

# Thermokinetic behavior of powdered phenol-formaldehyde (PPF) resins

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## Abstract

This study was conducted to investigate thermokinetic behavior of powdered phenol-formaldehyde (PPF) resins used for the production of wood-based panel products. Both fusion diameter and stroke cure time of the PPF resins were measured to characterize flow properties and reactivity of PPF resins. In addition, differential scanning calorimetry (DSC) was also used to obtain apparent glass transition temperature ( $T_g$ ) and activation energy ( $E_a$ ) of the PPF resins. The results showed that the stroke cure time of PPF resins was positively related with fusion diameter of the PPF resins. The  $T_g$  of PPF resins depended on the heating rate with a linear relationship established between heating rate and the  $T_g$ . The  $E_a$  of PPF resins depended on types of PPF resin and spray-drying temperatures.

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**Keywords:** Powder PF resin; Differential scanning calorimetry; Glass transition temperature; Heating rates; Activation energy

## 1. Introduction

Liquid phenol-formaldehyde (LPF) and powdered phenol-formaldehyde (PPF) resins are used for the production of wood-based panels. LPF and PPF resins share 59% and 27% of the total used for these products [1,2]. PPF resin has been used for oriented strand board (OSB) production since 1975 in North America. The last decade has seen much discussion of using LPF or PPF resins for OSB panel production. The advantages of using PPF resin include faster curing, lower resin usage, a better distribution, longer storage life, and lower transportation cost. But, disadvantages are spray-drying cost and dust control. Important physical properties of PPF resin for this application include powder particle geometry, bulk density, and particle size. Powder particle geometry is either spherical or fractured-irregular shapes. It is known that the latter is more efficient under marginal wax distribution condition [3].

Attaining adequate flow of adhesives has been recognized for the development of durable adhesive bond strength for

plywood [4]. Furthermore, the curing behavior is equally important to obtain suitable bond strength. In the case of PPF resin, the plasticity of the resin increases at the elevated temperature of hot pressing. The viscosity decreases up to a softening point (or glass transition temperature,  $T_g$ ) where the PPF resin starts to melt, and then increases to infinite viscosity as cross-linking process rapidly increases.

Poor flow of PPF resin was associated with low internal bond strength [5]. A resin flow to form a strong adhesive bond was also related to optimum number average molecular weight ( $M_n$ ) of PF resin [6]. Ellis and Steiner [6,7] reported that the fusion diameter decreased as the  $M_n$  increased for PPF resins [7].

In addition to inherent properties, processing parameters also impact the adhesion performance of PPF resin. For example, the particle size of PPF resins was dependent on spray-drying parameters such as inlet temperature, feed rate, and resin solids content, and the most important parameter was reported as the initial drying temperature [8].

Although limited studies on the flow properties of PPF resins are available, there is insufficient data on thermokinetic behavior for optimizing adhesive bond strength in the manufacture of wood-based panels. Therefore, this study was

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conducted to investigate the thermokinetic behavior of PPF resins.

## 2. Materials and methods

### 2.1. Materials

Two different types of PPF resins are being used for the manufacture of OSB, which is composed of three layers (two face layers and one core layer). The PPF resin used for the face layer is called ‘face resin’ while the one used for the core layer is called ‘core resin’. Thus, this study used two commercial PPF resins of both core and face resins from a local resin company in Que., Canada. In addition, a liquid PF resin was also synthesized in the laboratory to investigate the effect of spray-drying temperature on thermokinetics of PPF resin.

### 2.2. Fusion diameter and stroke cure time

The fusion diameter of powdered PF resin was measured to determine the flow properties of the PPF resins subjected to a specific temperature and pressure. Cylindrical pellets (12.0 mm in diameter, 5.0 mm in thickness) were prepared from 0.5 g of the powdered resin. Each pellet was placed on a hot plate at 150 °C followed by a weight sufficient to deliver an initial force of 0.47 MPa. The weight was removed in 3 min and the diameter of the pellet was measured at two different directions to get an average value of three replications.

As a measure of the reactivity of PPF resin, the stroke cure time was measured on a hot plate at 150 °C using 2 g of PPF resin. The stroke cure time is the time taken for a sample of powdered resin to melt and then cure on a hot plate.

Free formaldehyde in the prepared urea-formaldehyde resins was determined by a slightly modified sodium sulfite method [9]. A solution of 25 ml of 1 M sodium sulfite mixed with 10 ml HCl was added to 2–3 g of PPF resin sample dissolved in 100 ml of distilled water. Ten drops of 0.1% thymolphthalein was added and the solution, and then titrated with 1 N sodium hydroxide to determine the percent of free formaldehyde.

