

Differential Scanning Calorimetry Characterization of Urea–Formaldehyde Resin Curing Behavior as Affected by Less Desirable Wood Material and Catalyst Content

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ABSTRACT: Differential scanning calorimetry was applied to investigate the curing behavior of urea–formaldehyde (UF) resin as affected by the catalyst content and several less desirable wood materials (e.g., wood barks, tops, and commercial thinnings). The results indicate that the reaction enthalpy of UF resin increased with increasing catalyst content. The activation energy and peak temperature of the curing UF resin generally decreased with increasing catalyst content at lower levels of catalyst content. However, with further increases in catalyst content, the changes in the activation energy and peak temperature were very limited to nonexistent. The hydrolysis reaction of the cured UF resin occurred during the latter stages of the curing process at

both lower level (<0.2%) and higher level (>0.7%) catalyst contents. This indicates that there existed an optimal range of catalyst content for the UF resin. The curing enthalpy of the UF resin decreased with increasing wood raw materials present due to the effect of diffusion induced by the wood materials and the changes in the phase of the curing systems. This suggests that the curing reactions reached a lower final degree of conversion for the wood–resin mixtures than for the UF resin alone. © 2005 Wiley Periodicals, Inc. *J Appl Polym Sci* 98: 2027–2032, 2005

Key words: activation energy; catalysts; curing of polymers; differential scanning calorimetry (DSC)

INTRODUCTION

With the amount of forest resources declining and the concomitant rising cost of raw wood materials, it is becoming necessary for the wood industry to look for ways to use less desirable fiber resources for panel manufacturing, which include lower value raw materials such as wood barks, wood tops, and commercial thinnings. Changes in raw materials can have detrimental effects on the mechanical and physical properties of the panels and require changes in processing conditions, including in the resin system used. The acidity of the wood and the type and amount of acid catalyst mixed in the adhesive play very important roles in the curing behavior of urea–formaldehyde (UF) resin. To obtain optimum bond strength, the pressing parameters must be adapted to the curing behavior during panel manufacturing. If this correction is not precise, the resin will be uncured or overcured, which will result in lower bond strength and higher costs due to larger adhesive amounts needed to reach panel requirements. Understanding the effects

of various raw materials and catalyst contents on the curing behavior of UF resin is fundamental to the establishment of optimal processing parameters for the manufacture of wood-based composite products. Some effort has been put into the study of the curing behavior of UF resins by differential scanning calorimetry (DSC) as affected by the resin molar ratio, catalyst type, solid content, and heating rate.^{1–5} However, study on the curing behavior of UF resins as affected by wood raw materials and catalyst content has been very limited. The aim of this study was to investigate the effects of various less desirable raw materials and catalyst contents on the curing behavior of the UF resin by DSC and to generate useful information to optimize UF resin application for panel manufacturing.

EXPERIMENTAL

Raw materials

The raw materials for this study, as shown in Table I, were poplar (*Populus*) bark (PB), red pine (*Pinus resinosa*) bark (RPB), white spruce (*Picea glauca*) bark (WSB), 6-year poplar tops with bark (PT), red pine commercial thinnings without bark (RP), 6-year poplar commercial thinnings without bark (P₆), 10-year poplar commercial thinnings without bark (P₁₀), and

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TABLE I
Types and Codes of the Raw Materials

Type of raw material	Code
White spruce thinnings without bark	WS
White spruce bark	WSB
Red pine thinnings without bark	RP
Red pine bark	RPB
10-year poplar without bark	P ₁₀
6-year poplar without bark	P ₆
Poplar top with bark	PT
Poplar bark	PB

white spruce commercial thinnings without bark (WS). The commercial UF resin used was MDF-302 resin for medium density fiberboard from Borden Chemical, Inc. (Leves, PQ, Canada). The solid content of the resin was 65%, as measured by a solids pan technique. The pH value of the resin was 7.85. The catalyst used was a 10% NH₄Cl solution.

