Free Formaldehyde Reduction in Urea-formaldehyde Resin Adhesive: Modifier Addition Effect and Physicochemical Property Characterization

Keke Liu, Changqing Su, Weiwu Ma, Hailong Li, Zheng Zeng,* and Liqing Li *

Melamine, polyvinyl alcohol, and adipic acid dihydrazide as modifiers were added to urea-formaldehyde (UF) resin for reducing the free formaldehyde. The influence of addition amount and addition stage of modifiers on the physicochemical property and free formaldehyde content of UF resin was tested. Fourier transform infrared spectroscopy (FTIR) and thermogravimetric analyses (TGA) were used to determine the structural change and thermal stability of the resins. The results revealed that the UF resin added with 6% melamine had the lowest free formaldehyde content of 0.31%. Among all modified resins added with equal amount of modifier in different stages, the UF resin added with 3% polyvinyl alcohol in the second alkaline stage achieved the lowest free formaldehyde content of 0.33%. More importantly, the comprehensive effect of melamine, polyvinyl alcohol, and adipic acid dihydrazide on the free formaldehyde content of resin was studied. The free formaldehyde content in the UF resin added with the comprehensive modifiers achieved 0.24% content, and formaldehyde emission of this kind of adhesive was just 0.21 mg/g. Coupling the experimental results with the characterization data, comprehensive modifiers can reduce the formation of chemical bonds (methylene and ether bonds) in the resin and improve thermal stability of UF resin effectively.

Keywords: Urea-formaldehyde resin; Free formaldehyde; Modification; Melamine; Polyvinyl alcohol; Adipic acid dihydrazide

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INTRODUCTION

Urea-formaldehyde (UF) resins are used as adhesives for wood manufacturing (middle and high-grade wood composite boards), such as particleboard, medium density fiberboard, and hardwood plywood (Mao *et al.* 2013a). They have many advantages, such as high reactivity, clear glue line, good performance, and low cost (Lubis *et al.* 2017). However, the application of UF resins is limited due to the high content of free formaldehyde, poor water resistance, easy aging, and brittleness. The release of free formaldehyde from wood composite boards is harmful to human health. Modifying the resin or exploiting novel adhesives could promote the properties of UF resins and avoid the high content of free formaldehyde (Zhang *et al.* 2014; Sulaiman *et al.* 2018).

Controlling the free formaldehyde content in UF resins improves their physical and chemical properties. In various studies, UF resins have been modified with melamine (Altun and Tokdemir 2017), polyvinyl acetate (Kim and Kim 2005), tannin (Bacardit *et al.* 2014; Zhang *et al.* 2019), soybean protein (Liu and Li 2007), and lignin (Qiao *et al.* 2015).

Because the free formaldehyde in UF resins mainly comes from the decomposition of methylene and ether bonds (Mao *et al.* 2013b, 2013c), methylene and ether bonds in resins could be reduced after adding modifiers to the resins. For example, melamine contains one triazine ring structure and six reactive functional groups, each of which undergo a reaction with formaldehyde to form hydroxymethyl-melamine to reduce the free formaldehyde content (Lei and Frazier 2015).

The influence of the addition stage and allocation proportion of melamine on UF resins has been studied (Zhang *et al.* 2013a; Luo *et al.* 2015). The addition stage of melamine has a remarkable impact on the performance of melamine-urea-formaldehyde (MUF) resin. The resin with melamine added in the primary stage obtained the highest bond strength and the lowest formaldehyde emissions. A high allocation proportion increased the methylene ether group content, resulting in improved water resistance of the MUF resins, whereas a low allocation proportion decreased formaldehyde emissions. In addition, polyvinyl alcohol (PVOH) has great potential to improve the performance of UF resin; PVOH is very viscous, which improves the initial viscosity and bond strength of the resin (Pan *et al.* 2014). It has numerous hydroxyl groups, resulting in the reaction with formaldehyde to form polyvinyl formal under acidic conditions; this reduces the content of hydrophilic hydroxymethyl groups of UF resin and enhances the water resistance and the initial viscosity of the adhesive (Gungor and Kiskan 2018). Moreover, the structure formed by the reaction of PVOH with formaldehyde increases the water solubility of the adhesive and captures residual formaldehyde in the adhesive (Zhang *et al.* 2015). Under low temperature acidic conditions, the UF resin with PVOH exhibits better water resistance and lower free formaldehyde than the UF resin synthesized by the traditional process.

The use of UF resin with lower free formaldehyde content in the wood manufacturing has resulted in products with the lower emission of formaldehyde (Que *et al.* 2007). Formaldehyde emission in wood-based panel is mainly from two sources: residual free formaldehyde in panels and polymer hydrolysis due to broken chemical bonds (Costa *et al.* 2012). Formaldehyde emissions from particleboard decrease with the decreasing ratio of formaldehyde to urea in UF resins, but unfortunately, other physical and mechanical properties are also negatively affected (Hematabadi *et al.* 2012; Ayrilmis *et al.* 2016). The formaldehyde concentration emitted from fiberboard panels can be decreased by adding different modifiers, including acids (Dorieh *et al.* 2018), ammonium (Dorieh *et al.* 2019), and amines (Boran *et al.* 2011; Ghani *et al*. 2018).