### 2.3. DSC measurement

A pressurized differential scanning calorimetry (DSC; TA 2910, TA Instrument, USA) was used to evaluate the curing behaviors of the PPF resins with four different heating rates (5 °C/min, 10 °C/min, 15 °C/min, and 20 °C/min). For each scan, about 7 mg of PPF resin was added to an aluminum capsule. The capsule was sealed, and then heated from 25 °C to 280 °C at each heating rate. This multi-heating rate method was employed to determine the activation energy ( $E_a$ ) of the PPF resins using the Kissinger equation [10] expressed

as:

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

where  $\beta$  is the heating rate (°C/min) and  $T_p$  is the peak temperature. The  $E_a$  can be calculated from the slope and the pre-exponential factor from the intercept of a plot of  $-\ln(\beta/T_p^2)$  versus  $1/T_p$ . However, it does not give any information on reaction order. The same DSC curve was used to determine apparent glass transition temperature ( $T_g$ ) of the sample using the step analysis method for each sample.

## 3. Results and discussion

Table 1 shows characteristics of the PPF resins used in this study. The liquid PF resin spray-dried at two different outlet temperatures (92 °C and 105 °C) to obtain PPF resins.

Fig. 1 shows the relationship between the stroke cure time and fusion diameter of commercial PPF resins. Although there are large variations, the results show that stroke cure time increases with increasing fusion diameter. This result is reasonable since the fusion diameter decreases as the PPF resin cures in a short time, which prevents the flow of the resin during its cure.

Table 1  
Characteristics of PPF resins used in this study

Parameters	PPF resin		LPF resin
	Face resin	Core resin	
Moisture content (%)	4.4 ± 0.86	4.6 ± 0.91	42.2 <sup>a</sup>
Stroke cure time (s)	16 ± 4.64	16 ± 5.12	–
Fusion diameter (mm)	30 ± 9.25	25 ± 3.83	–
Free formaldehyde (%)	1.12	0.66	0.25
Viscosity (mPa s)	–	–	126.5

<sup>a</sup> The value represents non-volatile resin solids of the LPF resin.

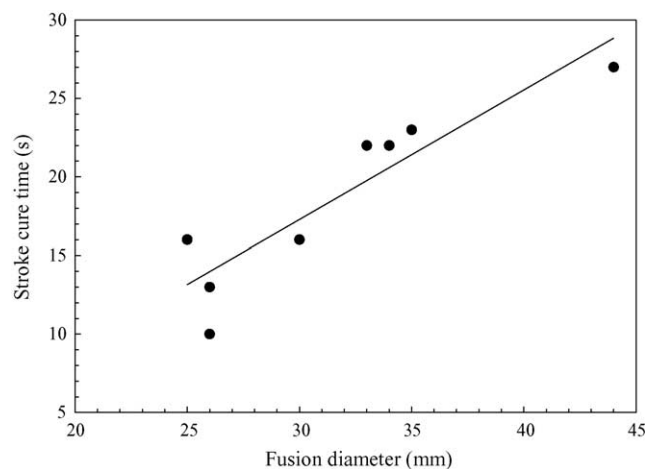


Fig. 1. The relationship between stroke cure time and fusion diameter of PPF resin.

