

Modelling the rheology of an unsaturated polyester moulding material during cure

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ABSTRACT

Results are presented of an investigation into the curing - rheological behaviour of an unsaturated polyester dough moulding compound using the techniques of rotational rheometry, capillary extrusion rheometry and differential scanning calorimetry. A model that incorporates the effects of the inhibition and curing reactions and the shear rate and temperature dependence of shear viscosity has been developed. The novel feature of this model is the allowance made for the inhibition phase which has a significant effect on the processability of such materials. The use of this model should enable predictions of the processing of unsaturated polyester materials to be made with far greater accuracy than was previously possible.

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1 INTRODUCTION

Polyester moulding compounds form one of the most widely used groups of thermoset materials. These materials offer a good cost to final property ratio and they can be used in most of the major processing operations. Knowledge of the rheology of this class of material is therefore essential if industry is to utilise the advantages to be obtained from making predictions of mould-filling using computer programme packages. Although the chemo-rheology of polyester moulding compounds has been studied for many years [1,2] the effect of inhibitors (added to improve storage life) on cure has generally been neglected. These inhibitors can have a significant effect on the cure behaviour which should be taken into account when developing models to predict the viscosity-cure relationship.

This report investigates the chemo-rheology of an unsaturated polyester dough moulding compound (DMC) using a rotational rheometer, capillary rheometer and a differential scanning calorimeter (DSC). Measurements have been conducted using both constant heating rate and isothermal test conditions. A model incorporating the effects of the inhibition and curing reactions and the shear rate and temperature dependence of viscosity has been developed.

2 MATERIALS

2.1 TEST MATERIALS

Two materials were investigated in the curing-rheology work. The materials were essentially the same with the exception that one material contained glass fibres and the other did not. Capillary extrusion rheometry measurements were performed on the material containing glass fibres to obtain the shear rate and temperature dependence of the shear viscosity before cure. The material without fibres was used to obtain the cure and viscosity kinetics using DSC and rotational rheometry respectively.

The material containing fibres had the following basic composition:

- 30 wt% of unsaturated polyester in styrene containing a thermoplastic shrinkage control additive, inhibitor, mould release agent and catalyst;
- 55 wt% inert filler;
- 15 wt% 6mm chopped 'E' type glass fibre bundles.

The material without fibres had the following composition:

- 35 wt% of unsaturated polyester in styrene containing a thermoplastic shrinkage control additive, inhibitor, catalyst and mould release agent;
- 65 wt% inert filler.

2.2 THE CURING OF UNSATURATED POLYESTERS

The curing reaction of unsaturated polyester resin is a free-radical chain growth cross-linking copolymerization between the unsaturated polyester molecules and styrene monomer. The cure process includes three major reactions : styrene - styrene, polyester vinylene - polyester vinylene and styrene - polyester vinylene.

The polymerisation process is initiated by the breakdown of catalyst (or initiator) molecules into free-radicals. The most common type of initiator used in polyester DMCs (and that used

in the polyester materials investigated herein) is benzoyl peroxide [4]. The benzoyl peroxide breaks down to form two benzoyloxy radicals which in-turn form two phenyl radicals and carbon dioxide. These phenyl radicals react with the carbon-carbon double bond in the styrene and polyester molecules thus opening them up to allow polymerisation to occur. Since the open bond is itself a radical and requires a further electron to stabilise the polymer the open bond reacts with the nearest available double-bonded unit, whether styrene or polyester, to either extend the polyester chain or form a cross-link.

Since benzoyl peroxide is highly reactive the shelf life of an uninhibited unsaturated polyester resin is relatively short at room temperature [4]. Thus inhibitors are usually added to a benzoyl peroxide catalysed polyester resin to extend the room temperature shelf life. Inhibitors prevent the cure reaction from taking place by scavenging the free radicals formed throughout the material and converting them into non-reactive substances [5]. After the inhibitor - free-radical reaction the inhibitor becomes inactive and is unable to prevent further cure. This results in a period of time, called the induction or inhibition period, during which the cure reaction is prevented by the inhibition reaction. After the inhibitor molecules are used up the polymerisation proceeds in the usual manner.