In this work, in addition to melamine and PVOH, an adipic acid dihydrazide as a modifier was utilized to improve the properties of UF resin and control free formaldehyde. An adipic acid dihydrazide with a symmetrical bifunctional structure can be acylated with aldehydes due to its active chemical properties, and it serves as a formaldehyde scavenger (Tao *et al.* 2018). The UF resin was modified by melamine, PVOH, and adipic acid dihydrazide. The free formaldehyde content in the UF resin with three modifiers added at different amounts and stages was studied. The optimal addition amount and stage of each modifier were used to synthesize a comprehensive-modified UF resin (CUF). The content of formaldehyde emission in UF resin and CUF resin was measured. Fourier transform infrared spectroscopy (FTIR) and thermogravimetric analysis (TGA) were used to characterize the property and structure of resins.

EXPERIMENTAL

Materials

Formaldehyde solution (37%), urea, sodium hydroxide, ammonium chloride, and formic acid were AR grade and purchased from Sinopharm Chemical Reagent Co., Ltd, Shanghai, China. Melamine was CP grade and purchased from Sinopharm Chemical Reagent Co., Ltd, Shanghai, China. Polyvinyl alcohol was AR grade and provided by Xilong Chemical Co., Ltd, Shantou, China. Adipic acid dihydrazide was AR grade from Tianyi Chemical Materials Ltd, Guanzhou, China.

Preparation of UF Resin

The UF resin with a formaldehyde/urea (F/U) molar ratio of 1.22:1 was synthesized by a traditional process (Zhang *et al.* 2013a; Luo *et al.* 2015). In the first stage, the formaldehyde solution was added to a four-necked flask and heated to 40 °C. The pH of the reaction system was adjusted to 8.0 to 8.5 with 3 M sodium hydroxide solution, and the first section of urea (U_1) was added at a F/U_1 ratio of 2:1. The temperature was gradually increased to 90 °C and kept for 60 min. During the second stage, the pH was adjusted to 5.0 to 5.5 with formic acid, and condensation of the reaction system was continued until the turbidity point. In the third stage, the pH was adjusted to 7.5 to 8.0 with 3 M sodium hydroxide solution. After that, the temperature was decreased to 75 to 80 °C, and the second section of urea (U_2) was added at a F/(U_1+U_2) molar ratio of 1.22:1. The temperature was maintained at 75 to 80 °C for a certain time before cooling to 40 °C.

Preparation of Modified UF Resin

Modifiers included melamine, polyvinyl alcohol, and adipic acid dihydrazide. Each modifier, accounting for 0.5%, 1%, 3%, and 6% of the mass of urea, was added in the first alkaline reaction stage, denoted as XUF0.5% resin, XUF1% resin, XUF3% resin, and XUF6% resin, respectively (Luo *et al.* 2015). The synthetic proportions are listed in Table 1. Modifier, accounting for 3% of the mass of urea, was added in the three reaction stages of alkaline, acidic, and alkaline, respectively. Modifier was added in the first stage (first alkaline stage), denoted as XUF_1 resin; modifier was added in the second stage (acidic stage), denoted as XUF_2 resin; and modifier was added in the third stage (second alkaline stage), denoted as XUF_3 resin (Zhang *et al.* 2013a). Besides, X represented M, P, and A, respectively when modifier added was melamine, polyvinyl alcohol, and adipic acid dihydrazide. The synthetic proportion is listed in Table 2.

Table 1. Urea-formaldehyde Resin with Different Amounts of Modifier

M/U Mass Ratio[a] (%)	Mass of Modifier (g)	Mass of U_1 (g)	Mass of U_2 (g)	Total Amount (g)	Mass of F (mL)
0	0.00	87.50	64.25	151.75	250
0.5	0.76	85.74	64.25	151.75	250
1	1.52	85.98	64.25	151.75	250
3	4.55	82.95	64.25	151.75	250
6	9.10	77.40	64.25	151.75	250

[a]M/U Mass Ratio is the mass ratio of modifier to urea in the modified UF resin

Table 2. Urea-formaldehyde Resin with Modifier Added in Different Stages

Adding Stage	First Stage	Second Stage	Third Stage
U_1 (g)	82.95	82.95	82.95
Modifier (g)	4.55	4.55	4.55
U_2 (g)	64.25	64.25	64.25
Total Mass (g)	151.75	151.75	151.75

Physicochemical Property of the Resin Measurement

The solids content of the resin was determined based on an oven-drying method. Approximately 1 g of resin was placed into a constant temperature oven for 2 h at 120 °C. The curing time was measured with the ammonium chloride solution. Next, 50 g of resin and 2 mL of ammonium chloride solution (25%) were added to the conical flask and stirred for 2 min; 10 g of the sample was moved into a tube, which was placed in a short-necked flask containing boiling water (started the time). The sample was stirred quickly until the stir bar suddenly failed to lift (stopped the time). In this way, the time was recorded. The viscosity of the resin was measured using the NDJ-5S digital viscometer provided by Shanghai Jitai Electronic Technology Co., Ltd., Shanghai, China. Beside, each experiment was repeated 3 times.

