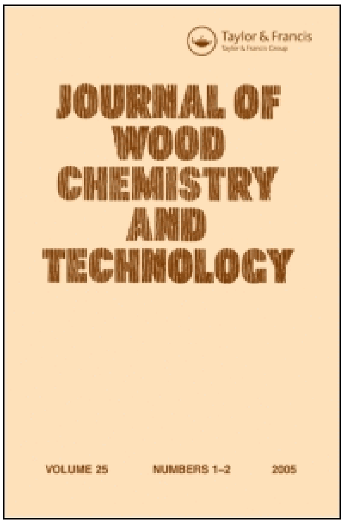

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Byung-Dae Park[a][b]; Bernard Riedl[a]; Hyeun-Jong Bae[c]; Yoon Soo Kim[d]
[a] Department of Wood and Forest Sciences, Faculty of Forestry and Geomatics, CERSIM, Laval University, Québec, QC., Canada [b] Forintek Canada Corp., Ste-Foy, Québec, Canada [c] Department of Plant Science, Laval University, Québec, QC., Canada [d] Department of Forest Products and Technology, Chonnam National University, Kwangju, Korea

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DIFFERENTIAL SCANNING CALORIMETRY OF PHENOL-FORMALDEHYDE (PF) ADHESIVES

Byung-Dae Park* **and Bernard Riedl**
Department of Wood and Forest Sciences, Faculty of Forestry and Geomatics,
CERSIM, Laval University, Québec, QC., G1K 7P4 Canada

Hyeun-Jong Bae
Department of Plant Science, Laval University, Québec, QC., G1K 7P4 Canada

Yoon Soo Kim
Department of Forest Products and Technology
Chonnam National University, Kwangju, 500-757, Korea

ABSTRACT

This paper discusses theoretical background of differential scanning calorimetry (DSC) and its application for phenol-formaldehyde (PF) adhesives to characterize their thermal curing behaviors. Three different scanning methods (single-heating rate, multi-heating rate and isothermal method) of DSC were used for liquid and powdered PF resins. The result showed that the single-heating rate method gave larger activation energy compared with that of the multi-heating rate method. The multi-heating rate method was successfully employed for the thermal characterization of powdered PF resin that showed two distinctive exothermic peaks. The isothermal method can provide an insight for how PF resin cures in hot-pressing process.

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*Current address: Forintek Canada Corp., 319, rue Franquet, Ste-Foy, Québec, G1P 4R4 Canada.

INTRODUCTION

One of the most important variables affecting the properties of thermosetting resin is the degree of cure. Thermosets are crosslinked through the curing process. The physical and mechanical properties change remarkably before and after the curing. Various methods are available for the determination of the degree of cure, including gravimetric analysis by chemical solvent, spectroscopic and chromatographic techniques, and thermal analysis. Thermal analysis methods are a group of techniques in which specific physical properties of a material are measured as a function of temperature, and include thermogravimetirc analysis (TGA), differential scanning calorimetry (DSC) and thermomechanical analysis (TMA). Thermal analysis data permit the estimation of the kinetics that take place during heating. For thermosetting adhesives, thermal techniques have been used to establish the degree and rate of cure, and to study chemical kinetics of curing reaction and the curing behavior itself.[1]

Phenol-formaldehyde (PF) resin is currently used as adhesives for the manufacture of wood-based composite panels such as plywood, oriented strand board (OSB), and laminated veneer lumber (LVL). The reaction mechanisms in PF resin include both formaldehyde addition to phenolic ring and condensation of methylolated phenol into infinite network polymer. These reaction mechanisms are well reviewed by Megason[2] and Pizzi.[3]

Early work on thermal behavior of PF resin has been done using differential thermal analysis (DTA), a precursor of DSC.[4-8] Using both DTA and infrared spectroscopy, Katovic[4] detected two main reactions, leading to the formation of methylene bridges and to dibenzyl ether linkages. The author also reported that the letter reaction is governed by a free-radical mechanism. Chow *et al.*[8] also used DTA and found two endothermic peaks for resole PF resins with different formaldehyde to phenol molar ratios from 0.75 to 2.4. They reported that the first peak was found around 115 to130°C, while the second peak occurred around 130 to 152°C. They attributed the appearance of endothermic peaks to the evaporation of water produced by the condensation reaction of PF resin.

Among many thermal methods, DSC has been used extensively to study the curing process of thermoset adhesives.[9-11] DSC is a powerful tool because it not only isolates the temperature dependent behavior for a given chemical process, but it also allows quantitative measurement of the heat associated with the process. Three main thermal analysis techniques available for DSC kinetic studies include i) single-heating rate method, ii) multi-heating rate method, and iii) isothermal method. These three techniques can provide data that allows a rapid estimation of reaction order (*n* or/and *m*), activation energy (E), pre-exponential factor (Z), and reaction rate (k).

