# The chemorheology of phenol-formaldehyde thermoset resin and mixtures of the resin with lignin fillers

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The chemorheology of phenol-formaldehyde (PF) resin, PF mixed with ammonium salt lignosulfonate (ALS) filler, and PF mixed with methylolated ALS (MALS) filler was studied in order to characterize their isothermal cure behaviours. The results show that both ALS and MALS have a lower reactivity than PF and act as diluents in the resin. The cure rate of the resin decreases when increasing the ALS or MALS content in the PF. In addition the cure rate constant increases when PF is mixed with ALS and decreases when PF is mixed with MALS. These results are in agreement with those obtained from differential scanning calorimetry (d.s.c.) studies. The viscosity can also be expressed as a function of the cure degree, which is calculated from the kinetic parameters of the d.s.c. measurements by using the Williams–Landel–Ferry (WLF) equation. This expression gives a better calculated profile than does the dual Arrhenius model, in particular for PF mixed with filler, above the gel point.

**(Keywords: chemorheology; phenol-formaldehyde resin; lignin filler)**

## INTRODUCTION

Phenol-formaldehyde (PF) resin is widely used as wood adhesive. To reduce its high cost, the partial replacement of some of the resin with low-cost substances has apparent attractiveness in industrial applications. Lignin, which is a by-product of the wood pulp industry, has a similar structure to the PF resin, but its cost is much lower than that of the latter. Many studies have been made concerning the incorporation of lignin into the thermosetting phenolic resin, but the replacement amount is limited, however, as a result of the low reactivity of industrial lignin. Normally, its reactivity can be improved either by methylolation with formaldehyde to provide methylol functionalities, or by phenolation with phenol to provide a reactive prepolymeric resole[1–3]. We have studied and compared the reactivity of the non-modified lignin, ammonium salt lignosulfonate (ALS), and methylolated ALS (MALS), by using differential scanning calorimetry (d.s.c.)[4,5]. The results show that the reactivity of ALS is improved by methylolation.

The cure behaviour is the most important characteristic of a thermosetting resin. To study the cure behaviour of PF, and PF mixed with different fillers, in detail, a number of chemical and physical characterization methods are available[6–8]; d.s.c. is very often used, while dynamic rheology is also one of the best techniques. The latter method can offer several observations which are very sensitive to the changes in molecular and phase structure which occur as the cure reaction proceeds[9–11]. In order to study the agreement between chemorheology and d.s.c. in studying the cure behaviour of thermosets, it is important to compare the cure kinetic parameters obtained from both of these techniques, and also correlate viscosity with the d.s.c. kinetic parameters. A dual Arrhenius model contains several parameters which show the effect of the cure reaction on the viscosity. Additionally, viscosity is dependent on free volume. The Williams–Landel–Ferry (WLF) equation can be used in combination with the d.s.c. results[12–14]. As far as we know, modelling the viscosity of PF and PF mixed with fillers, which are specific thermoset resin systems, has not been the subject of previous work. In this paper, the cure behaviour of PF, PF mixed with ALS, and PF mixed with MALS, at different levels of filler content, was followed by time-dependent dynamic viscosity, measured under isothermal conditions. A dual Arrhenius model was used to estimate the kinetic rate constants and the activation energy of the cure reaction. These parameters were compared with those obtained from d.s.c. The abilities of both the dual Arrhenius model and the WLF model to accurately follow the viscosity as a function of the cure reaction were compared.

## EXPERIMENTAL

The resin systems employed in the study are phenol-formaldehyde (PF), PF mixed with the non-modified lignin, ammonium salt lignosulfonate (ALS), and PF mixed with methylolated ALS (MALS), where the filler content is varied over the range from 0 to 40 wt%. PF is a product of Reichhold Limited (St-Thérèse, Qué., Canada), and has a solid content of ~60 wt%. ALS powder was supplied by Daishowa Chemicals (Québec,

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Qué., Canada). MALS was prepared using the same method as described in previous paper[15]. A PF aqueous solution was blended with either a ALS or MALS aqueous solution for ~15–20 min at room temperature. The pH was adjusted to almost the same value for all of the mixtures, which were then freeze-dried to produce powders suitable for rheological testing. Then, 2–3 g of powdered sample was pressed in a mould under a pressure of $1 \times 10^5\,\mathrm{N\,m^{-2}}$ for 2–3 min to obtain a disc with a thickness and radius of ~2.5 mm and 12.5 mm, respectively.

A Rheometric System IV instrument was used to carry out the rheological characterization. The sample chamber of the rheometer was preheated to 70°C, and the sample disc was then placed between the parallel plates (radius = 12.5 mm) as quickly as possible. The distance between the sample and the plates was adjusted until the sample adhered loosely to the latter. After a period of 2.5 min of equilibration at 70°C, the oven was then heated to reach a fixed temperature in order to study the isothermal chemorheology of the thermosetting resin. The strain and frequency used were 2% and $0.5\,\mathrm{rad\,s^{-1}}$, respectively.