As the number of cross-linking bridges increase during polymerisation the material reaches a point known as 'gel'. The gel point of a thermosetting polymer represents the formation of a fully three-dimensional cross-linked structure, after which the viscosity of the polymer rises rapidly due to reduced molecular mobility [1,2]. The gel point therefore represents a processing limit of the polymer. In unsaturated polyester materials the gel point occurs at relatively low polymerisation conversion levels of approximately 5-10%. This results in rapid viscosity increases early on in the cure reaction. Yang and Lee [6] have described the rheological changes that occur and the relatively low gel point of unsaturated polyesters in terms of micro-gel particle formation.

3 EXPERIMENTAL TECHNIQUES

3.1 CAPILLARY RHEOMETRY

Capillary extrusion measurements of the glass fibre filled material were made using an NPL/Carter-Baker Enterprises designed rheometer [7] with 4 mm diameter dies to prevent 'log jamming' of the glass fibres. Capillary dies of lengths from 5 to 60 mm were used to obtain entrance pressure drop corrections. Tests were performed at 30, 40, 50 and 60 °C to obtain the temperature dependence of viscosity. The shear rate dependence was measured over the range 5 to 500 s⁻¹.

3.2 DIFFERENTIAL SCANNING CALORIMETRY

DSC kinetics were obtained using a Perkin Elmer DSC7 [8,9]. Measurements were performed using constant heating rate and isothermal test conditions on the fibre-free material. Fibres were excluded from the material as a reproducible fibre-filled sample is difficult to obtain due to the small sample size (20 mg) and the long length of the fibres compared with the size of the sample holder. All samples were encapsulated in sealable aluminium pans which were filled to capacity to prevent loss or separation of styrene from the material.

3.3 ROTATIONAL RHEOMETRY

Oscillatory rotational rheometry was performed using a Carrimed CSL500 rheometer on the fibre-free material. Measurements were made at a frequency of 1 Hz with an angular displacement of 1×10^{-4} rad. The gap between the plates was varied in the range 0.2 to 1.0 mm. Disposable nickel coated copper plates of 10 mm and 20 mm in diameter were used. Improvements were made on the parallelism of the disposable plates using an NPL developed levelling system for the bottom plate. The samples were heated using a radio frequency (RF) field method which enabled rapid heating of the copper plates, which in turn heated the small sample. The samples were tested using isothermal and constant heating rate conditions.

It is noted that for highly filled materials there is no quantitative agreement between complex viscosity values obtained in oscillation with steady shear viscosity values obtained either in continuous rotation or by capillary extrusion rheometry. The strain rates used in the oscillatory technique were small in comparison with those in capillary extrusion rheometry and industrial processing, for example, injection moulding. Consequently the capillary rheometer measurements were used to scale the viscosity data during cure obtained using rotational rheometry. This scaling factor was determined from measurements of the viscosity of the uncured material using both techniques. This was considered to be the most reliable method of obtaining accurate curing-viscosity data on fibre-filled materials that was relevant to practical processing conditions.

4 RESULTS

4.1 CAPILLARY RHEOMETRY

Shear viscosity data for the material containing glass fibres were obtained at a number of shear rates at 30, 40, 50 and 60 °C, figure 1. The data shown on the graph are the mean of three measured values. It can be seen that the gradients of the viscosity, η , versus shear rate, $\dot{\gamma}$, curves are approximately of the same magnitude. As similar gradients were obtained for different temperatures it is assumed that the exponent, p , in the power-law viscosity model (equation 1) is independent of temperature over the range tested. It is further assumed that the power-law model can be extrapolated up to cure temperatures (7).

$$\eta = \bar{\eta}_0 \dot{\gamma}^{(p-1)} \quad (1)$$

The temperature dependence of viscosity, η , has been described using an Arrhenius expression $e^{q/\theta}$ [7]. Plots of log shear viscosity against the reciprocal of temperature, T (K), at constant shear rates have gradients that are proportional to the temperature coefficient, q . The model for shear rate and temperature dependence of shear viscosity is described by equation 2.

$$\eta = \bar{\eta}_0 \dot{\gamma}^{(p-1)} e^{\frac{q}{T}} \quad (2)$$

The values of the parameters of the above power-law viscosity model obtained from a least squares fit of the experimental data, figure 1, are shown below, with an analysis of their standard deviations (in brackets).

$$\begin{aligned}
\bar{\eta}_0 &= 41.8 \times 10^6 \text{ N s}^p \text{ m}^{-2} \quad (9 \times 10^6 \text{ N s}^p \text{ m}^{-2}) \\
p &= 0.381 \quad (0.06) \\
q &= 2800 \text{ K} \quad (300 \text{ K})
\end{aligned}$$

To assess the accuracy of the fit of the power-law model to the viscosity data the standard deviation of values calculated for the expression

$$\left[\frac{\text{experimentally measured shear viscosity values}}{\text{calculated shear viscosity values using the power law model}} \times 100\% \right]$$

was evaluated. The standard deviation was of the order of 7% for values over the shear rate range used in the experiments.