Using the single-heating rate (4°C/min) DSC technique, Sebenik and co-workers[9] determined the kinetic parameters for the curing reaction of resole PF resins. They identified two dominant reactions of both addition and condensation reaction. The activation energy (E) for the addition reaction changes from 99.2 to 80.8 kJ/mole and for the condensation reaction from 95.8 to 79.9 kJ/mole when the amount of NaOH was increased from 0.25 to1.0 percent. The reaction orders (*n*) for addition was 2 and for condensation 1. Using DTA multi-heating rate technique, Mizumachi [7] also measured the activation energy of urea-formaldehyde (UF) resins in the presence of wood flour. The author found that unfilled UF resin showed larger activation energy than that of filled resin and it ranged from 121.3 to 263.6 kJ/mole depending on wood species.

Comparing novolak with resole resins, Chow and Steiner[12] reported interesting DSC results showing an endothermic peak for a resole reaction and an exothermic peak for a novolak reaction. Their results provided an explanation about the nature of inconsistencies between exothermic or endothermic reactions for different types of resins (i.e., resole or novolak), and the state of resins (liquid or solid). Christiansen and Gollob[10] used DSC to determine relationships between formulation parameters and physical properties of PF resoles, and found two exothermic peaks. The first peak was attributed to the addition of free formaldehyde to phenolic rings while the second peak was assumed due to the condensation reaction of methylolated phenols. The second peak occurred at a higher temperature when a low formaldehyde-phenol mole ratio and a high total NaOH-phenol mole ratio were used for the resin synthesis. However, they did not find any discernible correlation for the DSC peak temperature with the initial NaOH-phenol mole ratio.

DSC has also been used to monitor the curing process of PF resin under different temperatures and humidities.[11] The authors found that the degree of resin cure increased with increasing pre-cure temperature and time. The results also showed that the rate of cure increased with increased pre-cure humidity while the rate of cure decreased with an increase in the initial moisture content of samples. They concluded that moisture within a sample could either advance or retard the resin cure. Moisture, on one hand, acts as a plasticizer to promote resin reactivity via molecular mobility, and on the other hand, moisture may dilute the reactive components of a resin, retarding the overall cure rate.

In summary, DSC has been used extensively to characterize the curing process of PF resins. However, limited results are available for the DSC analysis of the cure of PF resins by different analysis methods even though there are various methods of analysis for PF resins cure. This study was conducted to characterize thermal behavior of PF resole resins with DSC using different thermal analytical methods.

THEORY OF DSC

DSC is built based on the principle of converting the sample compartment of a DTA apparatus into a differential calorimeter that gives quantitative results.

The sample and reference materials are heated directly with separate coils. A heating coil increases the temperature of the reference material at a constant rate. A second coil is placed under the sample. The sample and reference are kept at equal temperature. When a phase change or weight loss occurs, the sample and reference temperature becomes slightly different, which generates a current in the thermocouple system measuring the temperature difference between two cells. Thus, the apparent heat capacity is obtained.

The basic assumption for the application of DSC to the cure of thermoset polymers is that the measured heat flow ($d\mathrm{H}/d\mathrm{t}$) is proportional to the reaction rate ($d\alpha/d\mathrm{t}$). In practice, it is often a good assumption.[1]

$$d\mathrm{H}/d\mathrm{t} \propto d\alpha/d\mathrm{t} \tag{1}$$

All kinetic models start with the basic rate equation that relates the rate of conversion at constant temperature, $d\alpha/d\mathrm{t}$, to a function of the concentration of reactants, $f(\alpha)$, through a rate constant, k,

$$d\alpha/d\mathrm{t} = k\ f(\alpha) \tag{2}$$

where α is the chemical conversion, or extent of reaction, k is the rate constant, and $f(\alpha)$ is assumed to be independent of temperature. Among several model categories of thermoset curing reactions, two typical models are nth-order and autocatalytic reaction. For thermosets that follow nth-order kinetics, the rate of conversion is proportional to the concentration of unreacted material (reactant concentration), expressed as;

$$d\alpha/d\mathrm{t} = k\ (1 - \alpha)^{n} \tag{3}$$

where *n* is the reaction order. In usual manner, the temperature dependence is assumed to reside in the rate constant through an Arrhenius relationship given by

