

Effects of Melamine Addition Stage on the Performance and Curing Behavior of Melamine-Urea-Formaldehyde (MUF) Resin

Jizhi Zhang, Xiaomei Wang, Shifeng Zhang, Qiang Gao,* and Jianzhang Li*

Three formaldehyde-based resins were prepared: urea-formaldehyde (UF) resin without melamine modifier (named UF0 resin) and melamine-urea-formaldehyde (MUF) resins with melamine modifier added at two different synthesis stages (named MUF1 resin and MUF2 resin). The effects of the melamine addition stage on the performance and curing behavior of MUF resin were studied. Three-ply plywood bonded by these adhesives was manufactured, and its bond strength and formaldehyde emissions were measured. The curing behavior and functional groups of the resins were measured by differential scanning calorimetry (DSC) and Fourier transform infrared spectroscopy (FT-IR). Their activation energies were calculated using the Kissinger equation and the Kissinger-Akahira-Sunose (KAS) method. The results showed that melamine addition and the addition stage had significant influences on the characteristics of resins. The plywood bonded by MUF1 resin showed the highest bond strength and the lowest formaldehyde emissions. The activation energies of UF0 resin, MUF1 resin, and MUF2 resin were significantly different; the values were 99.44 kJ/mol, 105.75 kJ/mol, and 150.65 kJ/mol, respectively. According to the FT-IR spectra, the amount of methylene and methylene-ether bonds in cured MUF2 resin was the lowest, which meant that the cross-linking degree of MUF2 resin was the lowest.

Keywords: Melamine-urea-formaldehyde resin; Melamine addition stage; Performance; Curing behavior; Activation energy

Contact information: College of Materials Science and Technology, Beijing Forestry University, 100083 Beijing, People's Republic of China;

* Corresponding author: gao200482@163.com, lijianzhang126@126.com.

INTRODUCTION

Urea-formaldehyde (UF) resins are used primarily as wood adhesives in the manufacture of plywood, medium density fiberboard (MDF), particleboard, and other non-structural wood products. UF resins have the advantages of high reactivity, fast curing, water solubility, and low price. However, they have poor water resistance and emit formaldehyde, which limits their application (Myers 1982, 1984, 1990; Dunky 1998). These issues have stimulated efforts to improve the performance of UF resins. Lowering the molar ratio of formaldehyde to urea is one of the most effective ways to reduce the formaldehyde emission, but the bond strength and water resistance of panels also deteriorate when this is done (Meyer *et al.* 1980; Pizzi *et al.* 1994; Ebewele *et al.* 1994; Bono *et al.* 2003; Fan *et al.* 2006).

The performance of UF resins can also be improved by introducing components such as melamine to modify it. Melamine has the potential to improve water resistance

and reduce formaldehyde emissions due to its high functionality, its stable molecular structure in comparison to urea, and its reaction with formaldehyde, which is similar to that of urea (No and Kim 2004, 2007; Hse *et al.* 2008; Hse 2009). However, melamine is much more expensive than urea; thus, low levels of melamine are used to modify UF resins to reduce formaldehyde emissions and improve water resistance.

The performance of MUF resins is closely related to the resin formulation. Previous research has shown that the synthesis parameters have significant effects on the resin properties, and much attention has been paid to molar ratio, melamine content, pH value, and catalysts. However, studies on the effects of the melamine addition stage on resin synthesis and performance have been limited. Shiau and Smith (1985) indicated that melamine addition is most effective in the methylation step of an alkaline-acidic process, and the amount of melamine incorporated into a UF resin is preferably at least 2% added in two stages, or at least 4% added in a single stage, for a substantial reduction in the formaldehyde emissions of particleboards. Studies by Paiva *et al.* (2012) found that the initial acidic stage is the most appropriate for melamine addition in a strongly acidic process and that particleboards produced with resins synthesized with a condensation pH value between 4.5 and 4.7 showed good overall performance, both in terms of internal bond strength and formaldehyde emissions. Xu *et al.* (2009) synthesized four types of MUF resins with melamine added at different stages and investigated the curing behavior and the adhesion performance of resins by dynamic mechanical thermal analysis (DMTA). They reported that, by adding melamine initially with the urea and formaldehyde, the cured resin showed the lowest thermal stability, rigidity ($\Delta E'$), temperature of $\tan\delta$ maximum ($T_{\tan\delta}$), wet shear strength, and pH value. However, by adding formaldehyde and melamine in two stages, the resin showed the highest wet shear strength.

Even though these authors investigated the effects of the melamine addition stage on resin synthesis and adhesion performance, studies on the curing activation energy of MUF resins synthesized with different melamine addition stages have not been reported. Therefore, this study was conducted to investigate the influence of the melamine addition stage on the curing behavior of MUF resins using DSC and FT-IR spectroscopy. The activation energy was calculated using the Kissinger equation and the Kissinger-Akahira-Sunose (KAS) method. The performance of MUF resins was investigated by measuring the bond strength and formaldehyde emissions of plywood bonded by these resins. The results of this investigation are expected to help develop new, environmentally friendly MUF resins and contribute to the production of plywood, both from a theoretical and a practical point of view.

EXPERIMENTAL

Materials

Formaldehyde (HCHO, 37 wt% aqueous, AR) and formic acid (HCOOH, AR) were purchased from Xilong Co., China. Solid urea (CON₂H₄) and melamine (C₃H₆N₆) were industrial reagents obtained from Lanyi Chemical Co., China. Sodium hydroxide (NaOH), ammonium chloride (NH₄Cl), and all other chemicals used were of AR grade from Beijing Chemical Works, China. For convenience, hereafter when referring to molar ratios, the letters F, U, and M may be used as abbreviations for formaldehyde, urea, and melamine, respectively.