## THEORY

### *Rheology*

*Dual Arrhenius model.* Several researchers[16–19] have proposed empirical models to correlate the isothermal viscosity data. The most extensively used model can be represented by the following equation:

$$\ln\eta = \ln\eta_0 + kt \tag{1}$$

where $\eta$ is the time-dependent viscosity, $\eta_0$ is the viscosity at time zero, $k$ is the polymerization rate constant (an apparent kinetic factor) and $t$ is the time.

The temperature dependence of both $\eta_0$ and $k$ is described by an Arrhenius equation. Therefore, for $T = \mathrm{a}$ constant, one can express the isothermal cure viscosity as a function of the cure temperature ($T$) and the time ($t$) by the following:

$$\ln\eta(t)_T = \ln\eta_\infty - \Delta E_\eta/RT + tk_\infty\exp(-\Delta E_k/RT) \tag{2}$$

where $\eta_\infty$ is the pre-exponential factor for the viscosity, which corresponds to the calculated viscosity of the uncured material at $T = \infty$, $\Delta E_\eta$ is the Arrhenius activation energy of chemoviscosity, $R$ is the gas constant, and $k_\infty$ and $\Delta E_k$ are the analogues of the terms $\eta_\infty$ and $\Delta E_\eta$, respectively.

For the temperature function $T = f(t)$

$$\ln\eta(T,t) = \ln\eta_\infty - \Delta E_\eta/Rf(t) + k_\infty\int\exp(-\Delta E_k/Rf(t))\,\mathrm{d}t \tag{3}$$

One obvious limitation of this representation is that it does not directly take into account $\alpha$, namely the cure degree of the resin, and thus the kinetic parameters are of an apparent type.

*Williams–Landel–Ferry (WLF) equation.* At any stage of advancement, the temperature dependence of the viscosity can be described by the Williams–Landel–Ferry (WLF) equation[12–14]:

$$\log\eta(t) = \log\eta_{T_s} - 26.8(T - T_s)/(13.4 + T - T_s) \tag{4}$$

where $\eta(T)$ is the viscosity at temperature $T$ and $\eta_{T_s}$ is the viscosity at a reference temperature $T_s$.

In this paper, the cure degree calculated from the d.s.c. kinetic parameters is used to characterize the resin advancement.

*Differential scanning calorimetry (d.s.c.)*[4,5]

For thermosets that cure according to $n$th-order kinetics, the kinetic parameters can be calculated by using the following equation:

$$\ln(\mathrm{d}\alpha/\mathrm{d}t) = \ln A - (E_a/RT) + n\ln(1-\alpha) \tag{5}$$

where $\mathrm{d}\alpha/\mathrm{d}t$ is the reaction rate, $A$ is the pre-exponential factor, $E_a$ is the activation energy, $R$ is the gas constant, $\alpha$ is the fractional conversion or degree of cure, and $n$ is the reaction order.

In a dynamic d.s.c. scan, equation (5) may be solved with a multiple linear regression expression of the general form $z = a + bx + cy$. The slope which is obtained by plotting $\ln(\mathrm{d}\alpha/\mathrm{d}t)$ against $1/T$ is $E_a$, while the slope which is found by plotting $\ln(\mathrm{d}\alpha/\mathrm{d}t)$ against $\ln(1-\alpha)$ is $n$ and the intercept is $\ln A - (E_a/RT)$. In addition, $\mathrm{d}\alpha/\mathrm{d}t$ can be obtained by dividing the peak height $\mathrm{d}H/\mathrm{d}t$ at temperature $T$ by the total peak area $\Delta H_t$, while $\alpha$ is obtained by measuring the ratio of the partial area $\Delta H_T$ at temperature $T$ to the total peak area $\Delta H_t$.

Equation (5) upon integration becomes

$$\alpha = 1 - [1 - A(1-n)]t\exp(-E_a/RT)^{1/(1-n)} \tag{6}$$

Thus, the cure degree at any time in an isothermal programme can be calculated. In this particular case, the use of a high pressure cell in the d.s.c. apparatus, necessary because of water being produced during the curing process, precludes the use of an isothermal technique to obtain $\alpha$. Then, as explained above, kinetic parameters which are obtained in either a dynamic or a temperature scanning mode are applied to predict the isothermal curing behaviour.

## RESULTS AND DISCUSSION

### *Rheological properties of PF resin*

*Figure 1* shows the viscosity, storage modulus and loss modulus of the PF resin for a dynamic/100°C isothermal

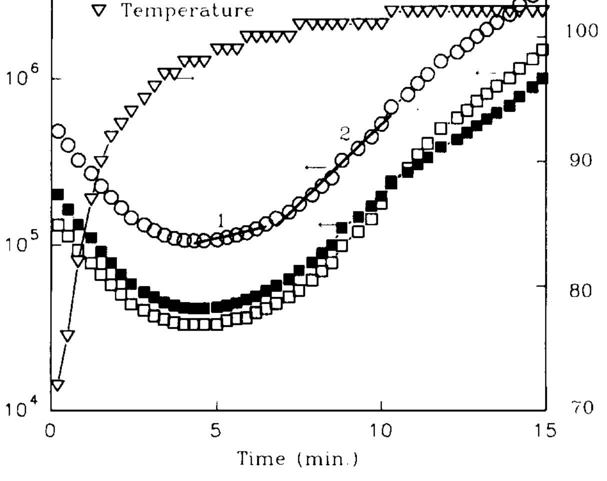

**Figure 1** Viscosity $\eta$ (○), storage modulus $G'$ (□), and loss modulus $G''$ (■) profiles of PF resin for a dynamic/100°C isothermal cure; (▽) temperature