$$k(\mathrm{T}) = \mathrm{Z} \exp(-\mathrm{E/RT}) \tag{4}$$

where Z is the pre-exponential factor or Arrhenius frequency factor (1/sec), E the activation energy (J/mole), R the gas constant (8.314 J/mole•K) and T the absolute temperature (K). Combining Equations (3) and (4) gives the complete rate equation for *n*th-order reactions;

$$d\alpha/dt = \mathrm{Z} \exp(-\mathrm{E/RT})\,(1-\alpha)^{n} \tag{5}$$

There are three methods of measuring the cure rate of thermoset resins; the single heating rate method (Borchardt-Daniels), the multi-heating rate method[13,14] and the isothermal method. The Borchardt-Daniels method is based on a single-heating rate run to analyze a curing reaction assuming *n*th-order kinetics expressed by Equation (6). Taking logarithms of Equation (5) gives:

$$ln\,(d\alpha/dt) = ln\,\mathrm{Z} - \mathrm{E/RT} + \mathrm{n}\,ln\,(1-\alpha) \tag{6}$$

A typical DSC exothermic thermogram (Figure 1) is used to measure the two basic parameters ($d\alpha/dt$ and α) required to solve Equation (6) which can be solved with a multiple linear regression. Z and E can be obtained from the intercept and slope of the regression line. The reaction rate is obtained by dividing the peak height (dH/dt) at time, t by the total heat of reaction, ΔH_0.

$$\mathrm{d}\alpha/\mathrm{dt} = (\mathrm{dH/dt})/\,\Delta\mathrm{H}_0 \tag{7}$$

The value α is determined by measuring the partial heat of reaction (ΔH_p) up to time t, and dividing by the total heat of the reaction.

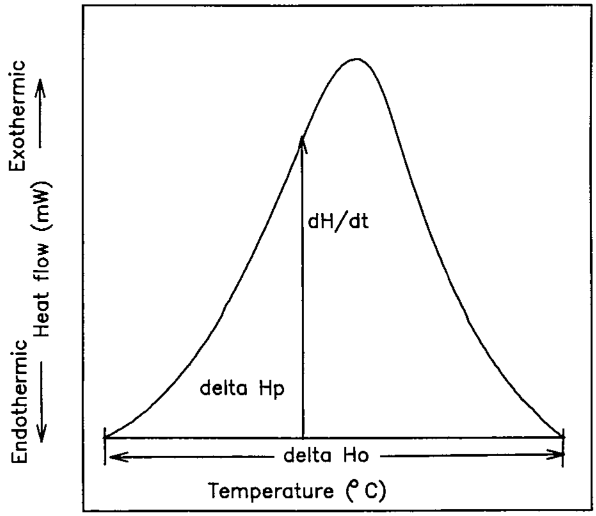

FIGURE 1. A typical exothermic reaction thermogram by the single-heating rate method.

$$\alpha = \Delta H_p / \Delta H_0 \tag{8}$$

This method is attractive because it provides a great deal of information from a single temperature-programmed dynamic experiment. However, it is not consistently reliable when used to predict the course of a reaction over a wide time-temperature range.[1] The criterion for judging the dynamic experiment is its ability to describe and accurately predict the isothermal behavior. This method yields accurate kinetic parameters for simple reaction systems. However, it is unsuitable for any reaction system presenting overlapping peaks, or multi peaks and autocatalytic kinetics.

A common multi-heating rate method based on the work of Ozawa[13] uses a simple relationship between the activation energy, E and the heating rate, β. Rewriting Equation (2) gives:

$$d\alpha/dt = f(\alpha)\, Z \exp(-E/RT) \tag{9}$$

If the sample temperature is changed by a controlled and constant heating rate β, the variation in the degree of conversion can be analyzed as a function of temperature, this temperature being dependent on the time of heating. Therefore, the reaction rate may be written as follows:

$$\frac{d\alpha}{dt} = \frac{d\alpha}{dT}\frac{dT}{dt} \tag{10}$$

The heating rate is defined as $\beta = dT/dt$. Equation (10) becomes

$$d\alpha/dt = \beta\,(d\alpha/dT) \tag{11}$$

A combination of Equations (9) and (11) leads to

$$\frac{d\alpha}{dt} = \beta\frac{d\alpha}{dT} = f(\alpha) Z e^{-E/RT} \tag{12}$$

