PROCESSING OF SHORT FIBER-THERMOSETTING MATRIX
COMPOSITES

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ABSTRACT

The fundamentals aspects of the processing of thermosetting matrix composites with short fibers in compression molding technologies are presented. The reaction kinetics and the rheology of compounds based on unsaturated polyester matrices have been characterized as a function of different processing variables: temperature and shear rate. The effects of the filler (calcium carbonate) and the reinforcement (glass fibers) on the curing kinetics of unsaturated polyester resins were studied by differential scanning calorimetry (DSC), and the rheological properties of the compounds were analyzed using parallel plates rheometry. The results of the DSC characterization were used to develop an empirical kinetic model accounting for diffusion control effects, while DSC and rheological measurements were combined to obtain correlations between viscosity, extent of reaction, temperature and shear rate. The complete chemorheological model was verified through rheological tests performed at different heating rates and angular frequencies. The model developed in this work has been integrated in a general processing model for the description of the molding behavior of thermosetting matrix compounds for automotive applications. Excellent agreement between model predictions and experimental results has been obtained.

INTRODUCTION

Unsaturated polyesters are widely used in composites because of their low cost and versatility. They offer advantages such as low weight, high strength and excellent mechanical properties. With the aid of fillers, reinforcements and additives, they are usually available in the form of compounds for compression molding (i.e. sheet molding compound, SMC), injection molding (i.e. bulk molding compound, BMC), resin transfer molding and pultrusion (1).

Typical resins contain 30-50 % styrene by weight, equivalent to about 2 mol styrene to 1 mol double bonds on the polyester. The curing reaction of unsaturated polyester resins involves the copolymerization between the styrene monomer and the unsaturated polyester molecule in the presence of an organic initiator (2). The initiator decomposes and creates free radicals in the system. The free radicals grow

and form long-chain molecules through connecting styrene monomers and polyester molecules by both inter and intramolecular reactions.

Extensive research has been devoted to the curing kinetics of unsaturated polyester resins in the literature (3-12). However, the effects of fillers and reinforcements on the curing behavior of unsaturated polyester resins have been less studied and relatively few data have been published on the rheology of this material. Kubota (13) studied the effect of filler (calcium carbonate, $CaCO_3$) on the curing behavior of a polyester resin. He reported that, as the amount of filler was increased, the curing started at a lower temperature and a lower final degree of curing was obtained. The experimental results of Lem and Han (14) revealed that the presence of fillers increased the rate of cure. Of the various fillers investigated ($CaCO_3$, clay, HDPE), calcium carbonate was found to be the most effective. The gel time was found shorter for mixtures of resin and particulates than for the neat resin alone. As reported by Blanc et al. (15), Algrave found that $CaCO_3$ has a negligible influence on the curing kinetics.

In this work a BMC compound based on an unsaturated polyester resins was studied by means of differential scanning calorimetry (DSC) and rheometry. The major goal was to investigate the effects of filler (calcium carbonate) and reinforcements (glass fibers) on its curing kinetics and rheology.

EXPERIMENTAL

Materials

The materials used in this study were provided by Fiat Research Center (CRF) in the form of neat resins and BMC compounds from Menzolit Inc. The compositions of the compounds are given in Table 1.

Table 1. Compositions of BMC compounds used in this study

	BMC-Paste 1	BMC-Paste 2
Unsaturated polyester resin in styrene + additives	26	30
Calcium carbonate	74	50
6 mm chopped glass fibers	0	20

Calorimetric measurements

The thermocalorimetric characterization was carried out in a Mettler TA 3000 differential scanning calorimeter (DSC), equipped with a liquid nitrogen cooling system. The tests were performed both in isothermal conditions at four different temperatures and dynamic conditions at three different heating rates under a nitrogen atmosphere. The samples were sealed in hermetic aluminum pans and weighed before and after the experiment to check if there was any loss of styrene

monomer during the cure reaction. The weight of the samples ranged between 10 and 20 mg for neat resins and between 20 and 30 mg for BMC pastes. The loss of mass was less than 5 % with respect to the initial mass of the neat resin. At the end of each isothermal run, samples were cooled rapidly to room temperature and then reheated to 200° C at heating rate of 10° C / min to determine the residual heat of reaction.