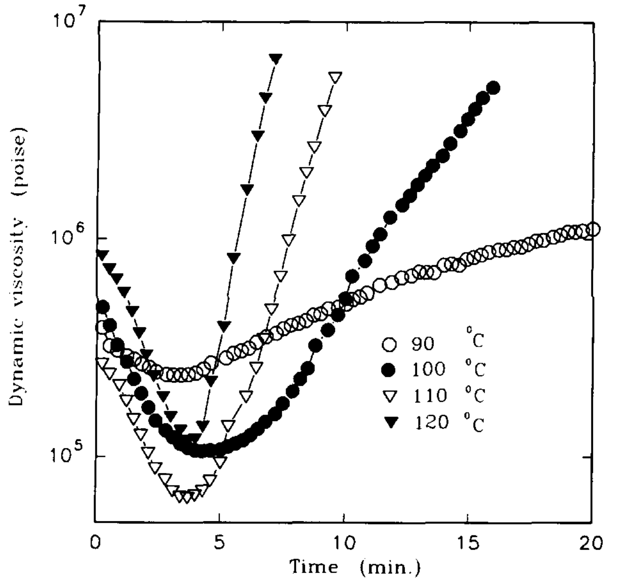

**Figure 2** Viscosity profiles of PF resin for dynamic/isothermal curing treatment at different isothermal temperature: (○) 90; (●) 100; (▽) 110 and (▼) 120°C

cure. The chemorheological behaviour for the curve can be qualitatively described by a initial decrease in the viscosity, due to the temperature dependence of the viscous flow term, until it reaches the isothermal temperature (at approximately the point of minimum viscosity), which is then followed by an increase in viscosity which occurs as the polymerization reactions proceed under constant temperature. It was observed that the viscosity profile shows a slight downward curvature after ~10 min. This point is related to the gel point[9]. As one can see in *Figure 1*, the curves for $G'$ (storage modulus) and $G''$ (loss modulus) also cross at this time, which is additional evidence for the occurrence of the gel point.

*Figure 2* shows the viscosity profiles of the PF resin for isothermal cures at different isothermal temperatures, i.e. at 90, 100, 110 and 120°C. As expected, the rate of change of the viscosity increases with temperature since this depends on the cure kinetics. The initial viscosity at the different isothermal temperatures decreases with temperature, except in the case of the measurements at 120°C, since the temperature dependence of the viscosity affects the reaction mixture more rapidly than the cure kinetics during this initial period. For an isothermal temperature of 120°C, the initial viscosity is higher than that measured at both 100 and 110°C. In this case it can be thought that the cure reaction begins before the isothermal temperature is reached and thus the viscosity increases.

The viscosity curves for the isothermal temperatures of 90, 100 and 110°C all show an inflection point, after 14.1, 9.7 and 5.3 min, respectively. These are indicative of gel points, as mentioned above. It is known, that for the same resin, the gel point should appear at the same cure degree, even for different isothermal temperatures[20]. In order to check this phenomenon in our resin system, the samples that had reached the gel point (according to the rheology measurements) were tested by using d.s.c. The chemical cure degree achieved at the gel point is calculated as follows:

$$\alpha_1 = 1 - (\Delta H_1 / \Delta H_2) \tag{7}$$

where $\alpha_1$ is the chemical cure degree achieved at the gel point, and $\Delta H_1$ and $\Delta H_2$ are the heats of reaction, at the gel point and for an uncured sample, respectively. The values of $\alpha_1$, listed in *Table 1* for the PF resin, are similar even though they do show a slight variation, which does strengthen the inference described above.

It is observed that upon reaching the isothermal temperature (i.e. at approximately the point of minimum viscosity), the viscosity profiles exhibit two relatively linear regions at the 90, 100 (shown in *Figure 1* as areas 1 and 2) and 110°C isothermal temperatures, or one linear region at an isothermal temperature of 120°C, before the gel point is reached (indicated by a downward curvature point). In the first case, the calculation of the viscosity corresponding to $t=0$ ($\eta_0$) and the apparent cure reaction rate constant $k$ at each isothermal temperature can be based on the method described by Dusi and May[19]. $\eta_0$ is calculated by using a linear regression process on the linear region (as shown in *Figure 1*) that directly occurs after the point of minimum viscosity. An Arrhenius plot of these values *versus* $T^{-1}$ ($T$ is the isothermal temperature) is set up to obtain the viscous flow material parameters $\Delta E_\eta$ and $\eta_\infty$. The profiles obtained exhibit a second linear region after the first linear region, which relates to the reaction kinetics of the system during cure. The individual slopes are calculated and then plotted *versus* $T^{-1}$ to yield the kinetic parameters $E_k$ and $k_\infty$. If the viscosity profile only exhibits one linear region between the beginning of the isothermal temperature and the gel point, the calculation of $\eta_0$ and $k$ is simpler. One can therefore directly use this linear relationship to obtain these parameters. However, the method used here assumes that there is no cure reaction occurring before reaching the isothermal temperature. If the resin cures before this, the cure degree will be different at the beginning of the different isothermal temperatures, and will affect the accuracy of four of the model parameters and the modelling of the chemorheology behaviour. For this reason the viscosity curve obtained at an isothermal temperature of 120°C was not used in the calculations of these parameters. It is impossible to keep the resin uncured before reaching the isothermal temperature, but the effect can be reduced by selecting a suitable test temperature and by reaching it as fast as possible. Since the experimental isothermal temperature is not exactly constant, its average value is used for the value of $T$ to calculate the material parameters. *Figures 3* and *4* display the Arrhenius plots used to determine these parameters.

