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Relationship between curing activation energy and free formaldehyde content in urea-formaldehyde resins

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This study investigated the effect on the curing behavior, activation energy (E_a) of the curing reaction, crystalline structure, crosslinking, and free formaldehyde content of the addition of the following scavengers in urea-formaldehyde (UF) resins: medium density fiber board flour, rice husk flour, silica powder, and tannin powder. The scavenger content was 3 and 7 wt% of the UF resin solid content. The curing behavior of UF resins was monitored by differential scanning calorimetry, thermogravimetric analysis, and X-ray crystallography. The curing E_a was correlated to the free formaldehyde content of the scavenger containing UF resins. The thermal stability of the UF resins increased but the curing E_a decreased with increasing scavenger content. After curing, the crystallinity of the UF resins decreased in the presence of scavengers. The unreacted free formaldehyde content was reduced in the tannin powder containing UF resins. The degree of crosslinking affects the formaldehyde emission from wood panels bonded with UF resin. This is especially true for wood panels in service for long periods of time and exposed to high humidity conditions. Once the free formaldehyde which influences considerably the emission has disappeared, the presence of the –CH_2– groups then becomes important. Hence, an increased resin crosslinking indicates a higher concentration of –CH_2– groups present, which may hydrolyze and emit formaldehyde slowly over time.

Keywords: activation energy; free formaldehyde; scavenger; UF resin; crystallinity

1. Introduction

Building and furnishing materials and consumer products are important sources of formaldehyde and other volatile organic compounds in the indoor environment. There is a growing concern about the significance of these indoor pollutants for the health and comfort of building occupants. As people generally spend over 90% of their time in indoor environments, the indoor air quality is an important consideration. Unsatisfactory indoor air quality has been associated with incidences of allergy, asthma, and other diseases and illnesses, including the nonspecific general symptoms referred to as the 'sick building syndrome.'

The major emission source of indoor air is formaldehyde, which is emission from urea-formaldehyde (UF) resin used in wood panels. UF resins are excellent adhesives for bonding wood and are considerably cheaper than other adhesives. UF resins are widely used as adhesives for the manufacture of interior grade wood products, in particular wood-based particleboard. However, the formaldehyde released by the UF binder during the board service life

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has been widely recognized as an indoor air pollutant. Thus, much research attention has been focused on reducing or controlling the formaldehyde emission from UF resin-bonded wood panels. The presence of free formaldehyde in the prepared UF resins is one of the reasons for formaldehyde emission [1]. Much attention has been paid to reduce or control formaldehyde emission from UF resin-bonded wood panels through resin synthesis. In general, UF resins are synthesized by a two-step reaction procedure (i.e. methylolation under alkaline condition and condensation under acidic condition using a large amount of formaldehyde). This synthesis method has been widely employed for the preparation of UF resins for many years. In the early 1970s, however, this method faced the serious problem of formaldehyde emission. So, lowering the formaldehyde to urea (F/U) mole ratio for the synthesis of UF resin was adopted as one of the approaches to reduce the formaldehyde emission from UF resin-bonded wood panels. One of the approaches for reducing formaldehyde emission is to lower the F/U molar ratio in the synthesized resin [2]. Beneficial approaches have included reducing the formaldehyde/urea molar ratio, synthesizing UF resin with acidic catalysts without first using an alkaline catalyst, impregnating the wood furnishing with a formaldehyde scavenger, and treating boards with formaldehyde scavengers or a barrier coating after manufacture. Therefore, many materials have been utilized as scavengers to reduce formaldehyde emissions from UF resins, including powdered glass, inorganic salts, and amine hydrochlorides [3,4].

In this study, UF resins containing sawdust of medium density fiber board (MDF flour), rice husk flour (RHF), silica powder and tannin powder as scavengers have been used, and E_1 and E_2 formaldehyde emission grade UF resins have been used.

After the curing process, the UF resin samples underwent thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) to provide simultaneous determination of the activation energy (E_a) of the curing process as well as the thermal stability of the cured resin. The percent crystallinity for the cured UF resins was determined by X-ray crystallography. The free formaldehyde contents of the scavenger containing UF resins were also determined, enabling the curing E_a to be correlated to the free formaldehyde content of the scavenger containing UF resins.

