

Curing Characteristics of Urea–Formaldehyde Resin in the Presence of Various Amounts of Wood Extracts and Catalysts

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ABSTRACT: The characteristics of urea–formaldehyde (UF) resin curing in the presence of wood extracts and a catalyst [ammonium chloride (NH₄Cl)] were investigated by differential scanning calorimetry (DSC). The effects of extracts from 16 wood species on resin curing behaviors were evaluated. A model developed in this study, $T_p = 53.296 \exp(-9.72C) + 93.104$, could be used to predict the resin curing rate in terms of the DSC peak temperature (T_p) as influenced by the NH₄Cl content (C). The results indicated that the curing rate of UF resin increased as the catalyst content increased and reached a maximum when the catalyst content ranged from 0.5 to 1.0% (solid basis over liquid UF resin weight). Further increases in the catalyst content had no effect on the resin curing rate. The

curing rates of UF resin in the presence of wood extracts increased with decreased pH values or increased base buffer capacities. It was also discovered that the activation energy could not fully explain the resin curing behavior when some species of wood extracts were present, and therefore, the pre-exponential factor had to be taken into account. The concept of the equivalent catalyst content (ECC) of wood extracts to the NH₄Cl content was introduced in this study; ECCs ranged from 0.0022 to 0.0331% among the 16 wood species. © 2007 Wiley Periodicals, Inc. *J Appl Polym Sci* 107: 1555–1562, 2008

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

INTRODUCTION

Urea–formaldehyde (UF) resin is the most common adhesive used in the manufacture of plywood, particleboard, medium-density fiberboard (MDF), and other nonstructural wood products. The initial pH value of UF resin is adjusted to be 7.0–8.5 for storage reasons. The condensation reaction (curing reaction) of UF resin with commercial applicability occurs under acidic conditions in combination with heat via hot pressing. In practice, a catalyst is indispensable for the rapid and efficient curing of UF resin; with a catalyst, UF resin increases its molecular weight by building chain lengths and forming crosslinks between chains.¹ It is well known that the degree of resin curing contributes to the properties of wood-based composites bonded by UF resin; a high degree of resin curing should be ensured. Insufficient catalyst will lead to a slow curing rate and will result in poor composite properties. Therefore, more resin would be required or a longer hot-press time would be needed to ensure desirable composite properties. Any such remedies would increase cost or reduce productivity. In MDF manufacturing, a superfluous

catalyst for UF resin could result in either a precured layer that is too thick and has to be sanded away from the MDF panel or the overcuring of the resin, which would result in poor panel properties.

Therefore, a knowledge of catalyst systems for UF resin is important for the efficient use of UF resin to achieve good bonding in the manufacturing of wood-based composites, such as plywood, particleboard, and MDF panels. Ammonium chloride (NH₄Cl) is traditionally a commonly used catalysts for UF resin curing due to its powerful catalysis and low cost.

Many studies have shown that UF resin curing is affected by wood species,^{2–7} pH, the buffer capacity of wood,^{3–6} and the soluble-acid and bound-acid contents.^{6,7} Hiroshi² appeared to be the first to evaluate the effects of wood species on UF curing by a differential thermal analysis technique in 1973. He classified wood species into two groups: one that had nearly no effect on the UF cure rate and one that had some influence on the reaction. Since then, some modern techniques such as differential scanning calorimetry (DSC)^{4,5,8} and dynamic mechanical analysis⁹ have been used to characterize UF curing. With dynamic scanning of UF resin with a single-heating-rate method, DSC analysis can provide ample information that is closely related to resin curing, such as total reaction heat, onset temperature,

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TABLE I
Chemical Properties of the 16 Species of Woods