**Table 1** The cure degree at the gel point obtained for different isothermal temperatures

| System | Temperature (°C) | Gel time at $G'=G''$ (min) | Cure degree (%) |
|---|---|---|---|
| PF | 90 | 14.1 | 39.0 |
| | 100 | 9.7 | 33.6 |
| | 110 | 5.3 | 40.6 |
| PF+ALS[a] | 100 | 12.5 | 67.8 |
| | 110 | 8.5 | 73.4 |
| | 120 | 6.7 | 75.1 |
| PF+MALS3H[b] | 100 | 17.1 | 67.9 |
| | 110 | 11.2 | 62.3 |
| | 120 | 7.9 | 66.6 |

[a] Contains 30 wt% filler

[b] ALS methylolated for 3 h; contains 30 wt% filler

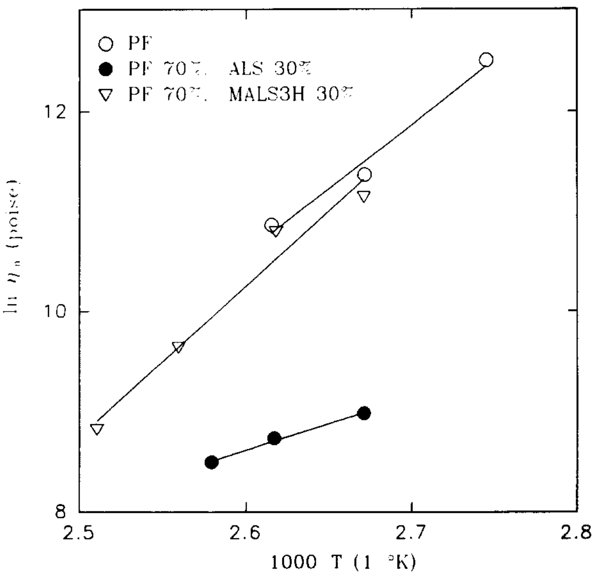

**Figure 3** The Arrhenius plots used to determine the viscous flow material parameters of PF (○), PF mixed with 30 wt% ALS (●), and PF mixed with 30 wt% MALS3H ( ALS methylolated for 3 h) (▽)

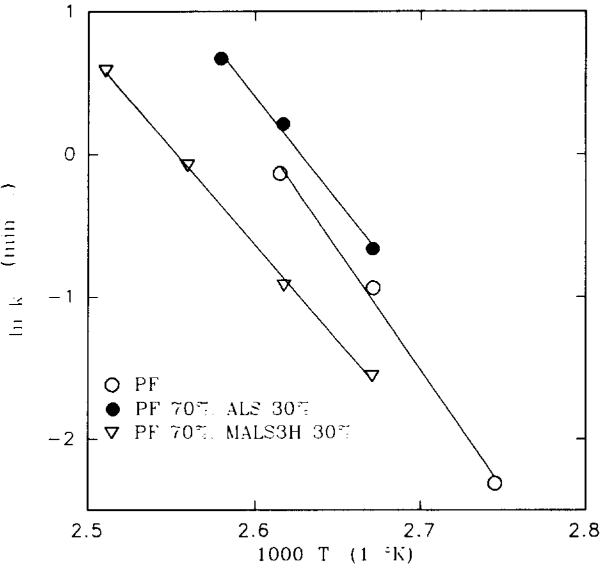

**Figure 4** The Arrhenius plots used to determine the kinetic parameters of PF (○), PF mixed with 30 wt% ALS (●), and PF mixed with 30 wt% MALS3H (ALS methylolated for 3 h) (▽)

**Table 2** The apparent kinetic parameters obtained from chemorheology measurements

| System | $\ln \eta_\infty$ (cp) | $\Delta E_\eta$ (kJ mol$^{-1}$) | $\ln k_\infty$ (min) | $\Delta E_k$ (kJ mol$^{-1}$) |
|---|---|---|---|---|
| PF | −22.7 | −106.0 | 37.6 | 120.4 |
| PF + ALS[a] | −5.13 | −43.9 | 38.0 | 121.9 |
| PF + MALS3H[b] | −29.0 | −125.5 | 34.4 | 112.2 |

[a] Contains 30 wt% filler

[b] ALS methylolated for 3 h; contains 30 wt% filler

The linear regression fit to the data points yielded the four model parameters mentioned above, and their values are listed in *Table 2*.

