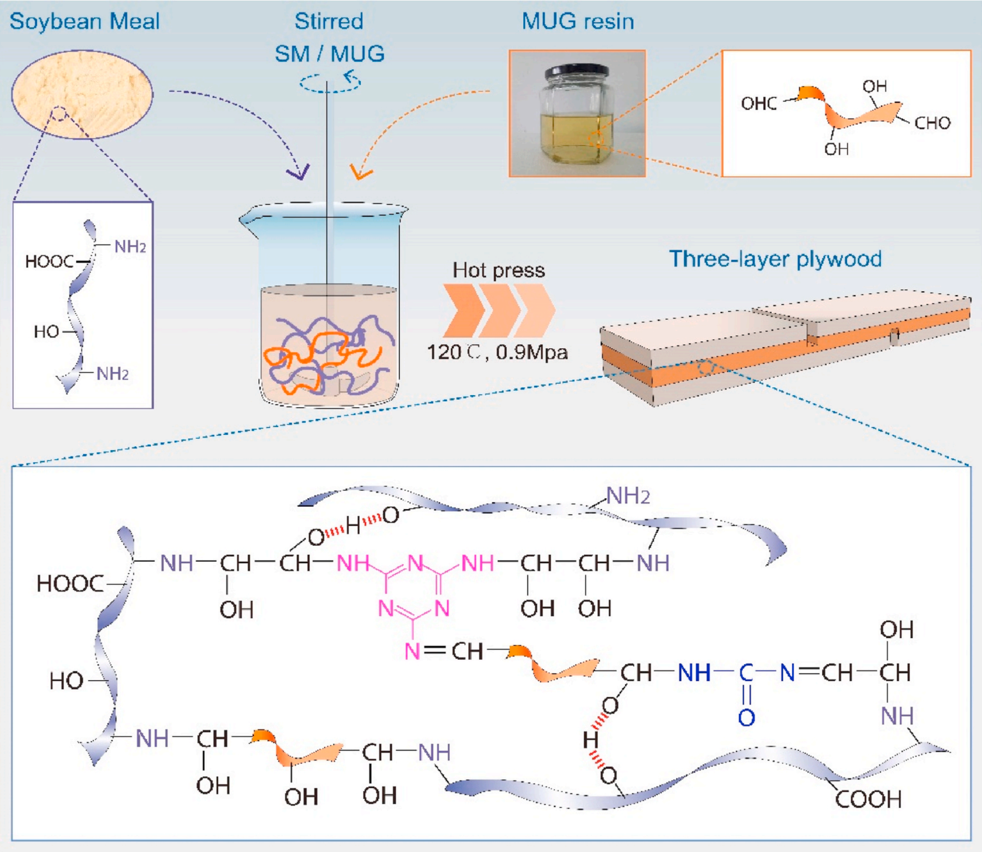

Fig. 3. Enhancement mechanism of MUG-modified SM-based adhesives.

Table 3
Viscosity and bonding strength of MUG-modified SM adhesive.

Adhesive ID	Viscosity (Pa·s)	Dry strength (MPa)	Wet strength (MPa)	Boiling-water-insoluble content (%)
SM slurry	128.4 ± 0.30^{e}	1.32 ± 0.21^{d}	N.A.	29.34 ± 0.05^{d}
SM/MUG-0	145.4 ± 0.19^{d}	1.59 ± 0.12^{c}	0.76 ± 0.07^{b}	45.91 ± 0.11^{c}
SM/MUG-5	183.6 ± 0.26^{c}	1.89 ± 0.19^{b}	$0.86 \pm 0.08^{a,b}$	46.21 ± 0.07^{c}
SM/MUG-10	204.8 ± 0.49^{a}	2.10 ± 0.34^{a}	0.92 ± 0.07^{a}	49.62 ± 0.33^{a}
SM/MUG-15	196.8 ± 0.53^{b}	1.90 ± 0.26^{b}	0.78 ± 0.05^{b}	48.51 ± 0.07^{b}
SM/MUG-20	186.4 ± 0.36^{c}	1.67 ± 0.20^{c}	0.70 ± 0.06^{c}	47.80 ± 0.16^{b}

Note: N.A. means no value because the specimens were all delaminated after soaking in water. The letters (a, b, c, d, and e) represent significant differences at $p < 0.05$.

