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Differential scanning calorimetry of phenol–formaldehyde resins cure-accelerated by carbonates

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Abstract

One of the drawbacks of phenol–formaldehyde (PF) resol resin is its slow cure which requires longer hot-pressing time for the manufacture of wood composite products, especially for thick fibreboard products. In this study, PF resol resin was modified with three carbonates (i.e. propylene carbonate, sodium carbonate and potassium carbonate) to accelerate the cure of the resin for the manufacture of medium density fibreboard. The thermal behaviour of carbonate-modified PF resol resins was characterized with differential scanning calorimetry (d.s.c.) using three different thermal scanning methods (single-heating rate, multi-heating rate and isothermal method). The results of the single-heating rate method were not consistent when compared to the other two methods. The rate constants were calculated with the activation energy and pre-exponential factor obtained by the multi-heating method. The calculated rate constant increased with increasing carbonate level and the temperature selected. The isothermal method revealed that the curing of propylene carbonate-modified resins follows autocatalytic kinetics while the other two additives showed *n*th-order kinetics with a partial autocatalytic effect.

Keywords: Phenol–formaldehyde resin; Cure acceleration; Carbonates

1. Introduction

Phenol–formaldehyde (PF) resin is currently used as an adhesive for the manufacture of wood-based composite panels such as plywood, oriented strand board (OSB), and fibreboard. Productivity for the manufacture of these panels depends on their main production steps such as drying, resination, and hot-pressing. Among these processes, the through-put of the hot-press critically influences the cost efficiency of the whole process. Hot pressing is the most costly unit operation. Therefore, a reduced pressing time has a strong influence on both the reduction of unit costs and productivity for panel production.

One of the main drawbacks that have prevented wider use of PF resins in the manufacture of wood composite panels is its relatively slow cure rate. There have been many attempts to cure PF resins faster, including using different catalysts, additives, or modified resin formulations. The cure speed of PF resins can be accelerated using various catalysts such as ammonia, amines, and amides [1]. Faster curing PF phenolic resins may also be prepared by metallic ion catalysis which increases the proportion of the free higher-reactive *para* positions available for the reaction during curing of the resin. Most bivalent metal ions accelerate phenol–formaldehyde reaction. The extent of acceleration depends on the type and amount of metal ion present. For example, Grenier-Loustalot et al. [2] reported a positive relationship between the characteristics of the catalyst (size and valence of cation) and the reaction rate. In other words, the greater the radius of hydrated cation, the faster the disappearance of formaldehyde in the reaction.

In order to improve the curing rate of PF resin, Daisy and Leeper [3] modified the sodium hydroxide addition step by replacing up to 50% by weight with potassium hydroxide. They found that comparable and, in many cases, superior strandboard and plywood could be made using potassium-modified PF resol resins when compared to conventional resin formulation.

Duval et al. [4] studied many catalysts, or additives such as hydrochloric acid, ammonia, sodium, lithium, barium, and zirconium hydroxides, to investigate the effect on the MW distribution of PF resins. They did not indicate,

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however, whether various catalysts accelerated the resin cure or not. Steiner [5] compared the effectiveness of $Ca(OH)_2$ with that of NaOH as a catalyst. The author found that the latter was a more effective catalyst for the PF resin system.

The cure acceleration of very alkaline PF resins for foundry core binders was pioneered in the early 1970s [6]. In this application, the addition of a considerable amount of an ester such as propylene carbonate, methyl formate, and glycerol triacetate in liquid (α-set) or a gaseous form (β-set) were found to accelerate resin curing. A possible mechanism for PF cure acceleration has been proposed [7,8]. The proposed mechanism is based on the carbanion behaviour of aromatic nuclei of phenate ions. In other words, the ester, or residue of its decomposition, attacks the negatively charged phenolic nuclei in a polycondensation, resulting in higher functionality (greater than 3) in addition to reactive methylol groups. This could lead to much earlier gelling of PF resin.

Using ester-modified PF resol resin, Pizzi and Stephanou [8] reported that the press time could be reduced to 2.5 min in making particleboard (12 mm thick). The internal bond strength was found to exceed the standard for exterior-grade board. Furthermore, they concluded that the preferred ester was glycerol triacetate which provided fast curing and a long pot-life for the adhesive.

Differential scanning calorimetry (d.s.c.) has been used to analyse the cure process for thermosetting polymer systems. D.s.c. is a powerful tool because it not only isolates the temperature-dependent behaviour for a given chemical process, but it also allows quantitative measurement of the heat associated with the process. The kinetic parameters for the curing reaction of PF resins were determined by Sebenik et al. [9]. They identified two dominant reactions; substitution and condensation reactions. For these reactions, the activation energies (E) were 99.2–80.8 and 95.8–79.9 kJ/mol, and the reaction orders (n) were 2 and 1, respectively. They also reported a decreased activation energy with increasing NaOH/phenol mole ratio.

Comparing novolak with resol resins, Chow et al. [10] reported interesting d.s.c. results showing an endothermic peak for a resol 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., resol or novolak), and the state of resins (liquid or solid).

Christiansen [11] used d.s.c. to determine relationships between formulation parameters and physical properties of PF resol, 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 discernible correlation for the d.s.c. peak temperature with the initial NaOH–phenol mole ratio.

D.s.c. has also been used to monitor the curing process of PF resin under different temperatures and humidities [12]. They 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 can either advance or retard the resin cure. Moisture, on one hand, acts as a plasticizer to promote resin reactivity via molecular mobility, on the other hand, moisture may dilute the reactive components of a resin, retarding the overall cure rate. Using both dynamic mechanical analysis (DMA) and d.s.c., Christiansen et al. [13] defined both the d.s.c. exothermic area as the rate of ‘chemical cure’ and the area under tan δ curves during DMA scans as the rate of ‘mechanical cure’. They found that the ‘chemical cure’ obtained from d.s.c. runs was much slower than that of the ‘mechanical cure’.