### *Effect of fillers on PF cure behaviour*

The d.s.c. results presented in *Table 3* show that, after PF is mixed with 30 wt% of either ALS or MALS, the reaction heat $\Delta H$ decreases. At the same replacement level, there is a larger decrease for the system where PF is mixed with ALS. The activation energy ($\Delta E_a$) decreases with the mixing of ALS and increases with the mixing of MALS, showing that methylolation improves the reactivity of ALS, which is still lower than that of pure PF. However, ALS has a catalytic effect on the cure of PF, with a reverse effect being observed after methylolation.

*Figure 5* shows the viscosity profiles of PF resin, PF mixed with 30 wt% ALS, PF mixed with 30 wt% MALS1H (ALS methylolated for 1 h), and PF mixed with 30 wt% MALS3H (ALS methylolated for 3 h), all for a dynamic/100°C isothermal cure. When PF is mixed with those fillers, clear inflection points can be seen in the viscosity curves. The $G'$–$G''$ cross-overs also occur at almost the same times, at these positions (not shown). For each type of resin system, the values of $\alpha_1$ (see *Table 1*) are similar for the different processing temperatures. The inflection points are considered to be indicative of the gel point. The results listed in *Table 1* show that, with ALS and MALS as fillers, the PF gels at a higher cure degree, and also cures more slowly. The four model parameters of the PF systems containing fillers (obtained by using the same method as described above) are presented in *Table 2*. The corresponding Arrhenius plots are also shown in *Figures 3* and *4*.

*Figures 3* and *4* show that the initial viscosity at the isothermal temperature decreases non-significantly for

**Table 3** The kinetic parameters obtained from d.s.c. measurements[5]

| System | $T_p$ (°C) | $\Delta H$ (J g$^{-1}$) | $\Delta E_a$ (kJ mol$^{-1}$) | $n$ | ln A |
|---|---|---|---|---|---|
| PF | 145.6 | 234.4 | 122.9 | 1.5 | 30.1 |
| PF + ALS[a] | 132.6 | 153.1 | 94.3 | 1.6 | 22.7 |
| PF + MALS3H[b] | 130.0 | 190.5 | 171.6 | 2.8 | 46.3 |

[a] Contains 30 wt% filler

[b] ALS methylolated for 3 h; contains 30 wt% filler

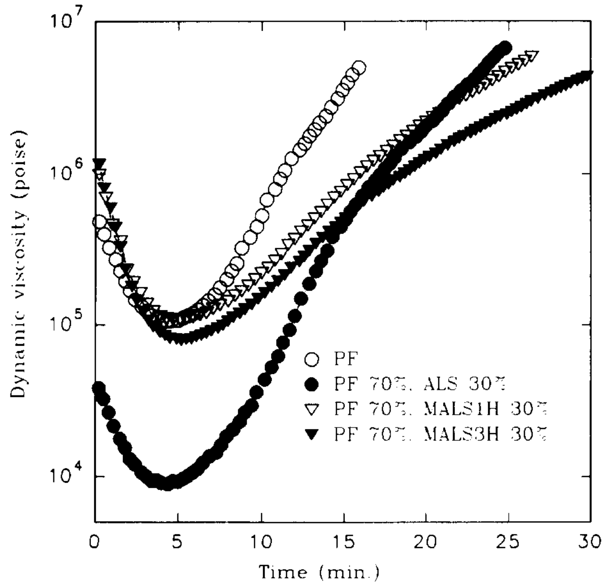

**Figure 5** Viscosity profiles of PF mixed with 30 wt% ALS (●), PF mixed with 30 wt% MALS1H (ALS methylolated for 1 h) (▽), and PF mixed with 30 wt% MALS3H (ALS methylolated for 3 h) (▼), for a dynamic/100°C isothermal cure

PF mixed with 30 wt% MALS, but significantly for PF mixed with 30 wt% ALS. The apparent cure reaction rate constant, $k$, of PF mixed with 30 wt% ALS, obtained from the slope of the $\log \eta$ *versus* $t$ curve, is higher than that of PF mixed with 30 wt% MALS, and even higher than that of PF. Therefore, material with a low initial viscosity does not necessarily have a low $k$ value. The two isothermal parameters, $\eta_0$ and $k$, appear to be totally independent of one another. This is because $\eta_0$ depends upon the structure of the resin, while $k$ depends upon its activation properties.