Commercial name	Botanical name	Hot-water extracts (%)	Wood pH	Base buffer capacity (mequiv)	Acid buffer capacity (mequiv)
Aspen	<i>Populus tremuloides</i>	1.34	4.75	3.83	4.49
Balsam fir	<i>Abies balsamea</i>	1.75	4.97	6.93	6.75
Black spruce	<i>Picea mariana</i>	1.56	4.72	2.25	4.44
Hemlock	<i>Tsuga canadensis</i>	1.38	4.90	3.57	7.19
Jack pine	<i>Pinus banksiana</i>	1.77	4.25	2.87	5.94
Red maple	<i>Acer rubrum</i>	1.33	5.30	2.67	6.67
Red oak	<i>Quercus rubra</i>	3.41	3.74	2.17	16.22
Red pine	<i>Pinus resinosa</i>	2.12	4.22	3.85	7.61
Sugar maple	<i>Acer saccharum</i>	1.62	6.32	3.88	5.66
White birch	<i>Betula papyrifera</i>	1.01	4.07	2.94	8.03
White cedar	<i>Thuja occidentalis</i>	1.97	4.49	1.86	11.90
White elm	<i>Ulmus americana</i>	1.03	5.46	5.20	5.30
White oak	<i>Quercus alba</i>	1.95	3.84	1.62	11.07
White pine	<i>Pinus strobes</i>	2.09	4.23	2.41	6.02
White spruce	<i>Picea glauca</i>	1.15	4.73	1.92	4.57
Yellow birch	<i>Betula alleghaniensis</i>	0.91	4.81	2.30	6.40

peak temperature, and activation energy. Therefore, the DSC technique was applied in this study.

The effect of wood species on MDF performance may be related to the chemical characteristics of the extracts present in the wood. Thus, the influence of wood species on UF resin curing can be minimized by the proper adjustment of the catalyst content. Currently, information available in the literature on UF curing as affected by wood extracts is limited. The purpose of this study was to investigate, with the DSC technique, the effect of wood extracts on UF curing. The results of this study should provide useful information on wood species and their impact on UF resin curing and bonding in composite panel manufacturing.

EXPERIMENTAL

Materials

A commercial UF resin designed for particleboard was used in this study. The solid content and pH value of the resin were 65.16% and 7.82, respectively. Gel time at 100°C with a 20% NH₄Cl solution was 50–60 s.

The NH₄Cl used was an ACS reagent grade chemical manufactured by Laboratoire Mat (Quebec, Canada). NH₄Cl was first prepared into an aqueous solution with 10 wt % concentration and then diluted into eight aqueous solutions with concentrations ranging from 0.162 to 7.494%, with different amounts of stoichiometric distilled water.

A total of 16 wood species grown in Eastern Canada were collected. All were used as raw materials in the manufacture of particleboard and MDF panels. For each wood species, fresh log was flaked into strands 76.2 mm long by 0.635 mm thick by random widths with a CAE waferizer (Surrey, B.C. Canada).

Next, the strands were dried to around 5% moisture content (MC) at 65°C. We then ground them into wood flours by passing them through a 2-mm (10-mesh) sieve with a Willey mill grinder (Swedesboro, NJ). The wood flours were extracted by hot water for 3 h. The mass ratio of wood to distilled water was 1 : 10. The extracted solutions from the 16 wood species were kept frozen before freeze drying for extracts. Freeze drying was done with equipment (a process called lyophilization).

The chemical properties of the 16 wood species, including pH value, acid buffer capacity, and base buffer capacity, are presented in Table I and were determined as follows: 25 g of wood flour (oven-dry basis) was added to 200 mL of boiled/distilled water in a 500-mL flask equipped with a condenser. This was refluxed for 20 min once the water began boiling. The mixture was cooled and then filtered. Finally, the flask was filled to 500 mL. The base buffer capacity in this study was defined as the milliequivalents of base needed to titrate 100 mL of extracted solution to a pH of 11.00 with a 0.025N sodium hydroxide solution. The acid buffer capacity in this study was defined as the milliequivalents of acid needed to titrate 100 mL of extracted solution to a pH of 3.00 with a 0.025N sulfuric acid solution. The initial pH value from the titration of the acid buffer capacity was reported as the wood pH.

To measure the interaction of a wood extract and UF resin, the extract was thoroughly dissolved in the resin before the DSC scan. Some extracts were not soluble in the resin or in water at room temperature. Therefore, each wood extract was dissolved in a 20% acetone aqueous solution (20/80 w/w acetone/water) to get an extract solution with a concentration of 4.875 wt %.