In summary, d.s.c. has been used extensively to characterize the cure process of PF resins. However, limited results are available for the d.s.c. analysis of the cure acceleration of PF resins although there are various approaches to cure PF resins faster. Most of the results are related to the elucidation of cure acceleration mechanisms and measurement of gel time. This present study was designed to characterize thermal behaviour of cure-accelerated PF resins using some additives. In order to achieve this objective, d.s.c. was chosen to follow the thermal behaviour of cure-accelerated PF resins.

2. Theory of d.s.c.

D.s.c. has been used extensively for the study of physical transformations and chemical reactions of materials. The basic assumption for the application of d.s.c. to the cure of thermoset polymers is that the measured heat flow (dH/dt) is proportional to the reaction rate ($d\alpha/dt$). The total heat detected during a reaction is identical to the heat evolved by the curing reaction. This assumes that no other enthalpic events occur, such as the evaporation of solvent or volatile components, enthalpy relaxation, or significant changes in heat capacity with conversion. In practice, it has proven to be a good assumption.

$$dH/dt \propto d\alpha/dt \tag{1}$$

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

$$d\alpha/dt = kf(\alpha) \tag{2}$$

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. In general, thermoset curing can be divided into several model categories. Two typical models of them are *n*th-order and autocatalytic reaction.

For thermosets that follow *n*th-order kinetics, the rate of conversion is proportional to the concentration of unreacted material (reactant concentration), expressed as;

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

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

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

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

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

In this study, we are concerned with three methods of measuring the cure rate of thermoset resins; the single heating rate method (Borchardt-Daniels), the multi-heating rates method [14,15], and the isothermal method. The Borchardt-Daniels method is based on a single-heating rate run to analyse a curing reaction assuming *n*th-order kinetics expressed by Eq. (6). Taking logarithms of Eq. (5) gives:

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

Eq. (6) can be solved with a multiple linear regression, and Z and E can be obtained from the intercept and slope of the regression line. This method is attractive because it provides a great deal of information potentially contained in a single temperature-programmed experiment. However, it is not consistently reliable when used to predict the course of a reaction over a wide time–temperature range [16]. The criterion for judging the dynamic experiment is its ability to describe and accurately predict the isothermal behaviour. This method yields accurate kinetic parameters for simple reaction systems. For the majority of thermoset cure reactions, this method consistently overestimates the activation energy and frequency factor when compared to values obtained from isothermal experiments.

A common multi-heating method is based on the work of Ozawa [14,17], and based on a simple relationship between the activation energy, E, and the heating rate, β. Rewriting Eq. (2) gives:

$$\mathrm{d}\alpha/\mathrm{d}t = f(\alpha)Z\exp(-E/RT) \tag{7}$$

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

$$\frac{\mathrm{d}\alpha}{\mathrm{d}t} = \frac{\mathrm{d}\alpha}{\mathrm{d}T}\frac{\mathrm{d}T}{\mathrm{d}t} \tag{8}$$

The heating rate is defined as $\beta = \mathrm{d}T/\mathrm{d}t$. Eq. (8) becomes

$$\mathrm{d}\alpha/\mathrm{d}t = \beta(\mathrm{d}\alpha/\mathrm{d}T) \tag{9}$$

A combination of Eq. (7) and Eq. (9) leads to

$$\frac{\mathrm{d}\alpha}{\mathrm{d}t} = \beta\frac{\mathrm{d}\alpha}{\mathrm{d}T} = f(\alpha)Z\,\mathrm{e}^{-E/RT} \tag{10}$$

Rearranging Eq. (10) in terms of two variables gives:

$$\frac{\mathrm{d}\alpha}{f(\alpha)} = \frac{Z}{\beta}\mathrm{e}^{-E/RT}\,\mathrm{d}T \tag{11}$$

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 $\alpha = \alpha_\mathrm{p}$, gives

$$\int_{\alpha_0}^{\alpha_\mathrm{p}} \frac{\mathrm{d}\alpha}{f(\alpha)} = \frac{Z}{\beta}\int_{T_0}^{T_\mathrm{p}} \mathrm{e}^{-E/RT}\,\mathrm{d}T \cong \frac{ZE}{\beta R}p(E/RT) \tag{12}$$

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 [18]. 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 $20 < E/RT < 60$:

$$\log p(E/RT) = -2.315 - 0.04567\,E/RT_\mathrm{p} \tag{13}$$

For thermoset curing, the extent of the reaction at the exothermic peak, α_p is constant and independent of the heating rate [19]. Therefore, the first integral in Eq. (12) is a constant, which leads to

$$\log\beta = \log p(E/RT) + \log(ZE/R) - \log F(\alpha) \tag{14}$$

where

$$F(\alpha) = \int_{\alpha_0}^{\alpha_\mathrm{p}} \frac{1}{f(\alpha)}\mathrm{d}\alpha.$$

Substituting Eq. (13) into Eq. (14) yields:

$$\log\beta = -2.315 - 0.4567E/RT_\mathrm{p} + \log(ZE/R) - \log F(\alpha) \tag{15}$$

The activation energy can be calculated from a plot of log β versus $1/T_\mathrm{p}$. Since this method uses the relationship between the peak exothermic temperature and its corresponding heating rate, the multi-heating method is an appropriate choice for cure characterization of resins that display low-energy cures, thermal instability, irregular baselines, solvent effects and some of the reactions with multiple exotherms [20–22].

For the calculation of the pre-exponential factor, rearranging Eq. (15) gives:

$$\beta = [ZE/RF(\alpha)]p(E/RT) \tag{16}$$

This equation is a two-parameter equation in which the first parameter, $ZE/F(\alpha)$, appears linearly, and the second parameter, E in the P-function, appears non-linearly. The pre-exponential factor is computed from the first parameter:

$$Z = (\text{1st parameter})[RF(\alpha)/E] \tag{17}$$

In order to calculate the Z value, $F(\alpha)$ must be known.