2. Experimental

2.1. Materials

The UF resins used for manufacturing particleboards were donated by a particleboard production enterprise in Korea. Depending on the degree of formaldehyde emission, the UF resins were classified as either E_1 or E_2 class (Table 1).

Sawdust of MDF flour was obtained from MDF board. In the mechanical processing (e.g. sawing and cut out) of the MDF board, 18.2% of the total input mass appears as waste (offcuts, chips, and sawdust), of which more than 90% is in the form of fine sawdust. RHF of particle size 30 μm was obtained from Saron Filler Ltd. in Korea. The wattle tannin (*Acacia mearnsii*, *Acacia mimosa*) in the form of powder with a moisture content of 8.8% was supplied by Bondtite (Australia).

The silica powder used was from Beijing Chemical Reagent of China. It was assayed to have 98.6% SiO_2.

Table 1. UF resins used.

	Formaldehyde emission class	Nonvolatile content (%)	Viscosity (mPa s)
UF-1	E_1	61.6	220 ± 25
UF-2	E_2	76.6	295 ± 20

2.2. Methods

2.2.1. Formulation of resins

MDF flour, RHF, silica powder, and tannin powder were premixed with the UF resin at either 3 or 7% by weight, and 10% NH_4Cl solution was added as a hardener.

2.2.2. Thermogravimetric analysis

The thermal stability of the cured UF resins as a function of scavenger content was determined by TGA in a nitrogen atmosphere at a heating rate of 10 °C/min from 30 to 800 °C with a thermogravimetric analyzer, TGA Q-5000 (TA Instruments, USA).

2.2.3. DSC analysis

All DSC measurements were made with DSC Q 1000 (TA Instruments, USA) that equipped with a TA Instrument thermal analysis system and software. The sample resins were tested by placing about 3 mg of each sample into a hermetic pan. Heating rates of 2, 5, 10, 20, and 40 °C/min and a scanned temperature range of 25–250 °C were selected.

2.2.4. X-ray crystallography

X-ray diffraction patterns of the cured resins were collected using the small-angle X-ray scattering technique with a Bruker General Area Detector Diffraction System (TA Instruments, USA) which recorded the intensity of the X-rays diffracted by the sample as a function of the Bragg angle using the Bruker software. Cu radiation ($\lambda = 1.5405$ Å) was used with a nickel filter. The exposure time was 300 s with a 0.02° (2θ) step.

2.2.5. Determination of free formaldehyde content in the UF resins

Free formaldehyde in the prepared UF resins was determined by a slightly modified sodium sulfite method [5]. A solution of 25 mL 1M sodium sulfite mixed with 10 mL HCl was added to 2–3 g of UF resin sample dissolved in 100 mL distilled water. The mixed solution containing about 10 drops of 0.1% thymolphthalein was neutralized with 1N sodium hydroxide. The percentage of free formaldehyde was determined by the equivalent of the amount of the consumed sodium hydroxide in titration [5,6].

3. Results and discussion

3.1. Curing behavior of UF resin determined by DSC and TGA

It is generally believed that in the presence of an acid catalyst, the exotherm arises from the polycondensation reaction of primary amino groups of unreacted urea with hydroxymethyl groups of resin. The curing reaction of UF resins is typically exothermic, so it was hypothesized that the reaction enthalpy would simply be proportional to the degree of conversion during the curing process. The DSC results in Figure 1 show that the peak temperature changed according to the type of scavenger.