Free Formaldehyde Content Measurement

The free formaldehyde and hemiacetal reacted with excess sodium sulfite solution at 0 °C to form hydroxymethyl sulfonate. The residual sodium sulfite solution was titrated with an iodine solution. Next, the hydroxymethyl sulfonate was decomposed with sodium carbonate solution to obtain the sodium sulfite, and the obtained sodium sulfite was decomposed with iodine solution. The free formaldehyde content was calculated from the volume of the iodine solution consumed by the sodium sulfite obtained by decomposition of hydroxymethyl sulfonate. Beside, each experiment was repeated 3 times.

Formaldehyde Emission Measurement

The formaldehyde emission from prepared resin was estimated by the diffusion method. The experimental device is shown in Fig. 1. The resin was placed in a petri dish in a 20 L sealed glass container. The closed glass container was placed in a chamber maintained at 25 °C and 60%. Before starting the experiment, nitrogen was passed through the glass container at 200 mL/min for 100 min. The formaldehyde emission was tested every 10 min with a measurement time of 2 min until the formaldehyde emission was steady. Beside, each experiment was repeated 3 times.

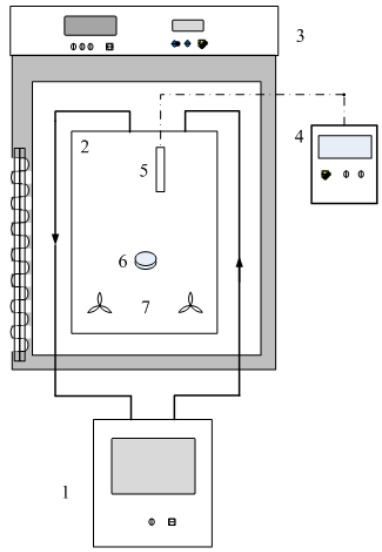

Fig. 1. The schematic diagram of the experimental system. 1: Interscan 4160, 2: Sealed glass capsule, 3: Constant temperature and humidity chamber, 4: Hygrothermograph, 5: Temperature and humidity sensor, 6: Petri dish, 7: Fans

FTIR Analysis of the Resin

FTIR spectroscopy (IS50 spectrometer, Thermo Electron Corporation, Waltham, MA, USA) was used for testing the functional groups of the resins. The spectra were obtained over the range of 400 to 4000 cm^{-1} with a 4 cm^{-1} resolution.

Thermal Stability Analysis of the Resin

Thermal stability analysis was carried out using a TGA1550 thermogravimetric analyzer (Shanghai Yingnuo Precision Instrument Co., Ltd., Shanghai, China). Approximately 7 mg of sample was placed in the crucible over a temperature range 25 to 600 °C at a heating rate of 10 °C/min under a nitrogen flow rate of 50 mL/min.

RESULTS AND DISCUSSION

Effect of Addition Amount of Modifier on Physicochemical Properties of the Resins

The UF resin was modified by melamine, PVOH, and adipic acid dihydrazide. Tables 3 to 5 show the physicochemical properties of blank UF resin and modified resin.

Effect of addition amount of melamine (M) on physicochemical properties of the resins

As shown in Table 3, after the addition of melamine to UF resin, the curing time of the resin increased, whereas the solid content and viscosity did not increase obviously. The melamine containing six reactive functional groups combines with more formaldehyde molecules to prompt the reactivity, and the curing time increases correspondingly (Lei and Frazier 2015). As the melamine was increased, the curing time of MUF resin was gradually shortened. This result indicates that the increased amount of melamine reduces the hydroxymethyl content and increases the hydroxymethyl-melamine content in MUF resin, which gradually seals off the hydrophilic groups and thus accelerates the curing rate of MUF resin (Jahromi 1999).

Table 3. Properties of the Resins with Different Melamine Amounts

Resins	Solid Content (%)	Curing Time (s)	Viscosity (mPa·s)
UF	51.5±1.3	62±2	18±3
MUF0.5%	50.7±1.3	78±4	18±3
MUF1%	51.4±1.4	75±3	20±4
MUF3%	52.4±1.8	72±3	20±3
MUF6%	51.6±1.7	71±2	20±4

Effect of addition amount of polyvinyl alcohol (P) on physicochemical properties of the resins

Table 4 shows that there was no obvious relationship between the curing time and the PVOH content. The solid content of PUF resins gradually increased from 54.1% to 54.4% as the mass ratio of PVOH/U increased from 0.5% to 3%, and then decreased to 50.6% when the mass ratio of PVOH/U was further increased to 6%. This result is attributed to the fact that the excess PVOH is not able to participate in the polycondensation reaction with the resin due to its large viscosity (Zhang *et al.* 2005; Huang *et al.* 2006). Moreover, the viscosity of PUF resin increased sharply with the addition of PVOH, as PVOH contains a large number of hydroxyl groups that react with formaldehyde to produce polyvinyl formal, and both polyvinyl alcohol and polyvinyl formal are viscous (Zhang *et al.* 2015).

