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Thermal analysis study of viscoelastic properties and activation energy of melamine-modified urea-formaldehyde resins

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Abstract—The objective of this research was to investigate the activation energy and viscoelastic properties of urea-formaldehyde (UF) resin, melamine-formaldehyde (MF) resin and UF-MF resin mixtures by differential scanning calorimetry (DSC) and dynamic mechanical thermal analysis (DMTA). The purpose of adding MF resin to the UF resin was to reduce the formaldehyde emission. As the MF resin content was increased in the UF-MF resin mixture, the formaldehyde emission decreased. The storage modulus (E'), loss modulus (E'') and loss factor ($\tan\delta$) of each resin were measured by DMTA. With increasing temperature, as the resin cured, the storage modulus (E') increased in all resin systems. The storage modulus (E') increased both as a function of increasing temperature and with increasing MF content. The activation energies (E_a) of the curing reactions of the UF and MF resins alone, as well as the mixed resins, on different substrates, were calculated on the basis of the variation of the temperature of the maximum of each DSC scan exotherm using the Kissinger equation. The E_a value of the UF resin decreased as the MF resin content ratio increased, and because of this lower activation energy the UF-MF resins cured faster than the UF resin. Formaldehyde is incorporated more easily and completely into melamine than into urea. The results showed that MF resin reacts with formaldehyde faster than UF resin because of its high $-$NH content.

Keywords: Melamine-formaldehyde resin; urea-formaldehyde resin; formaldehyde emission; DMTA; viscoelastic properties; DSC; activation energy.

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1. INTRODUCTION

Many building materials emit volatile organic compounds (VOCs), which may have an adverse effect on health and comfort. The level of formaldehyde emissions from wood based materials is usually determined in a reaction chamber at a predefined temperature, humidity and ventilation rate [1, 2]. Formaldehyde (HCOH) is a suspect human carcinogen that is known to be released from pressed-wood products used in home construction, including products made with urea-formaldehyde (UF) resins [3, 4]. Many consumer products containing formaldehyde-based resins release formaldehyde vapor, leading to consumer dissatisfaction and health-related complaints. These emissions have resulted in various symptoms, the most common of which is irritation of the eyes and the upper respiratory tract. These findings have led to an intensified concern about the indoor environment. Consumer products, specifically construction materials, are a major source of formaldehyde emissions in the indoor environment [5–9].

Amino resins are often used to modify properties of other materials. These resins are added during the processing of such products as textile fabrics to impart permanent press characteristics; automobile tires to improve the bonding of rubber to the tire cord; paper to improve its tear strength, especially of wet paper; and alkyds and acrylics to improve their curing properties. Amino resins are also used for molding products, such as electrical devices, jar caps, buttons and dinnerware, and in the production of countertops. These days, melamine-formaldehyde (MF) and urea-melamine-formaldehyde (UMF) resins are mainly used as thermosetting wood adhesives for wood-based panels. Both resins give excellent adhesive performance, good moisture resistance and tend to produce lower formaldehyde emissions than UF resins. Recently, the finding that hardening of UMF resins occurs mostly due to their melamine reactivity has led to the realization that development of a mechanism or system of hardening, to improve the performance or to lower the formaldehyde emissions of MF, can be more easily obtained with pure MF resins than with UMF resins [10, 11].

The reactions which occur during the synthesis of MF resin can be roughly divided into two different stages; methylolation and condensation. Following methylolation of melamine and formaldehyde, the second reaction step involves condensation, i.e., bridge formation, between the various (methylol) melamines, leading to the formation of a large number of different oligomers. In principle, two different types of linkages may form during the condensation step, the ratio of which depends strongly on the pH. At relatively low pH (7–8), methylene linkages are formed, whereas at pH values above 9 the formation of ether linkages is favored. Thus, a large number of oligomeric derivatives are formed, and cross-linked networking occurs during heating [12].

Thermal analysis is a powerful technique for studying the kinetics of physico-chemical processes [13]. Moreover, it is a useful technique for making time-temperature predictions and for the optimization of process variables. One of the most widely used techniques for the cure kinetic studies of thermosetting materials is the differential scanning calorimetry (DSC). In this particular case it has the advantage of being based on the same assumption as the heat equation, which is the proportionality between the rate of heat generation and the rate of reaction. Errors from different sources may affect the accuracy of the curing kinetic parameters determination based on DSC measurements, *viz.*, the use of an inappropriate kinetic model function, intrinsic defaults of the apparatus, or errors in the interpretation of the DSC thermogram [14]. It is well known that the baseline of a DSC scan experiment for a thermosetting resin is not a straight line, but to obtain its real shape is a complicated process. The type of baseline used is generally a simple straight line drawn from the beginning to the end of the exothermic signal [15].