4.2 DIFFERENTIAL SCANNING CALORIMETRY

It was found that the cure reaction of an unsaturated polyester DMC can be described using a combination of two separate expressions, further detail of which can be found in the NPL reports [8] and [9]. The first describes the effect of inhibitors added to the system [8]. The second is an autocatalytic model which describes the main curing reaction [9]. The total cure reaction, including inhibition, for isothermal testing conditions is then described by equations 3 - 5.

$$\alpha = \frac{[(n-1) K (t_i - t)]^{\frac{1}{n-1}}}{+ [(n-1) K (t_i - t)]^{\frac{1}{n-1}}} \quad (3)$$

where

$$t_i = \frac{1}{A_i} \exp \left[\frac{E_i}{R T} \right] \quad (4)$$

and

$$K = A \exp \left[-\frac{E}{R T} \right] \quad (5)$$

where α	conversion
n	curve shape constant
K	rate constant
R	gas constant, 8.32 kJ mol ⁻¹
t_i	inhibition time
A_i	rate constant for inhibition reaction
E_i	activation energy for inhibition reaction
T	temperature (K)
t	time (s)

However this expression for the conversion, α , is only valid when $(t_i - t) \geq 0$. For $(t_i - t) < 0$, $\alpha = 0$.

Fits to the experimental data using the above equations are shown in figure 2. The model provides a reasonable fit to all the experimental data, especially up to the gel point which is typically 5 to 10 % ($\alpha = 0.05$ to 0.1) for polyester materials. This is of great importance if DSC data are to be used to predict the rheological changes that occur up to gelation. The values obtained for the DSC cure model are given below.

$$\begin{aligned} A_i &= 8.52 \times 10^{17} \text{ s}^{-1} \\ E_i &= 140.4 \text{ kJ mol}^{-1} \\ n &= 1.48 \\ A &= 4.39 \times 10^{13} \text{ s}^{-1} \\ E &= 111.4 \text{ kJ mol}^{-1} \end{aligned}$$

Equation (5) can be expressed in an integral form, similar to that of equation (10), for use in fitting constant heating rate experimental data.

4.3 ROTATIONAL RHEOMETRY

Constant heating rate experiments were considered to be more suitable than isothermal experiments for modelling the curing-viscosity behaviour. These experiments are quick in comparison with isothermal experiments and cover the whole temperature range. Additionally constant heating rate experiments are also free of problems found in isothermal experiments wherein cure occurs during heating up to the test temperature. Also the temperature dependence of the model is obtained in one experiment.

Oscillatory rotational rheometry cure results are shown in figure 3. These data show the sigmoidal change in storage modulus, indicated by η'' , and the change in dynamic viscosity, η' . The dynamic viscosity rises due to cure and then passes through a peak. The viscosity after gelation is high and the material is effectively solid. Thus for the purposes of flow modelling an ability to predict the rheological behaviour only up to, or near the peak in dynamic viscosity is necessary. Consequently all the curing-viscosity data were truncated before the peak prior to modelling; the model is not required to fit the peak in viscosity which is a feature of the dynamic measurements.

A number of rheological cure models without an inhibition term were applied to the constant heating rate test data. The empirical model shown below was found to be the best solution.

$$\ln \eta = \ln \eta_o + \frac{E_v}{R T} + C \alpha \quad (6)$$

where η	viscosity
η_o	viscosity constant
C	constant dependent upon the viscosity and conversion at gelation
T	temperature
R	gas constant
E_v	activation energy

and where the conversion, α , at time t_a is given by the solution of the Kamal [3] equation below.

$$\text{conversion, } \alpha = \frac{\left[(n-1) A \int_0^{t_a} \exp \left[-\frac{E}{R\theta} \right] dt \right]^{\frac{1}{(n-1)}}}{1 + \left[(n-1) A \int_0^{t_a} \exp \left[-\frac{E}{R\theta} \right] dt \right]^{\frac{1}{(n-1)}}} \quad (7)$$

where θ is the temperature as a function of time t (T is the temperature at time t_a). For a constant heating rate experiment $\theta = \dot{\theta}t + T_0$, where $\dot{\theta}$ is the heating rate and T_0 the initial temperature.