Wood pH value and buffer capacity measurement

We prepared the aqueous extract by refluxing 25 g of dry furnish in 200 g of distilled water for 20 min. Two replicates for each sample were prepared. After refluxing, the mixture was filtered through a filter paper with a vacuum. The aqueous extract was diluted to 500 mL and cooled down to room temperature before titration. All pH and buffer capacity measurements were made with a Corning Pinnacle 530 pH meter. Before each titration, the pH meter was calibrated with a standardized buffer solution to a pH of either 4 or 7, depending on the type of measurement to be done. After calibration, 100 mL of extract solution were pipetted into a 200-mL beaker; the initial pH of the solution was recorded, and the solution was then titrated to a pH of 3 (for alkaline buffer capacity) or 8 (for acid buffer capacity) with a nominal 0.025N H₂SO₄ or 0.025N NaOH solution. For each titration, two replicate measurements were done. Thus, the initial pH value for each sample was the average of eight measurements, and each buffer capacity value was the mean of four determinations. Here, we define the absolute acid buffer capacity as the buffering capacity of the acid after the effect of alkaline buffering capacity in a solution was eliminated.⁶ It can be expressed as:

Absolute acid buffer capacity

$$= \text{Acid buffer capacity} - \text{Alkaline buffer capacity}$$

DSC sample preparation

Raw material chips for each sample were air-dried for 2 weeks and ground into particles by passage through a No. 9 mesh screen (2 mm in diameter). Classification

of the particles for each sample was done with a No. 40 mesh screen (0.425 mm in diameter) and a pan. The powder in the pan was used for this study. To determine the effect of the catalyst content on the UF resin curing behavior, 10 catalyst contents (0, 0.1, 0.2, 0.3, 0.4, 0.5, 0.7, 1, 1.5, and 3% based on dry weight) were used to prepare specimens for DSC. To study the effects of the wood materials on the UF resin curing behavior, samples were prepared by the mixture of UF resin with various wood powders and NH₄Cl solution homogeneously according to the designed dry weight ratio (UF/wood/NH₄Cl = 1:1:0.003).

DSC measurement

The prepared samples were placed between an aluminum cup and lid and sealed tightly to increase the contact area between the sample and the pan and to prevent collapse of the pan at high pressure. The hermetic pan could maintain the moisture content inside the pan during DSC scanning. The sealed pan was placed into a TA Instruments DSC-2910 pressure cell and pressurized to 1.6 MPa with nitrogen, which thereby shifted the water vapor temperature from 100 to 200°C and prevented water evaporation in the scanning temperature range. Heating rates of 5, 10, and 15°C/min and a scanned temperature range of 20–200°C were selected. The sample size ranged from 9.2 to 12.3 mg for the liquid UF resins and from 7.11 to 8.19 mg for the wood/resin mixtures. Three replicates were conducted for each sample.

RESULTS AND DISCUSSION

Variation of the curing reaction behavior as affected by the catalyst content

The curing reactions of UF resins are typically exothermic, so it was hypothesized that the reaction enthalpy (ΔH) would simply be proportional to the degree of conversion (α) during the curing process. The DSC results from Table II show that ΔH obviously increased with increasing catalyst content. This indicates that the final ΔH of the curing reaction of the UF resin was strongly related to the catalyst content. The effect of the catalyst content on the final ΔH of the curing reaction could be explained by the increase in the reactivity of reactive groups by the decreased pH value in the curing system. The endothermic reaction seen in the DSC curves after resin curing should not have been related to vapor loss because the analysis was conducted under pressure. The hydrolysis of the cured UF resin might have contributed to this endothermic phenomenon. As shown in Figure 1, the endothermic reaction after resin curing was more pronounced at both lower levels ($\leq 0.1\%$) and higher levels ($> 0.7\%$) of catalyst content, whereas it was not notable in the range of 0.2–0.7% catalyst content. The