Table 4. Properties of the Resins with Different PVOH Amounts

Resins	Solid Content (%)	Curing Time (s)	Viscosity (mPa·s)
UF	51.5±1.3	62±2	18±3
PUF0.5%	54.1±1.6	54±2	19±3
PUF1%	54.2±1.4	50±2	30±4
PUF3%	54.4±1.5	65±3	91±5
PUF6%	50.6±1.2	48±2	325±10

Effect of addition amount of adipic acid dihydrazide (A) on physicochemical properties of the resins

As shown in Table 5, the addition of adipic acid dihydrazide caused an increase of solids content of the resins and a decrease of initial viscosity of the resins. The AUF6% resin had the largest solid content of 54.3%, while the other three AUF resins had the same solids content of 53.2%. Moreover, with a symmetrical bifunctional structure, the increase of adipic acid dihydrazide content did not affect the viscosity of AUF resins (Xu *et al.* 2016). Thus, the addition of different amounts of melamine, PVOH, or adipic acid dihydrazide had different effects on the physicochemical properties of the resins regarding curing time, viscosity, or solid content.

Table 5. Properties of the Resins with Different Adipic Acid Dihydrazide Amounts

Resins	Solid Content (%)	Curing Time (s)	Viscosity (mPa·s)
UF	51.5±1.3	62±2	18±3
AUF0.5%	53.2±1.4	73±3	14±1
AUF1%	53.2±1.6	42±2	15±2
AUF3%	53.2±1.5	70±3	15±2
AUF6%	54.3±2.0	52±2	15±3

Effect of Addition Amount of Modifier on the Free Formaldehyde Content of

Resins

The free formaldehyde content is one of the most important factors to evaluate the properties of UF resin. Free formaldehyde released from the UF resin used for the wood-based panels in domestic environments causes great harm to human health. Therefore, it is necessary to control the free formaldehyde content in UF resin by adding modifiers. The effects of addition amount of melamine, PVOH, and adipic acid dihydrazide on the free formaldehyde content of UF resin are shown in Fig. 2.

The free formaldehyde content of blank UF resin was 0.44%. With the addition of melamine from 0.5% to 6%, the free formaldehyde content in MUF resin decreased gradually from 0.38% to 0.31%; three -NH_2 groups in melamine react rapidly with free formaldehyde to produce hydroxymethyl-melamine, which is associated with forming a three-dimensional network (Yuan *et al.* 2015). With the addition of PVOH, the free formaldehyde content in PUF resin decreased from 0.43% to 0.36% when the mass ratio of PVOH/U increased from 0.5% to 3%, and thereafter the free formaldehyde content increased with further increases in the mass ratio of PVOH/U from 3% to 6%. PVOH reacts with formaldehyde to generate polyvinyl acetal (Liu *et al.* 2018b). However, the ability of the resin to lower the free formaldehyde content is reduced by inadequate reactions or the small solubility of PVOH when the addition amount of PVOH is excessive (Pan *et al.* 2014). The free formaldehyde content decreased after adding adipic acid dihydrazide to the resin. The resin with adipic acid dihydrazide added with the mass ratio of A/U of 1% or 6% had the free formaldehyde content of 0.36%, which was reduced by 18.1% compared with the blank UF resin. Hence, melamine had the greatest effect on reducing the free formaldehyde content. The ability of adipic acid dihydrazide for decreasing the free formaldehyde content in the resin was lower than that of the melamine. The free formaldehyde in PUF resin decreased only when the proper PVOH amount was added.

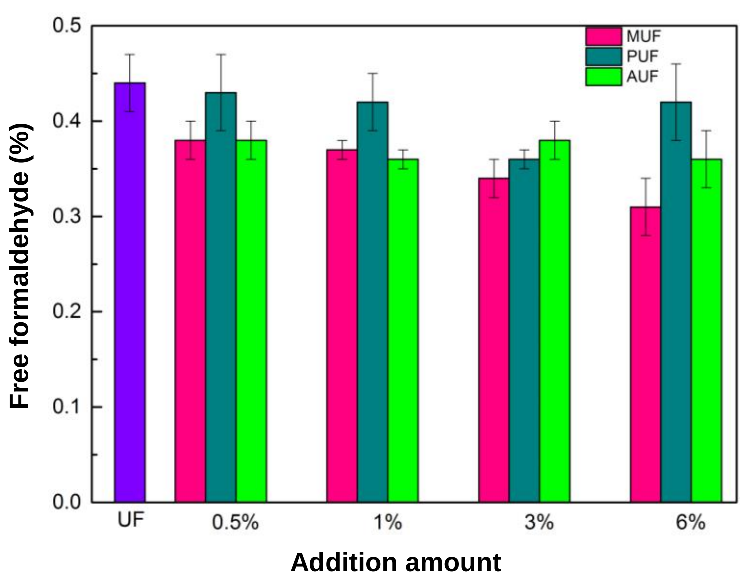

Fig. 2. Free formaldehyde content in the resins with different modifiers

Effect of Addition Stage of Modifier on Physicochemical Properties of the Resins

The UF resin was separately modified with melamine, polyvinyl alcohol, and adipic acid dihydrazide in the three reaction stages of alkaline, acidic, and alkaline, respectively. The mass ratio of each modifier to urea was 3%. The physicochemical properties of blank UF resin and the modified resins are shown in Tables 6 to 8.