UF Resin and MUF Resins Synthesis and Measurement

All resins were synthesized in the laboratory. Unmodified UF resin was synthesized as a control. The synthesis of UF resin, on which syntheses of MUF resins were based, was a typical three-step procedure (alkaline-acidic-alkaline). In the first stage, formaldehyde (F=446.0g) was poured into a three-necked flask, followed by the first urea portion ($U_1=168.4\text{g}$) at an F/U ratio of 2.0. The reaction mixture was blended using a stirrer. The pH value was adjusted to 8.5 to 9.0 with sodium hydroxide (30 wt%). Within 50 to 60 min, the temperature was gradually increased to 90 °C and maintained at this temperature for 1 h. During the second stage, the pH value was adjusted to 4.8 to 5.0 with formic acid (30 wt%) for condensation. The temperature was maintained at 90 °C until the end point was reached. The end point was determined by the cloudy appearance when dropping the solution mixture into a beaker of water at 20 °C. In the third stage, the pH value was adjusted to 7.5 to 8.0 with sodium hydroxide (30 wt%). The second urea portion ($U_2=42.1\text{g}$) was added, attaining a F/U ratio of 1.6. The temperature was decreased to 70 to 80 °C and maintained for 40 min. After that, the temperature was decreased to 60 to 70 °C and the third urea portion ($U_3=95.6\text{g}$) was added, with a final F/U ratio of 1.1. The reaction mixture was maintained at 60 to 70 °C for 30 min; then, the pH value was adjusted to 7.5 to 8.0, and the mixture was cooled to ambient temperature. UF resin was obtained and labeled UF0.

Based on UF resin, MUF resins were synthesized with a F/(U+M) ratio of 1.1 by adding melamine in the primary stage (with the addition of the first portion of urea, $F/(U_1+M)=2.0$) and in the late stage (with the addition of the second portion of urea, $F/(U_1+U_2+M)=1.6$) and labeled MUF1 and MUF2, respectively. In all cases, melamine was added in a single stage, and the amount of melamine was 10% by weight of urea (about 3.8% by weight of the resin mixture). As a curing agent, 1% ammonium chloride was used in all of the resins.

Characteristics of the resins were determined. The free formaldehyde content of the resins was measured using the ammonium chloride method. Five grams of resin was dissolved in 50 mL of distilled water in a 250 mL Erlenmeyer flask. Eight drops of bromocresol green-methyl red mix indicator were added and the mixture was carefully neutralized by titration with hydrochloric acid. Then 10 mL of 10% ammonium chloride solution and 10 mL of 1 mol/L sodium hydroxide solution were added to the mixture quickly. The mixture was sealed and stirred and then kept at 20 to 25 °C for 30 min. The resulting mixture was slowly titrated with the 1 N hydrochloric acid. The solids content was determined by evaporation of volatiles in 2 g of resin for 3 h at 120 °C. The curing time was determined at 100 °C after the addition of catalyst. Viscosity was measured with a NDJ-5S rotational viscometer at a constant temperature of 20 °C.

DSC Measurement

DSC analysis with a TA Instruments model Q2000 was used to evaluate the curing behavior of the MUF resins with four heating rates (5 K/min, 10 K/min, 15 K/min, and 20 K/min). Resin curing was catalyzed with 1% ammonium chloride (20 wt%). For each scan, about 8 to 10 mg of freeze-dried MUF sample was added to an aluminum pan. The pan was sealed and then heated from 30 °C to 160 °C in a 50-mL/min flow of N_2 at each heating rate. For each heating rate, the onset temperature, peak temperature, and heat of reaction were recorded, and an average value from at least two replications is presented.

Curing Kinetics Method

Based on dynamic DSC scans, various methods have been developed for the calculation of the activation energy for the curing reaction of resins. In this work, the activation energy was calculated with the Kissinger equation (Kissinger 1957) and the isoconversional method of KAS (Kissinger 1957; Sunose and Akahira 1971). For each DSC curve, the heat of the curing reaction was calculated as the total area under the exothermal curve, based on the extrapolated baseline. The degree of conversion (α) at a certain curing time (t) was calculated according to Eq. 1.

$$\alpha = \frac{\Delta H_t}{\Delta H_{Total}} \quad (1)$$

The equation for reaction rate, employed to study the kinetics of resin curing, can be expressed as:

$$\frac{d\alpha}{dt} = A \exp\left(-\frac{E_a}{RT}\right) f(\alpha) \quad (2)$$

By introducing the heating rate $\beta = dT/dt$ (K/min) into Eq. 2, namely,

$$\beta \frac{d\alpha}{dT} = A \exp\left(-\frac{E_a}{RT}\right) f(\alpha) \quad (3)$$

The integral form of the rate equation can be expressed as follows:

$$g(\alpha) = \int_0^\alpha \frac{d\alpha}{f(\alpha)} = \int_0^t A \exp\left(-\frac{E_a}{RT}\right) dt \quad (4)$$

The Kissinger equation was used to determine the activation energy of the resins. The equation can be expressed as,

$$-\ln\left(\frac{\beta}{T_p^2}\right) = \frac{E_a}{RT_p} - \ln\left(\frac{AR}{E_a}\right) \quad (5)$$

where β is the heating rate (K/min), T_p is the peak temperature (K), R is the gas constant (8.314 J/mol/K), E_a is the activation energy (kJ/mol), and A is the pre-exponential factor (1/s). The activation energy can be calculated from the slope, and the pre-exponential factor can be found from the intercept of the plot of $-\ln(\beta/T_p^2)$ versus T_p^{-1} .