The UF resins present exotherms in the temperature range with curing peak temperatures observed between 87.5 and 94.8 °C in Figure 1. Figure 1 shows the change in reaction heat of the UF resins during their curing. The peak area is the amount of energy required to complete the cure of the resin, which is the area under the exothermic DSC curve. The areas of these
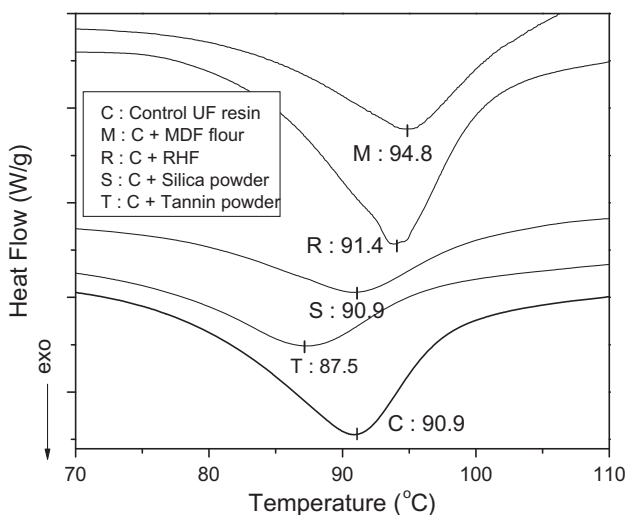
Figure 1. The peak temperature of UF resins (E_1) containing different scavengers at a heating rate of 10 °C/min.

peaks should, therefore, be proportional to the amounts of $-CH_2-O-CH_2-$ linkages in the UF resins [7,8]. Also, Figure 1 compares the curing exotherms for the UF resins at a heating rate of 10 °C/min. The DSC curves show an exotherm peak at a lower temperature for the tannin powder containing UF resin (87.5 °C), but at a higher temperature for that containing MDF flour (94.8 °C), compared to the control UF resin. Figure 1 indicates that the curing exotherm is shifted to a lower temperature with tannin powder addition compared to the UF control resin.

Tannin powder containing UF resin, as compared to the control UF resin, contains a larger amount of reactive hydroxymethyl groups, as demonstrated by the considerably lower curing peak temperature. On the other hand, the peak temperature for the other scavengers (MDF flour and RHF) was increased.

The thermogravimetric behavior of the various forms of UF resins was analyzed, and the results are given in Figures 2 and 3. Figure 2, compares the weight loss of the uncured control UF resin (E_2) and the scavenger containing UF resins in the temperature range from 30 to 800 °C. In the process of curing of tannin powder containing UF resin, as the tannin could react with the free formaldehyde in the curing system, the weight loss was lower than that of the control UF resin. The weight change of the silica powder containing UF resin was midway between that of the control resin and the tannin powder containing UF resin.

Figure 3 shows the weight loss of the control UF resin (E_2) and the scavenger-containing UF resins cured at 120 °C for 1 h. The cured UF resins showed thermal stability up to 200 °C. The results show that tannin powder-containing UF resin had lost up to 4% of its weight by the time it reached 200 °C. The tannin powder-containing UF resin (4% loss at 200 °C) had a higher thermal stability than the UF control resin (7% loss at 200 °C). As tannin is more reactive with formaldehyde, the thermal stability of the cured UF improved at the same curing conditions.

3.2. Activation energy (E_a) determined by DSC analysis

The E_a of the curing reaction of UF control resin and scavenger containing UF resins was calculated on the basis of the variation of the peak reaction temperature (T_{max}) as a function of the heating rate increase of the DSC scan, using Kissinger equation.
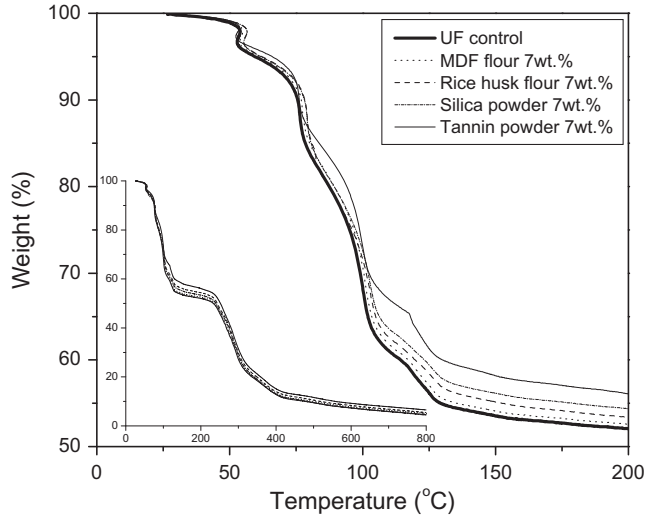
Figure 2. TGA thermograms of 7 wt% scavenger containing uncured UF resins (E_2), at a heating rate of 10 °C/min.
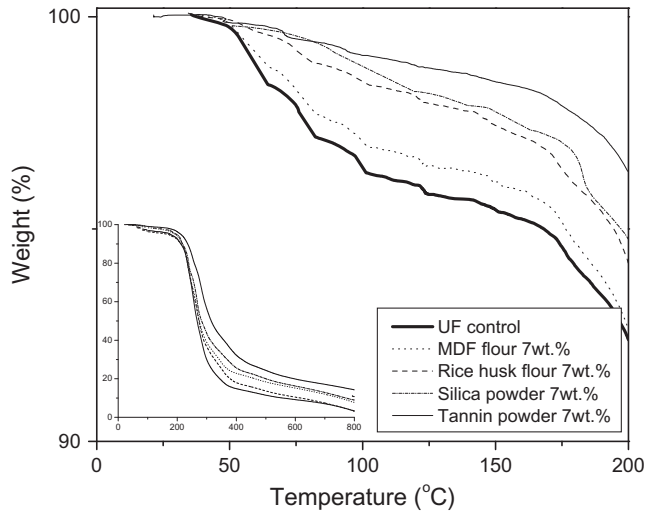