Rheological measurements

Rheological properties were measured with a Rheometrics dynamic spectrometer, RDS-II, with disposable parallel plates. The oscillatory shear flow measurements were conducted under isothermal conditions at different temperatures and dynamic conditions at different heating rates. Angular frequencies of 1 rad/s and 10 rad/s, and initial strain of 10% were applied.

RESULTS AND DISCUSSION

1. Effects of Filler and Reinforcements on the Curing Kinetics

The isothermal DSC experiments were performed at four different temperatures. The neat resin was characterized at 75° , 80°, 85° and 90° while BMC-Paste 1 and BMC-Paste 2 were characterized at 80°, 90°, 100° and 110° C. For temperatures higher than 90° in the case of the neat resin or 110° for the BMC-Paste 1 and BMC-Paste 2 the reaction rate was too fast to follow. For all the systems investigated, a second scan on the isothermally cured samples indicated that the curing reaction was not completed at any of the used temperatures. The sum of the heat release for the isothermally cured sample and the rescanned one was 16% lower than the heat release at the scanning mode. Similar observations are reported in the literature (16). Thus, when the conversion profiles were calculated, the reaction exotherms of the DSC dynamic tests were taken as the basis of the ultimate extent of reaction, namely,

$$\frac{d\alpha}{dt} = \frac{1}{H_T} \frac{(dH)}{dt} \qquad (1)$$

dH/dt is the rate of heat flow measured in DSC experiments. H_T is the total heat generated by curing reaction. Several dynamic DSC tests were performed at 3°, 5° and 10°C/min and the areas below the curves were integrated to calculate H_T. As reported in the literature (2,10) the value of H_T may not be an indication of 100 percent conversion.

The rate of reaction of the neat resin as a function of time for different curing temperatures is shown in Fig. 1. Similar curves were obtained for BMC-Paste 1 and BMC-Paste 2. In the investigated temperature range an induction period is observed; then the rate increases passing through a maximum and finally decreases till the final conversion is reached. The induction period is related to the consumption of radicals by inhibitors present in commercial formulations. An increase in temperature increases the value of the reaction rate at the maximum and decreases the induction time. Induction times can be described by the Arrhenius expression:

$$t_{in} = K_d \exp(E_{ad}/RT) \qquad (2)$$

where K_d is a pre-exponential factor, E_{ad} is the activation energy of the initial decomposition, R is gas constant and T is the absolute temperature. The experimental data, as ln t_{in} versus reciprocal temperature, were fitted to a straight line using the least-square method. As Fig. 2 shows, the results obtained for the neat resin are scattered and it is difficult to say if there is any influence of the filler on the induction period. For the investigated temperature range, fitting results indicate slightly shorter induction period for BMC-Paste 1 with respect to the neat resin. BMC-Paste 2 is characterized by a longer induction period in comparison to the neat resin. Some findings on the effect of calcium carbonate on the induction period are reported in the literature (14). In the study of the curing kinetics of particulate-filled unsaturated polyester resins by Lem and Han (15) $CaCO_3$ particles appeared to promote the decomposition of the benzoyl peroxide used as initiator and increased the rate of cure. In the present study, glass fibers showed opposite effect on the initiator decomposition in comparison with $CaCO_3$ (supposing that in all investigated systems the concentration and type of initiator and inhibitor were the same). The values of the k_d and E_{ad} given in Table 2.