Effect of addition stage of melamine (M) on physicochemical properties of the resins

As shown in Table 6, the melamine added in any stage did not improve the solid content of resins. The curing time of the resin increased gradually with the delay of melamine addition stage. The curing time of MUF_3 resin was almost equal to twice that of UF resin, whereas the viscosity of MUF_3 resin was lower than that of UF resin. The buffer performance of melamine makes the pH of the modified resin decrease slowly (Paiva *et al.* 2012). The reaction activity of melamine with urea-formaldehyde resin decreases from the delay of the melamine addition stage, so a longer time or higher temperature is required to cure the resin (Zhang *et al.* 2013a).

Table 6. Properties of the Resins Modified by Melamine

Resins	Solid Content (%)	Curing Time (s)	Viscosity (mPa·s)
UF	51.5±1.3	62±2	18±3
MUF_1	52.4±1.8	72±3	21±3
MUF_2	53.3±1.6	89±4	22±3
MUF_3	51.7±1.4	120±4	13±1

Effect of addition stage of polyvinyl alcohol (P) on physicochemical properties of the resins

Table 7 shows that the solid content of the resin modified by PVOH added in different stages was slightly increased compared with UF resin. The addition of PVOH in the first alkaline stage enhanced the viscosity of the resin, and the viscosity of the resin decreased gradually as the addition stage was delayed, due to the later addition stage resulted in the less reaction of PVOH in the solution. In addition, the addition of PVOH in the first or second alkaline stage lengthened the curing time, while the addition of PVOH in the acid stage shortened it.

Table 7. Properties of the Resins Modified by PVOH Added in Different Stages

Resins	Solid Content (%)	Curing Time (s)	Viscosity (mPa·s)
UF	51.5±1.3	62±2	18±3
PUF_1	54.4±1.5	65±3	91±5
PUF_2	53.2±1.4	60±2	78±5
PUF_3	54.0±1.7	72±3	26±3

Effect of addition stage of adipic acid dihydrazide (A) on physicochemical properties of the resins

As shown in Table 8, the presence of adipic acid dihydrazide increased the solids content of the resin and decreased the viscosity of the resin. The curing time of AUF_1 or AUF_3 resin was prolonged, and that of AUF_2 resin was shortened compared with the UF resin. The reaction of adipic acid dihydrazide with the free formaldehyde is a reversible reaction, and the equilibrium of the reaction shifts to the left under acidic conditions, resulting in releasing more formaldehyde to react with the curing agent (Saleem *et al.*

2013). When the pH of the system decreases, the molecular reactivity increases, and the collision rate accelerates.

Table 8. Properties of the Resins Modified Adipic Acid Dihydrazide Added in Different Stages

Resins	Solid Content (%)	Curing Time (s)	Viscosity (mPa·s)
UF	51.5±1.3	62±2	18±3
AUF_1	53.2±1.5	70±3	15±2
AUF_2	54.8±2.1	54±2	16±3
AUF_3	54.3±1.9	86±4	14±2

Effect of Addition Stage of Three Modifiers on the Free Formaldehyde of Resins

The free formaldehyde contents of resins modified by three modifiers added in three reaction stages are shown in Fig. 3. In the first alkaline addition stage, the melamine was more suitable for reducing the free formaldehyde in UF resin than PVOH and adipic acid dihydrazide. In the acidic addition stage, the adipic acid dihydrazide was superior. In the second alkaline addition stage, the PVOH modified resin had the lowest free formaldehyde content.

Compared with the UF resin, the free formaldehyde content of MUF_1 resin, MUF_2 resin, and MUF_3 resin was reduced by 23%, 16%, and 16%, respectively. One possible reason is that the free formaldehyde content increased with a decrease of the curing reaction of extent. Furthermore, the free formaldehyde content of PUF_1 resin, PUF_2 resin, and PUF_3 resin were decreased by 18%, 14% and 25%, respectively. In addition, with the delay of addition stage of adipic acid dihydrazide, the free formaldehyde content of resins decreased gradually. The free formaldehyde content of resin with adipic acid dihydrazide added in the second alkaline stage was 0.34%. In terms of the formaldehyde content, the PUF_3 resin had the best property. However, other physicochemical properties of resins, such as curing time, solid content and viscosity, also play important roles in determining the resin applicability.