Figure 3. TGA thermograms of 7 wt% scavenger containing UF resins (E_2) cured at 120 °C for 1 h (heating rate = 10 °C/min).

Kissinger [9] proposed that:

$$E_a\beta/(RT_p^2) = Ae^{-E_a/RT_p}, \tag{1}$$

where β is the heating rate and can be expressed as $\beta = dT/dt$, R the gas constant, T_p the curing peak temperature, and A the frequency factor. By taking the logarithm of Equation (1), the Kissinger equation is obtained as follows:

$$-\ln(\beta/T_\mathrm{p}^2) = -\ln(AR/\mathrm{E_a}) + (1/T_\mathrm{p})(\mathrm{E_a}/R). \qquad (2)$$

E_a can be obtained by plotting $-\ln(\beta/T_\mathrm{p}^2)$ against $1/T_\mathrm{p}$. In the DSC thermograms for the E_2 control resin and scavenger containing UF resins at different heating rates, the curing peak temperature in the temperature range of 62.5–94.7 °C corresponds to the process of crosslinking reaction (Table 2). With increasing heating rate, the curing peak temperature shifts to a higher value. The areas of these peaks should be proportional to the amount of –CH$_2$–O–CH$_2$– linkages in the UF resins [7].

   With increasing heating rate, the exotherm peak from the polycondensation reaction of UF resin was shifted to higher temperatures for all resins. The plots of $-\ln(\beta/T_\mathrm{p}^2)$ against $1/T_\mathrm{p}$ for control UF resin and scavenger containing UF resins are shown in Figure 4. Table 2 presents the curing peak temperature and the E_a of the resins for the curing process. The E_a values obtained for the UF control resin and the resin with silica powder contents of 3 and 7 wt% were 83.1, 78.7, and 76.9 kJ/mol, respectively. The values with tannin powder contents of 3 and 7 wt% were 78.0 and 75.2 kJ/mol, respectively (Table 2 and Figure 5). The E_a of UF resin decreased with increasing tannin and silica powder contents, suggesting that the lower E_a of the scavenger containing UF resins accelerated the curing compared to that of the control UF resin.

Table 2. Curing peak temperatures in DSC exotherms and activation energies (E_a) as calculated by the Kissinger equation.