Table 2. Parameters of the induction time model (Eq. 2)

	Neat resin	Bmc-Paste 1	Bmc-Paste-2
E_{ad}, (kj/mol)	125.1	119.2	152.7
K_d, (s-1)	$e^{-35.7}$	$e^{-33.8}$	$e^{-43.6}$

In addition to the influence on the initiator decomposition, the presence of filler and glass fibers in the resin increases the thermal conductivity and the viscosity of the curing system and reduces the number of the reactive double bonds per unit volume. The first two factors favorably affect the curing, while the last factor adversely affects the curing.

The partial integration of the areas under the curves Fig.1 leads to the computation of the extent of reaction, α, as a function of time (see Fig. 3). It is possible to note that the higher is the temperature the higher is the extent of reaction reached. As it is well known the isothermal curing of the thermosetting resins is usually characterized by gelation and vitrification (17). Vitrification occurs when the glass transition temperature of the reacting system approaches the temperature of cure, as a result of an increase in molecular weight. Near vitrification the reaction kinetics becomes diffusion-controlled which eventually leads to the cessation of reaction before completion.

Final extents of reaction, α_m, for three investigated systems are compared in Fig. 4. It is seen that in the investigated temperature range α_m linearly depends on the isothermal cure temperature

$$\alpha_m = p + qT \qquad (3)$$

As Fig. 4 shows in BMC-Paste 1 and BMC-Paste 2 a lower final extent of cure was obtained with respect to the neat resin. Similar results are reported by Kubota (13). Dynamic DSC experiments were also performed on the three systems at different heating rates. In particular, the reaction rate profiles of all three systems obtained at 10°C/min are compared in Fig. 5. It is seen that reaction rate profile of the BMC-Paste 2 is narrower with respect to that of the neat resin, it has higher maximum of

the rate of the reaction and it is shifted to higher temperatures. Following the longer induction time measured in isothermal experiments for this formulation, the reaction starts later, at higher temperatures which induce a faster reaction than the other two formulations. These differences are evident in Fig. 6 in terms of degree of reaction as function of time.

The essential step in the study of cure kinetics by DSC is fitting of the reaction rate profiles obtained from isothermal and dynamic experiments to a mathematical model. In this work the kinetic model proposed by Kenny et al (18) was applied to describe the experimental data:

$$d\alpha/dt = K\alpha^m (\alpha_m-\alpha)^n \qquad (4)$$

In Eq. 4, K is the reaction rate constant, α_m is the final extent of reaction, m and n are reaction orders. Parameters K, m and n were determined from each isothermal thermogram by the procedure proposed by Ryan and Dutta (19). The isothermal cure of unsaturated polyester was assumed to be a second order reaction (4,5,8,14,24), i. e. m+n=2.

The maximum rate of reaction in the isothermal cure occurs at a point where

$$\frac{d^2\alpha}{dt^2} = 0 \qquad (5)$$

Differentiating Eq. 4 with respect to α and setting the derivative to zero, were obtained:

$$m = 2\alpha_p/a_m \qquad (6)$$

where α_p is extent of reaction at the maximum cure rate, $(d\alpha/dt)_p$. The reaction orders m and n were found relatively insensitive to temperature and in the modeling the average values were used.

The rate constant K was calculated from

$$K = (d\alpha/dt)_p/(\alpha_p m(\alpha_m-\alpha_p)n) \qquad (7)$$

and its temperature dependence follows an Arrhenius relationship:

$$K = K_0 \exp(-E_a/RT) \qquad (8)$$

The computed parameters of the kinetic model are summarized in Table 3. The values of m and n are consistent with the values reported in the literature (4,5,7,18). As Table 3 shows, the presence of $CaCO_3$ in the resin results in a decrease of both the activation energy of the rate constant and the pre-exponential factor. In the presence of both $CaCO_3$ and glass fibers (BMC-Paste 2) higher values of E_a and K_0 with respect to the neat resin were obtained.

In Figs. 7 and 8 the comparison between the experimentally obtained isothermal profiles for the rate of reaction or extent of reaction and the kinetic model data is presented. For all investigated systems modeling predictions show good agreement with experimental data. As shown in Fig.8 the model is able to describe the incomplete cure caused by vitrification effects on the reaction kinetics.