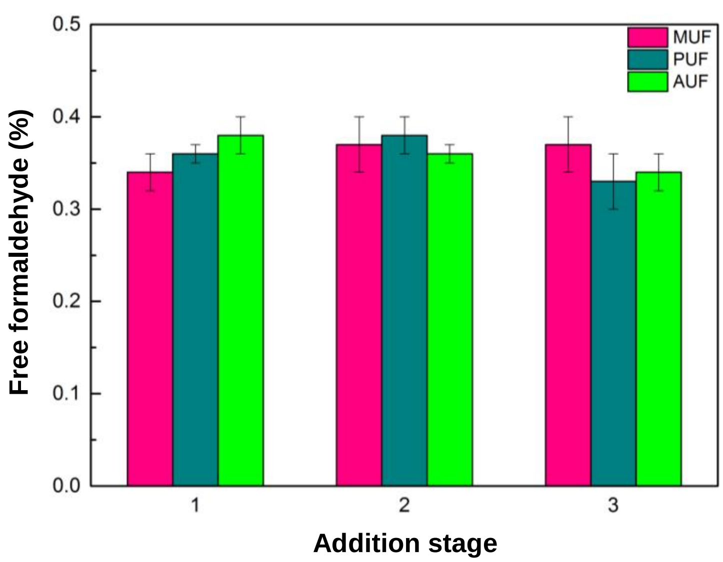

Fig. 3. The free formaldehyde content in the resins modified by different modifiers added in different stages

Comprehensive Effect of Three Modifiers on Properties of the Resins

A comprehensive-modified UF resin (CUF) was prepared by adding 3% melamine and 3% PVOH in the first alkaline stage and 3% adipic acid dihydrazide in the second alkaline stage, and the total mass of modifiers and urea in CUF resin was the same as the total mass of urea in blank UF resin. Figure 4 shows that the free formaldehyde contents in UF resin, MUF_1 resin, PUF_1 resin, AUF_3 resin and CUF resin were 0.44%, 0.34%, 0.36%, 0.34%, and 0.24%, respectively. Furthermore, CUF resin meets the technical requirements of the UF resin standard, as the free formaldehyde in adhesive applied in the wood production should be lower than 0.30%. It was concluded that both the melamine with high functional groups and PVOH presented as the formaldehyde capture agents to react with free formaldehyde, which were added at the first alkaline stage, and adipic acid dihydrazide added at the second alkaline stage plays an active role in reducing free formaldehyde.

To verify the free formaldehyde content results, the formaldehyde emission from prepared resins was tested by the diffusion method. Figure 5 shows the formaldehyde emission of UF resin and CUF resin. The addition of modifiers into UF resin obviously decreased the formaldehyde emission from UF resin. The formaldehyde emission in UF resin and CUF resin were 0.39 mg/g and 0.21 mg/g, respectively, as the equilibrium was reached, which corresponds to the results of free formaldehyde content in resins.