The dynamic mechanical technique, which involves application of a sinusoidally oscillating stress to the material and the analysis of the resultant strain, is now widely used as a polymer characterization technique. It has far greater sensitivity to both macroscopic and molecular relaxation processes than thermal analysis techniques based on the temperature probe alone. It is the viscous or time-dependent behavior of polymers that makes dynamic mechanical testing such a useful technique for their characterization. One of the most common uses of dynamic mechanical testing is the determination of the glass transition temperature (T_g) of the sample. Another important application area for dynamic mechanical thermal analysis (DMTA) is the monitoring of the resin curing process. The DMTA is very sensitive to this process, and isothermal experiments enable development of an ideal curing schedule [16].

In this study, we focus on the effect of adding MF resin, for the purpose of lowering the formaldehyde emission levels, on the activation energy and viscoelastic properties of UF resin. The activation energy (E_a) values for the thermal reaction were determined with differential scanning calorimetry (DSC) and the viscoelastic properties were measured by DMTA.

2. EXPERIMENTAL

2.1. Resin and formaldehyde emission testing

Each resin was synthesized in the laboratory. First, we synthesized urea-formaldehyde (UF) and melamine-formaldehyde (MF) resins. The compositions of these resins are given in Table 1. Their molar ratios were 1.25 (F/U) for urea-formaldehyde resin and 1.75 (F/M) for melamine-formaldehyde resin. As the catalyst, 10% NH_4Cl solution was used. Second, we mixed the UF resin and MF resin at two different weight ratios, *viz.*, 8 : 2 and 5 : 5. The viscosities and solid contents of these four resins were measured and are shown in Table 1. Their viscosity was measured with a Brookfield Viscometer Model DV II+, using an SC4-28 spindle with a viscosity range of 250–5 000 000 cP at room temperature (20°C). Medium density fiberboards (MDFs), with a specific gravity of 0.8 and dimensions of 270 mm × 270 mm × 8 mm, were fabricated using the above resins. The MDFs were fabricated by hot pressing

Table 1.
Weight formula, viscosity (at RT, 20°C) and solid content of resins

	UF	UF8 : MF2	UF5 : MF5	MF
Weight (g)	544			370
Urea				
38.5% Formaldehyde solution	600			600
Viscosity (cP)	29	31	39	75
Solid content (%)	50.7	51.7	51.6	50.9

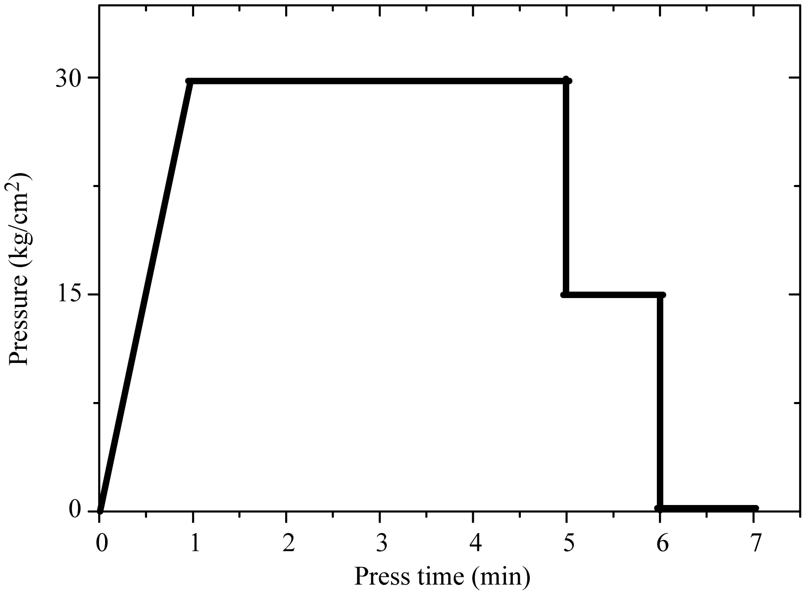

Figure 1. Hot-press schedule for MDF fabrication.

at a peak pressure of 30 kg/cm^2 and a temperature of 160°C. The press time was 5 min, with the pressure being released in two steps of 1 min each. The hot pressure schedule is shown in Fig. 1. The EN 120 (European Committee For Standardization, 1991) standard method based on the perforator test was used to measure the formaldehyde emission level.