The d.s.c. results[4,5] show that ALS cannot polymerize by itself, and has a weak reactivity with the PF resin. However, the value of $k$ for PF mixed with 30 wt% ALS (see *Figure 4*) is higher than that of the PF resin on its own. This can be explained as follows. Some filler additives also introduce new surfaces, thereby accelerating the cure reaction[21]. In this case, the filler acts both as a diluent and an accelerator. The rheological effects of dilution by ALS has been observed by changing the ALS content in PF, and this will be discussed later in this paper. The d.s.c. results[5] (presented in *Table 3*) also clearly represent these two actions. When PF is mixed with ALS, the overall reaction heat, $\Delta H$, decreases, showing the diluent action of the ALS. This decrease in activation energy illustrates the catalytic action of ALS. The cure reaction rate is proportional to the cure reaction rate constant and the concentration of reactant, and is determined by both of them. The combined rheological results show that PF resin has a shorter gel time than PF mixed with ALS (see *Table 1*).

For the system where PF is mixed with the MALS filler, there is also agreement between the d.s.c. and the rheology results. The former show that the heat of reaction of the PF/MALS system is higher than that of the corresponding PF/ALS system, at the same amount of replacement, but lower than that of the pure PF resin. This means that the reactivity of MALS is higher than that of ALS, as a result of the hydroxymethyl groups introduced into the ALS by the methylolation reaction, but its reactivity is still lower than that of pure PF. MALS has a diluent effect on the curing of PF, although to a lower extent than the ALS filler. This dilution effect of MALS on the rheological properties has been observed by varying the MALS content in the PF, and will be discussed later in this paper. The additional hydroxymethyl groups change the properties of ALS; MALS has an inhibitory effect on the cure of PF. The activation energy of PF mixed with MALS, from d.s.c., is higher than that of PF. In addition, the value of $k$ obtained from the rheological profiles is lower than other formulations. *Figure 5* shows that the inhibitory effect of MALS can be correlated with the methylolation degree. The value of $k$ for PF mixed with 30 wt% MALS is lower than that of PF mixed with the same amount of ALS. Furthermore, the value of $k$ for PF mixed with 30 wt% MALS3H is lower than that of PF mixed with the same amount of MALS1H, since the former has more hydroxymethyl groups[15]. This combination of the diluent and inhibitory actions of MALS leads to the PF/MALS mixed system having a lower cure reaction rate, i.e. a longer gel time, than either the PF resin or the PF/ALS mixed system (see *Table 1*).

$\Delta E_k$ is the cure reaction activation energy, obtained from rheology studies. The results presented in *Table 2* show that $\Delta E_k$ of PF mixed with 30 wt% ALS is almost equal to that of the PF resin, but is higher than that of the PF when mixed with 30 wt% MALS. This disagrees with the trend for $\Delta E_a$, the cure reaction activation energy, as obtained from d.s.c. studies, in spite of the fact that changes in the value of $k$ (from rheology studies) are in good agreement with $\Delta E_a$. This may be due to a variety of reasons. For example, the cure reaction rate, or cure reaction rate constant, based on an increase of the polymer number-average molecular weight $M_n$ (from d.s.c.), is directly related to the chemical kinetics, and not to an increase of the weight-average molecular weight $M_w$. Viscosity is more closely related to $M_w$ and the dependence of viscosity on $M_w$ changes from being linear at low-molecular-weight values to a 3.4-power dependence at high-molecular-weight values. Calculations of $k$ from rheology measurements, by using the change in viscosity (which is related to $M_w$) are not based on polymerization kinetics and cannot be related directly to resin chemistry[10,12,22]. Therefore, values of $k$ obtained from rheology profiles are apparent cure rate constants. During the cure process of a thermosetting resin, the rates of increase in $M_n$ and $M_w$ are different. If the rate of increase of $M_n$ for resin A is higher than that of resin B, it will also show the same trend in $M_w$. As observed above, the value of $k$ obtained from rheology measurements is in agreement with the results from d.s.c., and can give qualitative information. $\Delta E_k$ is taken from a regression calculation of the value of $k$, which is an apparent cure rate constant.

Values of $\Delta E_\eta$ given in *Table 2* show that $\eta_0$, the initial viscosity of PF when mixed with ALS, is less dependent on temperature than that of the pure PF system. After methylolation, a reversal in this trend is observed. $\Delta E_\eta$ and $\eta_\infty$ are both derived from a regression calculation of $\eta_0$, and are difficult to relate directly with the chemical reaction of the resin or the cure behaviour. However, their values can be changed by changing the molecular weight of the resin, or by a precuring treatment.

### *Effect of filler content on PF rheological properties*

The isothermal viscosity profiles of the PF system containing the ALS filler at loadings of 0, 10, 20, 30, and 40 wt%, for a dynamic/120°C isothermal cure, are shown in *Figure 6*. All of these profiles are similar in shape, and in addition they all show a downward curvature at various points in the polymerization region of the curves. In general, variation in the filler content may significantly alter the $G'$–$G''$ cross-over point, especially at high values of the filler concentration. Here, however, this effect is not clearly seen, even when the ALS or MALS content is as high as 40 wt% (not shown). Compared with the pure PF system, the curves all show a decrease in value of the initial viscosity. The variation of $\eta_0$ with different ALS loadings, at a constant temperature, is not strictly proportional to the filler content. The different $\eta_0$ values shown in *Figure 6* may arise for a number of reasons, such as experiment error, differences in the pellet forming conditions, humidity, density, etc.