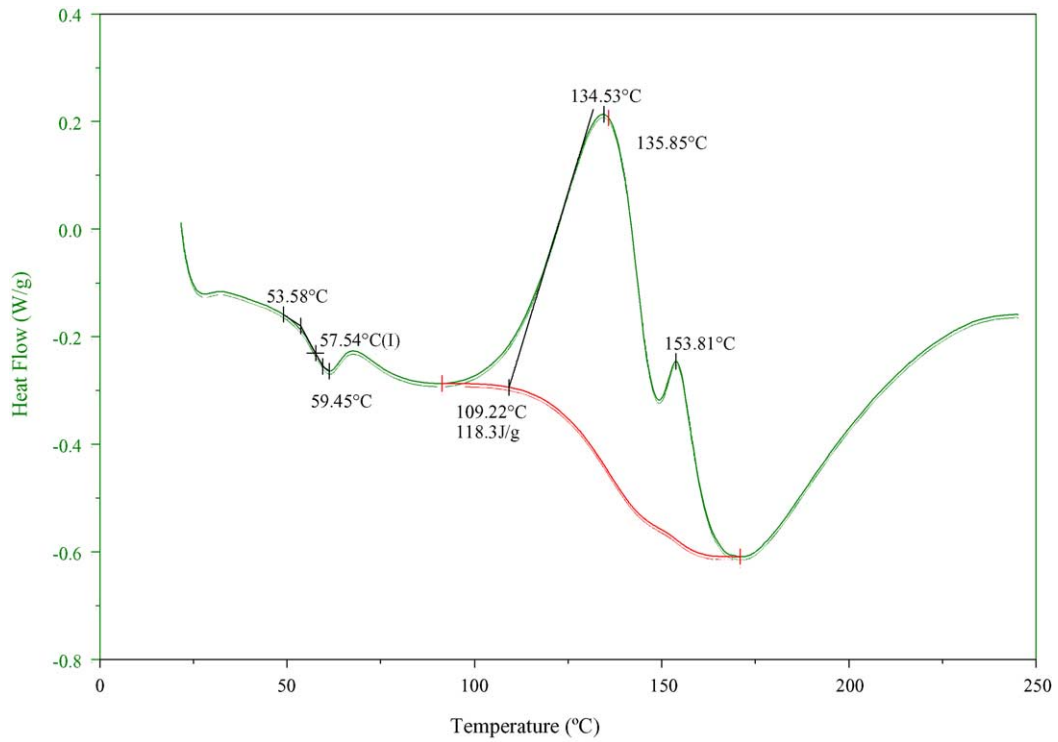


Fig. 2. A typical DSC curve of face PPF resin, showing a glass transition and double exothermic peaks at 10 °C/min.

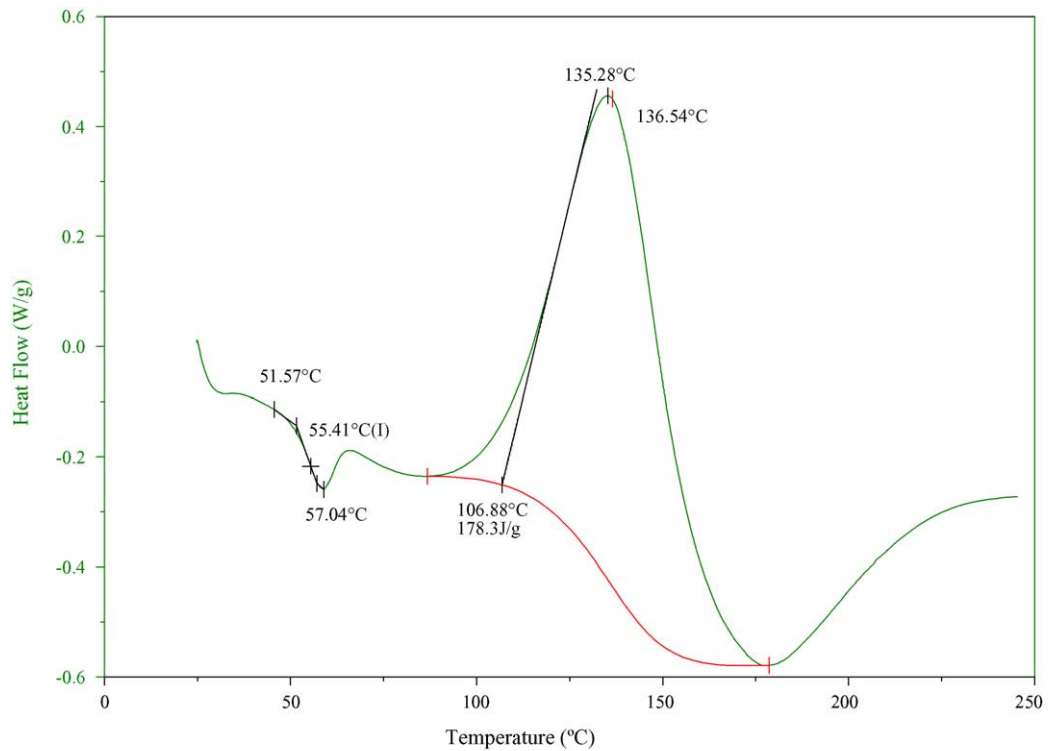


Fig. 3. A typical DSC curve of core PPF resin, showing a glass transition temperature and an exothermic peak temperature at 10 °C/min.