2.2. *Dynamic mechanical thermal analysis (DMTA)*

The viscoelastic properties of each sample were determined from 30 to 230°C at a heating rate of 5°C/min using a dynamic mechanical thermal analyzer (DMTA; Rheometric Scientific DMTA MARK IV). As the resins were in a viscous liquid state, the DMTA samples were prepared by sandwiching the resins between two layers of beech wood veneer, each having a thickness of 0.6 mm, and a three-point bending mode was applied [17]. The resin thickness was 0.2 mm and the sample dimensions were 28 × 5 × 1.4 mm. During the DMTA experiments, the static force was kept at 20% of the dynamic force and the frequency was maintained at 1 Hz with a strain of 0.05.

2.3. Differential scanning calorimetry (DSC)

DSC analysis with a TA Instruments model Q-1000 equipped with a Thermal Analysis Data Station enabled curing exotherms of the UF, MF and UMF resins to be determined. This study was done using a sealed liquid type aluminum capsule pan, under a nitrogen atmosphere, at five different heating rates, 2, 5, 10, 20 and 40°C/min, between 25 and 300°C.

3. RESULTS AND DISCUSSION

3.1. Formaldehyde emissions

The evolution of formaldehyde from UF products is well known. Over the past 40 years, investigators have extensively examined the structures of the components of urea-formaldehyde resin systems and the physical chemistry of their formation and degradation in aqueous solutions. Classical kinetic, chromatographic and NMR techniques have been applied to the study of this process [18]. We can conclude from these studies that the reactions, leading to the formation of UF products, occurred during UF resin synthesis and curing were reversible. In the forward direction, water is eliminated; therefore, the reverse reaction can be viewed as hydrolysis, which leads to the release of formaldehyde. Because most, if not all, of these reactions are catalyzed by acid, the use of an acid catalyst to hasten bond curing, unfortunately, also increases the rate of hydrolysis and formaldehyde liberation.

Figure 2 compares the formaldehyde emission behavior of the MF and UF resins used in this study. According to the European standard, the formaldehyde emission level of the MDF panels made using the UF resin was E_2 grade. To reduce their formaldehyde emission levels, MF resin was added. Figure 2 demonstrates the dramatic reduction in formaldehyde emission obtained through the addition of MF resin. In general, reducing the level of formaldehyde emission from products bonded with UF adhesive resins has been achieved by employing one or more of several technological methods [5]. However, in this study, MF resin was used as a low-formaldehyde-emission adhesive containing amino groups. It was found that as the MF resin content increased, the formaldehyde emission values decreased by an equivalent amount.

3.2. Viscoelastic properties

It is important to understand the thermal properties of UF and MF resins, because, as thermosetting adhesives, they are both strongly affected by, and indeed cured

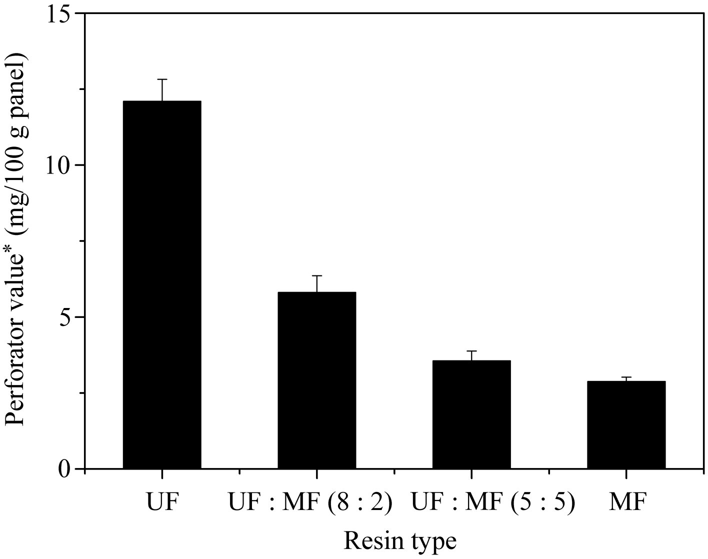

Figure 2. Formaldehyde emission from MDFs fabricated with UF and MF resins. *Perforator value (Formaldehyde emission level), E_0: Under 0.8 mg/100 g panel, E_1: Under 6.5 mg/100 g panel, E_2: Under 15 mg/100 g panel.