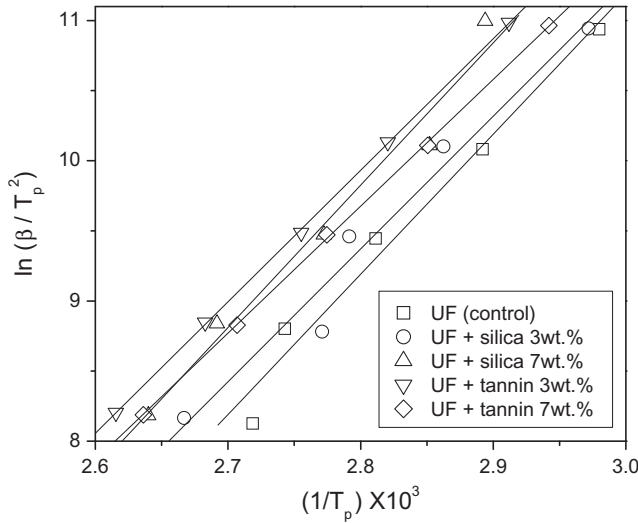|	Heating rate (°C/min)	Curing peak temp. (°C)	$\ln(\beta/T_\mathrm{p}^2)$ vs. $1/T_\mathrm{p}$	Activation energy (kJ/mol)
UF resin	2	62.6	$Y = 10.00X - 18.80$,	83.1
	5	72.8	$R^2 = 0.975$	
	10	82.7		
	20	91.6		
	40	94.8		
UF resin + 3 wt% silica	2	63.5	$Y = 9.47X - 17.14$,	78.7
	5	76.4	$R^2 = 0.967$	
	10	85.3		
	20	87.9		
	40	102.0		
UF resin + 7 wt% silica	2	61.8	$Y = 9.25X - 16.68$,	76.9
	5	73.0	$R^2 = 0.998$	
	10	81.1		
	20	91.1		
	40	98.9		
UF resin + 3 wt% tannin	2	70.4	$Y = 9.38X - 16.34$,	78.0
	5	81.5	$R^2 = 0.999$	
	10	90.0		
	20	99.7		
	40	109.3		
UF resin + 7 wt% tannin	2	66.9	$Y = 9.05X - 15.66$,	75.2
	5	77.8	$R^2 = 0.999$	
	10	87.5		
	20	96.4		
	40	106.3		

Figure 4. Plot of $\ln(\beta/T_p^2)$ vs. T_p^{-1} for UF resins (E_1) containing different contents of silica and tannin powder.
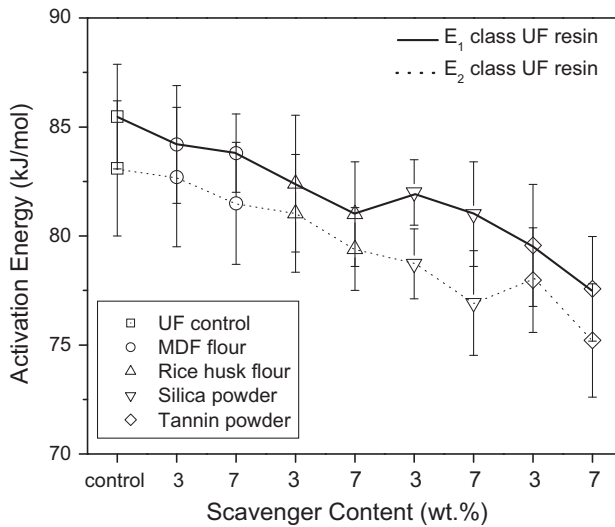

Figure 5. Activation energies of unmodified and modified UF resins with different scavengers using the Kissinger equation.

3.3. *Crystalline structure and crosslinking of UF resin*

Figure 6 shows the results of the crystallinity of the control UF resin (E_1) as a function of curing temperatures. The diffraction peaks with 2θ values of 22.5° and 25° were attributed to a partially crystalline UF resin. This crystallinity corresponds to an ordered arrangement of UF oligomers as demonstrated by molecular mechanics calculations [10]. Different packing configurations have similar energies, suggesting that the observed crystallinity was due to a random distribution of variously ordered arrangements of UF oligomers.
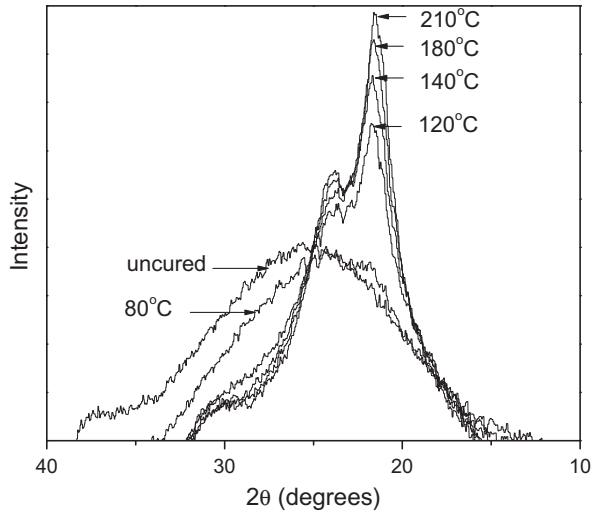
Figure 6. X-ray diffraction traces of unmodified UF resins (E_1) at different curing temperatures.