Rearranging Equation (12) in terms of two variables gives:

$$\frac{d\alpha}{f(\alpha)} = \frac{Z}{\beta} e^{-E/RT}\, dT \tag{13}$$

Integration of this equation from an initial temperature, T_0, corresponding to a degree of conversion, α_0, to the peak temperature, T_p, where $\alpha = \alpha_p$, gives

$$\int_{\alpha 0}^{\alpha p} \frac{d\alpha}{f(\alpha)} = \frac{Z}{\beta}\int_{T0}^{Tp} e^{-E/RT} dT \cong \frac{ZE}{\beta R} p\,(E/RT) \tag{14}$$

where α_p represents the conversion or degree of cure at the exothermic peak, and β the heating rate, and p(E/RT) the P-function defined by Doyle.[15] It is assumed that Z, E and $f(\alpha)$ are independent of temperature. If T_0 is low, it may be reasonably assumed that $\alpha_0 = 0$. Values for p (E/RT) were tabulated by Doyle. For 20<E/RT<60:

$$\log p(E/RT) = -2.315 -.04567\ E/RT_p \tag{15}$$

For thermoset curing, the extent of the reaction at the exothermic peak, α_p, is constant and independent of the heating rate.[1] Therefore, the first integral in Equation (14) is a constant, which leads to

$$\log \beta = \log p(E/RT) + \log (ZE/R) - \log F(\alpha) \tag{16}$$

where $F(\alpha) = \int_{\alpha_0}^{\alpha_p} \frac{1}{f(\alpha)} d\alpha$. Substituting Equation (15) into Equation (16) yields:

$$\log \beta = -2.315 -0.4567\ E/RT_p + \log (ZE/R) - \log F(\alpha) \tag{17}$$

The activation energy can be calculated from a plot of log β versus $1/T_p$. Since this method uses the relationship between the peak exothermic temperature and its corresponding heating rate, the multi-heating rate method is an appropriate choice for cure characterization of resins that display low-energy cures, thermal unstability, irregular baselines, solvent effects and some reactions with multiple exotherms.[16-18]

Another useful and accurate expression for the pre-exponential factor for *n*th-order reactions, which relates E, β, and T_p, was derived by Kissinger:[19]

$$Z = \frac{\beta E e^{E/RTp}}{RT_p^2[n(1-\alpha_p)^{n-1}]} \tag{18}$$

Kissinger argued that $n(1-\alpha_p)^{n-1} \approx 1$ and is independent of the rate of heating. Equation (18) can be rewritten as:

$$Z = \frac{\beta E e^{E/RTp}}{RT_p^2} \tag{19}$$

Rearranging and taking logarithm of Equation (19) yields

$$-\ln\left(\frac{\beta}{T_p^2}\right) = \frac{E}{RT_p} - \ln\left(\frac{ZR}{E}\right) \tag{20}$$

which is the equation of a straight line between $-\ln(\beta/T_p^2)$ and $1/T_p$. From a fitted straight line, the activation energy (E) can be calculated from the slope and the pre-exponential factor from the intercept. From these data and the Arrhenius law, the rate constants may be derived. However, it does not give any information on reaction order.

The isothermal method is a thermal analysis technique to measure the time dependence of curing at constant temperature, and recommended for complete characterization and modeling of the cure process. In general, isothermal methods can best distinguish between different reaction mechanisms and they give the most accurate and reliable description of curing reaction.[1] For a *n*th-order reaction, the reaction rate is expressed by Equation (3), and the rate constant and the reaction order can be obtained from the intercept and the slope of log ($d\alpha/dt$) versus log ($1-\alpha$) plot. Taking the logarithm of Equation (3) yields:

TABLE 1.
Summary of DSC results of a single heating rate (10°C/min) method for liquid PF resole resins.

Resin type[1)]	ΔH (J/g)	E (kJ/mole)	*n*	T_p (°C)
A	493.7	215.9	2.7	150.1
B	517.3	148.7	2.1	144.3
C	378.9	142.1	2.2	151.1

1) The resin A and B are commercial resins, and C is the synthesized resin.

$$\log (d\alpha/dt) = \log k + n \log (1-\alpha) \tag{21}$$

Equation (21) can also be solved by a multiple linear regression using an isothermal DSC thermogram as shown in Figure 5.

RESULTS AND DISCUSSION

The results of dynamic scans by a single heating rate (Bochardt-Daniels method) for liquid PF resole resins are summarized in Table 1. The single-heating rate method produces abundant kinetic information by one dynamic scan such as total reaction heat (ΔH), activation energy (E), reaction order (*n*), and peak temperature of a reaction. Therefore, this method is an appropriate choice for the comparison of thermal characteristics of different resins in relatively short time. Two commercial resins (A and B) showed relatively larger total reaction heat than that of the resin C synthesized in laboratory. The ΔH is measured as the integrated area under the exothermic curve of DSC thermogram divided by the amount of resin solids. So, the ΔH is highly dependent on the reaction advancement of a resin.[20]