The single activation energy obtained from the Kissinger equation does not offer complete information about the characteristics of the curing process. Therefore, the KAS kinetic method was employed to obtain the activation energy at a given degree of conversion, which is described by Eq. 6. The basic assumption of the model-free isoconversional method is that the reaction rate at a constant rate of conversion is only a function of temperature (Vyazovkin and Sbirrazzuoli 1996). The model-free kinetics method follows every point of conversion, obtaining the activation energy at each point. It is suitable for the characterization of the curing reaction of resins.

$$-\ln\left(\frac{\beta}{T^2}\right) = \frac{E_a}{RT} - \ln\left(\frac{AR}{E_a g(\alpha)}\right) \quad (6)$$

where T is the temperature at a given degree of conversion (K). In both cases, the conversion-dependence function ($f(\alpha)$ or $g(\alpha)$) is not required. However, this equation does not give any information about reaction order.

FTIR Analysis

FTIR spectroscopy (Nicolet FT-IR spectrometer series 6700) in transmittance mode was used for the characterization of the functional groups of the MUF resins. All samples were heated at 120 °C for 3 h and then ground to powder. KBr pellets with 1 mass% of the powdered material were produced. The spectra were obtained by 32 scans of the spectral area from 4000 to 400 cm^{-1} with a resolution of 4 cm^{-1} .

Preparation and Performance Measurement of Plywood

Three-ply plywood was manufactured from poplar veneers with dimensions of 410 mm \times 410 mm \times 1.5 mm on a laboratory hot press under the following conditions: the adhesive formulation was 100 parts resin, 1 part ammonium chloride, and 20 parts wheat flour, the glue spread amount was approximately 280 to 300 g/m^2 (double glue line), the hot press temperature was 120 °C, the hot press pressure was 1.1 MPa, and the hot press time was 6 min. The bond strength (soaked in 63 °C water for 3 h) and formaldehyde emissions of plywood were tested according to Chinese National Standard GB/T 17657-1999. The formaldehyde emissions of plywood were determined using the desiccator method. Ten specimens (150 mm \times 50 mm) per panel were placed in a 9-11 L sealed desiccator that contained a crystallizing dish (12 cm \times 6 cm) holding 300 mL of distilled water. After being closed, the desiccator was kept at 20 ± 2 °C for 24 h. The dish was then removed and the water was analyzed for formaldehyde content. The results were expressed as mg/L of formaldehyde in the air.

RESULTS AND DISCUSSION

Performance of MUF Resins

Some technical characteristics of the UF and MUF resins are presented in Table 1. In addition, the bond strength and formaldehyde emissions of plywood bonded by the resins are shown in Fig. 1.

Table 1. Characteristics of the UF and MUF Resins

Parameters	UF0	MUF1	MUF2
Free formaldehyde content [%]	0.38 ± 0.04	0.23 ± 0.02	0.22 ± 0.03
Solids content [%]	56.6 ± 2.0	55.8 ± 1.5	56.3 ± 1.9
Curing time [s]	96 ± 3	120 ± 3	260 ± 5
Viscosity [mPa·s]	235 ± 10	200 ± 10	275 ± 10

As can be seen in the table, the solids content and density of all resins were quite similar. Compared to UF0 resin, the free formaldehyde content of MUF resins decreased

by approximately 40% with the addition of low levels of melamine, regardless of the addition stage. This can be explained by melamine's high functionality and the fact that the incorporation of formaldehyde into melamine occurs more easily and completely than its incorporation into urea (Kim *et al.* 2006). However, the curing time of MUF resins was longer than that of UF0 resin and the curing time of MUF2 resin was longer than that of MUF1 resin. One possible reason for this is the slower decrease in pH value of MUF resins due to the buffer capacity of melamine. As the melamine addition stage was delayed, the reactivity of melamine with the UF-based resin decreased and the amount of free melamine increased. Therefore, a higher temperature or longer time was needed to cure MUF resins.

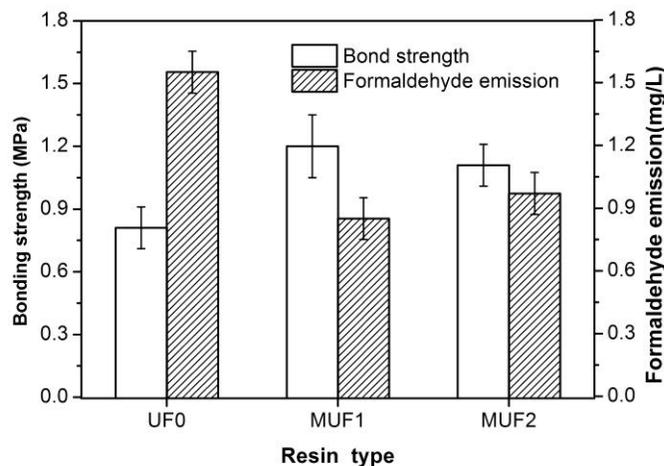


Fig. 1. Bond strength and formaldehyde emissions of plywood bonded by resins

The effects of melamine addition stage on the mechanical and physical properties of MUF resins in terms of bond strength and formaldehyde emissions are shown in Fig. 1. The bond strengths of plywood bonded by UF0 resin, MUF1 resin, and MUF2 resin after soaking in 63 °C water for 3 h were 0.81 MPa, 1.23 MPa, and 1.10 MPa, respectively. The MUF resins endowed plywood with higher bond strength than UF0 resin. The addition of melamine to UF resin enhanced the bond strength, and the efficiency decreased when the addition stage was delayed. One possible reason is that the content of free melamine increased with the delayed melamine addition stage, resulting in a slower decrease in pH value of MUF resins due to the buffer capacity of melamine. Therefore, the degree of the curing reaction of MUF resins decreased and the amount of cross-linked structures in the cured resins also was reduced, leading to deterioration of bond strength. Improvements in the degree of curing reaction, higher curing temperature, and/or longer curing time are necessary for plywood to achieve higher bond strength. The formaldehyde emissions of plywood were 1.56 mg/L, 0.86 mg/L, and 0.98 mg/L for UF0 resin, MUF1 resin, and MUF2 resin, respectively. Plywood with MUF1 resin yielded the lowest formaldehyde emissions, at 45%, which was less than UF0 resin. According to Chinese National Standard GB/T 9846.3-2004, the formaldehyde emissions of plywood manufactured with MUF resins can reach E1 grade ($0.5 \text{ mg/L} < E1 \leq 1.5 \text{ mg/L}$), while UF0 resin is E2 grade ($1.5 \text{ mg/L} < E2 \leq 5.0 \text{ mg/L}$). It should be noted that the addition of melamine to UF resin reduced the formaldehyde emissions of plywood significantly. This can be explained as follows: the bonds of a methylene carbon to an amide group from a melamine ring are more stable than the bonds to nitrogen from urea, which are quite