by, heating. These resins are in the liquid state at room temperature and become solid at higher temperatures after curing has taken place. DMTA is able to detect some of the transitions that occur, such as gelation and vitrification, by measuring the change in the mechanical properties. In this study, the storage modulus (E'), loss modulus (E'') and loss factor ($\tan\delta$) of each resin system were obtained by DMTA. Figure 3 shows the storage modulus (E'), loss modulus (E'') and $\tan\delta$ of the mixed resin (UF5 : MF5). By using the DMTA thermogram, we can check the viscoelastic properties of a thermosetting resin that is in the liquid state by using wood veneer. The DMTA thermogram in Fig. 3 shows that the storage modulus initially increased with increasing temperature as water evaporated from the sample in this temperature range. The storage modulus increased again as the temperature was further increased as a result of cross-linking induced by the curing reaction of the resin. The storage modulus reached a maximum when the curing reaction was completed. The increase in the storage modulus from the flat portion of the curve following evaporation of the water to the maximum value was the result of the consolidation of the resin network. This difference ($\triangle E'$) was used to evaluate the rigidity of the cured resin. As the temperature increased, the storage modulus (E') increased and the resin was cured above 170°C. The curing temperature was obtained from the $\tan\delta$ peak.

The $\tan\delta$ peaks are shown in Fig. 4. The $\tan\delta$ value increased sharply up to its maximum value, due to the increase in viscosity, and then decreased as the temperature was further increased. Finally, the $\tan\delta$ value slightly increased again

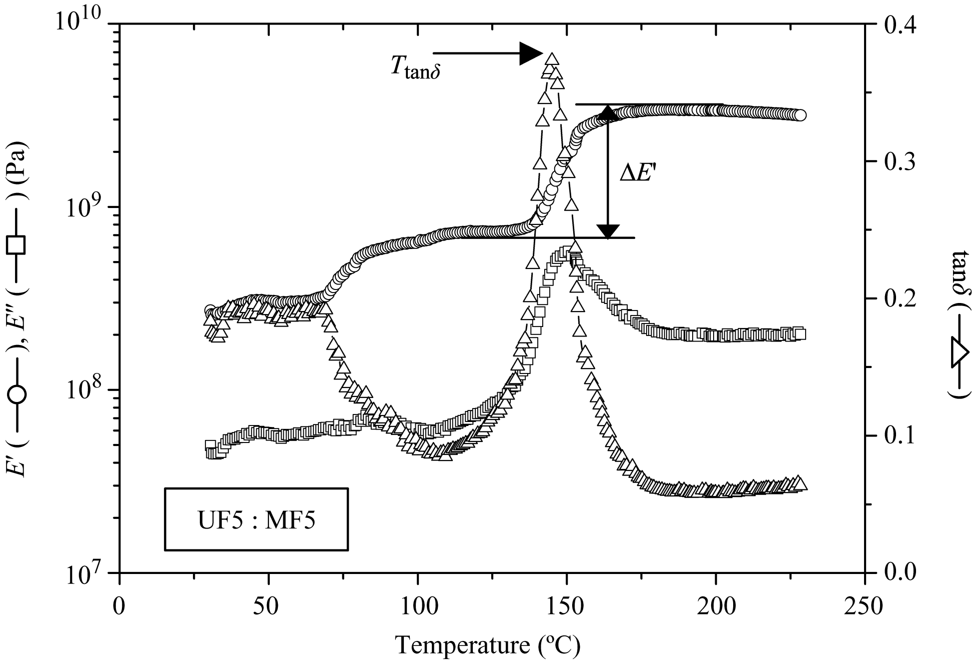

Figure 3. DMTA thermogram of UF5 : MF5 (heating rate 5°C/min).

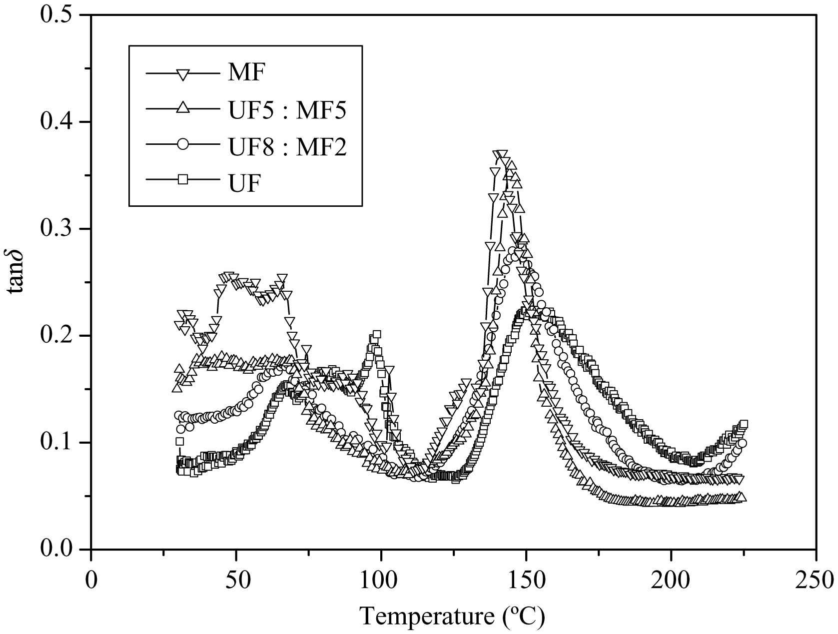

Figure 4. Loss factor (tan δ) of different resins (heating rate 5°C/min).