Table 3: Parameters of the thermokinetic model

	Neat resin	BMC-Paste 1	BMC-Paste 2
Heat of reaction (J/g) :	365	365	365
Activation energy, Ea, (kJ/mol) :	73.1	49.9	92.2
Pre-exponential factor of Eq. (9), ko, (s^{-1}):	$e^{19.1}$	$e^{12.2}$	$e^{26.2}$
Reaction order, m	0.43	0.48	0.59
Reaction order, n	1.57	1.52	1.41
Coefficient of eq (3), p	-1.407	-2.544	-2.214
Coefficient of eq (3), q, $(10^{-3} K^{-1})$	6.17	8.98	7.79

One of the drawbacks of isothermal curing is the limited temperature range where useful kinetic information may be obtained. The prediction of real processes usually requires a knowledge of the curing kinetics in a broad temperature range. In order to check if the kinetic expressions arising from isothermal runs are valid outside the range of temperatures used for parameter computation, the cure in dynamic conditions, at constant heating rates, was also simulated. By means of Eq.(2) the initial temperature of cure, Ti, was calculated. It was supposed that no monomer reacts until the number of all initiator radicals created is equal to the effective number of inhibitor molecules initially presented. For isothermal tests this condition is fulfilled at time $t=t_{in}$. For dynamic tests, the same condition can be written in the following way:

$$\int_{t=0,T=T0}^{t=t_{in}} \frac{dt}{Kd \cdot \exp(E_{ad}/RT)} = 1 \qquad (9)$$

The initial temperature of cure was determined experimentally from DSC curves at the crossover of the tangent at the first inflection point and the base line. The comparison between estimated and experimentally obtained initial temperatures of cure, for different heating rates is reported in Table 4. It is seen that the theoretical data agree fairly well with experimental findings.

Table 4: Initial temperature of cure at different heating rates for BMCsystems

Heating Rate (°C / min)	Neat Resin T_i (K)		BMC-Paste 1 T_i (K)		BMC-Paste 2 T_i (K)	
	DSC	Eq.(10)	DSC	Eq. (10)	DSC	Eq. (10)
3	369.1	368.6	366.7	367.5	377.9	378.5
5	372.8	373.0	373.3	372.2	381.6	382.3

| 10 | 376.0 | 379.2 | 378.9 | 378.7 | 388.0 | 387.7 |

Reaction rate profiles of dynamic DSC experiments obtained at different heating rates are compared to the kinetic model data in Fig. 9. Zero time corresponds to the temperature of 70 °C. Fairly good agreement was obtained for all investigated systems.

Chemorheological behavior

Isothermal complex viscosity, η^*, of the system in the unreacted state, as a function of angular frequency is plotted in Fig. 10. It is seen that the resin exhibits shear thinning behavior. Polyester resins are reported as Newtonian liquids (20,21). Although the composition of the resin was not disclosed by the producer we believe that it contains a low-profile additive such as poly(methyl methacrylate) which contributes to the non-Newtonian behavior (21). Such additives are commonly used in BMC to reduce the resin shrinkage on curing. The observed shear thinning behavior is attributable to breakage of the particle agglomerates as the shear rate is increased. Such behavior is typical for concentrated suspensions (14).

In the investigated range of angular frequencies the following empirical equation was found to fit the experimental data:

$$\eta^* = \exp(A(T) + B(T)\ln \omega + C(T) (\ln \omega)^2) \qquad (10)$$

where ω is the angular frequency. Supposing the validity of the Cox-Merz rule (22), Eq.(10) can be written in terms of the shear viscosity and the shear rate. The case when C=0 corresponds to the power-low behavior.