TABLE II
DSC Results of UF Resins Mixed with Varied Catalyst Contents

Catalyst content (%)	ΔH (J/g)	E_a (kJ/mol)	T_p (°C)		
			5°C/min	10°C/min	15°C/min
0	—	54.8	128.1	135.5	139.4
0.1	—	46.7	108.5	115.46	120.1
0.2	90	43.5	95.01	102.51	107
0.3	98.5	40.6	87.24	96.24	100.07
0.4	110.3	37.8	86.45	95.69	99.5
0.5	113.9	36.9	84.93	94.53	97.73
0.7	122.2	36.4	83.11	92.28	96.21
1.0	134.8	36.4	82.9	91.98	96.04
1.5	162.1	36.4	82.8	91.98	95.88
3.0	172.3	36.4	82.55	91.98	95.49

following factors might have been the main reasons for these observations. At lower levels of added catalyst, the pH value of the curing system was relatively high. Thus, the reaction rate would have been lower. To cure the resin, more time would have been needed. However, with increasing temperature, a hydrolysis reaction occurred and became more intense with time. The hydrolysis reaction would have retarded or even stopped the curing reaction. Thus, the endothermic reaction occurred at the latter stages of the curing process. On the other hand, higher catalyst content resulted in lower pH values in the curing system. Much evidence exists that low pH accelerates not only the rate of cure of UF resins but also their rate of hydrolysis after resin curing.^{7-11,3,12} It is, therefore, of critical importance to add catalyst and to control hot-pressing time precisely to obtain optimal bond strength in a panel. A range of catalyst content of

0.2–0.7% would be desirable in the panel manufacturing for this UF resin.

The activation energy (E_a) at the peak point of the DSC curve was calculated by standard method ASTM E 698-79.¹³ The method involves a plot of $\log(\Phi/T_{max}^2)$ against $1/T_{max}$, which gives a straight line, where Φ is the heating rate, and T_{max} is the peak temperature of the DSC scanning curve. E_a is given by

$$E_a = \text{Slope of the line} \times R$$

where R is the universal gas constant ($8.314 \text{ J mol}^{-1} \cdot \text{K}^{-1}$).

In general, E_a of the catalyst/resin mixture was lower than that of the UF resin alone. Furthermore, E_a decreased with increasing catalyst content in the UF curing systems at lower levels of catalyst content ($\leq 0.5\%$). However, E_a seemed unchanged at higher

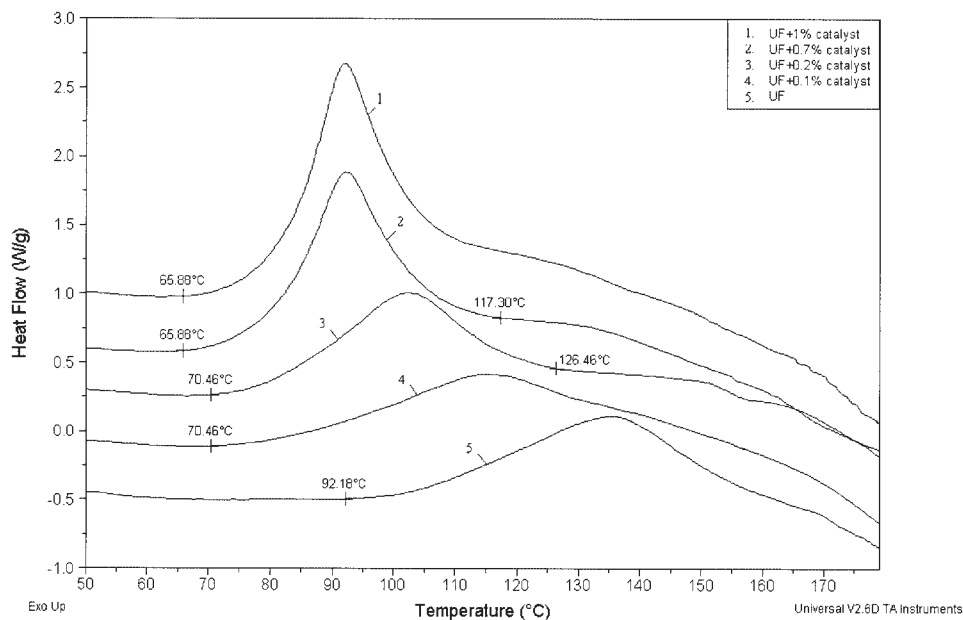


Figure 1 DSC curves of the mixture of the UF resin and catalyst (heating rate = 10°C/min).