susceptible to hydrolysis and can release formaldehyde due to a reverse methylation reaction. Therefore, MUF resins yield lower formaldehyde emissions. The formaldehyde emissions of plywood bonded by MUF resins increased as the addition stage was delayed. A possible reason is that the degree of the MUF2 resin curing reaction was lower than that of MUF1 resin, which is supported by the DSC analysis and FT-IR spectra. In general, a lower curing degree of the adhesive leads to greater formaldehyde emissions and lower bond strength.

Overall, the addition of low levels of melamine to UF resin for bonding plywood enhanced the bond strength and reduced the formaldehyde emissions. The plywood bonded by MUF1 resin yielded the highest bond strength and the lowest formaldehyde emissions.

Curing Behavior of MUF Resins

Figure 2 shows typical DSC curves of the UF resin and MUF resins at a heating rate of 10 K/min in the temperature range of 50 to 160 °C. As thermosetting polymers, the curing of UF resin and MUF resins was an exothermal reaction.

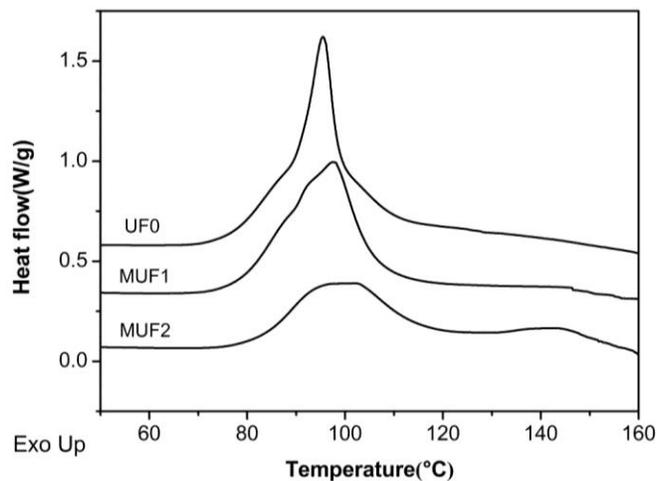


Fig. 2. DSC curves of the UF resin and MUF resins at a heating rate of 10 K/min

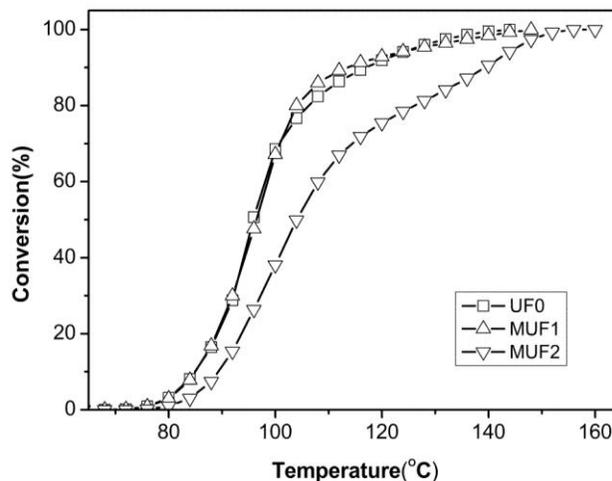


Fig. 3. The conversion degree of the UF resin and MUF resins at a heating rate of 10 K/min

An obviously exothermic peak was observed during the curing process. For UF0 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 (-CH₂OH) (Siimer *et al.* 2003). For MUF 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 melamine with hydroxymethyl groups. With an increase in free melamine content, the curing process of MUF resins proceeded in larger temperature ranges than UF0 resin, especially MUF2 resin. Smooth exothermic peaks followed by a plateau were observed. This result suggested that the reactivity of the curing reaction of MUF resins declined as the melamine addition stage was delayed. A post-curing reaction took place at higher temperatures in the case of MUF2 resin. As shown in Fig. 3, the conversion degree of MUF1 resin was quite similar to UF0 resin, whereas the conversion degree of MUF2 resin was the lowest among the resins. It can be concluded that the curing process of MUF2 resin is prolonged and a high temperature is necessary.

Table 2. Curing Parameters for Resins at a Heating Rate of 10 K/min

Resin type	Onset temperature [°C]	Peak temperature [°C]	Heat of reaction [J/g]
UF0	76.58	95.00	181.5
MUF1	81.70	97.13	159.1
MUF2	81.79	102.09	129.9