Another useful and accurate expression for the pre-exponential factor for nth-order reactions, which relates E, β and T_p, was derived by Kissinger [23]:

$$Z = \frac{\beta E\ \text{e}^{E/RT_\text{p}}}{RT_\text{p}^2[n(1-\alpha_\text{p})^{n-1}]} \tag{18}$$

Kissinger argued that $n(1-\alpha_\text{p})^{n-1} \approx 1$ and is independent of the rate of heating. The Eq. (10) can be rewritten as:

$$Z = \frac{\beta E\ \text{e}^{E/RT_\text{p}}}{RT_\text{p}^2} \tag{19}$$

Rearranging and taking logarithm of Eq. (19) yields

$$-\ln\left(\frac{\beta}{T_\text{p}^2}\right) = \frac{E}{RT_\text{p}} - \ln\left(\frac{ZR}{E}\right) \tag{20}$$

which is the equation of a straight line if $y = -\ln(\beta/T_\text{p}^2)$ and $x = 1/T_\text{p}$. From a plot of y versus x and fitting a 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.

Autocatalysed thermoset cure reactions are the type where one of the reaction products is also a catalyst for further reaction. The kinetics of autocatalysed reactions are described by an equation expressed as;

$$\text{d}\alpha/\text{d}t = (k_1 + k_2\alpha^m)(1-\alpha)^n \tag{21}$$

where k_1 and k_2 are the rate constants for primary and secondary reactions. This equation indicates that the maximum rate of cure and corresponding exothermic peak in isothermal d.s.c. occur at $t > 0$, and that the rate of cure at $t = 0$ is finite. Thus, an autocatalysed reaction of thermoset polymers is characterized by a maximum conversion rate, typically occurring between 20 and 40% conversion [16].

Following Kissinger's method as shown by the Eq. (18), the pre-exponential factor for autocatalysed reactions can also be approximated by an equation [22]:

$$Z \cong \frac{\beta E\ \text{e}^{E/RT_\text{p}}}{RT_\text{p}^2[2\alpha_\text{p} + 2B\alpha_\text{p} - 3\alpha_\text{p}^2 - B]} \tag{22}$$

where B is a stoichiometric parameter. For example, epoxide is reacted with amine which is a curing agent in an amine–epoxide curing reaction. $B = 1$ when the quantities of reactive epoxide and amine are equal to each other [16]. Rewriting Eq. (22) gives an equation which is similar to Eq. (20):

$$-\ln\left(\frac{\beta}{T_\text{p}^2}\right) = \frac{E}{RT_\text{p}} - \ln\left(\frac{ZR[2\alpha_\text{p} + 2B\alpha_\text{p} - 3\alpha_\text{p}^2 - B]}{E}\right) \tag{23}$$

This equation is also used to obtain the activation energy using the linear relationship between $y = -\ln(\beta/T_\text{p}^2)$ and $x = 1/T_\text{p}$. The intercept of the straight line can be used to calculate the pre-exponential factor.

Isothermal method is a thermal analysis technique to measure the time dependence of curing at constant temperature. Isothermal methods are 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 cure [16].

As previously mentioned, most thermosetting cure reactions can be represented by either autocatalysed or nth-order rate equations. For an nth-order reaction, the reaction rate is expressed by Eq. (3), and the rate constant and the reaction order can be obtained from the intercept and the slope of $\log(\text{d}\alpha/\text{d}t)$ versus $\log(1-\alpha)$ plot.

For an autocatalysed reaction, on the other hand, the reaction rate is given by an equation as:

$$\text{d}\alpha/\text{d}t = k\alpha^m(1-\alpha)^n \tag{24}$$

where m is also a reaction order. Taking the logarithm of Eq. (24) yields:

$$\begin{aligned}\log(\text{d}\alpha/\text{d}t) &= \log k + \log \alpha^m(1-\alpha)^n \\ &= \log k + n\log \alpha^{m/n}(1-\alpha)\end{aligned} \tag{25}$$

This equation can also be solved by the linear relationship between $\log(\text{d}\alpha/\text{d}t)$ and $\log\alpha^{m/n}(1-\alpha)$. The slope of the straight line is n and the intercept is $\log k$. The value m is calculated by substituting n and k, and then solving Eq. (25). In addition, for an autocatalysed reaction, a plot of $\log(\text{d}\alpha/\text{d}t)$ versus $\log[\alpha^{m/n}(1-\alpha)]$ is used for comparison of experimental results and the best-fit line.

For thermal analysis using the isothermal method, the two basic parameters, $\text{d}\alpha/\text{d}^\text{t}$ and α, are required and can be obtained from the d.s.c. exotherm. The reaction rate is obtained by dividing the peak height $\text{d}H/\text{d}t$, at time t by the total heat of reaction, ΔH_0.

$$\text{d}\alpha/\text{d}t = (\text{d}H/\text{d}t)/\Delta H_0 \tag{26}$$

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.

$$\alpha = \Delta H_\text{p}/\Delta H_0 \tag{27}$$

3. Materials and methods

3.1. Resin synthesis

To prepare PF resin for d.s.c. analysis, liquid phenol (90%) and paraformaldehyde were used as supplied. PF resin was synthesized in a 2 L reaction kettle according to a modified method [25]. The reactor was charged with phenol (90%), paraformaldehyde (45.6%), and water.

After heating the components to 40°C in the reactor, the initial sodium hydroxide (50%) was slowly added over 10 min. When the temperature rose to 100°C, the resin was cooked for 2–3 min and then cooled to 65°C where cooking was continued for 65 min. The temperature was held at 65°C until the Gardner–Holdt viscosity ranking (25°C) was KL. The resin was then cooled to 30–40°C, and the second portion of sodium hydroxide (50%) was added. The solids content of the synthesized resin was determined by a pan solids technique [26]. The gelation time was measured with a Sunshine Gel Time meter with 1 g of resin at 120°C.