associated with the vibration of O–H/N–H bonds and the symmetric and asymmetric stretching vibrations of the $–CH_2$ group of the peptide chains [28], while the peaks detected at 1643, 1526, and 1237 cm^{-1} were ascribed to the C=O stretching (amide I), N–H bending (amide II), and N–H/C–N stretching vibration (amide III), respectively [29]. Notably, Fig. 4B shows that after thermal curing, the IR absorption at approximately 1685 cm^{-1}, related to the C=O stretching of aldehyde in the freeze-dried MUG resin, disappeared while the IR absorption of N–H bending (amide II) at 1526 cm^{-1} was obviously weaker, indicating that the free aldehyde groups of the MUG resin reacted with the amino groups of soybean protein to form more three-dimensional networks, as illustrated in Fig. 3, which provided a basis for the improved bonding and water resistance [30].

Fig. 4C illustrates the FTIR spectra (colored lines) of the cured MUG-modified SM adhesive. However, no significant variations were observed, as the same adhesive formulation was used, except for the melamine content in the MUG resin. After 4 h of water boiling treatment in the sol-gel test to remove soluble and unstable components from the cured SM sample, the FTIR spectra (black lines in Fig. 4C) detected stronger IR absorptions at 3276 cm^{-1} and 1515 cm^{-1} that were assigned to soybean protein; however, the weaker IR absorptions at 1036 cm^{-1}, which were ascribed to -C-O- bonds in carbohydrates and MUG resins, imply that the components removed from the cured adhesive in the sol-gel test were mainly dissoluble carbohydrates due to the poor cross-linking of carbohydrates to the MUG resin.

The solid-state ^{13}C NMR spectra in Fig. 4D were employed to further investigate the crosslinking of SM and MUG. The overlapping signals in the ranges of 46–68, 26–45, and 16–22 ppm were ascribed to the α-C, β-C, and methylene/methyl groups, respectively [31]. The detected peak at 162.5 ppm was attributed to the –C=N groups from the dehydrated MUG (Fig. 1C) and the triazine rings of melamine in cured adhesives of SM/MUG-0 and SM/MUG-10. Meanwhile, the decreased peaks of α-C and β-C compared to the MUG-modified SM adhesive with pure SM adhesive suggested that the main chemical crosslinking reaction between the MUG resin and soybean protein occurred, as illustrated in Fig. 3. Furthermore, the MUG-modified SM adhesive had a larger relative integral area in the peak at 82.1 ppm, indicating that intermolecular hydrogen bonds formed between SM and MUG with abundant –CHOH groups [32].

In addition, the melamine content in the MUG resin also had an important effect on the viscosity of the SM adhesive, which is defined by both the initial viscosity (molecular weight) of the MUG resin and intermolecular interactions between the MUG resin and SM molecules. The test results in Table 3 show that the viscosity of the adhesive reached