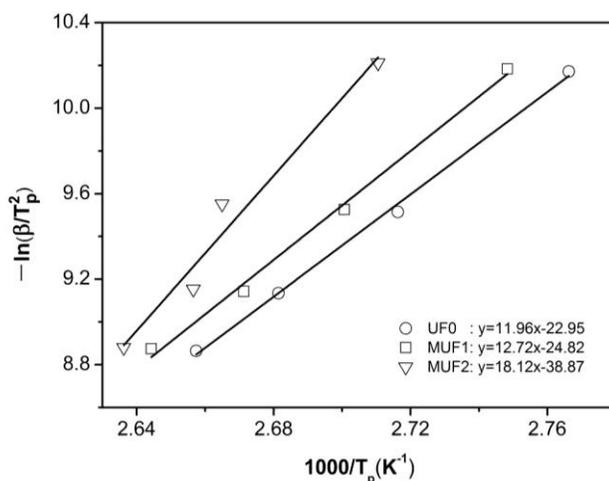


Fig. 4. A graph of $-\ln(\beta/T_p^2)$ versus T_p^{-1}

In addition, the average onset temperature, peak temperature, and heat of reaction during the curing reaction of the three resins are summarized in Table 2. From the table, it can be seen that the onset temperatures of MUF resins shifted to higher temperatures, *i.e.*, 81.70 °C to 81.79 °C, while that of UF0 was 76.58 °C, indicating that the polymerization of MUF resins started at higher temperatures. The onset temperature increased with the addition of melamine, regardless of the addition stage. The peak temperature increased slightly with the addition of melamine, and the highest peak temperature was 102.09 °C, obtained from MUF2 resin. The temperatures at which the polymerization of MUF resins reached the maximum conversion rate were higher than that of UF0 resin, especially MUF2 resin. The heat of curing reaction (ΔH) was determined as the area under the

exothermic thermogram of a DSC curve. The ΔH values at a heating rate of 10 K/min were 181.5 J/g, 159.1 J/g, and 129.9 J/g for UF0, MUF1, and MUF2 resins, respectively. The ΔH decreased with the addition of melamine, and the lowest value was obtained from MUF2 resin. These results indicated that the reactivity of curing reaction of MUF resins decreased with the addition of melamine, and more energy was required to complete the curing of MUF resins, especially MUF2 resin.

The activation energy could be used as a reference in the evaluation of the curing behavior of the UF resin, although it did not reveal all the characteristics of resin curing (Gao *et al.* 2008). Figure 4 shows a plot of $-\ln(\beta/T_p^2)$ versus T_p^{-1} , which was used to calculate the activation energies of the UF and MUF resins.

Table 3. Kinetic Analysis of Resins Using the Kissinger Equation

Resin type	T_p /K				E_a /KJ/mol	A	R^2
	5 K/min	10 K/min	15 K/min	20 K/min			
UF0	361.50	368.15	372.94	376.31	99.44	1.11×10^{14}	0.997
MUF1	363.86	370.28	374.35	378.18	105.75	7.65×10^{14}	0.995
MUF2	368.93	375.24	376.43	379.33	150.65	1.38×10^{21}	0.968

As shown in Table 3, the activation energies of the UF and MUF resins cured with 1% ammonium chloride as the catalyst were calculated using the Kissinger equation. The activation energy of UF0 resin was 99.44 kJ/mol, which was higher than that reported in the literature, ranging from 73.35 to 77.71 kJ/mol (Popović *et al.* 2011). This result might be due to the freeze-drying treatment of resins in this work, which reduced the mobility of molecules.

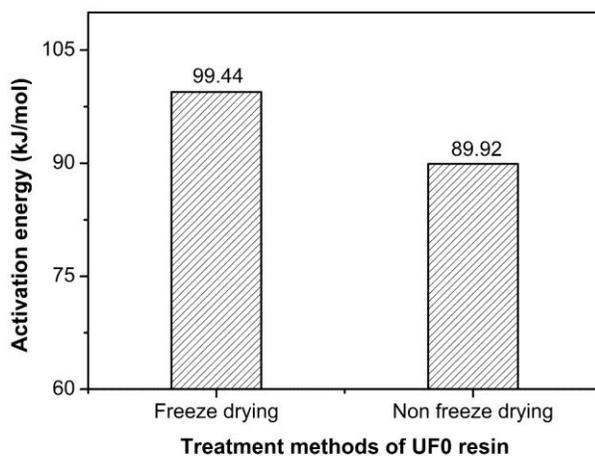


Fig. 5. The curing activation energy of UF0 resin with and without freeze-drying treatment

The activation energy was also influenced by the curing conditions. Figure 5 shows that the activation energy of UF0 resin without freeze-drying was 89.92 kJ/mol, which was lower than the resin with freeze-drying treatment. Water plays an important role in the curing reaction and affects the activation energy. In addition, the activation energy of UF0 resin was lower than that reported in the literature (Kim *et al.* 2006); the activation energy of pure UF resin with an F/U molar ratio of 1.25 was reported to be 287.2 kJ/mol. According to the literature (Park *et al.* 2006), the E_a increases with increasing F/U molar ratio, indicating that UF resin with a lower F/U molar ratio requires

less energy to spontaneously initiate the curing reaction than resins with a higher F/U molar ratio. For the curing reaction of MUF resins, the activation energy was 105.75 kJ/mol and 150.65 kJ/mol for MUF1 resin and MUF2 resin, respectively. The activation energies varied significantly by adding melamine at different synthesis stages. There was a positive correlation between the curing time and curing activation energy. MUF2 resin appeared to have the highest activation energy with the longest curing time. In general, resin with higher activation energy always shows a slower curing reaction at a given temperature than resin with lower activation energy. From the results, the conclusion can be drawn that melamine addition had adverse effects on the curing behavior of the UF resin, which contrasts with the research of Kim *et al.* (2006). They added MF resin to UF resin for the purpose of reducing formaldehyde emissions and found that the E_a value of the UF resin decreased as the MF resin content ratio increased. This can be explained by the fact that MF resin reacts with formaldehyde faster than UF resin in the early stages of the reaction because of its high $-NH$ content. This research indicated that the curing mechanism of UF resin mixed with MF resin was different than that of MUF resin.

The pre-exponential factor A is another important kinetic parameter used to determine the rate constant of resin curing according to the well-known Arrhenius equation. The pre-exponential factors of the curing reactions were 1.11×10^{14} , 7.65×10^{14} , and 1.38×10^{21} for UF0 resin, MUF1 resin, and MUF2 resin, respectively. This tendency is consistent with the change in activation energy. According to the collision theory (Nordman and Blinder 1974), a high pre-exponential factor implies that the total number of successful collisions resulting in a reaction is large. Therefore, to obtain a sufficient number of successful collisions for the curing reaction, the resin with a higher pre-exponential factor value needs to be heated to a higher temperature to cure completely. This result is compatible with the peak temperature and heat of curing reaction described above.