The activation energy is a physical quantity that takes into account the fact that thermodynamically favorable reactions do not proceed spontaneously.[1] In other words, the activation energy is the energy needed to start a reaction. The

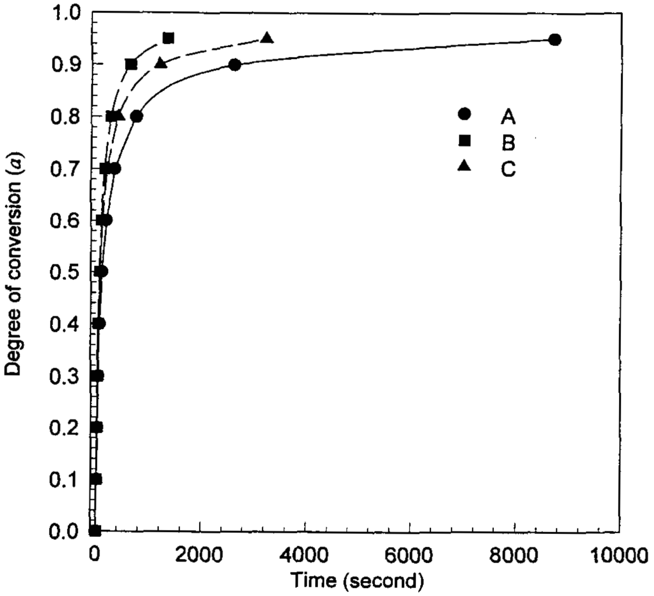

FIGURE 2. Comparison of the conversion rates of liquid PF resins at 150°C.

resin A had the largest activation energy followed resin B and C. This result means that the resin A needs more energy to start its curing reaction than those of resin B and C.

The single-heating rate method has two assumptions; 1) the reaction follows *n*th order reaction, and 2) the temperature dependence of the reaction rate follows the Arrhenius expression. The reaction order (n) ranged from 2.7 to 2.1 for liquid PF resins. The observed reaction orders appear to be reasonable, and are in the range of PF resin by other authors.[9] The peak temperature is a temperature where the conversion rate ($d\alpha/dt$) reaches the maximum during a dynamic scan of the reaction. The peak temperatures ranged from 144 to 151°C for three liquid PF resins. To compare the reaction rate of liquid resins, the degree of conversion (α) was plotted as a function of the conversion time, and was shown in Figure 2. A

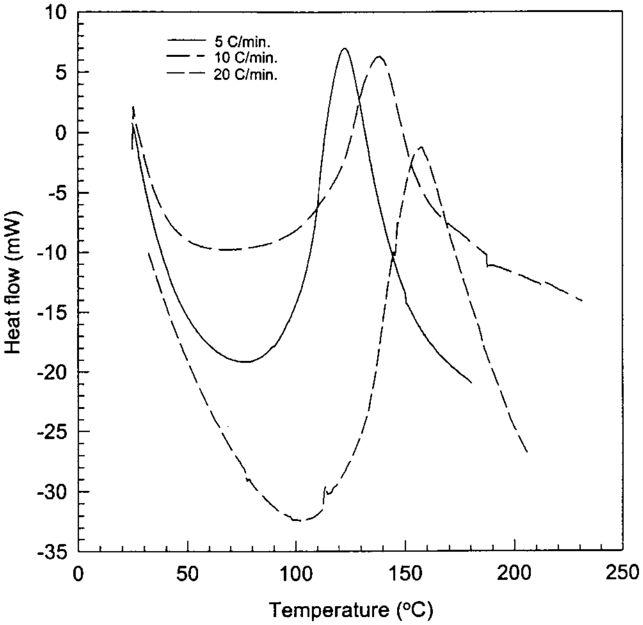

FIGURE 3. Typical DSC thermograms of multi-heating rate method for powder PF resin.

commercial resin (B) showed the fastest reaction rate followed by C and A. This result along with the lowest peak temperature indicated that the resin B is a fast curing resin (Table 1).

As described in the theory section, another thermal characterization technique is the multi-heating rate method. The detail procedures of this method are explained in the ASTM method.[14] Typical DSC thermograms of multi-heating rate method for the resin C is shown in Figure 3. This method uses the relationship between the peak temperature and its corresponding heating rate to arrive at a calculated value for the activation energy. This method requires only the identification of the peak temperature at three or more heating rates. This

TABLE 2.
Results of the multi-heating rate method for the PF resin C.