The amount of $-CH_2-$ crosslinks in the cured UF resin is high in amorphous structures. The amorphous resins must, therefore, include some structural characteristics which under all conditions increase the amount of crosslinking, and hence sufficiently cured resin. In contrast, insufficiently cured resin must have some structural characteristics causing a decrease in crosslinking of the cured resin [10].

The crystallinity proportion of the cured resin was 28.4% for the control UF resin (E_1), 27.2–26.9% for MDF flour, 25.9–24.5% for RHF, 25.3–23.9% for silica UF resins, and 23.4–21.6% for tannin UF resin (Figure 7). At same temperature and with increasing scavenger
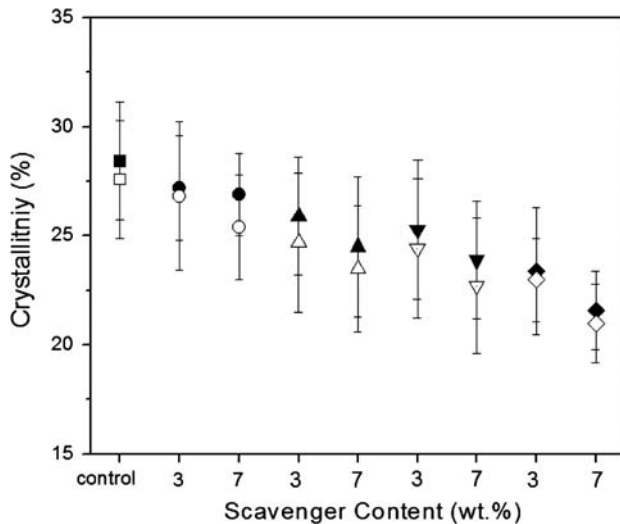

Figure 7. Crystallinity of all UF resins as a function of scavenger content.
■ UF control(E1), ●:MDF flour, ▲:Rice husk flour, ▼:Silica flour, ◆: Tannin flour, □: UF control(E2), ○:MDF flour, △:Rice husk flour, ▽:Silica flour, ◇: Tannin flour.
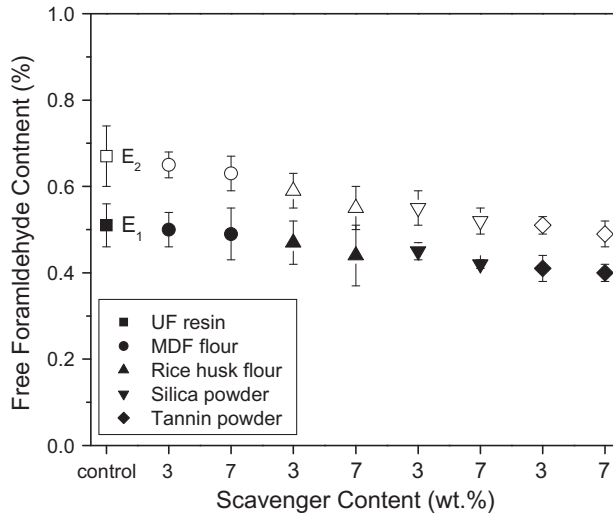
Figure 8.   Free formaldehyde content in UF resins as a function of scavenger content.

percentage from 3 to 5%, the trend of crystallinity of the cured resin decreased. Consequently, there should be some correlation between the crystallinity extent of the resin when cured and the strength of the same UF resin when used as an adhesive. In other words, increasing the crystallinity should decrease the extent of three-dimensional crosslinking, and hence weaken the strength of the hardened resin [11,12].