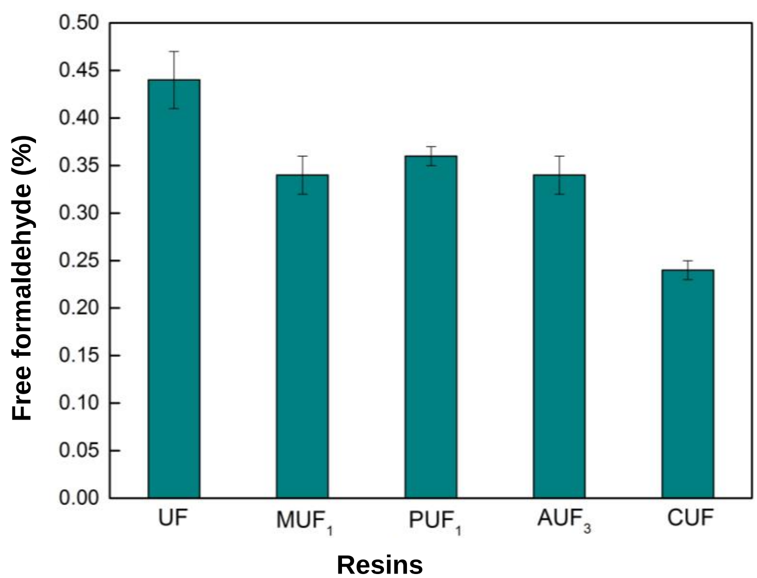

Fig. 4. The free formaldehyde content in different resins

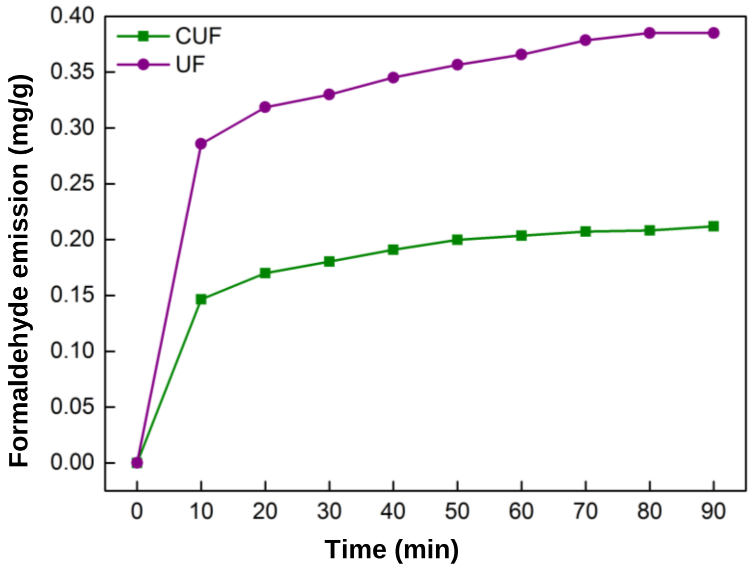

Fig. 5. The formaldehyde emission from UF resin and CUF resin

FTIR Analysis of UF, MUF_1, PUF_1, AUF_3, and CUF Resins

The FTIR spectra of the cured resins are shown in Fig. 6. The broad peak at 3340 cm^{-1} is attributed to the stretching vibration of O-H and N-H bonds (Ong *et al.* 2018). The band at 2956 cm^{-1} is due to the symmetric stretching vibration of $-CH_2$ (Li *et al.* 2009; Li *et al.* 2016). The peak at 1634 cm^{-1} is assigned to powerful adsorption of C=O belonging to primary amides, while the peak at 1551 cm^{-1} is assigned to the C-N stretching of secondary amides (Liu *et al.* 2018a). The C-N stretching of CH_2-N is the adsorption band of the resins, which is found at 1386 cm^{-1}, and the peak at 1252 cm^{-1} is a characteristic of adsorption band of the C-N and N-H in tertiary amine (Luo *et al.* 2015). The band at 1131 cm^{-1} is attributed to the stretching vibration of C-O in aliphatic ether bonds. The peak at 1023 cm^{-1} is a broad-strong peak assigned to the O-H stretching of hydroxymethyl group combined with the C-O stretching of ether bonds (Tejado *et al.* 2007; Wang *et al.* 2017). The hydroxymethyl group and ether bonds are present in all urea-formaldehyde resins, and the addition of modifiers reduces hydroxymethyl groups and ether bonds of the resins. The spectra of all resins had a small band at 899 cm^{-1}, which belongs to flexural vibration of the C-H in unsaturated hydrocarbyl (Yu *et al.* 2018).

The position of characteristic absorption peaks of the resins did not change after mixing modifiers to the resins. In addition, there was no new adsorption band in the infrared spectrum, which could be due to the similar curing reactions of the five resins. The addition of modifiers weakened the absorption intensity of all characteristic adsorption peaks, which indicates that the modifiers reduce the formation of many chemical bonds in the resins, including methylene and ether bonds.

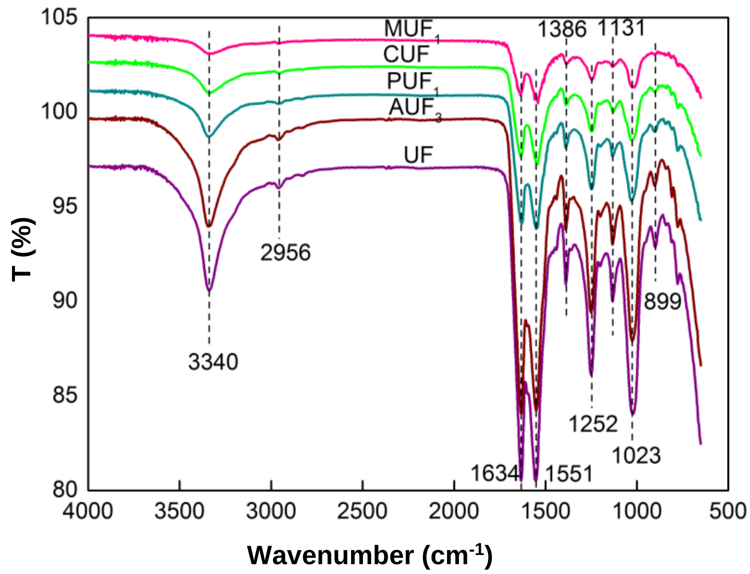

Fig. 6. The FTIR spectra of different resins

Thermal Stability Analysis of UF, MUF_1, PUF_1, AUF_3, and CUF Resins

The thermal degradation curves of the cured resins express the relationship between the weight loss of resins and thermal degradation temperature (Zhang *et al.* 2013b). The addition of comprehensive modifier had a great impact on improving thermal stability of the resin, followed by the melamine, but the presence of PVOH in the first alkaline stage and adipic acid dihydrazide in the second alkaline stage did not improve the thermal stability. As thermosetting polymers, the curing of resins is an exothermal reaction. For UF resin, the exothermic peak could be attributed to the heat released from the polycondensation reaction of primary amino groups of free urea with hydroxymethyl groups (Siimer *et al.* 2003). For modified resins, these exothermic peaks could also be attributed to the heat released from the formation of the branched-type methylene bridge cross-links from free modifiers with hydroxymethyl groups. As shown in Fig. 7, the curve of MUF resin was quite similar to UF resin, whereas the curve peaks of CUF resin moved back. It can be concluded that the addition of modifiers improved the thermal stability of the resin.