β (K/min.)	T_p (K)	1000/T_p	-*ln* (β/T_p^2)	E (kJ/mole) 1)
5	412.1	2.42	10.4	73.46
10	424.2	2.36	9.8	
20	437.9	2.28	9.2	

1) The activation energy was obtained with three heating rates

method is useful for the characterization of resins that display lower-energy cure such as melamine-formaldehyde resin, solvent effects, poorly resolved base lines, or multiple reaction phenomena. The laboratory synthesized resin (C) was selected for its thermal characterization by the multi-heating rate method, and the results are presented in Table 2. A linear equation obtained by using Equation (20) is expressed as $-\ln(\beta / T_p^2) = -14.455 + 10.125 \times 1000 / T_p$.

The calculated activation energy (73.46 kJ/mole) was lower than that obtained by a single-heating rate method (142.1 kJ/mole). This might be due to thermal lag that occurred in transferring heat from the capsule to the sample resin inside the capsule at high heating rate. In other words, there is a difference between the programmed temperature and the sample temperature inside the capsule. This result indicates that the activation energy measured by the single-heating rate method is inconsistent with that of the multi-heating rate method. For the majority of thermoset cure reactions, this method consistently produces larger the activation energy and frequency factor when compared to values obtained from isothermal heating method.[1]

This multi-heating rate method can also be used for a resin that displays multiple reaction phenomena for which the single heating rate method is inapplicable. The dynamic single scanning method assumes that the reaction follows *n*th order reaction, which is not the case for multiple reaction phenomena. A commercial PF powder resin that displays two exothermic peaks was used to

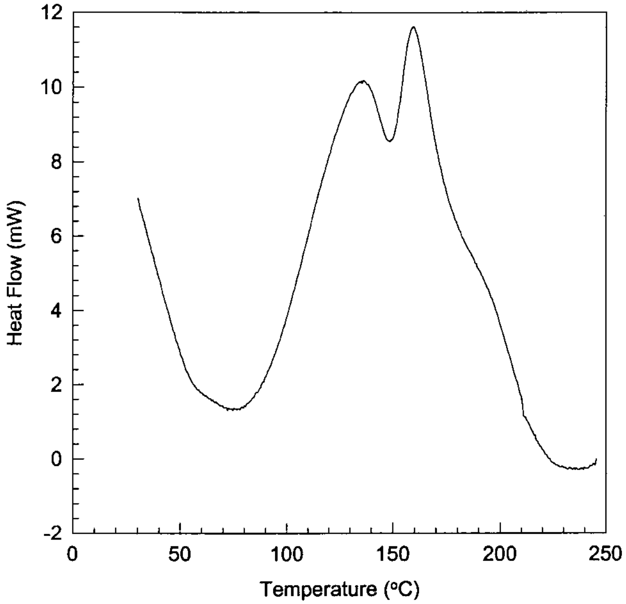

FIGURE 4. A DSC thermogram with two exothermic peaks of powder PF resin.

characterize its thermal behavior. Figure 4 shows a typical DSC thermogram of the powder PF resin, showing two exothermic peak temperatures occurring at 130°C (T_{p1}) and 159°C (T_{p2}). Three different heating rates (5, 10, and 20°C/min.) were used for the powder resin.

Depending on heating rates, the first peak varied from 120 to 142°C, while the second one varied from 153 to 165°C. These peak temperatures of the powder resin are slightly higher than those of liquid PF resole resins (i.e. two exothermic peaks observed at 98-129°C and 139-151°C)[10] The authors did not use multi-heating rate method, however. It is well known that there are two major chemical reactions in PF resins; methylolation and condensation.[3] The methylolation is a nucleophilic addition of formaldehyde into phenol ring while the condensation is

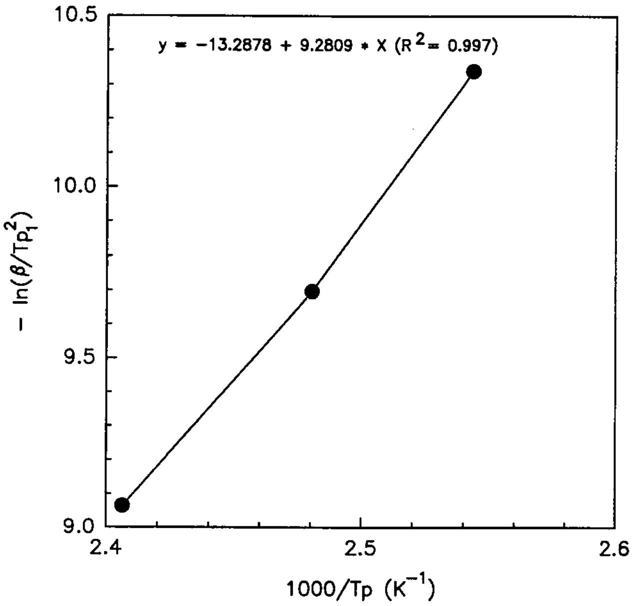

FIGURE 5. Arrhenius plot for the first peak (T_{p1}).