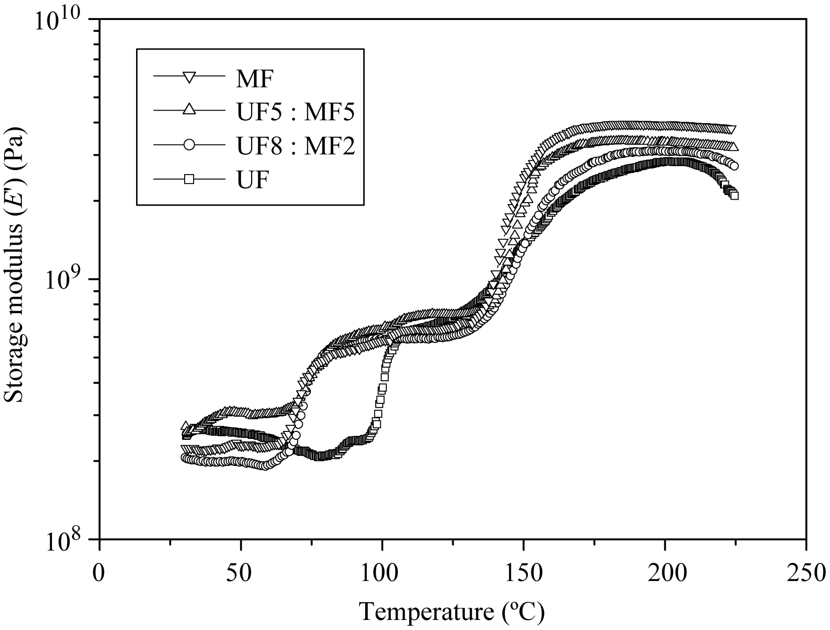

Figure 5. Storage modulus (E') of different resins (heating rate 5°C/min).

after the curing reaction was completed. The temperature of the active curing reaction can be determined from the maximum value of the tan δ in this temperature range. The storage modulus (E') results for the resins are shown in Fig. 5. The storage modulus (E') increased both as a function of increasing temperature and with increasing MF content.

Furthermore, the storage modulus of MF is the highest and, in general, the higher the MF content, the higher the storage modulus at a temperature of around 200°C after curing. Based on these results, the rigidities ($\triangle E$) of the resins are shown in Fig. 6. The rigidity ($\triangle E$) increased as the MF content increased.

The higher the storage modulus of the MF resin compared to that of the UF resin can probably be attributed to the molecular structure and reaction mechanism of the former. The reactions that occur during the synthesis of both UF and MF resins can be roughly divided into two different stages: methylolation and condensation. The condensation reaction of melamine with formaldehyde is similar to that between urea and formaldehyde. However, the incorporation of formaldehyde into melamine occurs more easily and completely than its incorporation into urea. The amino group in the melamine easily accepts up to two molecules of formaldehyde. Thus, a complete methylolation of melamine is possible, whereas it is not possible with urea. Up to 6 molecules of formaldehyde can be attached to 1 molecule of melamine. The methylolation step thus leads to generation of a series of methylol compounds, with 2–6 methylol groups. Because melamine is less soluble in water than urea, the hydrophilic stage proceeds more rapidly in the case of MF resin