The three additives used were propylene carbonate (98%), sodium carbonate (Na_2CO_3) and potassium carbonate (K_2CO_3). All additives were diluted to an aqueous solution; propylene carbonate was prepared as a 1 mol solution (10.4 wt%); both sodium carbonate and potassium carbonate were prepared as a 2.5 mol solution (Na_2CO_3 26.5 wt% and K_2CO_3 34.5 wt%). The prepared additive solutions were mixed with the synthesized PF resin in a small vial. The additive concentrations (2, 4, 8 and 10%) were determined by the relative weight percentage of the non-volatile solids for the resin synthesized.

3.2. D.s.c. analysis

All d.s.c. 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 vapour pressures up to 10 MPa. Dynamic scans (Borchardt–Daniels method) were made with a single heating rate of 10°C/min and a scanning temperature range from 30 to 240°C. Analysis of the results of these dynamic scans produced inconsistent thermal kinetic parameters for the reaction order, n for the modified PF resins. Therefore, a multi-heating rate method (ASTM E-698 method) was employed for thermal characterization of modified PF resins. 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. For isothermal scanning, four different temperatures were employed; 80, 110, 120 and 130°C with a scanning time range of 30–65 min.

4. Results and discussion

Fig. 1 shows the measurements of gelation time at 120°C as a function of the level of additives. As expected, all additives tested were effective in accelerating the cure of PF resin. The gel time decreased rapidly when propylene carbonate (referred to as PC hereafter) was used. Both sodium carbonate (referred to as NC hereafter) and potassium carbonate (referred as to KC hereafter) use resulted in moderate decreases in the gel time. In general, PC-modified resins showed the shortest gel time with NC-modified resins having an intermediate range, and KC-modified resins having the longest gel time as the concentrations of additives increased.

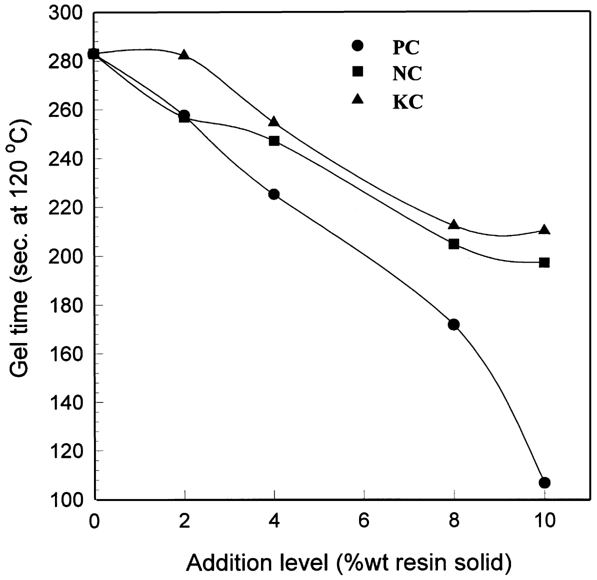

Fig. 1. The gel time of cure-accelerated PF resins with carbonates.

As mentioned earlier, dynamic scan of modified PF resins showed inconsistent nth-order thermal kinetic parameters. The results are summarized in Table 1, including total and partial reaction heat, peak temperature and conversion rate. The peak temperature for dynamic scanning at 10°C/min showed a unique trend as the additive levels increased. For PC-modified resin, the peak temperature decreased up to 4% concentration and then rapidly increased. However, both NC- and KC-modified reins showed a consistent decrease in the peak temperature as the additive amount

Table 1
The peak temperature and its corresponding maximum conversion rate obtained from a dynamic heating method at 10°C/min

Additive types	Concentration (wt%)	ΔH_p (J/g)[a]	ΔH_0 (J/g)[b]	T_p (K)[c]	α_p^d
Base resin	0	135.9	386.9	422.05	0.351
PC	2	94.9	405.5	414.05	0.234
	4	95.6	394.6	415.05	0.242
	8	85.2	339.9	418.75	0.250
	10	64.9	330.4	420.55	0.196
NC	2	133.1	433.2	416.25	0.307
	4	130.8	423.9	413.15	0.308
	8	124.6	458.5	409.15	0.271
	10	114.9	452.4	408.35	0.253
KC	2	141.5	438.1	417.25	0.322
	4	130.6	393.6	414.55	0.331
	8	137.8	543.5	410.65	0.253
	10	126.5	474.2	409.85	0.266

[a] The partial reaction heat up to the peak temperature
[b] The total reaction heat
[c] The peak temperature
[d] The maximum conversion rate at the peak temperature