a cross-linking reaction by methylolated phenol into polymer molecules. Observing two exothermic peaks, Christiansen and Gollob[10] related the first peak to the methylolation reaction, and the second one to the condensation reaction of PF resin. Since a commercial powder PF resin used for this study, it is not clear whether the first peak is due to the methylolation reaction like in liquid PF resin because the amount of free formaldehyde in such resin is known to be very low. Other possible reason might be due to additives that accelerate the curing of PF resin. Another possibility might be a wide distribution of weight average molecular weight species in the PF resin. In other words, higher molecular weight species will cure at lower temperatures, while lower molecular weight species will cure at higher temperatures. It is well known that multiple procedures of resin synthesis are being used for PF resin synthesis.[21]

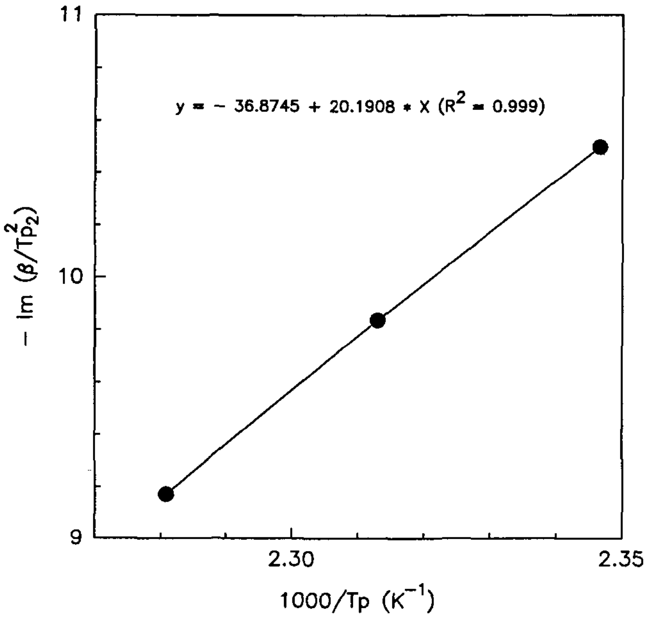

FIGURE 6. Arrhenius plot for the second peak (T_{p2}).

For each heating rate and exothermic peak, the necessary parameters were calculated to build linear regression line, and the activation energies for two exothermic peaks were calculated using the Equation (20). Both Arrhenius plots and derived linear relationships for two exothermic peaks are shown in Figures 5 and 6. The slopes of each curve were used to calculate the activation energy corresponding to the peaks. The calculated activation energies for the first and second peak are 77.2 and 167.9 kJ/mole, respectively. The first exothermic reaction appeared to have lower activation energy than that of the second exothermic reaction. In general, the methylolation reaction is exothermic and favored at lower temperature while the condensation reaction predominates at higher temperature.[21]

TABLE 3.
Rate constants k_1 and k_2 at different temperatures for the first and second exothermic peak of the powder PF resin.

T (K)	k_1 (s^{-1})	k_2 (s^{-1})
338.15	1.09×10^{-4}	4.07×10^{-8}
358.15	5.09×10^{-4}	1.14×10^{-6}
378.15	2.00×10^{-3}	2.25×10^{-5}
398.15	6.87×10^{-3}	3.29×10^{-4}
418.15	2.09×10^{-2}	3.73×10^{-3}
438.15	5.77×10^{-2}	3.38×10^{-2}

Using the intercept of the derived linear relationship between $-ln\ (\beta/T_p^2)$ and $1/T_p$, the pre-exponential factor (Z) was calculated, and used to get the rate constants using the Equation (4). The calculated rate constants of k_1 for the first peak and k_2 for the second peak for different temperatures are shown in Table 3. The two rate constants increased with increasing temperature as expected. In general, the first exothermic peak showed a larger rate constant than that of the second one. This result indicates that the first reaction is faster than the second reaction in the powder PF resin.