TABLE II
 T_p Values of the UF Resin with Different Catalyst Contents

Catalyst concentration (%)	Catalyst content (%) ^a	T_p (°C)	Predicted T_p (°C)
0	0	144.24	146.40
0.162	0.032	135.67	132.15
0.325	0.065	123.30	121.44
0.569	0.114	107.60	110.70
0.812	0.162	102.22	104.14
2.437	0.487	95.27	93.57
4.875	0.975	93.51	93.11
6.248	1.250	93.10	93.10
7.494	1.499	92.81	93.10

^a The catalyst content refers to the percentage of solid NH_4Cl over the liquid UF resin.

DSC measurement

To prepare the DSC samples, 5 ± 0.005 g of UF resin was weighed and put in a 10-mL beaker; 1.0 mL of a catalyst solution or wood extract solution was pipetted into the resin. This was followed by blending for 40 s. Next, about 3.5–4.5 mg of the blended mixture was sealed in a DSC hermetic pan. For each DSC scan, the total time for sample preparation was controlled within 8–10 min.

For each DSC measurement, pressure DSC (DSC 2910, TA Instrument Co., New Castle, DE) was used. Heating rates of 10, 15, and 20°C/min in a scanning temperature range of 20–220°C were selected, and a pressure of 4 MPa with nitrogen gas was used during the DSC scanning.

Activation energy analysis

There are several methods for calculating the activation energy of resin curing with DSC. In many studies involving resin curing, the Kissinger equation and the Ozawa equation have been the most common models used.^{2,10–13} In this study, the Kissinger activation energy and the Ozawa activation energy, which were calculated from the Kissinger equation and the Ozawa equation, respectively, had negligible differences with relative variances of less than 2.58%. Therefore, the Kissinger equation was selected as the model equation because it could be used to calculate not only the activation energy but also the pre-exponential factor, as shown in eq. (1). Unless stated otherwise, *activation energy* refers to the Kissinger activation energy:

$$-\ln\left(\frac{\beta}{T_p^2}\right) = \frac{E_a}{RT_p} - \ln\left(\frac{ZR}{E_a}\right) \quad (1)$$

where β is the heating rate (°C/min), E_a is the activation energy (kJ/mol), R is the gas constant (8.314 J·mol⁻¹·K⁻¹), T_p is the peak temperature (K), and Z is the pre-exponential factor (1/s).

On the basis of the equation, there was a straight line between $-\ln(1/T_p^2)$ and $1/T_p$; from this, the activation energy and the pre-exponential factor could be calculated from the slope and the intercept, respectively. Theoretically, more than four heating rates are needed, in general, for eq. (1) to obtain accurate activation energies and pre-exponential factors. However, because our goal was to focus on the evaluation of commercially available wood species for particleboard and MDF, there were only three heating rates applied in this study; we expected that this would provide information on the general effect of wood extracts on UF curing, which is very important in wood-panel composite manufacturing.

RESULTS AND DISCUSSION

UF resin curing in the presence of different catalyst contents

In practice, catalyst use generally ranges between 0.5 and 1.25% in a solid basis over UF resin in a liquid basis. To compare the catalytic effect of wood extracts on UF resin curing, a series of DSC scans at a heating rate of 15°C/min were made for the resins with different catalyst contents ranging from 0.032 to 1.5%, as shown in Table II. A control was also prepared by the mixing of 5 ± 0.005 g of UF resin with 1.0 mL of water to investigate the catalytic effect of NH_4Cl on UF resin curing. In other words, this control had 0% catalyst content.