In order to analyze the contribution of the polymerization reaction to the viscosity changes the rheological measurements were performed under identical isothermal conditions as the thermocalorimetric measurements. Isothermal complex viscosity, measured at angular frequencies of 1 and 10 rad / s, as a function of time is plotted in Fig. 11. As expected from results presented in Fig. 10, at higher angular frequency lower values of the viscosity were obtained. At a fixed temperature and shear rate, any variation of the system viscosity is determined by the molecular structural changes such as growth, branching and crosslinking of the polymer molecules. The incipient formation of an infinite network of crosslinked polymer molecules results in a physical event, gelation, and the transformation of a viscous liquid to a rubbery state. Gelation occurs at a fixed extent of reaction as long as the reaction mechanism is not a function of temperature (23). In this work the gel time was determined from the inflection point on the isothermal η^* vs time curve (24). Comparing Figs. 1 and 11 it was seen that induction times determined by DSC are even higher than gelation times obtained from rheological measurements. It should be noted that after the sample was placed on the parallel plate it took about two minutes to start the measurement. Even with this correction the gelation times were shorter than induction times obtained by means of DSC. It seems that evaporation of styrene may cause observed differences in induction period.

In order to relate the isothermal viscosity changes to the reaction kinetics the induction times characteristics of the rheological measurements must also be determined. However this determination is difficult as a consequence of the constant increase of the viscosity due to the styrene evaporation. Then, the isothermal viscosity was related to the extent of reaction measured in DSC

experiments presented in Fig. 3. We are aware of uncertainties included in η versus α relationship due to the fact of intrinsic differences between processing conditions in both experimental techniques. In the investigated temperature range for the extent of reaction at the gel point, α_g, the average value of 0.024 was obtained. The following empirical equation was found to fit η versus α data:

$$\eta = \eta_i(T) \cdot \frac{\alpha_g}{\alpha_g - \alpha}^n \qquad (11)$$

η_i is the initial viscosity at temperature T. The exponent n was found to depend on the frequency but independent on the temperature. For the frequencies of 1 and 10 rad/s, n values of 4.6 and 3.7 were obtained, respectively. Combining Eqs. (10) and (11) the following model which describes viscosity as a function of angular frequency, temperature and the extent of reaction was obtained:

$$\eta = \exp(A(T) + B(T)\ln\omega + C(T)\ln(\omega)^2)(\alpha_g / (\alpha_g - \alpha))^n \qquad (12)$$

A, B, and C were found to depend on the temperature following Arrhenius relationship. By means of data presented in Fig. 10 the following equations were obtained:

A=-12.601+4946.2/T
B=0.523-279.3/T
C=-0,100+36,434/T

The characterization of the filled formulations was performed through capillary rheometry. The results are shown in Fig. 12 in terms of viscosity measured as a function of the shear rate for different temperatures. A similar non-Newtonian behavior as in the case of the neat resin was observed. In order to verify the developed model, rheological measurements were performed under dynamic conditions at different heating rates and angular frequencies. Two simulations, corresponding to the different induction times obtained by DSC and rheometry, were done for each experiment. A comparison between experimental results and the model data, as complex viscosity versus temperature, is given in Fig. 12. Fairly good prediction capability of the developed model regarding the viscosity of system in unreacted state is observed. Better agreement between experimental and the model data was obtained when induction period was calculated by means of DSC data.

CONCLUSIONS

The curing of unsaturated polyester resins as components of bulk molding or sheet molding compounds were studied by means of differential scanning calorimetry and rheometry. The effects of filler (calcium carbonate) and reinforcements (glass fibers) on the curing kinetics were investigated. It was found that induction period is slightly affected by the presence of CaCO3-filler. In general, the addition of filler results in an increase of the cure reaction time. In the presence of both CaCO3-filler and glass-fiber reinforcements a longer induction period with respect to the neat resin was observed. At a constant heating rate the reaction is characterized by a higher onset temperature, higher reaction rate and shorter reaction time with

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respect to the neat resin. The kinetic behavior of investigated systems was described by an empirical model accounting for diffusion control effects.