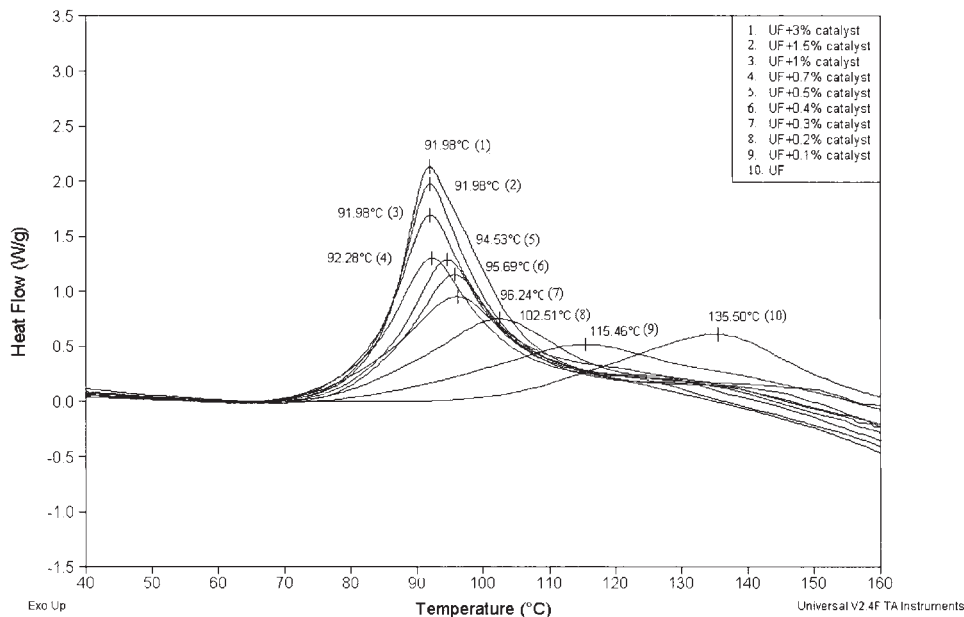


Figure 2 T_p as affected by the catalyst content (heating rate = $10^{\circ}\text{C}/\text{min}$).

levels of catalyst content. Several factors may have influenced the changes in the activation energies of the curing systems. The variation of the pH values in the curing systems was the most probable contributor. Because curing of UF resin occurs under acidic conditions, with the introduction of catalyst, the resulting decrease in pH in the UF curing system may have led to a decrease in E_a of the UF curing reaction. With increasing catalyst content, most reaction groups were activated. Thus, with further increases in catalyst content, the change of E_a was very limited.

The peak temperature (T_p) is the temperature at which the conversion rate reaches a maximum during a dynamic scan of the reaction. The T_p 's ranged from 82 to 128°C for a heating rate of $5^{\circ}\text{C}/\text{min}$, from 92 to 135°C for a heating rate of $10^{\circ}\text{C}/\text{min}$, and from 95 to 139°C for a heating rate of $15^{\circ}\text{C}/\text{min}$. The decrease in T_p with increased catalyst content was very significant at lower levels of catalyst content ($\leq 0.3\%$), whereas no significant change was observed at higher levels of catalyst content ($> 0.3\%$), as shown in Figure 2.

The initiation (start) temperature (T_s) is the temperature where the curing reaction starts; this value was obtained from the DSC curves. With a heating rate of $10^{\circ}\text{C}/\text{min}$, T_s of the curing reaction decreased by more than 20°C by the addition of 0.1% catalyst, as shown in Figure 1. With further increases in catalyst content ($> 0.1\%$), the resulting decreases in T_s were very limited.

Variation of the curing reaction behavior as affected by wood raw materials

The DSC results of the UF resin and its mixtures with wood raw materials and 0.3% catalyst are summarized in Table III.

ΔH obviously decreased when wood raw material was added in the curing systems of the UF resin. This indicates that the final ΔH 's of the curing reaction for the mixtures of UF resin with wood were lower than those for the UF resin alone. The main factors could have been diffusion control and the change in the reaction phase of the curing system.¹⁴ When dry wood powder is introduced into UF resin, the powder will absorb some water in the resin. As a result, the viscosity of the UF resin increases. Consequently, the diffusion and mobility of UF resin molecules are reduced. Therefore, the curing reactions of UF resin may be influenced by diffusion because the mobility of the molecules and their reactive groups decrease 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 conversion during the curing process of UF resins. The phase of a UF resin changes from a homogeneous solution to a heterogeneous system