The test results are summarized in Table II and illustrated in Figure 1. The control sample without catalyst showed a peak temperature of 144.24°C. The peak temperature related to the curing rate of UF resin decreased significantly with increased catalyst content up to 0.487% in the resin. After this, a further increase in the catalyst content only slightly lowered the peak temperature, especially above

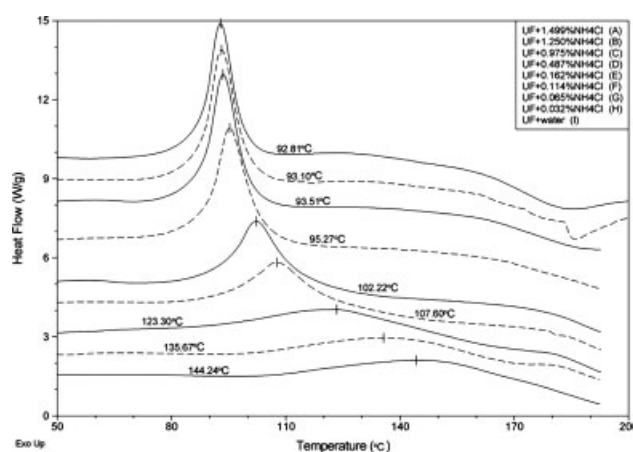


Figure 1 DSC curves of the UF resin cured with different catalyst contents (heating rate 15°C/min).

0.975%. Because the reaction of formaldehydes with the catalyst (NH_4Cl) generates hydrochloric acid that catalyzes UF resin curing,¹⁴ the reduced curing rate was attributed to a limitation in the free formaldehyde available for crosslinking reactions of the resin system. This study indicated that a catalyst content of 0.5–1.0% was critical to UF resin curing. We also observed that an increase in the catalyst level resulted in taller and narrower temperature peaks, which implied that the resin cured more completely. When the catalyst content was less than 0.162%, the DSC peak became too broad to accurately ascertain the onset and end temperatures of the curing peak; therefore, it was impossible to draw the baseline and measure the area under the peak or the total heat of the reaction.

The correlation between the DSC peak temperatures and catalyst contents shown in Table II could be expressed by eq. (2):

$$T_p = 53.296 \exp(-9.720C) + 93.104 \quad (2)$$

where T_p is the DSC peak temperature ($^{\circ}\text{C}$) and C is the catalyst content (%) on a solid basis over the UF resin in a liquid basis.

We observed that the resin curing rate, expressed as the DSC peak temperature, was strongly correlated to the catalyst content ($R^2 = 0.988$). The extrapolated value of the DSC peak temperature was 93.104°C , which was the lowest DSC peak, or the maximum curing temperature, that could be obtained for a given UF resin with an infinite increase in the catalyst (NH_4Cl) level. This theoretical value seemed to be reached when NH_4Cl was used at about 1.0% catalyst content in this study. The predicted peak temperatures calculated from eq. (2) are shown in Table II; the variation between the predicted and experimental peak temperatures was less than 2.88%. Thus, eq. (2) could be used to predict the DSC peak temperature of the UF resin curing within a certain range of catalyst content.

UF resin curing in the presence of different wood extracts

Hot-water extracts, as part of wood components, possibly influence UF resin curing during hot pressing. The hot-pressing process used in the manufacture of plywood, particleboard, and MDF panels normally involves wood MC of about 9–11% and temperatures ranging from 100 to 220°C . The contents of hot-water extracts for the 16 wood species varied between 0.91 and 3.41% on a dry wood basis, as shown in Table I. For the DSC test, each aqueous extract solution was prepared with a 4.875% concentration; 1.0 mL of the aqueous extract solution was mixed with 5 g of the liquid UF resin. Thus, the

extract content in the resin was 0.975% on a solid basis over liquid UF resin.

Two control samples were prepared by the mixing of 5 ± 0.005 g of UF resin with 1.0 mL of a 20% acetone aqueous solution (acetone/water) and with 1.0 mL of a 20% acetone aqueous solution containing 0.975% NH_4Cl , respectively. The first control sample was used to investigate the effect of acetone introduced in resin curing, and the second sample was used to investigate the catalytic effect of wood extracts. The DSC peak temperatures (heating rate = $15^{\circ}\text{C}/\text{min}$) of the UF resin mixed with the acetone/water solution were similar to those of the UF resin mixed with water only (144.63 vs 144.24°C , as shown in Tables III and II, respectively). This result indicates that acetone introduced for the dissolution of the wood extracts had a minor effect on resin curing.