The kinetic model was verified through isothermal and dynamic calorimetric tests performed at different temperatures and heating rates. The rheological properties of neat resins and a bulk molding compound (without reinforcements) were studied using a parallel-plate rheometer. In all investigated systems shear thinning behavior was observed. A chemorheological model was proposed that may be useful for predicting the viscosity variation during BMC processing. The model acquires information on relationships between the system viscosity in the absence of chemical reaction and the shear rate at different temperatures as well as information on the variation of the extent of reaction as the cure reaction progresses. The theoretical predictions were found to agree fairly well with experimental results.

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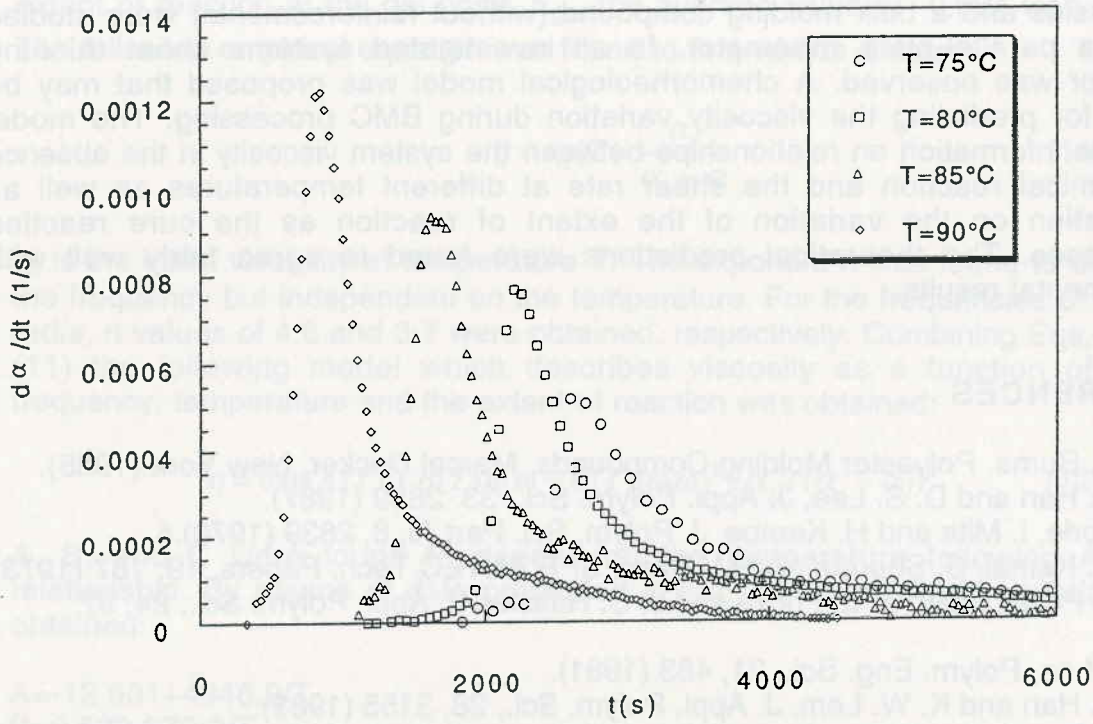24. J. M. Kenny and M. Opalicki, Makromol. Chem., Macrom. Symp., 68, 41 (1993).