After an initial increase the value of $k$ is then reduced with increasing ALS content (see *Figure 7*) even though this filler has a catalytic action on the cure of PF. It can be considered that a lower concentration of functional groups in the resin will lower the value of $k$. The catalytic effect of ALS may not grow clearly with an increasing ALS content, but the effect of dilution is proportional to the amount of the ALS component, and this results in a

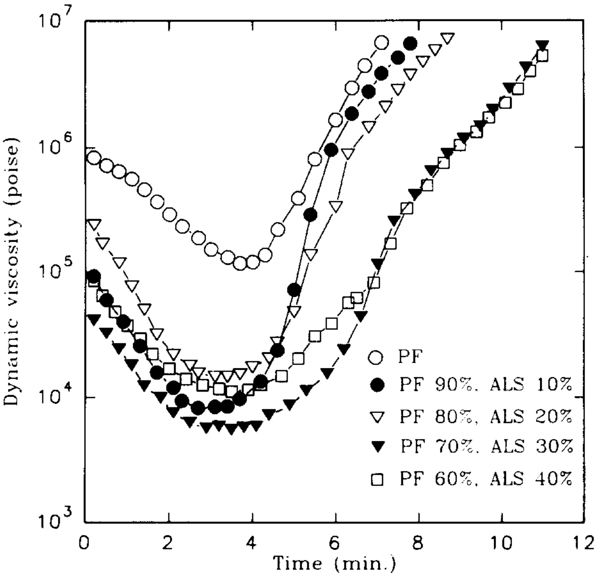

**Figure 6** Viscosity profiles of PF mixed with ALS at different loadings for a dynamic/120°C isothermal cure: (○) 0; (●) 10; (▽) 20; (▼) 30 and (□) 40 wt%

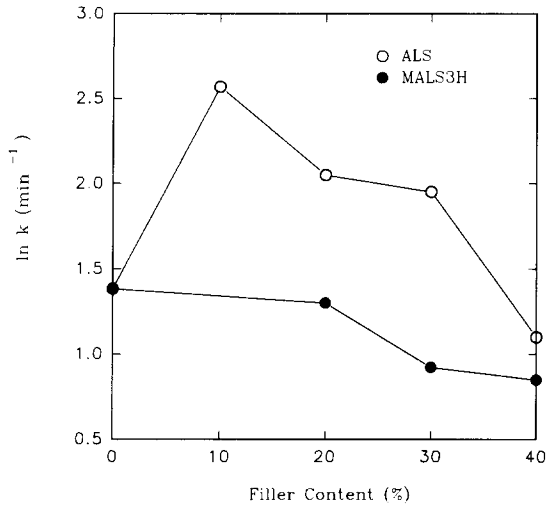

**Figure 7** The relationship between ln $k$ and the filler content of the mixed PF sysems: (○) ALS and (●) MALS3H (ALS methylolated for 3 h)

decrease in $k$. As shown from the d.s.c. results[4], the heat of reaction of the PF/ALS system is reduced, while the activation energy is virtually unchanged, with increases with the ALS content.

The general variation in the viscosity profiles of PF when mixed with MALS over the same range of filler contents, measured at constant temperature (not shown), is similar to that of the PF/ALS system, except the values of $k$ are lower than that of pure PF. *Figure 7* shows that the variation of $k$ in the PF/ALS system is more sensitive to the filler content than that in the corresponding PF/MALS system.

### *Monitoring viscosity profiles*

Calculated viscosity profiles, obtained by employing the parameters given in *Table 2* in the Arrhenius equation, were compared to the experimental profiles. *Figures 8* and *9* show the experimental viscosity profiles and the corresponding calculated profiles (obtained by using the dual Arrhenius model), for the PF and the PF/30 wt% MALS3H systems, respectively. These show that, at both the ramping temperature and the isothermal temperature, the calculated viscosities agree well with the experimental data before the gel point is reached. Minor differences between the experimental and model curves arise because the parameters used were average optimum values and also because of experimental error. However, there are more significant differences between the profiles after the gel point, in particular for the PF mixed system. This shows that in the isothermal mode, ln $\eta$ is a linear function of the cure time for both PF and for PF when mixed with either ALS or MALS before the gel point is achieved. After the gel point the polymerization kinetics are generally changed. Since this model does not contain any information concerning the mechanism of cure, it serves only a limited purpose. If one combines viscosity data with polymerization kinetics, a better result should be obtained. Tajima and Crozier[12,13] used the WLF equation to relate its parameters to the cure degree of

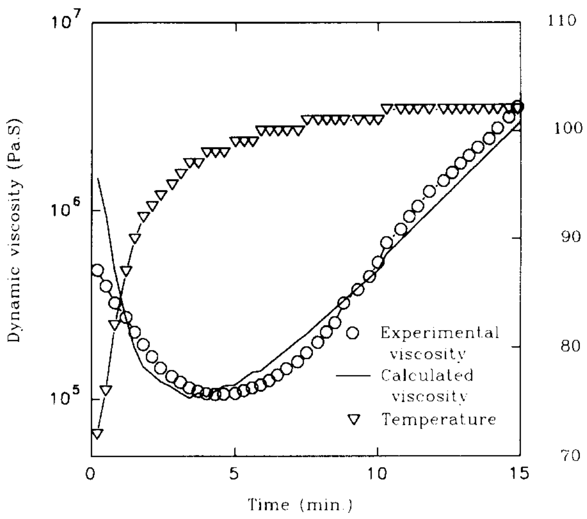

**Figure 8** Comparison of the calculated curve (——), obtained using the dual Arrhenius model, and the experimental viscosity profile (○) of PF for a dynamic/100°C isothermal cure; (▽) temperature