The dependence of the activation energy on the degree of conversion and the complexity of the curing process can be revealed by the model-free isoconversional method (Vyazovkin and Sbirrazzuoli 2006). The activation energy at a degree of conversion ranging from 5% to 95% was calculated using the model-free KAS method, and the dependence of activation energy on the degree of conversion is presented in Fig. 6.

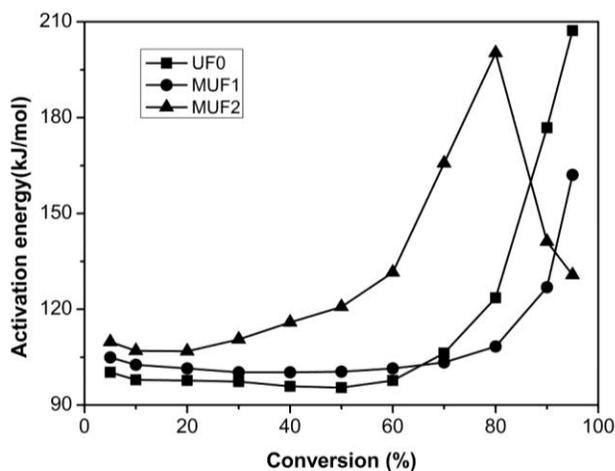


Fig. 6. Activation energy dependency on the degree of curing by applying the KAS isoconversional model

It can be seen that the activation energy values remained relatively constant when the degree of conversion ranged from 5% to 70% and increased significantly toward the end of the curing reaction for UF0 and MUF1 resins. In the early stage of the curing process of UF0 and MUF1 resins, methylene and ether bridges were formed. The activation energy values remained relatively low and stable, indicating that the curing reactions proceeded quickly and that the curing reaction at this stage can be described by a single curing mechanism. As the curing reactions proceeded, the mobility of molecules was greatly reduced and the curing reactions became diffusion-controlled. Therefore, activation energy values increased significantly in the final stage of the curing reaction due to increased diffusion hindrance caused by the increasing molecular weight of the resin (Pizzi and Panamgama 1995). For MUF2 resin, the activation energy values gradually increased to the maximum value when the degree of conversion was 80%, and then decreased to approximately 125 to 130 kJ/mol. The decrease in activation energy might be attributed to the reversibility of hydroxymethyl groups of MF resin components in the curing of MUF2 resin at elevated temperatures. Some of the hydroxymethyl groups (bonded to melamine molecules) migrated to the urea that was added after melamine by dissociation into formaldehyde and reaction with urea (No and Kim 2004). Overall, the melamine addition stage had a clear effect on the curing behavior of MUF resins. The curing mechanism of MUF1 resin was similar to that of UF0 resin, whereas MUF2 resin was different from UF0 and MUF1 resins.

Structure of Cured MUF Resins

The structure of cured MUF resins was closely related to the resin synthesis procedure and the curing process. In the synthesis of MUF1 resin, the reaction mechanism of melamine with formaldehyde was similar to that of urea with formaldehyde. Melamine underwent two different reaction stages: methylation and condensation. First, melamine and formaldehyde were reacted in a weakly alkaline pH to form various methylolmelamines. Second, methylolmelamines and methylolureas polymerized by forming methylene and methylene-ether bonds in acidic conditions during the condensation step, leading to the formation of a large number of oligomers. Some formaldehyde was liberated from dimethylene ethers by dehydroxylation, raising the amount of free formaldehyde. Cross-linked networking structures were obtained during curing.

In the case of MUF2 resin, melamine added with the second urea reacted with residual free formaldehyde in the reaction mixture in alkaline conditions to form monomeric methylolmelamines, reducing the free formaldehyde content of the resins and modifying resin properties. For MUF resins, there was a small amount of melamine remaining in the resins as free melamine and monomeric methylolmelamines.

The effects of melamine addition stage on the molecular structures of resins were analyzed by FTIR spectroscopy. Figure 7 shows the FTIR spectra of the cured UF0 and MUF resins. In addition, the assignments of absorption bands are tabulated in Table 4 according to the literature (Padgett and Hamner 1958; Myers 1981; Jada 1988; Socrates 1994). A distinct peak at 814 cm^{-1} was detected for each MUF resin, which was attributed to the stretching of the triazine ring structure of melamine. The peak at 814 cm^{-1} was chosen as a reference because the triazine ring was not expected to change during curing. Based on the fact that the intensities of the peaks at 814 cm^{-1} were basically identical, the intensity of other bands was an indication of the amount of relevant chemical structures present in the cured MUF resins.