The results of DSC measurement with different wood extracts and their kinetic analyses are summarized in Table III. The curing peak temperature of UF resin in the presence of each wood extract was in the range 131.72 – 145.25°C when the heating rate was $15^{\circ}\text{C}/\text{min}$. The sharp curing peaks were similar to those of UF cured with NH_4Cl at contents lower than 0.162%. From these peaks, it was not possible to ascertain the onset and end temperatures; therefore, the total heat produced from the curing reaction could not be measured.

We also found that activation energies of the UF resin cured in the presence of different wood extracts were in the range 86.28 – 234.09 kJ/mol. For two control samples, the activation energy was 132.00 kJ/mol for UF with a 20% acetone aqueous solution and 75.28 kJ/mol for UF with NH_4Cl . These test results indicate that NH_4Cl was more powerful than any wood extract in the catalysis of UF resin curing. The catalytic effects of wood extracts on UF resin curing were dependent on the wood species. On the basis of the curing activation energy (132.00 kJ/mol) for the UF resin with a 20% acetone aqueous solution (no catalyst), the 16 species could be classified into following three groups:

1. No or minor catalytic effect (activation energy = 118 – 145 kJ/mol): the activation energy for the UF resin with wood extracts varied $\pm 10\%$ from the activation energy of the UF control without catalyst (132 kJ/mol). This group, which included hemlock, jack pine, white cedar, and white spruce, appeared to have little or no effect on UF resin curing. The $\pm 10\%$ variances from the control were the estimated value ranges that may have resulted from experimental errors of DSC analysis and/or the actual variation of activation energies.
2. Positive catalytic effect (activation energy = 86 – 118 kJ/mol): this group of species seemed

TABLE III
DSC Results for the UF Resin in the Presence of Wood Extracts of 16 Species

Extract species or control	T_p (°C)			E_a (kJ/mol)	Z	R^2
	10 (°C/min)	15 (°C/min)	20 (°C/min)			
Aspen	133.74	137.46	143.87	86.28	7.95×10^{10}	0.9328
Balsam fir	135.44	138.56	144.62	95.13	1.07×10^{12}	0.916
Black spruce	136.99	143.12	146.05	100.03	3.87×10^{12}	0.9866
Hemlock	138.04	143.45	143.02	138.08	3.46×10^{17}	0.7556
Jack pine	134.77	137.59	142.22	120.15	2.24×10^{15}	0.9410
Red maple	137.24	139.08	145.59	97.39	1.95×10^{12}	0.8247
Red oak	126.28	131.72	134.41	106.41	6.54×10^{13}	0.9888
Red pine	135.85	137.66	140.47	198.60	3.49×10^{25}	0.9496
Sugar maple	139.69	145.25	148.20	109.11	4.87×10^{13}	0.9923
White birch	136.06	139.10	142.22	95.89	1.49×10^{12}	0.9897
White cedar	132.06	137.41	141.12	141.50	1.42×10^{18}	0.9656
White elm	137.26	142.89	145.57	109.60	6.88×10^{13}	0.9866
White oak	128.12	133.23	136.71	103.38	2.21×10^{13}	0.9997
White pine	137.63	139.50	141.18	234.09	1.15×10^{30}	0.9612
White spruce	139.72	142.74	147.07	126.51	9.49×10^{15}	0.9582
Yellow birch	136.52	142.41	146.65	90.91	2.55×10^{11}	1.0000
Acetone/water (control)	140.10	144.63	146.26	132.00	4.46×10^{16}	0.8772
NH ₄ Cl (control)	86.40	93.55	94.77	75.28	5.95×10^{10}	0.9042

favorable to UF resin curing and included aspen, balsam fir, black spruce, red maple, red oak, sugar maple, white birch, white elm, white oak, and yellow birch. The activation energies of these species were less than the activation energies of the UF control without catalyst, minus a 10% variance.

- Negative catalytic effect (activation energy = 145–234 kJ/mol): this group contained two species, red pine and white pine. These species did not seem to favor UF resin curing because the activation energies were much higher than those of the UF control without catalyst, plus a 10% variance.