This model, as defined by equations 6 and 7, includes terms which describe the change in viscosity with temperature and with cure conversion. The temperature dependence part of the equation ($\ln \eta_0 + E_v/RT$) was determined from a least squares fit of the constant heating rate curve before cure, figure 3. Once obtained, these values were fixed and the other constants allowed to float in the data fitting routine. The activation energy E_v is related to the temperature dependence of viscosity q in equation (2) by the relation $E_v = q \times R$. However, the value for q presented in section 4.1 is for a fibre-filled material whereas E_v is used herein to represent the activation energy for the unfilled system. The shear rate or frequency dependence of viscosity is not covered by this equation as the oscillatory testing was carried out at a fixed frequency: this factor is incorporated into the full model in section 5.

Typical fits obtained using this model (equations 6 and 7) are shown in figure 4. This model can be seen to be inadequate for accurate viscosity modelling. However a rough estimate of the viscosity change is obtained. The experimental data show a more rapid viscosity rise at the start of cure compared with that given by the fit of the model (equations 6 and 7). The model therefore requires an additional term to sharpen the curing process.

In constant heating rate experiments an inhibition reaction delays the start of curing with the consequence that a higher temperature is reached before the cure reaction starts. As a consequence, when the inhibition reaction finishes the cure process commences at a faster rate and the viscosity rise is more rapid. Allowing for an inhibition reaction would sharpen the response of the model. The model was modified using a term which activated the cure model after the inhibition reaction was completed, equation 8. The equation describes the viscosity (η) as a function of time (t_a).

$$\ln \eta = \ln \eta_0 + \frac{E_v}{RT} + C \frac{\left[(n-1) A \int_0^{t_a-t_i} \exp \left[-\frac{E}{R\theta} \right] dt \right]^{\frac{1}{(n-1)}}}{1 + \left[(n-1) A \int_0^{t_a-t_i} \exp \left[-\frac{E}{R\theta} \right] dt \right]^{\frac{1}{(n-1)}}} \quad (8)$$

where C is a constant and t_i is given by equation (4). This expression is valid for $(t_a - t_i) \geq 0$.

If $t_a - t_i < 0$ then

$$\ln \eta = \ln \eta_0 + \frac{E_v}{RT} \quad (9)$$

The values of A_i , E_i , n and A were determined from DSC measurements, and η_0 and E_v/R from oscillatory rheometry measurements as described above. The values of these parameters, presented in table 1, have been used with equation (8) to obtain a least squares fit to the experimental data, thereby yielding an optimum value for C of 11.6. The excellent fit of this model to the data is shown in figure 5. This result indicates that DSC reaction kinetics can be used for modelling rheological changes during cure by the use of equations 8 and 9.

5 PROPOSED FULL RHEOLOGICAL MODEL

Using all the data obtained, table 1, provides the input to the model, equation 10, that describes the change in viscosity with cure, including inhibition effects. This model is capable of predicting the shear rate, temperature and cure dependence of viscosity.

$$\ln \eta = \ln \bar{\eta}_0 + \frac{q}{T} + (p-1) \ln \dot{\gamma} + C \frac{\left[(n-1) A \int_0^{t_a-t_i} \exp \left[-\frac{E}{R\theta} \right] dt \right]^{\frac{1}{(n-1)}}}{1 + (n-1) A \int_0^{t_a-t_i} \exp \left[-\frac{E}{R\theta} \right] dt} \quad (10)$$

6 DISCUSSION

The chemo-rheology of the unsaturated polyester DMC investigated in this work must be modelled taking into account the inhibition reaction. Failure to do so prevents the accurate prediction of the viscosity change with cure. When inhibition reaction kinetics is incorporated into the chemo-rheological model a good prediction of the viscosity during cure is obtained.