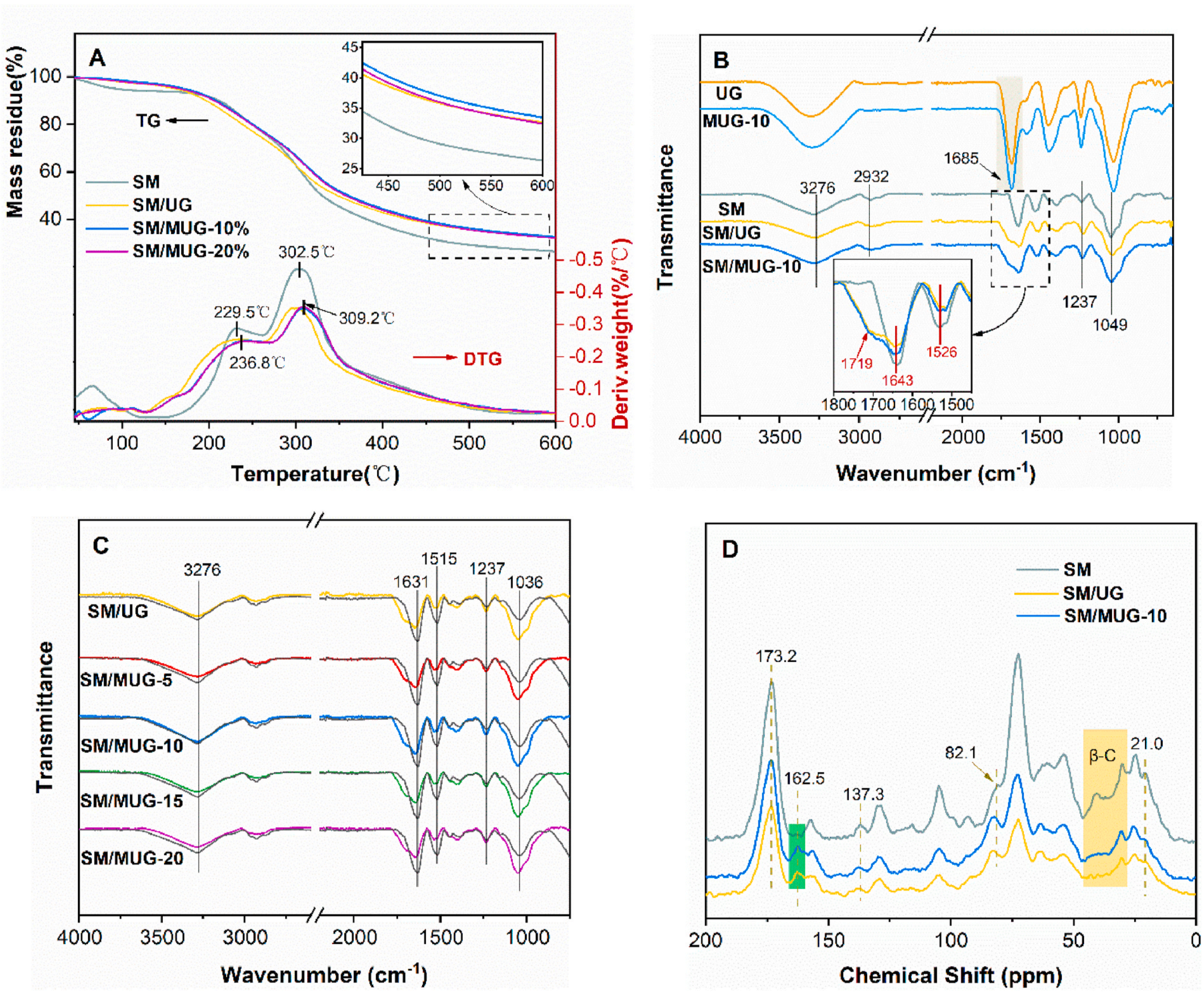

Fig. 4. (A) TGA and DTG curves, (B) FTIR spectra of freeze-dried MUG resins and cured SM adhesives, (C) FTIR spectra of cured adhesives before and after water-boiling treatments, and (D) Solid state ^{13}C NMR spectra of cured SM adhesives.

Table 4
Effect of M dosage on the thermal stability of cured SM adhesives.

Sample ID	Peak degradation temperature (°C)		Mass residue (%)
	Stage II	Stage III	
SM slurry	229.5	302.5	24.2
SM/UG	211.5	299.3	30.5
SM/MUG-5	235.2	308.2	31.1
SM/MUG-10	236.8	309.2	31.8
SM/MUG-15	236.3	308.4	30.9
SM/MUG-20	236.4	308.2	30.0

a maximum at 10% melamine content, which was similar to the viscosity of the MUG resin alone. This implies that the adhesive viscosity was mainly determined by the initial viscosity of the MUG resin or the effects of melamine content on the structure of the MUG resin, rather than by the number of aromatic triazine rings in the MUG.

3.3. Storage stability of MUG resin

Due to the high reactivity of melamine and its derived components, the residual amino groups from the melamine probably reacted with the free aldehyde groups in MUG resin during storage at room temperature. Photographs of MUG solutions after various storage times at 20–25 °C are presented in Fig. 5. Insoluble sediment was observed in MUG-15 and MUG-20 after storage at room temperature for 15 days, and the sediment increased with prolonged storage. This fact evidenced the high reactivity of MUG resin, and its storage time might have an important effect on the MUG resin and the modified SM adhesive.