Activation energy is a kinetic parameter independent of curing temperature, but it reflects the sensitivity of a resin to temperature. Activation energy is usually calculated from the changes in the level of DSC peak temperature as heating rate changes. Therefore, a resin curing with a lower activation energy indicates that the curing rate is more sensitive to temperature change compared to that of a resin with a higher activation energy. In addition, the activation energy could be used as a reference in the evaluation of UF resin curing behavior.

The activation energy did not, however, reveal the whole picture of resin curing when certain wood extracts were present; the activation energy was often influenced by the curing conditions. For example, the peak temperatures of UF curing were 128.12, 123.23, and 136.71°C for extracts from white oak, whereas the peak temperatures were 136.99, 143.12, and 146.05°C for extracts from black spruce at heat-

ing rates of 10, 15, and 20°C/min, respectively, as shown in Table III. Thus, the use of white oak extracts resulted in lower peak temperatures compared with the use of black spruce extracts; this result indicates that white oak extracts had a stronger catalytic effect on resin curing than black spruce extracts. However, the activation energies of these two species were quite similar (103.38 vs 100.03 kJ/mol). Table III also shows another example in which the aspen/UF sample displayed a higher peak temperature than the white oak/UF sample at each heating rate. However, the aspen/UF sample had a much lower activation energy than the white oak/UF sample (86.28 vs 103.38 kJ/mol, respectively). These two cases imply that other kinetic variables, such as the pre-exponential factor, should also be considered to better understand the cure kinetics of UF resin curing in the presence of wood extract.

According to the well-known Arrhenius equation, shown in eq. (3), the rate constant of UF curing is determined by both the activation energy and the pre-exponential factor. When UF curing is evaluated by DSC, the peak temperature corresponds to the curing rate of the UF resin or is directly proportional to the rate constant. According to the collision theory,¹⁵ the pre-exponential factor is equivalent to the total number of successful collisions that result in a reaction; these successful collisions occur as a result of reactant particles coming sufficiently into contact with each other. Collision theory also indicates that the number of successful collisions is defined by both temperature and the characteristics of the reactant particles. Furthermore, vast differences in the nature and amount of the various chemical components within wood extracts can be found even

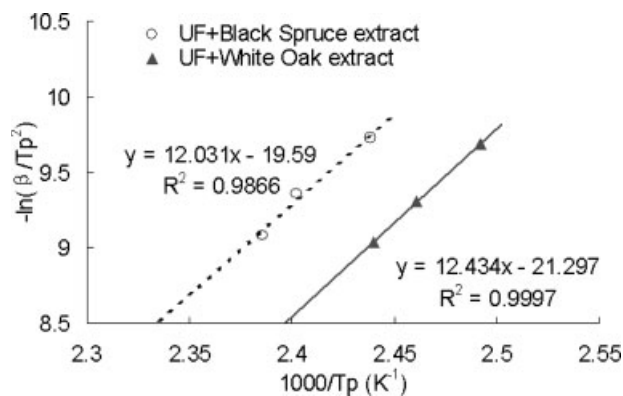


Figure 2 Kissinger plots for the UF resin in the presence of black spruce and white oak extracts.

within a single species, depending on the age and growth site of the trees sampled and the sampling location within the log, for example. Therefore, each wood extract may have different effects on successful collisions and may, therefore, affect the curing reaction of UF resin at the same temperature:

$$k = Z \cdot \exp(-E_a/RT) \quad (3)$$

where k refers to the rate constant of a chemical reaction, Z is the pre-exponential factor or Arrhenius frequency factor, R is the gas constant, E_a is the activation energy, and T is the absolute temperature of the reaction taking place.

A plot of $-\ln(\beta/T_p^2)$ versus $1/T_p$, as shown in Figure 2, was used to calculate the activation energies of the UF resins cured in the presence of black spruce extract and white oak extract. Figure 2 shows that the two lines had similar slopes, and, therefore, two similar activation energies were obtained. However, the data in Table III indicate that the UF resin cured faster with white oak extract than with black spruce extract, as indicated by the peak temperatures. In this case, Z should be taken into consideration. The line for the black spruce extract showed a smaller intercept than the line for white oak extract (19.59 vs 21.30), which resulted in a lower Z value for black spruce extract than for the white oak extract (3.87×10^{12} vs 2.21×10^{13} 1/s), on the basis of eq. (1).