TABLE III
DSC Results of the UF Resin and Its Mixtures with Wood Raw Materials

Sample	ΔH (J/g)	Reduction of ΔH (%)	T_p ($^{\circ}\text{C}$)	T_s ($^{\circ}\text{C}$)
UF	103.78	0	95.53	65.75
P ₆	93.36	10.00	100.92	69.54
RP	92.82	10.56	97.56	66.18
WS	86.75	16.41	98.39	65.59
PB	83.55	19.49	101.14	65.26
PT	83.09	19.94	103.54	69.82
WSB	75.67	27.09	94.23	55.19
RPB	66.77	35.66	91.56	56.55
P ₁₀	—	—	105.73	71.89

TABLE IV
pH and Buffer Capacity of the Raw Materials

Sample	pH	Acid buffer capacity (mmol/L)	Alkaline buffer capacity (mmol/L)	Absolute acid buffer capacity (mmol/L) ^a
WS	4.79	0.44	0.69	-0.25
WSB	4.76	1.74	1.18	0.56
RP	4.72	0.41	0.64	-0.23
RPB	4.55	1.31	0.96	0.35
P10	6.85	0.17	1.64	-1.47
P6	6.17	0.33	1.2	-0.87
PT	5.28	1.54	1.94	-0.40
PB	5.05	4.14	4.69	-0.55

^a Absolute acid buffer capacity = Acid buffer capacity - Alkaline buffer capacity.

when the UF resin is mixed with wood. As a result, the UF resin disperses many droplets on the surface of the wood powder. These droplets cannot be linked with each other, and a portion of the available functional groups remain unreacted. The reduction of 10–20% ΔH on the addition of P₆, RP, WS, PB, and PT might have been due to these factors. Another major factor affecting ΔH was the reaction between formaldehyde and the wood extractives during the resin curing process. The significantly lowered ΔH 's of the UF resin mixed with RPB and WSB might have been due to these materials' rich extractives, such as tannin, which could have reacted with the free formaldehyde in the curing system. Moreover, this decrease in free formaldehyde content in the curing system also reduced

the final ΔH because formaldehyde in the curing system was needed to bring the required reaction to a crosslinked and glass-like solid.¹⁵ The pH values and buffer capacities of the UF resin mixed with wood materials might have played a role in the observed ΔH 's. However, there was no evidence that these factors had significant effects on the curing enthalpy of the UF resin. The DSC curves of the UF resin mixed with P₁₀ at 0.3% added catalyst content showed that the curing rate was lower than that of the UF resin mixed with other wood materials. As a result, the hydrolysis reaction occurred at the latter stages of the curing process. There are two ways to avoid hydrolysis at the latter stages of the curing process during DSC scanning. One is to increase the curing reaction rate by the addition of the correct amount of catalyst. Another is to use a lower heating rate.

T_p and T_s of the UF in the presence of hardwood (poplar) were higher than those of UF in the presence of softwood (white spruce and red pine). The increased pH values of the wood–resin mixtures caused by the introduction of poplar powder, which had a higher pH than softwood powders (Table IV), were likely to be the main contributors to this effect. The acid buffer capacity of the wood (estimated here by the absolute acid buffer of the wood extracts) should also be considered because this can also influence the change in pH value of the resin. The absolute acid buffer capacity (Table IV) had a strong relationship with T_p and T_s as shown in Figures 3 and 4.