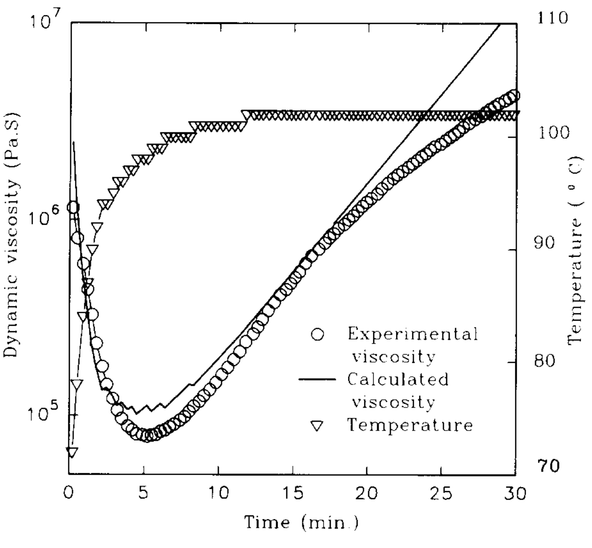

**Figure 9** Comparison of the calculated curves (——), obtained using the dual Arrhenius model, and the experimental viscosity profile (○) of the PF/30 wt% MALS3H (ALS methylolated for 3 h) system for a dynamic/100°C isothermal cure; (▽) temperature

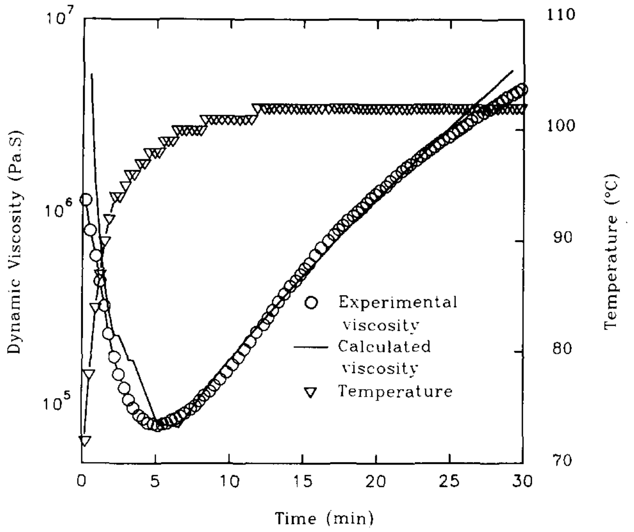

**Figure 10** Comparison of the calculated curve (—) obtained using the WLF equation, and the experimental viscosity profile (○) of the PF/30 wt% MALS3H (ALS methylolated for 3 h) system for a dynamic/100°C isothermal cure; (▽) temperature

the resin, and obtained good results. Here, we combine the parameters of this equation with the kinetic parameters which were obtained from d.s.c. measurements. The amount of reacted resin is defined by the cure degree which is calculated by using equation (6).

Regression analysis of the viscosity and the cure degree of the resin indicate that $\log T_s$ is directly proportional to $\log \alpha$, i.e.

$$\log T_s = 0.261 \log \alpha + 2.05 \tag{8}$$

In addition, the viscosity at $T_s$ is an exponential function of the temperature:

$$\log \eta_{T_s} = 28.47 - 0.035\, T_s \tag{9}$$

By combining equations (4), (8) and (9), the viscosity can then be calculated as a function of the cure degree of the resin. A better monitoring profile for the system where PF is mixed with 30 wt% MALS3H, is shown in *Figure 10*. As can be seen, this also shows good agreement after the gel point, in spite of the fact that the d.s.c. parameters obtained from dynamic testing do not give a reasonable $\alpha$ under isothermal conditions.

## CONCLUSIONS

The apparent cure rate constant $k$ and the gel time obtained by chemorheology measurements can reflect the cure behaviour of the thermoset. The value of $k$ has a direct relationship with the effective cure rate constant and also the concentration of functional groups in the resin. The ALS and MALS fillers have a lower reactivity than PF and act as diluents in the PF system. The cure rate of the resin decreases with increasing ALS or MALS content. However, the cure rate constant increases when PF is mixed with ALS but decreases when PF is mixed with MALS. These observations are in agreement with the results obtained from d.s.c. measurements. Additionally, viscosity can be expressed as a function of the cure degree, which is calculated from the kinetic parameters obtained from d.s.c. by using the WLF equation. This equation gives a better fit to the viscosity data than the dual Arrhenius model, in particular for PF mixed with filler, after the gel point has been reached.

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