According to the collision theory, the lower Z value of UF curing in the presence of black spruce may have been a result of some of the chemical characteristics of the extract that were unfavorable for resin curing; as a result, a higher temperature was needed to ensure that the reaction would take place. Table III clearly shows that the peak temperatures of the UF cured with black spruce extract at heating rates of 10, 15, and 20°C/min were all higher than those of the resin cured with white oak extract.

In addition, the chemical characteristics shown in Table I indicate that compared with the white oak extract, the black spruce extract had a higher pH value (4.72 vs 3.84) and a much lower base buffer capacity (4.44 vs 11.07 mequiv). The lower pH and higher base buffer capacity were favorable for UF curing because acidic conditions are preferable for the curing reaction of UF resin. Therefore, to obtain a sufficient number of successful collisions for the curing reaction, UF resin in the presence of black spruce extract needed to be heated up to a higher reaction temperature. It seems, from this study, that the pre-exponential factor was useful in the overall evaluation of the curing behaviors of the resins.

Correlation of wood characteristics with the peak temperature and activation energy

The curing reaction of UF resin is essentially polycondensation under acid conditions, and the polymerization rate, or curing rate, is controlled by the acidity. Therefore, in this study, we attempted to correlate the wood chemical characteristics involved with acidity with the peak temperature at a heating rate of 15°C/min in the presence of wood extracts. The wood chemical characteristics of extracts from 16 wood species, including the pH value, acid buffer capacity, and base buffer capacity, are given in Table I. There were some correlations established between the peak temperature and both the pH value ($R^2 = 0.58$) and base buffer capacity ($R^2 = 0.56$), as shown in Figures 3 and 4, respectively. The lower pH value demonstrated that the extract solution was more acidic. The base buffer capacity in this study was defined as the total amount of base needed to gradually raise the pH to 11.00, and the higher base buffer capacity demonstrated that the wood extract solution had a greater capacity to maintain acidity in the system. Therefore, the peak temperature of UF resin in the presence of wood extracts decreased with

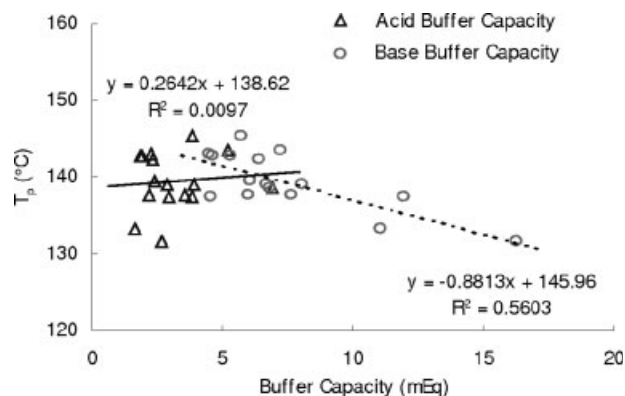


Figure 3 Correlations between T_p and the buffer capacity of wood extracts.

decreasing pH or increasing base buffer capacity. However, it seemed that no correlation existed between the peak temperature and the acid buffer capacity ($R^2 < 0.01$).

An attempt was also made to correlate the wood chemical characteristics with the activation energy of the UF resin in the presence of wood extracts. However, no correlations were found, as indicated by the lower R^2 values (0.06 for pH, 0.02 for base buffer capacity, and <0.01 for acid buffer capacity).

Equivalent catalyst content (ECC)

As shown in Table II and Figures 3 and 4, the 16 wood species had different catalytic effects on UF resin curing, on the basis of activation energy values or peak temperatures. To further characterize the catalysis of wood extracts, the concept of ECC of wood extract to NH_4Cl was introduced in this study. The ECC could be calculated from eq. (3), which was derived from eq. (2) by substitution of the catalyst content for the ECC:

$$\text{ECC} = -\ln[(T_p - 93.104)/53.296]/9.72 \quad (4)$$

where ECC (%) refers to wood extracts with respect to NH_4Cl and T_p ($^{\circ}\text{C}$) is the DSC peak temperature at a heating rate of $15^{\circ}\text{C}/\text{min}$.