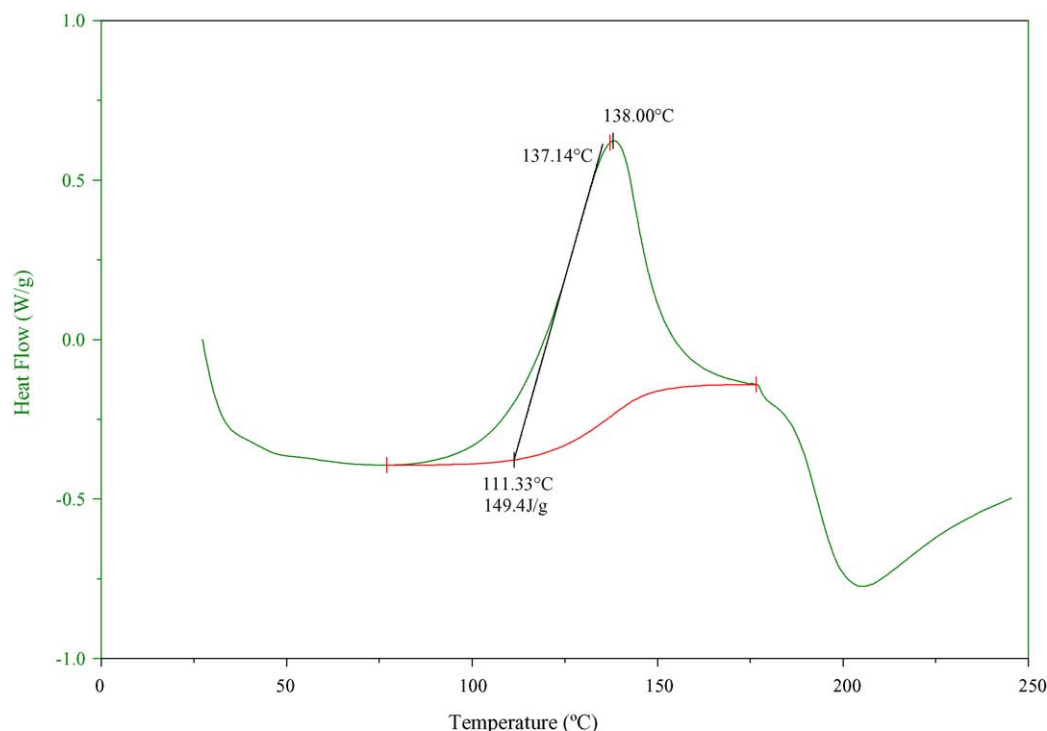


Fig. 4. A typical DSC curve of core PPF resin after gelation at 120 °C at 10 °C/min.

A typical DSC curve obtained with a commercial face PPF resin at 10 °C/min is shown in Fig. 2. The resin shows an endothermic transition at lower temperature and two exothermic peaks at higher temperature. The endothermic transition was assumed as the apparent glass transition temperature ( $T_g$ ).

Two exothermic peaks, at 134.5 °C and 153.8 °C, were observed for the face PPF resin. However, the interpretation of these peaks is not clear. One interpretation attributes the first peak to the methylation reaction and the second to the condensation reaction of PF resin [11]. Two exothermic peaks were also reported for novolak PPF resin [12]. The first, around 95 °C, was ascribed to melting of the resin, while the second, around 115 °C, was not explained. The double peaks for PPF resins deserve further study of the effects of molecular weight distribution, different catalysts, or different synthesis procedures.

Fig. 3 is a DSC curve of the core PPF resin at the heating rate of 10 °C/min, showing one exothermic peak at higher temperature. The  $T_g$  of this resin decreased to 55.4 °C while the peak temperature slightly increased to 135.3 °C. These results indicate that the core PPF resin possesses a better flow behavior than the face PPF resin at lower temperature. But the peak temperatures of these two PPF resins both were occurred around 135 °C, which indicates a similar rate of cure.

Fig. 4 shows a DSC curve of the core PPF resin after stroke cure time measurement at 120 °C. An interesting result is the disappearance of the glass transition. This result is attributed to the polymerization when gelled at 120 °C.

To determine an inherent  $T_g$  of PPF resin, the  $T_g$  was plotted as a function of heating rate. Fig. 5 shows a linear relationship between heating rate and  $T_g$  for both face and core PPF resins. The intercept was assumed as an apparent  $T_g$  of sample. The apparent  $T_g$  values of face and core PPF resins were calculated as 79.7 °C and 48.9 °C, respectively.