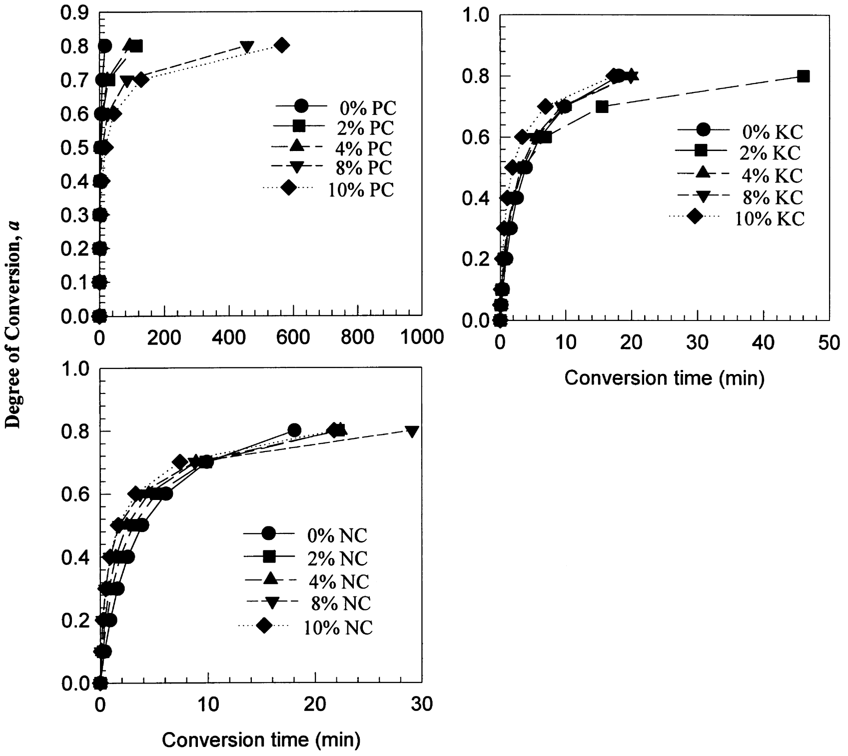

Fig. 2. The degree of conversion of modified PF resins with three carbonates.

rose. Results also indicate that the cure acceleration effects are present for each additives tested.

For the comparison of conversion rate versus time of modified PF resins, the degree of conversion, α, was plotted as a function of the conversion time at 140°C as shown in Fig. 2. All data were obtained from dynamic scanning at a heating rate of 10°C/min. The PC-modified resins showed longer conversion time than that of the base resin for all concentration levels (Fig. 2a). The NC-modified PF resins were quite different from the PC-modified resins (Fig. 2b). As the level of NC increased, the conversion time was lower up to the conversion rate of about 0.7 compared with the base resin. Above the 70% conversion level, the conversion time became longer than that of the base resin. The NC-modified PF resins had much lower conversion time than those for the other two carbonate-modified resins as indicated by the conversion time scale shown. The KC-modified PF resins had similar conversion time to that of NC-modified resins (Fig. 2c), and had a shorter conversion time than that of the base resin. However, it seemed that the longer conversion time at the 2% concentration level is an extreme. In general, the KC-modified resins resulted in slightly longer conversion time than those for NC-modified resins.

In addition, the conversion time of modified PF resins at selected conversion rates (i.e. 30, 50 and 70%) is presented in Table 2. Both NC- and KC-modified resins showed a decrease in conversion time when the concentration of additives was increased. PC-modified PF resins also followed a similar trend for both lower PC concentrations (i.e. up to 4%) and lower degree of conversion (i.e. 30%). However, the conversion time was lengthened above 4% PC concentration and at higher degrees of conversion (i.e. 50 and 70%). A similar result was already observed in Fig. 2a. These results indicate that PC-modified resins might be cured fast and that the curing process might be in a transition from a chemical-controlled reaction to a diffusion-controlled reaction at these conditions. For example, at higher PC concentration levels, the PC-modified resins prepared for d.s.c. scanning started to gel even at room

Table 2
The conversion rate versus time for modified PF resins

Additive types	Concentration (wt% of resin solid)	Conversion time (s)		
		$\alpha 30^a$	$\alpha 50$	$\alpha 70$
Base resin	0	95.1	228.0	567
PC	2	67.4	279.0	1767
	4	64.4	291.0	2349
	8	107.0	453.0	3045
	10	148.1	168.6	22 206
NC	2	67.6	179.8	525
	4	42.5	138.1	582
	8	29.6	104.7	507
	10	28.0	101.8	546
KC	2	62.1	207.0	894
	4	61.5	169.6	543
	8	45.2	134.2	486
	10	35.0	114.5	414

All conversion rates were obtained by a single heating method at 140°C
[a] α30, 50 and 70 mean the conversion rate at 30, 50 and 70%, respectively.

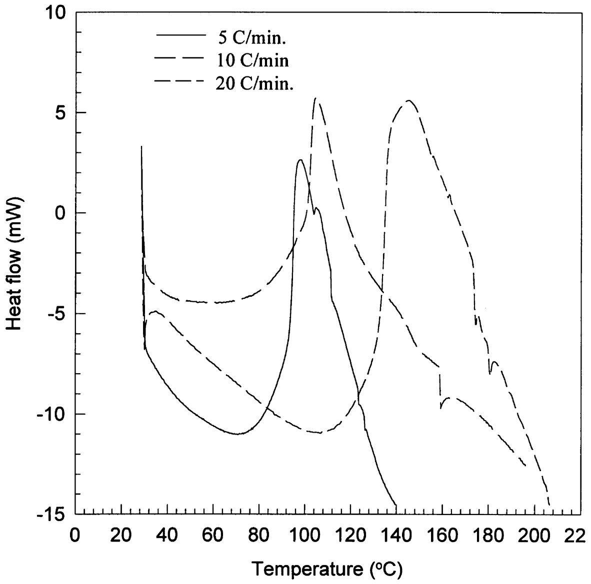

Fig. 3. Typical d.s.c. thermograms of KC-modified PF resins using the multi-heating rate method.

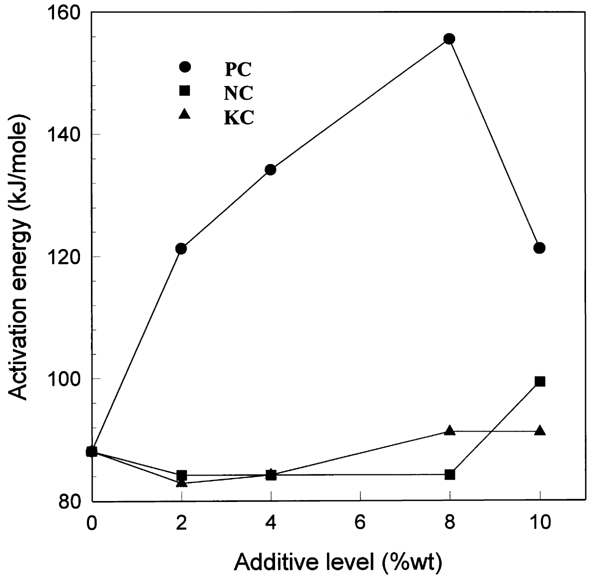

Fig. 4. The activation energy of modified PF resins obtained by multi-heating rate method.

temperature in about 15 min. The gel time measurement also supports this phenomena.