Since DSC cure kinetics were used to model the chemo-rheology, it follows that the DSC reaction can be modelled using rheologically derived parameters. However, it is essential that the heat production of the exothermic reaction during cure is known for mould filling calculations. Failure to predict the exothermic temperature rise results in large errors when predicting viscosity changes. For example, it has been shown that a 10 °C temperature rise can result in a 30% fall in viscosity [7]. It is therefore unlikely that rheological kinetics in isolation can be used in mould filling software packages.

7 CONCLUSIONS

A model is proposed that adequately describes the development of viscosity during cure for an unsaturated polyester resin. This model requires data from capillary rheometry, rotational rheometry and DSC measurements.

A key feature of the model is its ability to account for inhibition which is of great importance for commercial materials.

The incorporation of this new model into existing mould filling software should enable industrial processing of unsaturated polyester thermosets to be predicted with much greater accuracy than is currently possible.

8 FUTURE WORK

It is proposed that the curing viscosity model described in this document is incorporated into mould filling simulation software. Predictions of injection mould filling can then be compared with measurements made on commercial moulding processes.

9 ACKNOWLEDGEMENTS

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Table 1: Terminology and values of parameters used in the modelling

Parameter or variable	Description	Value / units (standard deviation in brackets)
$\bar{\eta}_0$	zero shear viscosity constant (fibre-filled material)	$41.8 \times 10^6 \text{ N s}^p \text{ m}^{-2}$ ($9 \times 10^6 \text{ N s}^p \text{ m}^{-2}$)
p	shear rate dependence constant	0.381 (0.06)
q	shear viscosity temperature dependence constant	2800 K (300 K)
n	curve shape constant	1.48
A_i	rate constant for inhibition reaction	$8.52 \times 10^{17} \text{ s}^{-1}$
E_i	activation energy for inhibition reaction	$140.4 \text{ kJ mol}^{-1}$
A	rate constant for cure reaction	$4.39 \times 10^{13} \text{ s}^{-1}$
E	activation energy for cure reaction	$111.4 \text{ kJ mol}^{-1}$
R	gas constant	8.32 kJ mol^{-1}
η_0	zero shear viscosity constant (unfilled material)	7.02 N s m^{-2}
E_v/R	viscosity temperature dependence (unfilled material)	1700 K
C	constant dependent upon the viscosity and conversion at gelation	11.6
$\dot{\gamma}$	shear rate	s^{-1}
T	temperature	K
α	conversion (0 - 1)	-
t_i	inhibition time	s
K	cure reaction rate constant	s^{-1}
η	viscosity	N s m^{-2}
t_α	time to conversion α	s
θ	temperature history $\eta = \eta(t)$	K