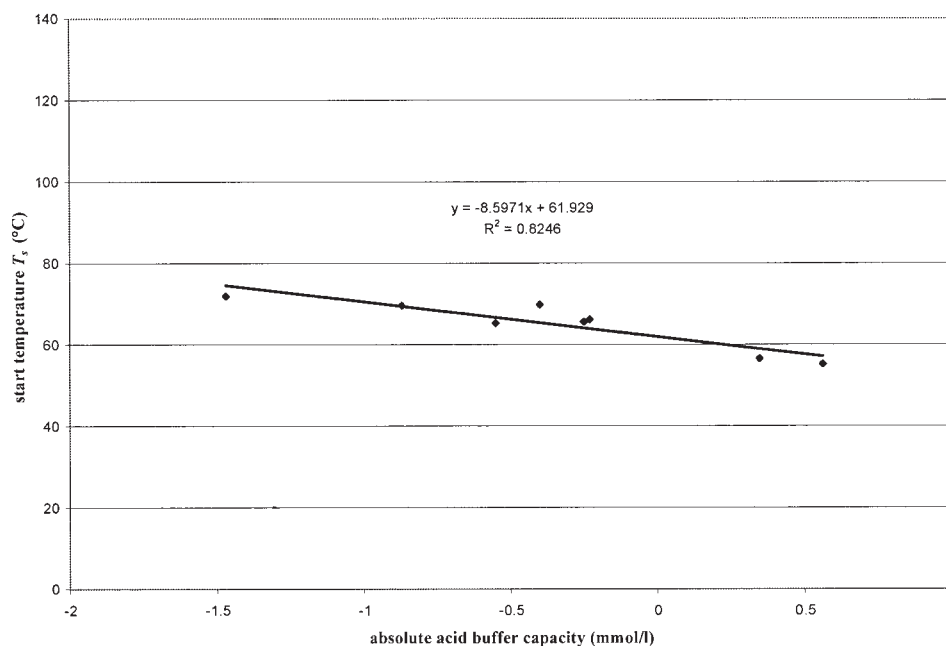


Figure 3 Curing T_s of the UF resin as affected by the absolute acid buffer capacity of the wood raw materials (heating rate = 10°C/min).

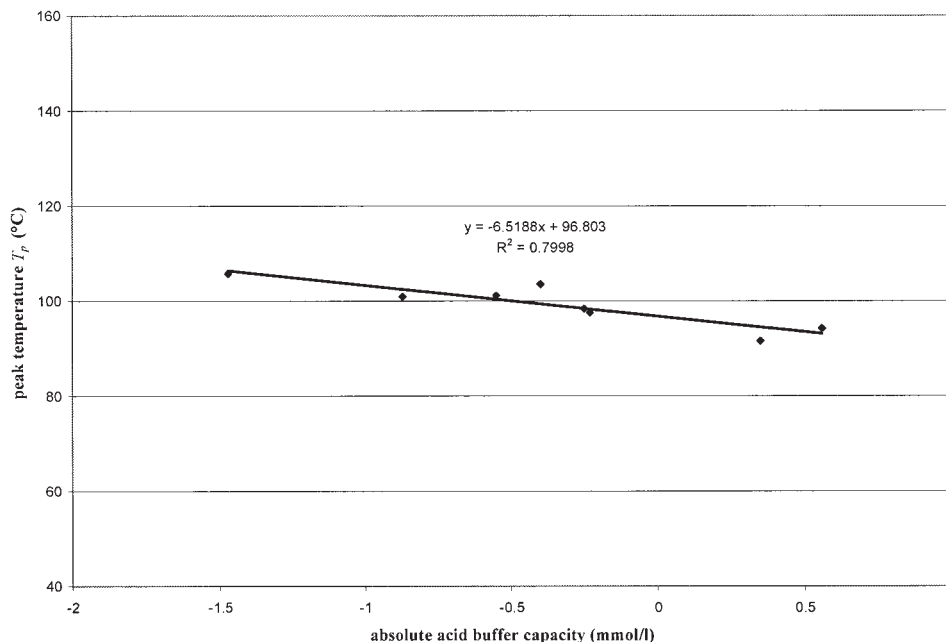


Figure 4 Curing T_p of the UF resin as affected by the absolute acid buffer capacity of the wood raw materials (heating rate = 10°C/min).

CONCLUSIONS

From this study, the major findings and conclusions are as follows. Catalyst content played a very important role in the UF resin curing, ΔH , E_a , T_p , and the stability of the cured resin. ΔH increased with catalyst content. E_a and T_p decreased with increased catalyst contents in the range 0–0.5%. The changes in E_a and T_p with further addition of the catalyst were very limited. Both lower and higher catalyst contents cause hydrolysis to occur during the latter stages of the curing process. An optimal range of catalyst content used for the UF resin existed.

The curing behavior of the UF resin was affected by the presence of wood raw materials in the curing system. In general, the curing enthalpy of the UF resin decreased with the presence of wood materials. Moreover, the presence of barks decreased curing enthalpy more than wood did.

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