The ECC of wood extracts ranged from 0.0022% (the minimum for sugar maple extracts) to 0.0331% (the maximum for red oak extracts), as summarized in Table IV. These results indicate that among the 16 wood species, red oak and sugar maple extracts had the strongest and weakest catalytic influences, respectively, on UF resin curing. This result seemed to be closely related to the wood chemical characteristics, as shown in Table I. Red oak and sugar maple had the lowest and the highest pH values, respectively. In addition, red oak also had the highest base buffer capacity, whereas sugar maple had a relatively lower one than the other species.

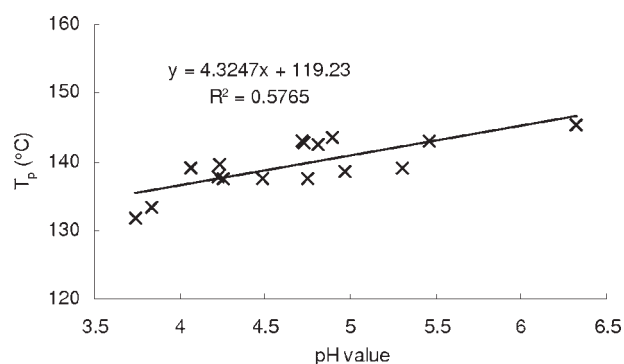


Figure 4 Correlations between T_p and the pH value of wood extracts.

TABLE VI
ECC of Wood Extractives and T_p at a Heating Rate of $15^{\circ}\text{C}/\text{min}$

Species of wood extractive	T_p ($^{\circ}\text{C}$)	ECC (%)
Aspen	137.46	0.0189
Balsam fir	138.56	0.0164
Black spruce	143.12	0.0065
Hemlock	143.45	0.0059
Jack pine	137.59	0.0186
Red maple	139.08	0.0152
Red oak	131.72	0.0331
Red pine	137.66	0.0184
Sugar maple	145.25	0.0022
White birch	139.10	0.0152
White cedar	137.41	0.0190
White elm	142.89	0.0070
White oak	133.23	0.0292
White pine	139.50	0.0143
White spruce	142.74	0.0073
Yellow birch	142.41	0.0080

Some correlations were made between ECC and pH value, acid buffer capacity, and base buffer capacity. Correlations were apparent for pH ($R^2 = 0.57$) and base buffer capacity ($R^2 = 0.59$), whereas no correlation seemed to exist between ECC and acid buffer capacity ($R^2 = 0.0097$).

CONCLUSIONS

The main findings from the study can be summarized as follows. A catalyst level of 0.5–1.0% (solid NH_4Cl to liquid UF resin) was critical to UF resin curing; such a level resulted in the resin curing reaching its maximum curing rate. On the basis of DSC analysis, the model developed in this study, $T_p = 53.296 \exp(-9.72C) + 93.104$, could be used to effectively predict the resin curing rate in terms of the DSC peak temperature (T_p) as influenced by the NH_4Cl content (C).

The 16 wood species used as raw materials for the manufacture of particleboard and MDF panels in Eastern Canada could be classified into three groups on the basis of the activation energy of UF in the presence of wood extracts: (1) positive catalytic effect (aspen, balsam fir, black spruce, red maple, red oak, sugar maple, white birch, white elm, white oak, and yellow birch), (2) no or minor catalytic effect (hemlock, jack pine, white cedar, and white spruce), and (3) negative catalytic effect (red pine and white pine). The activation energy did not fully explain the resin curing behavior when some wood extracts were present; thus, other kinetic parameters, such as the pre-exponential factor, should also be taken into account. Resin curing rates, in terms of peak temperature, increased with decreasing pH value or increasing base buffer capacity.

The concept of ECC of wood extracts to NH_4Cl was developed in this study. ECC values were 0.0022% (the minimum for sugar maple extractives) and 0.0331% (the maximum for red oak extractives) among the 16 species. These results indicate that red oak and sugar maple had the strongest and weakest catalytic effects, respectively, on UF resin curing.

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