The thermal degradation of the resins occurred in three main stages (Fig. 8). The first weight loss stage represents the evaporation of moisture, which occurs from 50 to 200 °C (Siimer *et al.* 2010). The mass loss of UF, MUF_1, PUF_1, AUF_3 and CUF resins in the first weight loss stage were 7.94%, 7.03%, 11.11%, 9.78%, and 5.49%, respectively. The second weight loss stage occurs from 200 to 350 °C, which is due to the degradation of polymer in the adhesive and the disintegration of the polymer structure network (Samaržija-Jovanović *et al.* 2011). The percent of mass loss at second weight loss stage was 69.14%, 62.26%, 71.03%, 70.26%, and 53.54% for UF, MUF_1, PUF_1, AUF_3, and CUF, respectively. In the first two stages, the weight loss rate of CUF resin was the smallest among the five resins, which suggests that the comprehensive modifier improved the thermal stability of the adhesive. The third weight loss stage occurred in the range of 350 to 600 °C. The mass loss in this stage includes the decomposition of the methylene bond in the adhesive, releasing the free formaldehyde. The mass loss of UF, MUF_1, PUF_1, AUF_3, and CUF resins in this stage were 8.81%, 11.73%, 9.73%, 9.75%, and 8.3%, respectively.

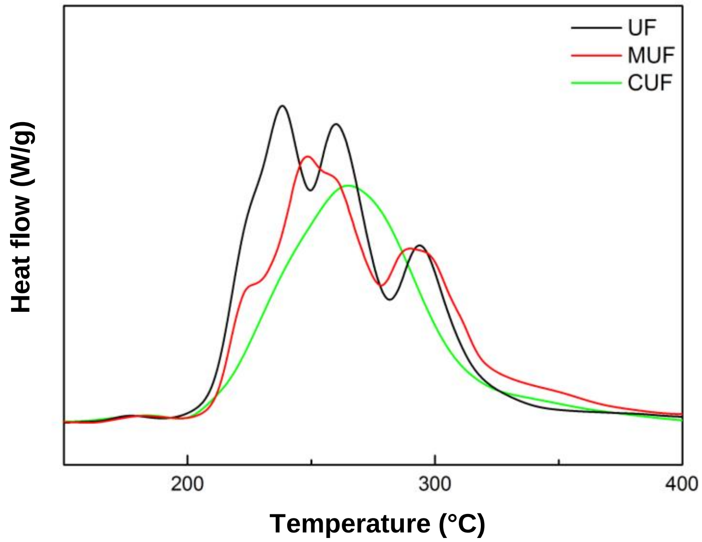

Fig. 1. The curves of exothermic peaks of the resins

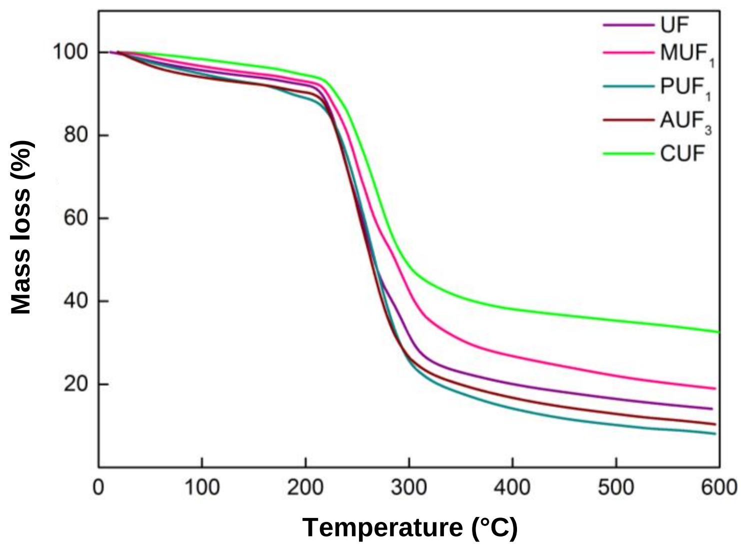

Fig. 8. The curves of thermal degradation of different resins

CONCLUSIONS

1. The addition of melamine, polyvinyl alcohol, and adipic acid dihydrazide as modifier was beneficial for reducing free formaldehyde and improving the performance of urea formaldehyde (UF) resins.
2. When modifiers were added in the same stage, for melamine, UF resin with 3% melamine gave the best physicochemical properties, while UF resin with 6% melamine yielded the lowest free formaldehyde content (0.31%). For polyvinyl alcohol, UF resin with 3% polyvinyl alcohol had the best physicochemical properties and yielded the lowest free formaldehyde content (0.36%). For adipic acid dihydrazide, UF resin with 6% adipic acid dihydrazide had the best physicochemical properties and yielded the lowest free formaldehyde content (0.36%).

3. When modifiers were added with an equal amount in different stages, the addition of melamine, polyvinyl alcohol, and adipic acid dihydrazides yielding the lowest free formaldehyde content occurred in first stage, third stage, and third stage, respectively; the addition of melamine, polyvinyl alcohol, and adipic acid dihydrazide with the best physicochemical properties occurred in second stage, first stage, and third stage, respectively.
4. The UF resin with comprehensive modifier containing the optimal amount of each component had the lowest free formaldehyde of 0.24%. The formaldehyde emission of CUF resin was 0.21 mg/g. Furthermore, the modifiers did not change the position of adsorption characteristic peaks. Thermogravimetric analysis confirmed that the thermal stability of UF resin was enhanced by the comprehensive modifier.
5. This work may be of interest to people working in the field of urea-formaldehyde resin focusing on reducing the free formaldehyde content.

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