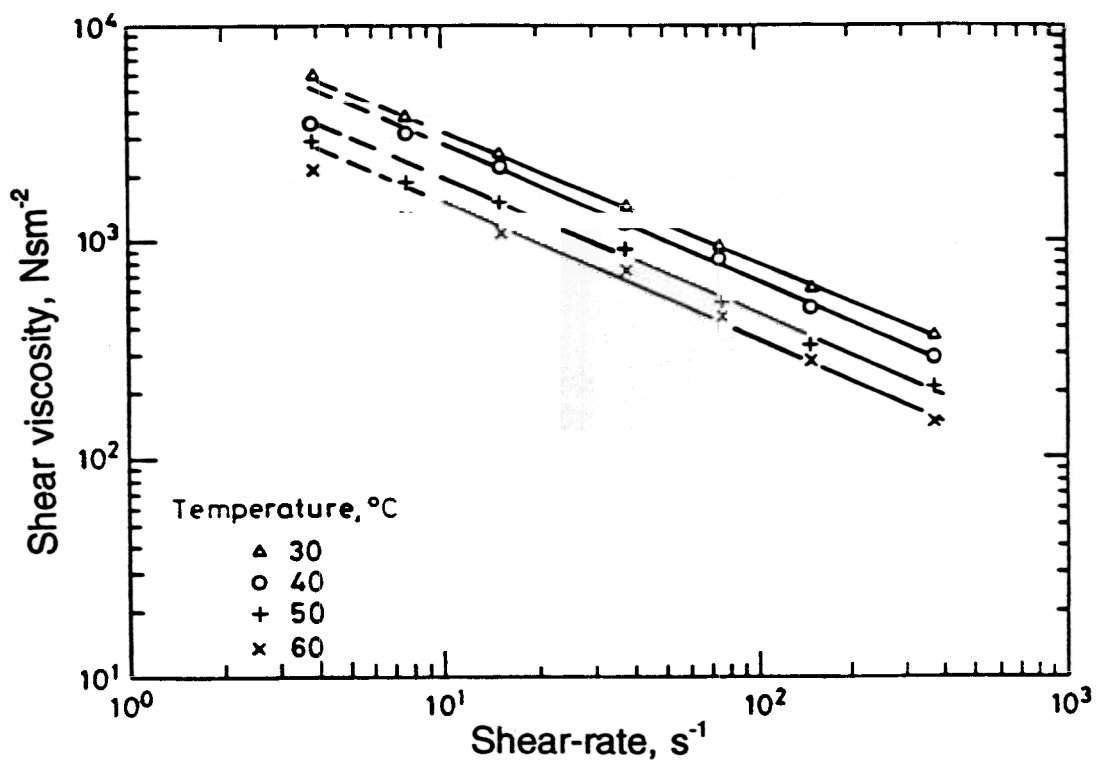


Figure 1 Effect of shear-rate and temperature on the viscosity of DMC L7049.

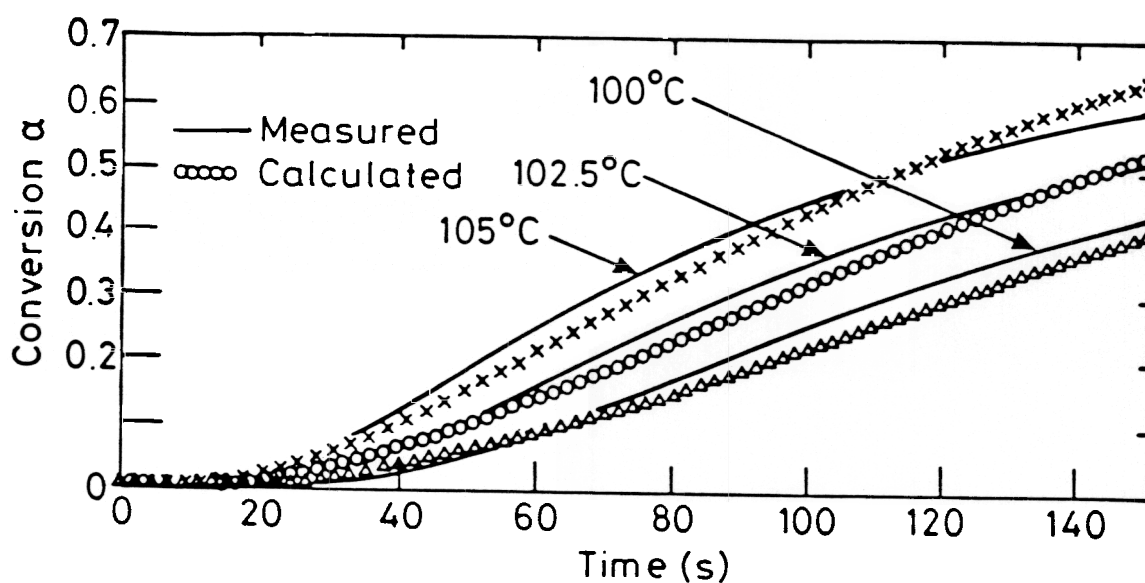


Figure 2 Measured and predicted DSC cure conversion data.