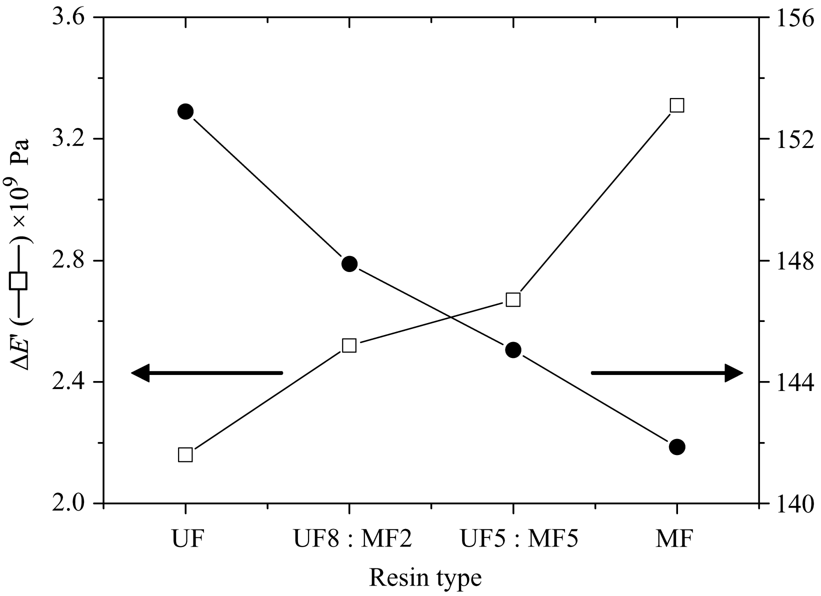

Figure 6. The rigidity ($\triangle E'$) and the temperature of tan δ maximum ($T_{\tan\delta}$) of different resins.

formation. Therefore, the hydrophobic intermediates of the MF condensation appear early in the reaction. The higher storage modulus of MF resin is likely because of the higher cross-link density and greater rigidity of the ring structure of melamine as compared to the more flexible structure of urea.

In the case of UF resin, in the first stage, urea is hydroxymethylolated by the addition of formaldehyde to the amino groups. This reaction is, in reality, a series of reactions that lead to the formation of mono-, di- and tri-methylolureas. Tetramethylolurea is apparently not produced, at least not in any detectable quantity. The second stage of urea-formaldehyde resin synthesis consists of condensation of methylolureas to produce low molecular weight polymers. The rate at which these condensation reactions occur is dependent on the pH and, for all practical purposes, these reactions occur only at acidic pH. At the start of the resin synthesis, melamine reacts with formaldehyde leading to the formation of a series of nine different methylolmelamines.

In the tan δ data in Fig. 4, this tendency is shown in detail. The temperatures corresponding to the maximum values of tan δ were in the order of increasing MF content ratio. From the tan δ results, the tan δ peak temperature values were 141.9°C for MF resin, 145.1°C for the mixed resin (UF5 : MF5), 147.9°C for the mixed resin (UF8 : MF2) and 152.9°C for UF resin. The heights of the tan δ peaks were also different. The highest peak was observed for the MF resin, with the tan δ peaks being in the order MF > UF5 : MF5 > UF8 : MF2 > UF. The results for tan δ peak temperature are shown in Fig. 6 along with the rigidity ($\triangle E$) values of the resins. These results show that MF resin reacts with formaldehyde faster than UF resin in the early stages of the reaction, because of its high —NH content.

3.3. Activation energy of chemical curing by DSC analysis

The activation energies of the curing reactions of the UF and MF resins alone, as well as mixed resins, on different substrates, were calculated on the basis of the variation in the temperature of the maximum of each DSC scan exotherm as a function of increasing temperature rate of the DSC scan, using the Kissinger equation. Thus, as reported in the literature [19], n-th order and autocatalytic kinetics are the two reaction mechanisms used to describe the curing reaction. They can be expressed as follows: for the n-th-order kinetics:

$$\mathrm{d}\alpha/\mathrm{d}t = k(1-\alpha)^n, \tag{1}$$

where α, the extent of the curing reaction, is defined as $\triangle H_t/\triangle H_{\text{Total}}$, where $\triangle H_t$ and $\triangle H_{\text{Total}}$ are the enthalpies of the curing reaction at time t and at the end of the curing process, respectively, and can be determined from DSC thermograms.

The rate constant can be expressed as

$$k = Ae^{-E_\mathrm{a}/RT}, \tag{2}$$

where A is the frequency factor and E_a is the activation energy. Then

$$\ln k = \ln((\mathrm{d}\alpha/\mathrm{d}t)/(1-\alpha)^n) = \ln A - E_\mathrm{a}/RT. \tag{3}$$

When the order of this reaction is properly estimated, a plot of $\ln k$ *vs.* $1/T$ allows to predict A and E_a.

Kissinger [19] proposed that

$$E_\mathrm{a}\beta(RT_\mathrm{p}^2) = Ae^{-E_\mathrm{a}/RT_\mathrm{p}}, \tag{4}$$

where β is the heating rate and can be expressed as $\beta = \mathrm{d}T/\mathrm{d}t$. By taking the logarithm on both side of equation (4), the Kissinger equation is obtained as follows:

$$-\ln(\beta T_\mathrm{p}^2) = -\ln(AR/E_\mathrm{a}) + (1/T_\mathrm{p})(E_\mathrm{a}/R), \tag{5}$$

where A and E_a can be obtained by plotting $-\ln(\beta T_\mathrm{p}^2)$ *vs.* $1/T_\mathrm{p}$.