The H NMR tracking results in Fig. 5 and Table 5 indicate that all MUG resins exhibited obvious changes in structures corresponding to signal peak 1 (δ = 5.15–5.18 ppm) and peak 3 (δ = 5.01–5.07 ppm), while a high melamine addition could (>10%) also lead to important changes in structures corresponding to signal peak 4 (δ = 3.9–4.0 ppm), indicating a more reactive or less stable MUG with more melamine. According to the NMR chemical shifts shown in Table 2, a decrease in signal peak 1 and increase in signal peak 3 were associated with the further reaction of free aldehyde groups with the residual terminal –NH_2 of urea and melamine, forming –NH– and two hydroxyl groups, as shown by Equation 1 in Fig. 6. The increase in the integral area of peak 3 was greater than the total decreased areas of peaks 1 and 4, indicating that the hydration of free aldehyde groups into hydroxyl groups occurred, as illustrated by Equation 2 in Fig. 6. The hydration was further evidenced by the decreased C=O stretching of aldehyde groups at 1685 cm-1 and the increased –OH stretching at 3286 cm^{-1} and C–O stretching at 1031 cm^{-1} due to the formation of hydro ethylene, as shown by the FTIR of the frozen-dry MUG in Fig. 7.

With the combination of the best bond strength, water resistance (Table 3), and thermal resistance (Table 4) of the modified SM adhesives, MUG-10 was identified as the preferred crosslinking agent for the SM adhesive. The bonding stability against storage time was evaluated weekly. The test results in Fig. 8 and Table S1 indicate that both the dry

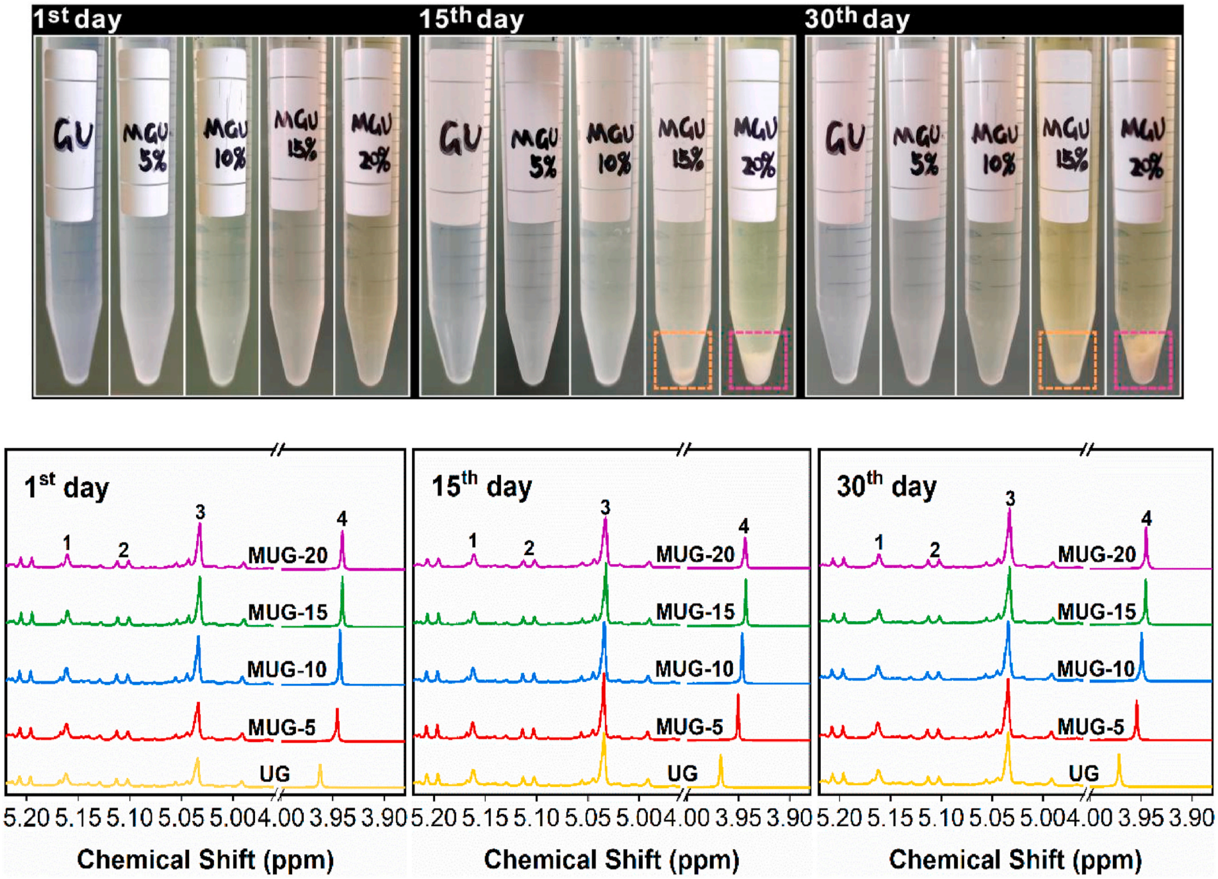

Fig. 5. Real product and ^{1}H NMR spectra of UG and MUG resins with different storage times.