Since the results of a single heating dynamic d.s.c. scans were inconsistent and difficult to interpret, the multiple-heating rate method was employed with two additional different heating rates (5 and 20°C/min). As mentioned in an earlier section, peak temperatures of d.s.c. thermograms are closely related to the corresponding heating rates. Fig. 3 shows typical thermograms of three different heating rates (5, 10 and 20°C/min). In this study, the relationship between heating rate [$-\ln(\beta/T_p^2)$] and peak temperature ($1/T_p$) was used to obtain a straight line. The slope and intercept of the line were used to calculate the activation energy and pre-exponential factor, respectively.

For PC-, NC- and KC-modified PF resins, linear relationships are obtained and the equations are presented in Table 3. All equations had high regression coefficients ranging from 0.98 to 0.99. The changes in the slopes of the PC-modified resins were inconsistent while those for NC- and KC- modified resins showed consistent trends with increasing additive levels.

Fig. 4 shows the activation energy of the cure reactions for modified PF resins as a function of additive levels. The calculated activation energies and pre-exponential factors are also presented in Table 4. As shown by the graph, the activation energy of PC-modified resin increases up to 8% level and then decreases to that of 2% level. For the NC- and KC-added PF resins, the activation energies were slightly lower at lower additive levels than that of the base resin while increasing above the base resin at a very high additive level (10%).

This result indicates that there are cure-accelerating effects at lower additive concentrations. Investigating PF resins with various weight average molecular weights, Park et al. [27] reported that the gel time at 120°C decreased as the molecular weight increased. The authors also reported that the activation energy decreased with increasing molecular weight. In other words, a lower activation energy is needed for higher molecular weight resins which cure

Table 3
The linear relationships between $y = -\ln(\beta/T_p^2)$ and $x = 1/T_p$ for the calculation of the activation energy and pre-exponential factor

Additive level (wt%)	Additive types		
	PC	NC	KC
2	$y = 14.4582x - 25.1451$ ($R^2 = 0.997$)	$y = 9.8465x - 13.908$ ($R^2 = 0.997$)	$y = 9.6326x - 13.3578$ ($R^2 = 0.980$)
4	$y = 16.1398x - 29.0908$ ($R^2 = 0.978$)	$y = 9.8551x - 14.1412$ ($R^2 = 0.998$)	$y = 9.8098x - 13.9231$ ($R^2 = 0.997$)
8	$y = 18.7554x - 34.9297$ ($R^2 = 0.993$)	$y = 9.8638x - 14.3064$ ($R^2 = 0.998$)	$y = 10.7167x - 16.3078$ ($R^2 = 0.999$)
10	$y = 14.5828x - 24.8301$ ($R^2 = 0.996$)	$y = 11.7643x - 19.1427$ ($R^2 = 0.997$)	$y = 10.725x - 16.4397$ ($R^2 = 0.999$)

The equation for the base resin is $y = 10.2607x - 14.68$ ($R^2 = 0.958$).

Table 4
The calculated activation energy and pre-exponential factor from the linear relationship established

Additive types	Concentration (wt%)	E_a (kJ/mol)	Z (1/s)
Base resin	0	85.31	4.06×10^{8}
PC[a]	2	120.2	4.9×10^{15}
	4	134.2	2.4×10^{17}
	8	155.9	8.6×10^{19}
	10	121.2	2.6×10^{16}
NC	2	81.9	1.8×10^{8}
	4	81.9	2.2×10^{8}
	8	82.0	2.6×10^{8}
	10	97.8	4.0×10^{10}
KC	2	80.1	1.1×10^{8}
	4	81.6	1.8×10^{8}
	8	89.1	2.1×10^{9}
	10	89.2	2.4×10^{9}

[a] The pre-exponential factor of the PC-modified PF resin was calculated by autocatalysed reaction model (Eq. (22))

faster than lower molecular weight resins. Thus, a lower activation energy at lower additive concentrations for both NC- and KC-modified PF resins could be attributed to the cure-acceleration effect of these additives. However, higher activation energy at higher additive concentrations might be due to the diffusion-controlled reaction. That is to say, higher NC and KC level has accelerated the cure of PF resin so fast that there is no longer a chemically controlled reaction. After a chemically controlled reaction, a diffusion-controlled reaction limits the rate of cure [16]. Therefore, higher activation energy at higher NC and KC level might be due to diffusion-controlled reactions. This explanation can be applied for PC-modified PF resins which show increasing activation energy even at lower concentrations (i.e., 2 and 4%). The other possible explanation might be related to localized curing of the PF resin when the base resin is mixed with PC.

The rate constants for modified PF resins were calculated using the activation energy and pre-exponential factor from the linear relationship between multi-heating rates and corresponding peak temperatures. The results are presented in Table 5. The pre-exponential factor, Z was calculated using Eq. (22) where B was 0.73. B, a stoichiometric parameter was obtained by considering the reactivity of the phenol ring and the formaldehyde/phenol molar ratio which was 2.2 in this experiment. So, it was assumed that each reactive site of the phenol ring has 0.73 mol of formaldehyde to react with (i.e., $2.2/3 = 0.73$). In order to calculate the pre-exponential factor, the peak temperature and maximum conversion rate were obtained from selected dynamic scanning at 10°C/min and the results are summarized in Table 4.