The DSC curing curves for the UF resin as a function of the heating rate are shown in Fig. 7. It can be seen that there is an exothermic peak in the curing process. The DSC curves of pure MF and pure UF also show exothermic peaks, but at a lower temperature in the case of MF and at a higher temperature in the case of UF. The MUF resin also presents exotherms in the temperature range 153–177°C (Table 2), which is situated between the UF (164–181°C) and MF (146–181°C) curing peak temperatures. The curing peak temperature range of 164–181°C corresponds to the cross-linking reactions. The area of these peaks should, therefore, be proportional to the frequency of occurrence of the $-\mathrm{CH_2}-\mathrm{O}-\mathrm{CH_2}-$ linkages in the UF resin [20]. In the DSC analysis, because of polymerization of the adhesives, the peaks were shown at higher temperatures with increasing heating rates. Upon increasing the heating rate, a shift of the condensation reaction to higher temperature was observed for all resin types. The plots of

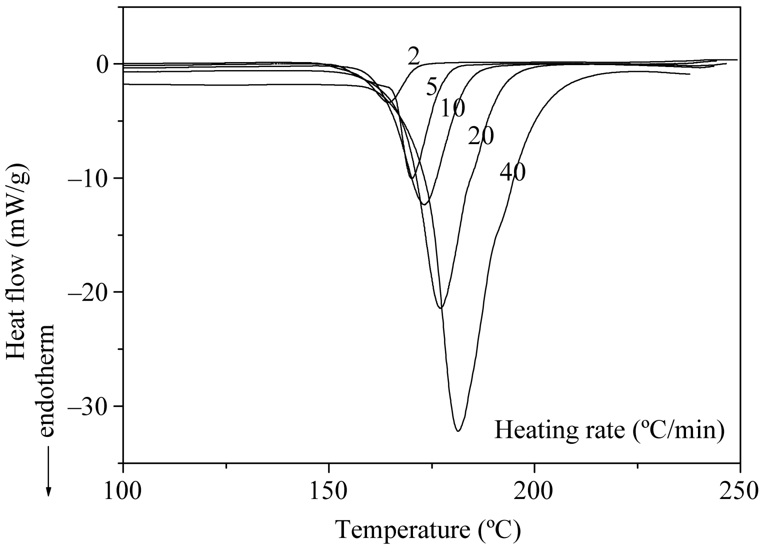

Figure 7. DSC thermograms for the UF resin at heating rates (°C/min) as indicated on the curves.

Table 2.
Kinetic parameters of resins obtained by Kissinger's analysis

Resin	Heating rate (β, °C/min)	Peak temp. (T_p, °C)	$\triangle H$ (J/g)	$\ln(\beta/T_p^2)$ *vs.* T^{-1}	E_a (kJ/mol)
UF resin	2	164.3	1127	$Y = 34.6X - 67.5$	287.2
	5	170.1	1175	$R^2 = 0.99$	
	10	173.3	1009		
	20	177.1	996.9		
	10	181.4	865.7		
UF8 : MF2	2	161.6	1048	$Y = 33.9X - 66.4$	281.7
	5	154.6	1168	$R^2 = 0.99$	
	10	168.5	988.3		
	20	174.5	945.3		
	40	177.0	916.4		
UF5 : MF5	2	153.0	981.8	$Y = 24.5X - 45.9$	203.4
	5	161.6	982.4	$R^2 = 0.98$	
	10	166.5	942.6		
	20	169.0	930.6		
	40	176.0	854.2		
MF resin	2	146.4	796.5	$Y = 15.2X - 24.9$	126.7
	5	158.5	830.1	$R^2 = 0.99$	
	10	166.5	741.8		
	20	174.5	734.1		
	40	181.5	706.1		

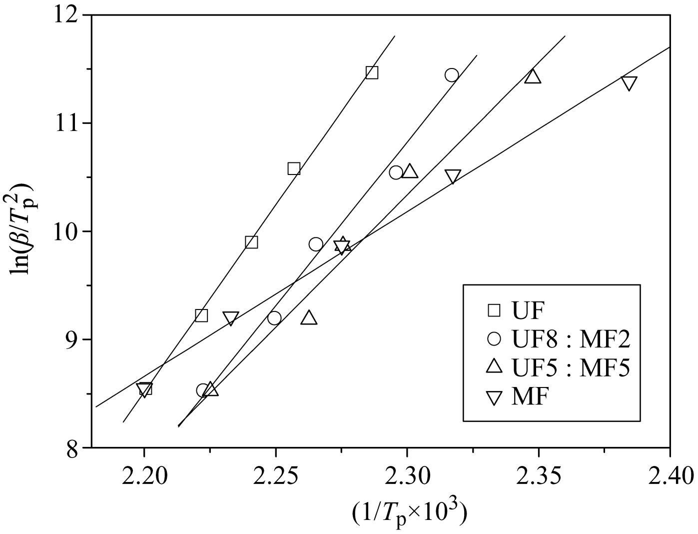

Figure 8. Plot of $\ln(\beta/T_p^2)$ *vs.* T_p^{-1} for the various resins.