Table 5
^{1}H- relative integral area of MUG resins with different storage times.

Peak ID	Relative integral area (%) for various storage time (day)														
	UG			MUG-5			MUG-10			MUG-15			MUG-20		
	1	15	30	1	15	30	1	15	30	1	15	30	1	15	30
1	7.2	6.7	6.5	7.0	6.5	6.5	6.4	6.2	5.9	6.2	5.9	5.8	6.0	5.3	4.9
2	3.8	3.9	3.8	3.9	3.9	3.9	3.9	3.8	3.8	3.9	3.9	3.7	3.8	3.4	3.6
3	12.5	17.4	17.4	14.6	18.7	18.7	15.6	19.4	19.4	15.8	20.8	19.7	15.5	18.7	20.2
4	3.9	3.9	4.0	4.3	4.5	4.5	6.2	6.3	6.3	5.8	5.8	5.4	5.7	5.2	5.4

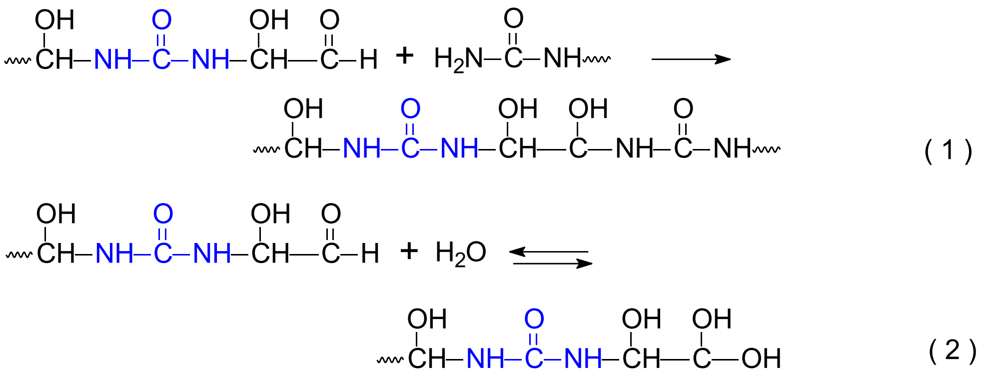

Fig. 6. Possible reactions of MUG resin during storage at room temperature.

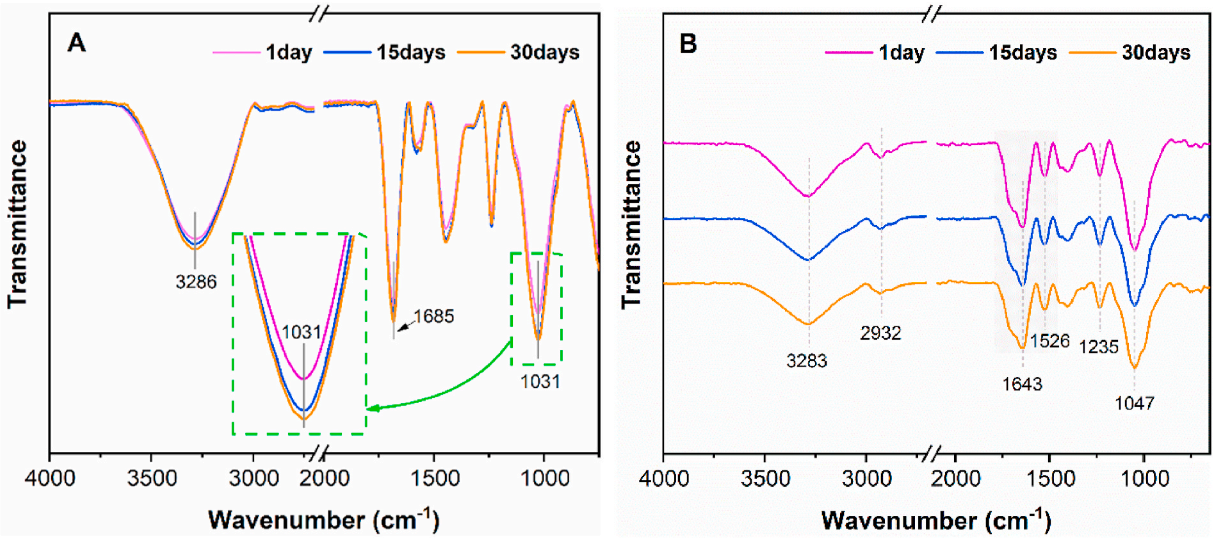

Fig. 7. FTIR spectra of uncured MUG-10 resin (A) and thermally cured SM/MUG-10 adhesive (B) with various storage times.