The calculated rate constants for modified PF resins were lower than that of the base resin. As expected, the rate constant decreased when temperature increased. For PC-modified resins, the rate constant decreased up to 8% level and then increased at all temperatures selected. This result is inconsistent with the results of the activation energy. This lack of agreement can be explained by the occurrence of an autocatalysed reaction for PC-modified resins, as suggested in isothermal scans. In contrast, the rate constants of both NC- and KC-modified resins showed consistent trends with increasing temperatures and additive levels. However, the rate constants increased rapidly at 140°C.

Isothermal scanning of modified resins was conducted. The results including total reaction heat (ΔH), and reaction order for both nth-order and autocatalysed reactions are summarized in Table 6. Fig. 5 shows the ΔH of modified PF resins at different isothermal temperatures. All additive levels are constant as 4% based on the solids content of the base resin. The PC-added resins showed the lowest ΔH at lower temperatures (80 and 110°C) while both NC- and KC-modified resins had the lowest ΔH at higher temperatures (120 and 130°C). Thus, less heat is needed to cure PC-modified resin at lower temperatures than NC- and KC-modified resins.

Table 5
The calculated rate constant [$k(1/\mathrm{s}) = Z\,\mathrm{e}^{-(E/RT)}$] using the calculated activation energy and pre-exponential factor from linear relationships

Additive types	Concentration (wt%)	Temperature (°C)			
		80	100	120	140
Base resin	0	9.9769×10^{-5}	4.637×10^{-4}	1.877×10^{-3}	6.642×10^{-3}
PC[a]	2	8.221×10^{-3}	7.379×10^{-2}	0.530	3.140
	4	3.496×10^{-3}	5.051×10^{-2}	0.365	2.666
	8	7.449×10^{-4}	1.283×10^{-2}	0.165	1.664
	10	3.056×10^{-2}	2.796×10^{-1}	2.039	12.285
NC	2	0.842×10^{-4}	3.751×10^{-4}	1.435×10^{-3}	4.823×10^{-3}
	4	1.700×10^{-4}	7.588×10^{-4}	2.907×10^{-3}	9.789×10^{-3}
	8	1.995×10^{-4}	8.913×10^{-4}	3.418×10^{-3}	1.151×10^{-2}
	10	1.375×10^{-4}	8.203×10^{-4}	4.075×10^{-3}	1.735×10^{-2}
KC	2	1.452×10^{-4}	6.263×10^{-4}	2.327×10^{-3}	7.6109×10^{-3}
	4	1.521×10^{-4}	6.962×10^{-4}	2.650×10^{-3}	8.871×10^{-3}
	8	1.694×10^{-4}	7.272×10^{-4}	3.132×10^{-3}	1.172×10^{-2}
	10	1.593×10^{-4}	8.114×10^{-4}	3.499×10^{-3}	1.311×10^{-2}

Table 6
Summary of isothermal d.s.c. results

Isothermal temp. (°C)	Additive types[a]	D.s.c. parameters		
		ΔH (J/g)	n	m
80	Base	63.7	0.6	*
	PC	41.5	0.5	*
	NC	47.0	0.8	*
	KC	53.8	0.6	*
110	Base	299.8	0.5	*
	PC	214.3	0.8	1.12
	NC	258.6	1.6	0.85
	KC	294.3	1.6	0.75
120	Base	289.5	1.5	*
	PC	285.4	2.2	0.95
	NC	244.1	2.1	0.6
	KC	255.8	2.0	0.47
130	Base	205.0	1.3	*
	PC	178.2	1.6	0.56
	NC	187.5	1.7	*
	KC	204.0	1.5	*

[a] The additive levels used were 4% by weight of the non-volatile solid of base resin

[b] All asterik-marked combinations are not valid for autocatalysed reaction model

Fig. 6 shows the plots of the conversion rate versus conversion time at different isothermal temperatures. In general, the conversion time decreased as the temperature increased. At lower temperatures (80–120°C), the PC-modified resins showed the largest conversion time while it showed the lowest conversion time at 130°C. In addition, the NC- and KC-modified resins also showed longer conversion times at 130°C than that of the control resin.

Typical thermograms of isothermal scans are shown in Fig. 7. For the control, NC- and KC-modified resins, all peaks of heat evolution occurred within 1 min. However, the peak heat evolution of PC-modified resins occurred at about 4 min. As shown in Table 6, the nth-order reaction model was applicable to all modified resins, while the autocatalysed reaction model was partially valid except below 110°C. The base resin did not fit at all for autocatalysed kinetics regardless of the isothermal temperature. In general, PF resin is believed to follow nth-order reaction kinetics. Above 100°C, the autocatalysed kinetics model had a good fit for NC- and KC-modified resins at both 110 and 120°C. The PC-modified resin was the only one whose kinetics agreed with an autocatalytic model at all isothermal temperatures.

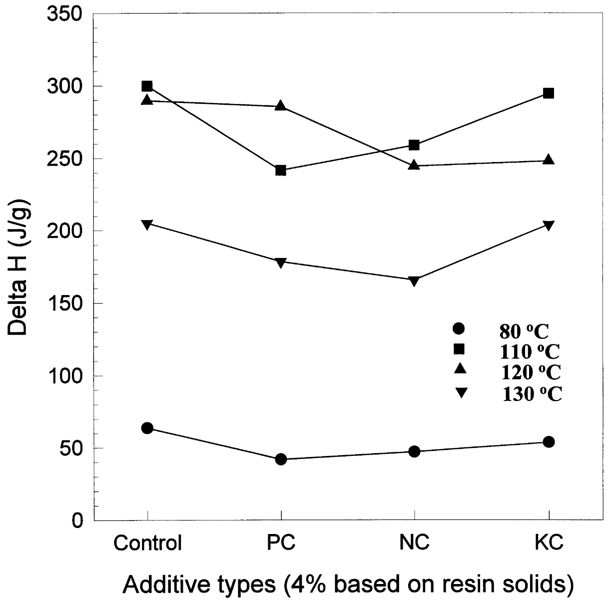

Fig. 5. The reaction heat (ΔH) of isothermal scans at different temperatures.