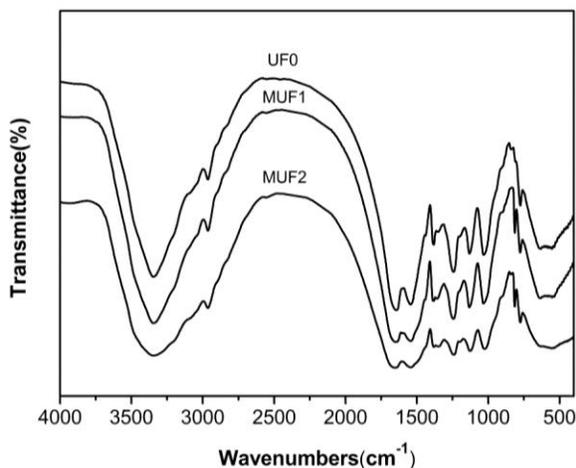


Fig. 7. FTIR spectra of the UF and MUF resins

Table 4. Absorption Band Assignment of FT-IR Spectra of Resins

Absorption Band (cm ⁻¹)	Chemical Structure Assignment	Observed Band (cm ⁻¹)		
		UF0	MUF1	MUF2
3350-3340	NH stretching of primary aliphatic amines	3349	3346	3346
2962-2960	-O-CH ₃ , aliphatic ethers	2964	2964	2964
1654-1646	C=O stretching of primary amide	1643	1647	1658
1560-1550	C-N stretching of secondary amines	1543	1543	1544
1400-1380	C-H mode in CH ₂ and CH ₃	1381	1381	1380
1380-1330	C-N stretching of CH ₂ -N	1351	1359	1349
1260-1250	C-N and N-H stretching of tertiary amides	1243	1243	1241
1150-1130	C-O stretching of aliphatic ether	1132	1133	1126
1050-1030	C-N or NCN stretching of methylene linkages (NCH ₂ N)	1032	1033	1023
815-813	Triazine ring stretching	-	814	814
780-750	C=O deformation of the NCON skeleton	776	776	775

A sharp peak at 1381 cm⁻¹ with a shoulder band around 1350 cm⁻¹ appeared in the cured UF0 resin. In the cases of MUF resins, a weak doublet peak was observed for each resin. The bands around 1650 cm⁻¹ and 1550 cm⁻¹, assigned to C=O stretching of primary amides and C-N stretching of secondary amines, decreased for all MUF resins. The C=O stretching of primary amides was the most dominant absorption band in the FTIR spectra of UF resin. The bands around 3340 cm⁻¹, due to NH stretching of primary aliphatic amines, become broader with the melamine addition stage delayed. This indicated that the amount of free -NH₂ increased with the melamine addition stage delayed, which provided evidence for the lower reactivity of melamine with the UF base resin. The free -NH₂ functionality would be available to form cross-links with formaldehyde during the curing reaction. Peaks at 1126 cm⁻¹ and 1023 cm⁻¹, corresponding to C-O stretching of aliphatic ether and C-N or NCN stretching of methylene linkages (NCH₂N), were

relatively weak for MUF resins, and the weakest region was obtained from MUF2 resin. These bands could have resulted from the cross-linkage of methylolureas and/or methylolmelamines. This result suggests that the amount of methylene and methylene-ether bonds in the cross-linked networking structures of cured MUF2 resin was the lowest, which is consistent with the highest activation energy and the lowest heat of reaction during the curing process obtained from dynamic DSC. From these results, it can be concluded that MUF2 resin had a lower degree of cross-linking, which is the reason that the bond strength of MUF2 resin was lower than that of MUF1 resin. As for the formaldehyde emissions, the free formaldehyde content and the methylene-ether linkages are major sources for the later formaldehyde emissions of plywood. The amounts of the free formaldehyde content and the methylene-ether linkages in MUF resins were lower than that of UF resin, which provided evidences for the lower formaldehyde emissions of MUF resins. It should be noted that the formaldehyde emissions of MUF2 resin was higher than that of MUF1 resin while the methylene-ether linkages of MUF2 resin was lower than MUF1 resin. The possible reason is that the lower degree of cross-linking of MUF2 resin may lead the methylene-ether linkages to split off of water and formaldehyde more likely. Although the curing degree of MUF2 resin was the lowest, the bond strength of MUF2 resin was higher than that of UF0 resin due to melamine's high functionality and stable molecular structure, which can improve the water resistance of resin and reduce formaldehyde emissions from plywood.

CONCLUSIONS

1. Low-level melamine-modified urea-formaldehyde resins endowed plywood with higher bond strength and lower formaldehyde emissions than UF0 resin. The plywood bonded by MUF1 resin yielded the highest bond strength and the lowest formaldehyde emissions.
2. The melamine addition stage had a significant influence on the characteristics of MUF resins. In general, a later melamine addition stage prolonged the curing time of resins, decreased the bond strength, and increased the formaldehyde emissions of plywood.
3. Compared with UF0 resin, the curing process of MUF resins shifted to higher, larger temperature ranges, especially for MUF2 resin. The activation energy increased significantly with the melamine addition stage delayed. The values were 99.44 kJ/mol, 105.75 kJ/mol, and 150.65 kJ/mol for UF0 resin, MUF1 resin, and MUF2, respectively. According to the FTIR spectra, a distinct peak at 814 cm^{-1} was observed for each MUF resin, which was attributed to the stretching of the triazine ring structure of melamine. The bands around 3340 cm^{-1} became broader with a delayed melamine addition stage, indicating that the amount of free $-\text{NH}_2$ increased and the reactivity of melamine declined. The amount of methylene and methylene-ether bonds in the cross-linked networking structures of cured MUF2 resin was the lowest, indicating that MUF2 resin had a lower degree of cross-linking, as well as the highest activation energy and the lowest heat of reaction during the curing process.

ACKNOWLEDGMENTS

The authors are grateful for the support of the Fundamental Research Funds for the Central Universities (No. BLX2012026), the National Natural Science Foundation of China (Project 30972310/C040302), and the Special Fund for Forestry Research in the Public Interest (Project 201004006-2).