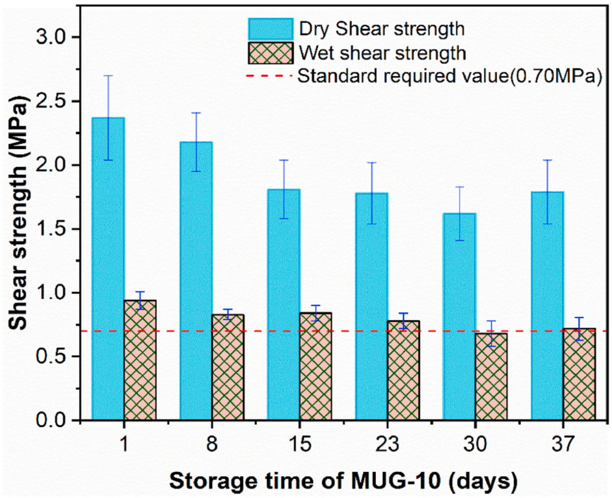

Fig. 8. Bonding properties of plywood bonded with different MUG-10 storage times.

strength and wet strength of the SM adhesive modified by MUG-10 decreased as the storage time increased. Compared to the SM adhesive modified by fresh MUG-10 (synthesized for 1 day), after a 3-week storage, MUG-10 bonded plywood had a dry strength of 1.78 MPa (dropped by 24.9%) and a wet strength of 0.79 MPa (reduced by 15.9%). When stored for 30 days, the bond strength decreased from 2.37 to 1.62 MPa (31.6%), and the water resistance in terms of wet strength decreased by 27.7% (from 0.94 to 0.68 MPa). As a result, the water resistance of the SM adhesive-modified MUG-10 stored for 30 days could not meet the required value (>0.7 MPa) for interior use according to the Chinese standard GB/T 9846–2015.

The deteriorated bond property was attributed to the further reaction of residual free aldehyde groups with the amino groups, as evidenced by NMR (Table 5) and FTIR (Fig. 7A) analyses. Consequently, the crosslinkable aldehyde groups were consumed during storage, which led to reduced crosslinking with soybean protein, as confirmed by the decreased FTIR absorptions at 1635 cm^{-1} and 1526 cm^{-1} assigned to the amide I and II groups of soybean protein, respectively. Therefore, the maximum allowable storage of MUG-10 resin is 3 weeks, preferably for 2 weeks, to ensure the necessary water resistance or bonding quality of plywood panels.

4. Conclusions

A cost-effective and formaldehyde-free crosslinking agent for formulating an interior-use SM adhesive was developed via the copolymerization of melamine, urea, and glyoxal. The melamine content had important effects on the structure and properties of the MUG resin and MUG-modified soybean adhesive. The most preferable melamine content was 10%, which resulted in the greatest improvement in bonding property; the dry strength increased by 32.1% and water resistance increased by 21.1% compared with MUG resin without melamine addition (UG). This improvement was mainly attributed to the incorporation of aromatic triazine rings, with good thermal resistance, into the aliphatic UG chains, the greater reactivity and functionality of melamine than urea, and the crosslinking reaction of the remaining aldehyde groups with soybean protein. Storage can obviously decrease the bonding property and water resistance of the MUG-modified SM adhesive owing to the further reaction of the remaining aldehyde with the amino groups of the MUG resin. Storage of MUG-10 resin at room temperature for 30 days significantly decreased the bond strength by 31.6% and the water resistance in terms of wet strength by 27.7%, resulting in deteriorated bonding properties that are lower than the required value for interior use according to the Chinese standard GB/T 9846–2015. The longest allowable storage of MUG-10 resin is 3 weeks, preferably for 2 weeks, to ensure the bonding quality of plywood panels.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.ijadhadh.2021.102986.

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