A typical isothermal DSC thermogram is shown in Figure 7. The maximum heat evolution occurrs near starting time (i.e. $t = 0$). This result clearly shows that the reaction follows the *n*th order rate expression.[1] However, autocatalyzed reactions are characterized by a maximum heat evolution at 30 % to 40% of the reaction in the isothermal DSC signal.[1] An autocatalyzed reaction is reported for PF resin modified by the addition of cure accelerating additives.[22] So, the isothermal DSC method provides a means of determining whether a given reaction follows autocatalyzed or *n*th order reaction kinetics. Isothermal experiments are time consuming, but they generate more reliable kinetic parameters. This is because the isothermal method introduces fewer experimental variables into a single measurement so that the scope for ambiguity in the interpretation of data is reduced.[1]

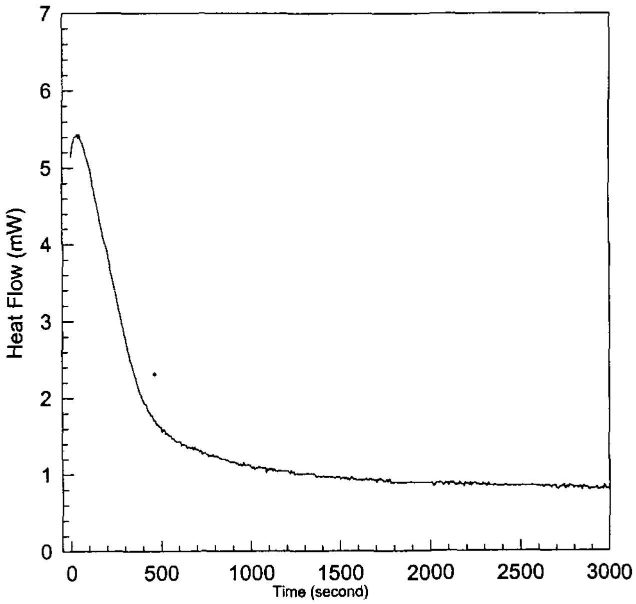

FIGURE 7. Typical isothermal DSC thermogram of the resin (C) at 120°C.

The degree of conversion (α) versus conversion time obtained from the isothermal scanning for 50 minutes is shown in Table 4. As expected, the conversion time increased with increasing the degree of conversion. Other degree of conversion versus conversion time results can also be obtained by running other isothermal scans at different temperatures. Therefore, the isothermal method is useful tool for characterizing the thermal behavior of a sample at different temperatures. At the same time, the results of isothermal analysis could provide an insight on how a PF resin cures in hot-pressing conditions.

CONCLUSIONS

DSC analysis techniques using three different thermal scanning methods (single-heating rate, multi-heating rate and isothermal method) were used to

TABLE 4.
Summary of isothermal DSC scans of the resin C at 120°C for 50 min.

Degree of conversion, α (%)	Conversion time, t (min.)
10	0.7
30	2.02
50	3.75
70	7.01
90	18.43

characterize thermal behaviors of liquid and powder PF resins. The results obtained showed that the single-heating rate method is fairly rapid and produces abundant reaction kinetic parameters that are useful for the comparison of different PF resins. However, it produced larger activation energy when compared to that of the multi-heating rate method. The multi-heating method was applied successfully to characterize thermal behavior of a powder PF resin that displays two exothermic peaks. Depending on heating rate, the first peak varied from 120 to 142°C and the second one varied from 153 to 165°C. The isothermal method can provide a means of determining a reaction type, and give an insight for how PF resin cures in hot-pressing conditions.

EXPERIMENTAL

According to a modified method,[23] a liquid PF resin for DSC analysis was synthesized in laboratory with a formaldehyde/phenol and NaOH/phenol molar ratio of 2.3 and 0.34, respectively. The details of resin synthesizing procedures was reported in the reference.[20] The solids content of the synthesized resin was determined by a pan solids technique.[24] The properties of the synthesized resin (C) are summarized in Table 5. To compare with the synthesized resin, both two commercial liquid PF resole resins (A and B) and a commercial powder PF resin for OSB from Neste Resins Canada (Toronto, Ont., Canada) were used for DSC analysis.

TABLE 5.
The resin properties of the synthesized PF resin C.

Parameters	Value
Nonvolatile solid (%)	45.7
PH	10.2
Viscosity (mPa.s)	79
Free CH_2O (%)	0.17
Specific gravity (g/cm^3)	1.17

All DSC measurements were made on a Mettler DSC 20 with a Mettler TA400 thermal analysis system, using large sealed capsules (ME-29889/V). The capsule with a volume of 270 μl can withstand vapor pressures up to 10 MPa. Dynamic scans (single-heating rate method) were made with a single heating rate of 10°C/min and a scanning temperature range from 30 to 240°C. A multi-heating rate method was employed for thermal characterization of both the resin C and a commercial powder PF resin. In addition to the single heating rate, two different heating rates (5 and 20°C/min) were used in order to have at least three different heating rates. An isothermal scanning was done with a laboratory synthesized PF resole resin at 120°C for 50 min. At least three DSC scans were repeated made for each heating-rate method, and then the average value was reported.

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