3.4.   *Free formaldehyde content in UF resins*

The free formaldehyde content of the UF resins as a function of scavenger content is summarized in Figure 8. UF odor is caused by the high volatility of formaldehyde, but the cause of the presence of free formaldehyde is complex. It can stem from a variety of partly related sources such as free, unreacted formaldehyde in the resin, formaldehyde dissolved in the moisture on the surface of wood panels bonded with UF resin, and variations in vapor pressure and release rate according to the humidity of the air and panels. The presence of free formaldehyde in the prepared UF resins is one of the reasons for formaldehyde emission. The control UF resin showed higher free formaldehyde than the other four resins, indicating that the free, unreacted formaldehyde is bonded with the scavenger in the UF curing reaction. The highest free formaldehyde was in the control UF resin and the overall free formaldehyde was in the order: control UF > UF + MDF flour > UF + RHF > UF + silica powder > UF + tannin powder.

3.5.   *Relationship between E_a and free formaldehyde content*

The E_a values calculated by the Kissinger equation for the control UF resin and scavenger containing UF resins are shown in Figure 5.

   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 scavenger content increased. In other words, the E_a of scavenger containing UF resin leads to its curing faster than control UF resin. These differences are clearly due to the different reaction mechanisms

described above. The incorporation of formaldehyde into scavenger occurs more easily and completely than its incorporation into urea.

When RHF and MDF flour are incorporated into the UF resin, the scavenger will absorb some water in the resin, thereby increasing the viscosity of the UF resin and decreasing the diffusion and mobility of the UF resin molecules. Therefore, the curing reactions of UF resin may be influenced by diffusion because the mobility of the molecules and their reactive groups decreases when the molecular weight increases, and crosslinking occurs between molecules at the latter stages of the curing process. The phase change in the curing system also affects the extent of conversion during the curing process of the UF resins [13]. The phase of a UF resin changes from a homogeneous solution to a heterogeneous system, when the UF resin is mixed with MDF flour and RHF. As a result, the UF resin disperses many droplets on the surface of the MDF flour and RHF. These droplets cannot be linked with each other, and a portion of the available functional groups therefore remains unreacted. The reduction of curing enthalpy observed with the addition of RHF and MDF flour might have been due to these factors [13].

The significantly lowered E_a of the UF resin containing tannin powder might have been because of the OH functional groups, reactivity with the free formaldehyde in the curing process. Moreover, this decrease in free formaldehyde content in the curing process also reduced the final curing enthalpy because formaldehyde in the curing system was required to bring the required reaction to a crosslinked [10]. It is of some importance that some less-favored reactions become more favored by the addition of tannin, to the detriment of the more commonly occurring reactions that do not appear to occur in the pure UF resin.

Figures 9 and 10 show the chemical structures of wattle tannin (*A. mearnsii*) flavonoid, according to Pizzi et al. [14], and of silica, respectively. The flavonoid units in such tannin extracts contain predominantly phloroglucinol or resorcinol A-rings and catechol or pyrogallol B-rings. The free C6 and/or C8 sites on the A-ring are reactive with formaldehyde because of their strong nucleophilicity. Some tannins contain A-rings which are resorcinolic in nature, while others contain A-rings which are phloroglucinolic in nature. The resorcinolic A-rings show reactivity toward formaldehyde comparable to that of resorcinol, while phloroglucinolic A-rings possess reactivity comparable to that of phloroglucinol. Tannins containing the greater amount of polymeric carbohydrates appear to react faster than other scavengers. Generally, a lowered E_a means the reaction will proceed faster under given curing conditions. These results also show that the formaldehyde emission was minimized at 7 wt% tannin.

A schematic illustration of the relationships between curing behaviors and free formaldehyde content is shown in Figure 11. The curing E_a of the UF resins decreased with
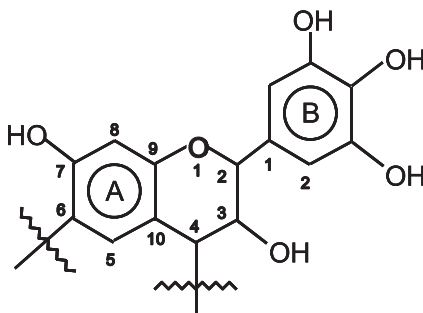

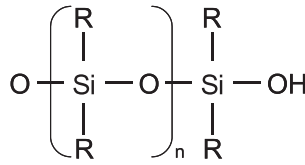Figure 9.   Chemical structure of wattle tannin flavonoid used.