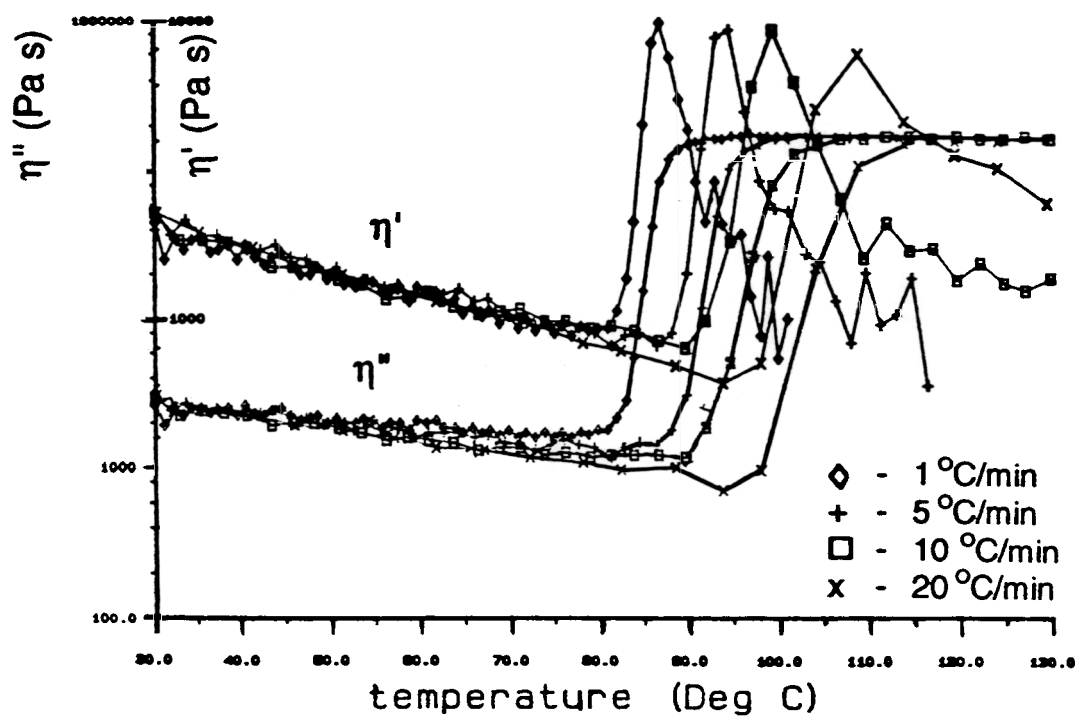


Figure 3 Constant heating rate rheological data obtained for DMC L7049.