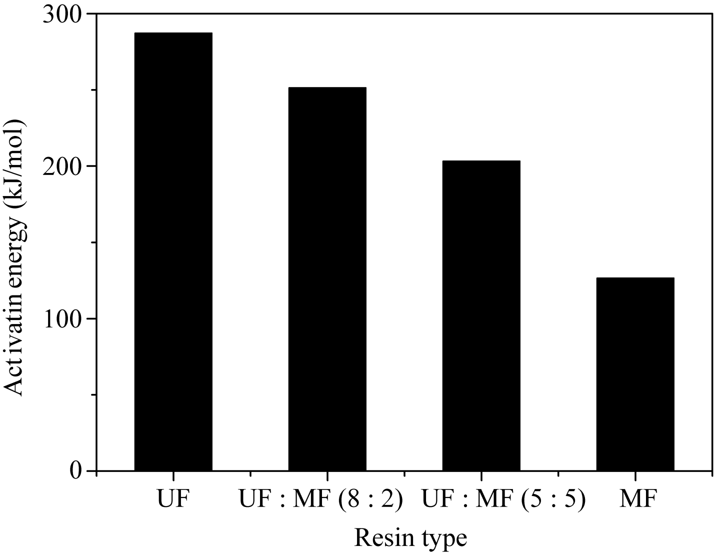

Figure 9. Activation energy of resins using the Kissinger expression.

$-\ln(\beta/T_p^2)$ against $1/T_p$ for the UF and MF resins are shown in Fig. 8. The value of E_a obtained for UF resin is 287.2 kJ/mol and that for MF resin is 126.7 kJ/mol. Figure 9 shows activation energy of the resins for the curing process. The activation energy is an important kinetic parameter, which describes the effect of temperature on the curing reaction. The E_a of UF resin decreased as the MF resin content increased. In other words, the E_a of MF resin leads to its curing faster than that of UF resin. These differences are clearly due to the different reaction mechanisms described above. The incorporation of formaldehyde into melamine occurs more easily and completely than its incorporation into urea. The amino group in melamine accepts easily up to two molecules of formaldehyde. Thus, up to 6 molecules of formaldehyde can be attached to 1 molecule of melamine. The methylolation step leads to a series of methylol compounds with 2–6 methylol groups [21, 22]. The mechanism of the further reaction of methylol-melamines to form hydrophobic intermediates is the same as for UF resins, with the splitting off of water and formaldehyde. Methylene and ether bridges are formed. The formation of the resin increased rapidly. The final curing process transforms the intermediates into the desired insoluble and infusible MF resins through the reaction of amino and methylol groups, which are still available for reaction.

4. CONCLUSIONS

In this study, the viscoelastic properties and activation energies of UF resin, MF resin and mixtures of these two resins were investigated. Usually, the MF resin is added to the UF resin to reduce the level of formaldehyde emission from wood-based panels that are made using UF resin. We evaluated changes in the viscoelastic properties and activation energies of the UF resin as the MF resin content was increased. At increased temperature, the resins showed viscoelastic properties. They were in the liquid state at low temperature and changed into the solid state as the temperature increased. The storage modulus (E') increased both as a function of increasing temperature, as well as increasing MF content. The higher storage modulus of the MF resin is due to the higher crosslink density and greater rigidity of the ring structure of melamine, as compared to the more flexible structure of urea. The highest $\tan\delta$ peak was observed for MF resin, with the $\tan\delta$ peaks being in the order: MF $>$ UF5 : MF5 $>$ UF8 : MF2 $>$ UF. The activation energy of the UF resin was determined by DSC as a function of the MF resin content. The UF resin had a higher activation energy than the MF resin. This means that less heat is needed to cure MF resin than the UF resin. In general, a lower activation energy indicates that the reaction proceeds faster at a given temperature. These results showed that MF resin reacts with formaldehyde faster than UF resin in the early stages of the reaction, because of its high $-$NH content. We found that the viscoelastic properties and activation energies pertaining to the curing behavior of the formaldehyde-based thermosetting resins examined in this study were dependent on the number of functional groups in the resin.

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