Fig.1: Rate of reaction as a function of time obtained from isothermal DSC experiments at four different temperatures for the neat resin.
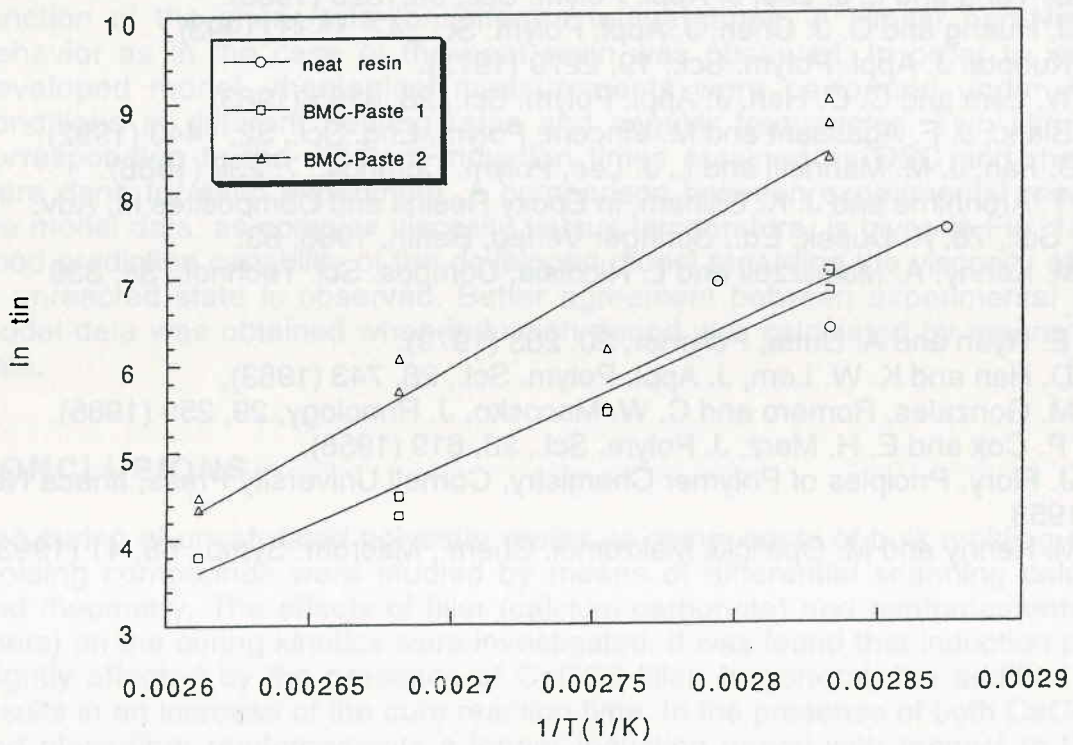

Fig.2: Logarithm of induction time as a function of reciprocal temperature

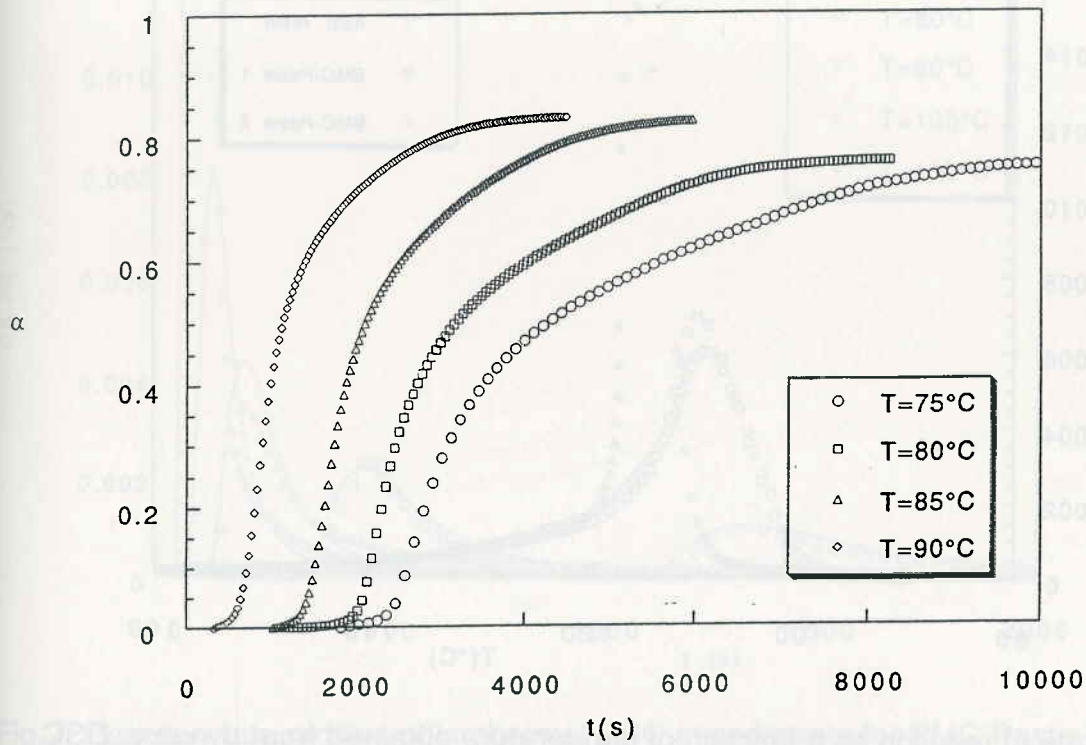Fig.3: Exte
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Fig.4: Final
function of