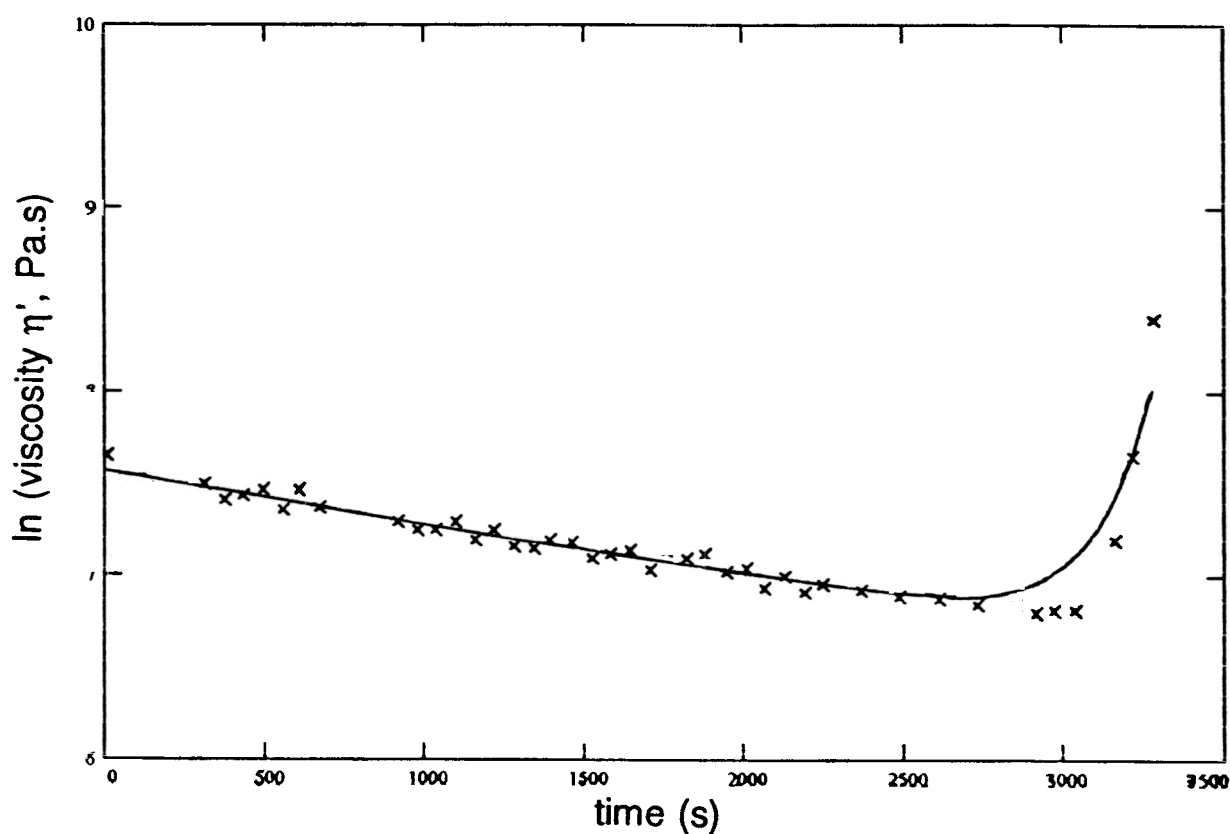


Figure 4 Comparison of measured data and cure model without an allowance for the inhibition reaction. Data obtained at a constant heating rate of 1°C/min .

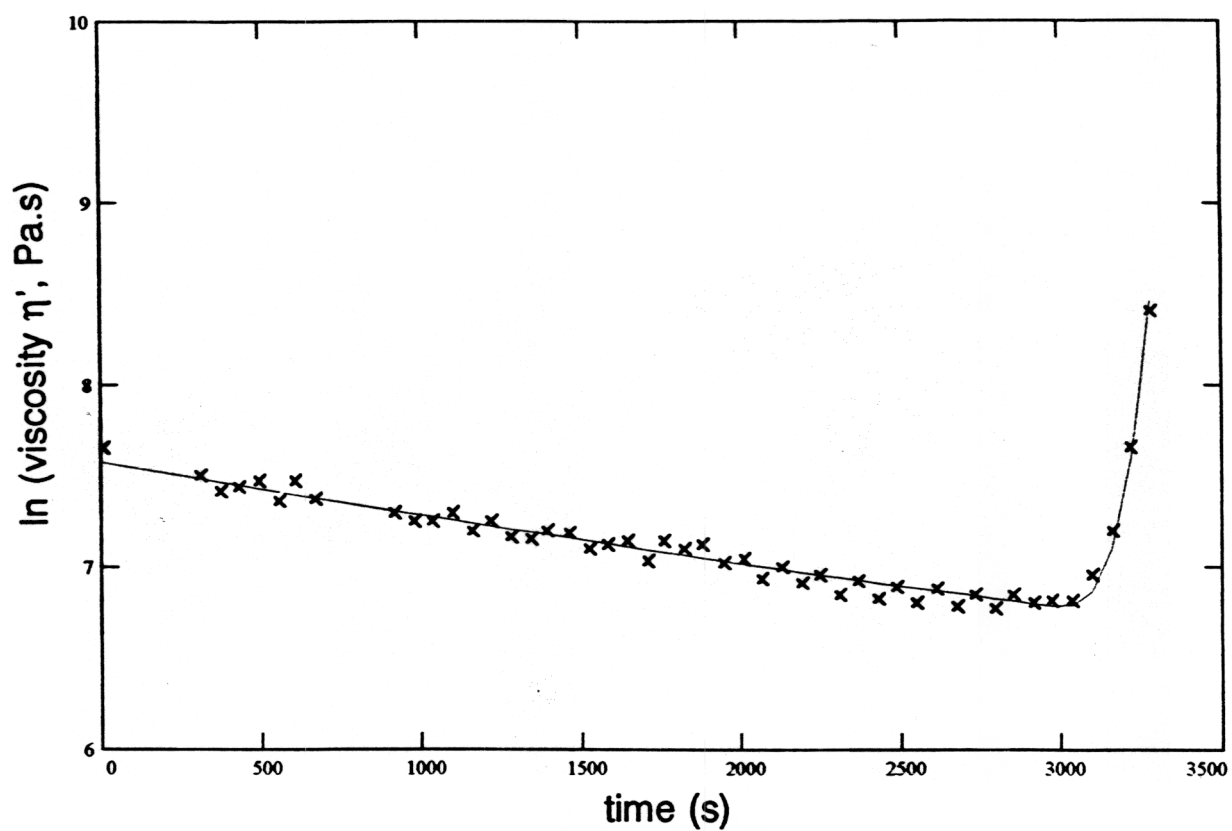


Figure 5 Comparison of measured data and cure model including an allowance for the inhibition reaction. Data obtained at a constant heating rate of 1°C/min.