This result indicates that the PC-modified resin follows autocatalysed reaction kinetics. In general, autocatalysed reactions are characterized by a maximum heat evolution at 20–40% of conversion [16]. The autocatalytic effect is due to the formation of some intermediate species, which markedly accelerates the reaction. A significant portion of the epoxy systems used in industry follow autocatalysed kinetics [16,28,29].

However, it should be pointed out that cure is not necessarily limited to one chemical reaction, and the kinetics may be those of an overall process when the chemical reactions occur simultaneously. Curing by two or more consecutive reactions is also possible. For example, Lau [30] found that cure associated with ambient chemical aging of an amine–epoxy system proceeded first by combined nth-order and autocatalytic processes, then became predominately autocatalytic, and finally became a diffusion-controlled reaction.

Thermal analysis of carbonate-modified PF resin indicated that all carbonates tested are capable of accelerating the cure rate of PF resin. Among the three carbonates, PC showed the fastest curing, and then NC and KC in that order. The results suggest that all carbonates can be used as additives for PF resin to reduce the pressing time for manufacture of panels. However, the PC may cause too short a pot life for the resin to be handled. The mixing of PC with PF resin in a processing line might avoid this problem. The NC-modified PF resins showed a consistent and controllable cure acceleration, suggesting that the NC can be a good additive for PF resin. The KC-modified resins cured slower than the NC-modified resins.

5. Conclusions

Carbonate additives used are capable of accelerating the cure of PF resol resin. The gel time measured at 120°C decreased with increasing the additive levels. PC-modified resins took less time to gel than either NC- or KC-modified resins. A dynamic single heating (Borchardt–Daniels) method was difficult to apply for carbonate-modified PF resins in the thermal behaviour analysis with d.s.c. because of inconsistencies in the thermal parameters. Thus, a multi-heating rate method was employed to obtain the activation energy and pre-exponential factor of the resins. A lower

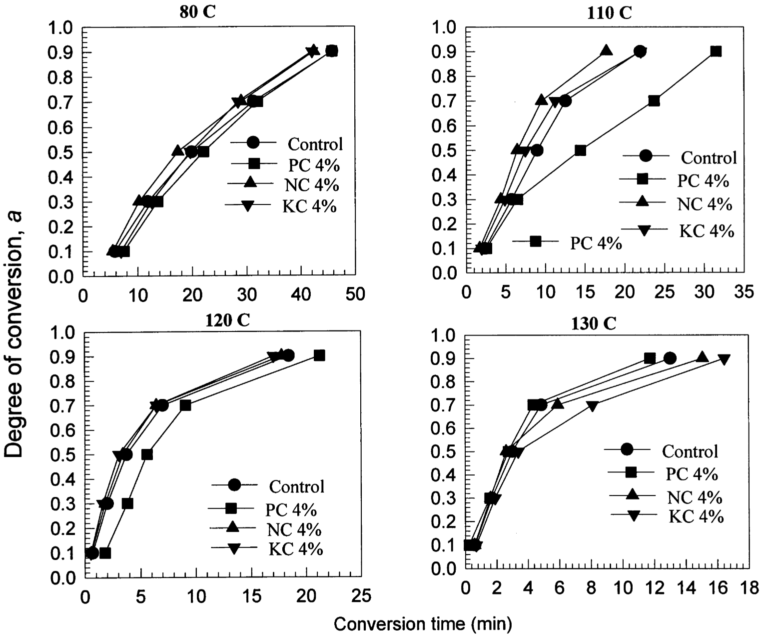

Fig. 6. Typical isothermal thermograms of modified PF reins at 120°C.

activation energy was obtained by a multi-heating rates method compared with that of a single heating rate method. These two parameters were used to calculate the rate constant for modified PF resins. The rate constant increased with increasing additive level and temperature selected. Isothermal scanning revealed that PC-modified PF resin follows autocatalytic kinetics above 110°C. The other two additives (NC and KC) also showed a partial autocatalytic reaction but can be expected to follow the *n*th-order reaction as the base resin does. The results obtained in this experiment indicate that all carbonates used can accelerate the cure rate of PF resin and could reduce the pressing time for panel manufacture. Among the three carbonates, sodium carbonate produced a consistent and controllable cure acceleration effect.

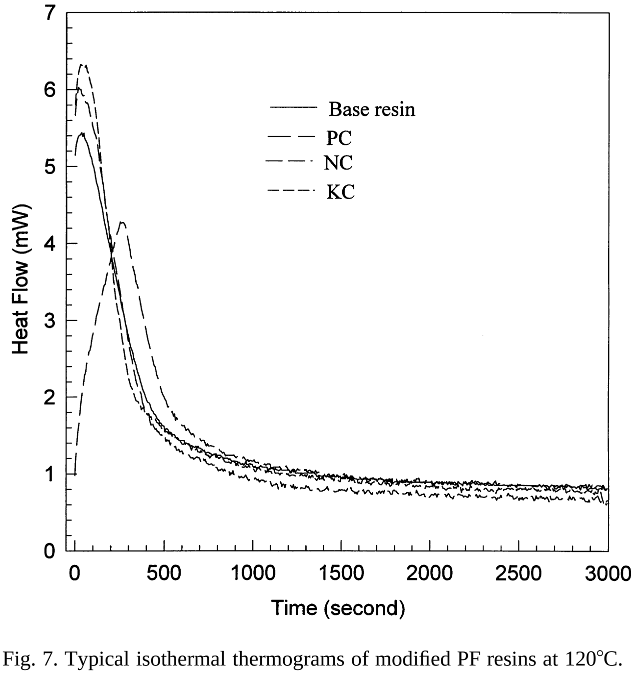

Fig. 7. Typical isothermal thermograms of modified PF resins at 120°C.

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