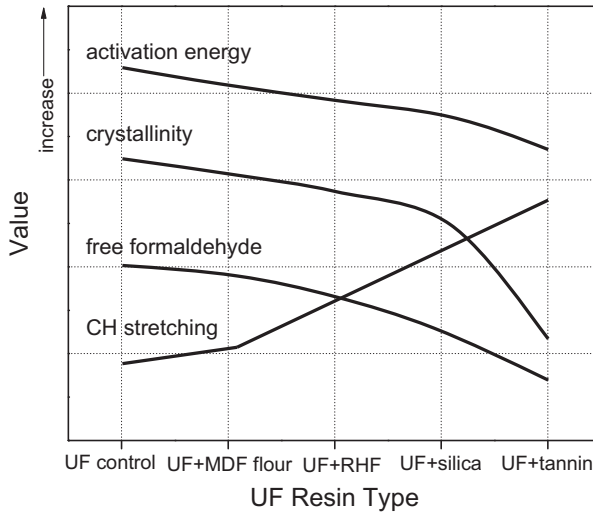Figure 10.   Chemical structure of silica used.

Figure 11.   Curing properties of UF resin as a function of scavenger kind.

scavenger addition. After curing, the crystallinity of the UF resins decreased in the presence of scavengers.

The extent of crosslinking should also have some influence on the formaldehyde emission from the wood panels bonded with UF resin. This is especially true for wood panels in service for long periods of time and exposed to high humidity conditions. Once the free formaldehyde that largely influences the emission has disappeared, the presence of the –CH$_2$– groups then becomes important. Hence, an increase in resin crosslinking means that there is a higher concentration of –CH$_2$– groups present, which with time might slowly hydrolyze and emit formaldehyde.

The most important factors determining the properties of the reaction products are (1) the relative molar proportions of urea and formaldehyde and (2) the reaction temperature and time [15]. The molecular species produced from the methylolation include mono-, di-, and tri-methylolureas. Tetramethylolurea has never been isolated. Low temperature and weak acidic pH condition favor the formation of methylene ether bridges (–CH$_2$–O–CH$_2$–) over methylolation. Each methylolation step has its own rate constant (k), with different k values for the forward and backward reactions. The reversibility of this reaction is one of the most important aspects of UF resins. This feature is responsible for both the low resistance against hydrolysis and the subsequent formaldehyde emission [15]. This indicates that formaldehyde emission could be related to E_a for the curing process of the resin.

4. Conclusions

The curing E_a of the UF resins was decreased with scavenger addition, as was the crystallinity of the UF resins after curing. The extent of crosslinking also affects the formaldehyde emission from wood panels bonded with UF resin, particularly those wood panels in service for long periods of time and exposed to high humidity conditions. Once the free formaldehyde that influences the emission has disappeared, the presence of the –CH$_2$– groups then becomes important. Hence, an increased resin crosslinking indicates a higher concentration of –CH$_2$– groups present, which may hydrolyze and emit formaldehyde slowly over time. The overall E_a value was in the order: control UF resin > UF resin + MDF flour > UF resin + RHF > UF resin + silica powder > UF resin + tannin powder.

After curing, the crystallinity of the UF resins decreased in the presence of scavengers. The amount of –CH$_2$– crosslinks in the cured resin was clearly higher in the amorphous structures, suggesting that the amorphous resins must include some structural characteristics which increase the degree of crosslinking and strengthen the resin under all conditions. The crystallinity of the cured UF resins decreased with increasing scavenger content in the order: control UF resin > UF resin + MDF flour > UF resin + RHF > UF resin + silica powder > UF resin + tannin powder. The unreacted free formaldehyde content was reduced with scavenger addition.

The results presented in this study support the important role played by MDF flour, RHF, silica powder, and tannin powder as scavengers in the curing process for UF resin.

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