REFERENCES CITED

- Bono, A., Beng, Y. K., and Siambun, N. J. (2003). "Melamine-urea-formaldehyde resin: The effect of the number of reaction stages and molar ratio on resin properties," *J. Tekhnologi*. 38, 43-52.
- Dunky, M. (1998). "Urea-formaldehyde (UF) adhesive resins for wood," *Int. J. Adhes. Adhes.* 18(2), 95-107.
- Ebewele, R. O., River, B. H., and Myers, G. E. (1994). "Behavior of amine-modified urea-formaldehyde-bonded wood joints at low formaldehyde/urea molar ratios," *J. Appl. Polym. Sci.* 52(5), 689-700.
- Fan, D. B., Li, J. Z., and Mao, A. (2006). "Curing characteristics of low molar ratio urea formaldehyde resins," *J. Adhes. Interface*. 7(4), 45-52.
- Gao, Z. H., Wang, X. M., Wan, H., and Yu, L. (2008). "Curing characteristics of urea-formaldehyde resin in the presence of various amounts of wood extracts and catalysts," *J. Appl. Polym. Sci.* 107(3), 1555-1562.
- Hse, C. Y., Fu, F., and Pan, H. (2008). "Melamine-modified urea formaldehyde resin for bonding particleboards," *Forest Prod. J.* 58(4), 56-61.
- Hse, C. Y. (2009). "Development of melamine modified urea formaldehyde resins based on strong acidic pH catalyzed urea formaldehyde polymer," *Forest Prod. J.* 59(5), 19-24.
- Jada, S. S. (1988). "The structure of urea-formaldehyde resins," *J. Appl. Polym. Sci.* 35(6), 1573-1592.
- Kim, S., Kim, H. J., Kim, H. S., Lee, Y. K., and Yang, H. S. (2006). "Thermal analysis study of viscoelastic properties and activation energy of melamine-modified urea-formaldehyde resins," *J. Adhes. Sci. Technol.* 20(8), 803-816.
- Kissinger, H. E. (1957). "Reaction kinetics in differential thermal analysis," *Anal. Chem.* 29(11), 1702-1706.
- Meyer, B., Johns, W. E., and Woo, J. K. (1980). "Formaldehyde release from sulfur-modified urea-formaldehyde resin systems," *Forest Prod. J.* 30(3), 24-31.
- Myers, G. E. (1981). "Investigation of urea-formaldehyde polymer cure by infrared," *J. Appl. Polym. Sci.* 26(3), 747-764.
- Myers, G. E. (1982). "Hydrolytic stability of cured urea-formaldehyde resins," *Wood Sci.* 15(2), 127-138.
- Myers, G. E. (1984). "How molar ratio of UF resin affects formaldehyde emission and other properties: A literature critique," *Forest Prod. J.* 34(5), 35-41.
- Myers, G. E. (1990). "Formaldehyde liberation and cure behavior of urea-formaldehyde resins," *Holzforschung* 44(2), 117-126.
- No, B. Y., and Kim, M. G. (2007). "Evaluation of melamine-modified urea-formaldehyde resins as particleboard binders," *J Appl Polym Sci.* 106(6), 4148-4156.

- No, B. Y., and Kim, M. G. (2004). "Syntheses and properties of low-level melamine-modified urea-melamine-formaldehyde resins," *J. Appl. Polym. Sci.* 93(6), 2559-2569.
- Nordman, C. E., and Blinder, S. M. (1974). "Collision theory of chemical reaction," *J. Chem. Educ.* 51(12), 790-791.
- Padgett, II, W. M., and Hamner, W. F. (1958). "The infrared spectra of some derivatives of 1,3,5-triazine," *J. Am. Chem. Soc.* 80(4), 803-808.
- Paiva, N. T., Henriques, A., Cruz, P., Ferra, J. M., Carvalho, L. H., and Magalhaes, F. D. (2012). "Production of melamine fortified urea-formaldehyde resins with low formaldehyde emission," *J. Appl. Polym. Sci.* 124(3), 2311-2317.
- Park, B. D., Kang, E. C., and Park, J. Y. (2006). "Effects of formaldehyde to urea molar ratio on thermal curing behavior of urea-formaldehyde resin and properties of particleboard," *J. Appl. Polym. Sci.* 101(3), 1787-1792.
- Pizzi, A., Lipschitz, L., and Valenzuela, J. (1994). "Theory and practice of the preparation of low formaldehyde emission UF adhesives," *Holzforschung* 48(3), 254-261.
- Pizzi, A., and Panamgama, L. A. (1995). "Diffusion hindrance vs. wood-induced catalytic activation of MUF adhesive polycondensation," *J. Appl. Polym. Sci.* 58(1), 109-115.
- Popović, M., Budinski-Simendić, J., Jovičić, M., Mursics, J., Điporović-Momčilović, M., Pavličević, J., and Ristić, I. (2011). "Curing kinetics of two commercial urea-formaldehyde adhesives studied by isoconversional method," *Hem. Ind.* 65(6), 717-726.
- Shiau, D. W., and Smith, E. (1985). "Low formaldehyde emission urea-formaldehyde resins containing a melamine additive," *US Pat.* No. 4,536,245.
- Siimer, K., Kaljuvee, T., and Christjanson, P. (2003). "Thermal behavior of urea-formaldehyde resins during curing," *J. Therm. Anal. Calorim.* 72(2), 607-617.
- Socrates, G. (1994). *Infrared Characteristic Group Frequencies*, 2nd Ed., Wiley, New York.
- Sunose, T., and Akahira, T. (1971). "Method of determining activation deterioration constant of electrical insulating materials," Research Report, Chiba Institute of Technology (Sci & Technol), Narashino, Chiba, Japan.
- Vyazovkin, S., and Sbirrazzuoli, N. (1996). "Mechanism and kinetics of epoxy-amine cure studied by differential scanning calorimetry," *Macromol.* 29(6), 1867-1873.
- Vyazovkin, S., and Sbirrazzuoli, N. (2006). "Isoconversional kinetic analysis of thermally stimulated processes in polymers," *Macromol. Rapid Commun.* 27(18), 1515-1532.
- Xu, G. Z., Eom, Y. G., Lee, Y. K., Lim, D. H., Lee, B. H., and Kim, H. J. (2009). "Curing behavior and adhesion performance of urea-melamine-formaldehyde (MUF) resin by staged addition of melamine," *J. Adhes. Interface.* 10(2), 84-89.

Article submitted: April 24, 2013; Peer review completed: May 27, 2013; Revised version received: August 11, 2013; Accepted: September 11, 2013; Published: September 13, 2013.