Fig. 6 shows linear relationships between  $-\ln(\beta/T_p^2)$  and  $1/T_p$  for face and core PPF resins. The  $E_a$  of PPF resins were calculated with the relationship in Eq. (1) [13]. The  $E_a$  calculated was 95.3 kJ/mol and 79.6 kJ/mol, respectively, for face

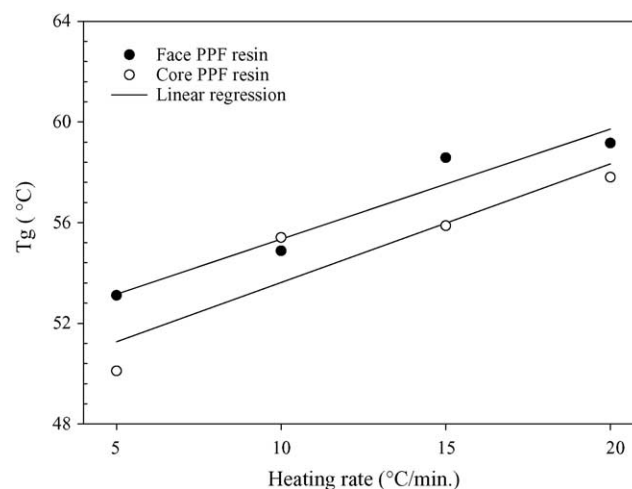


Fig. 5. The relationship between glass transition temperature ( $T_g$ ) and heating rate.

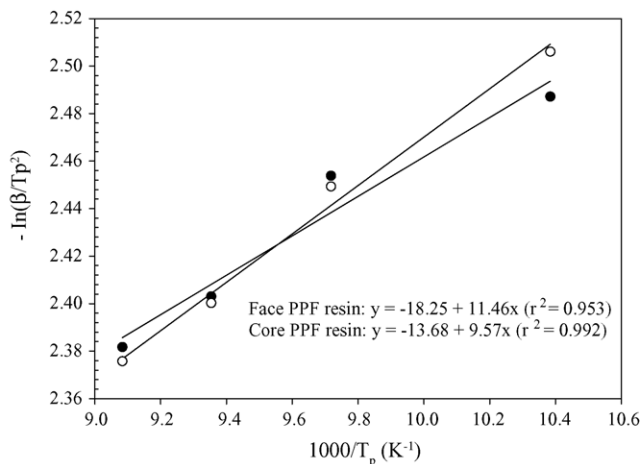


Fig. 6. Linear relationships between heating rate and peak temperature of face and core PPF resins plotted according to Eq. (1). (●) Face resin and (○) core resin.

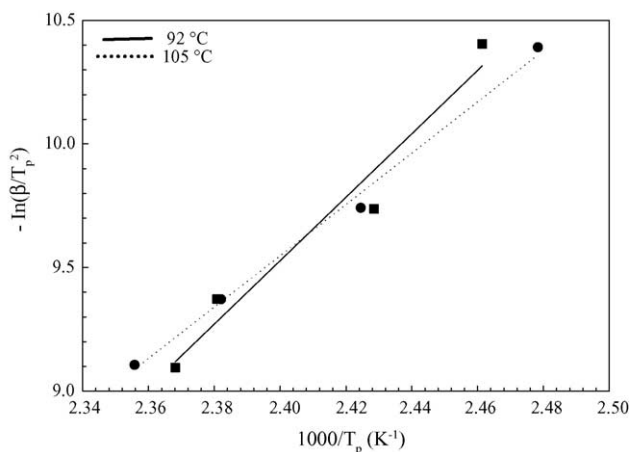


Fig. 7. Linear relationships between heating rate and peak temperature of PPF resins produced at two different spray-drying temperatures plotted according to Eq. (1).

and core PPF resins. The face PPF resin has a higher inherent  $T_{\text{eg}}$  and greater  $E_a$  than the core PPF resin. In general, the  $T_{\text{eg}}$  of thermosetting polymers increases with the degree of conversion [14]. Thus, the  $E_a$  of PPF resins in this study are quite compatible with other results [15].

A liquid PF resin synthesized in the laboratory was spray-dried at two different outlet temperatures in order to see the effect of spray-drying temperature on the thermokinetics of PF resin. The  $T_{\text{g}}$  values of the PPF resins obtained at 92 °C and 105 °C were determined as 50.9 °C and 49.4 °C, respectively.

Fig. 7 shows linear relationship between heating rate and peak temperature for the PPF resins. Although the two PPF resins were produced from the same liquid PF resin, the  $E_a$  values were quite different for the two different spray-drying temperatures, 92 °C and 105 °C, were found to have 86.2 kJ/mol and 106.7 kJ/mol, respectively. These results indicate that the spray-drying temperature advanced the degree of cure of PPF resin. This result is compatible with other results [8].

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