Fig.3: Extent of reaction as a function of time obtained from isothermal DSC experiments at four different temperatures for the neat resin.
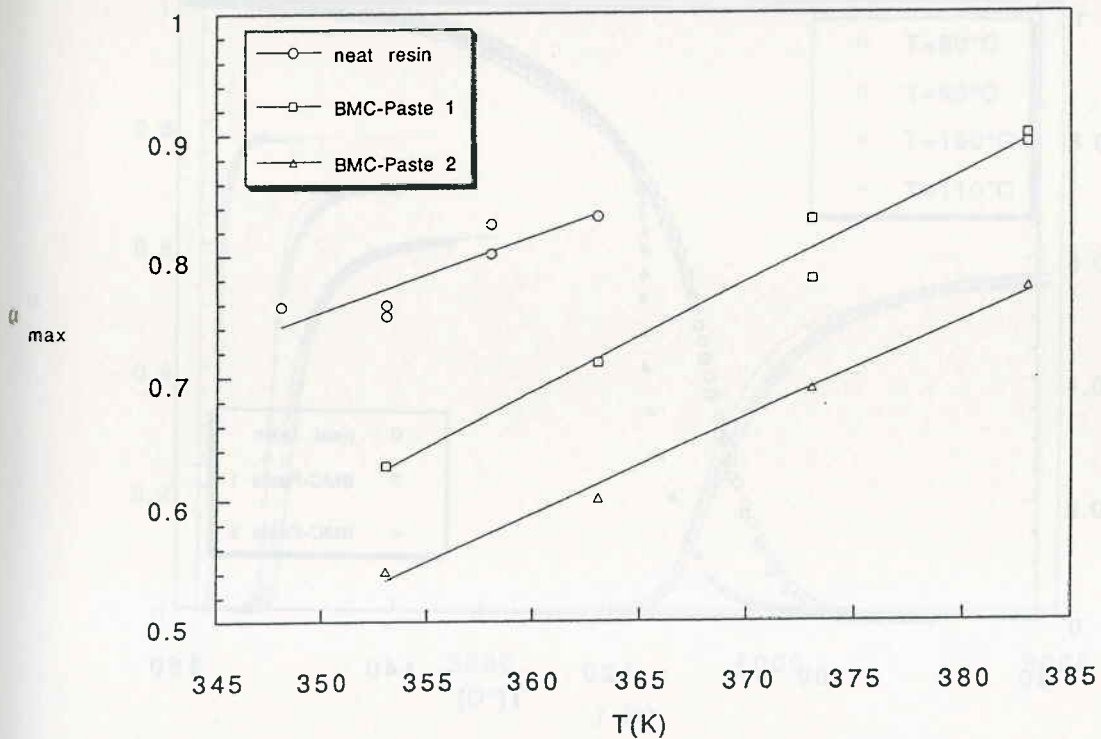

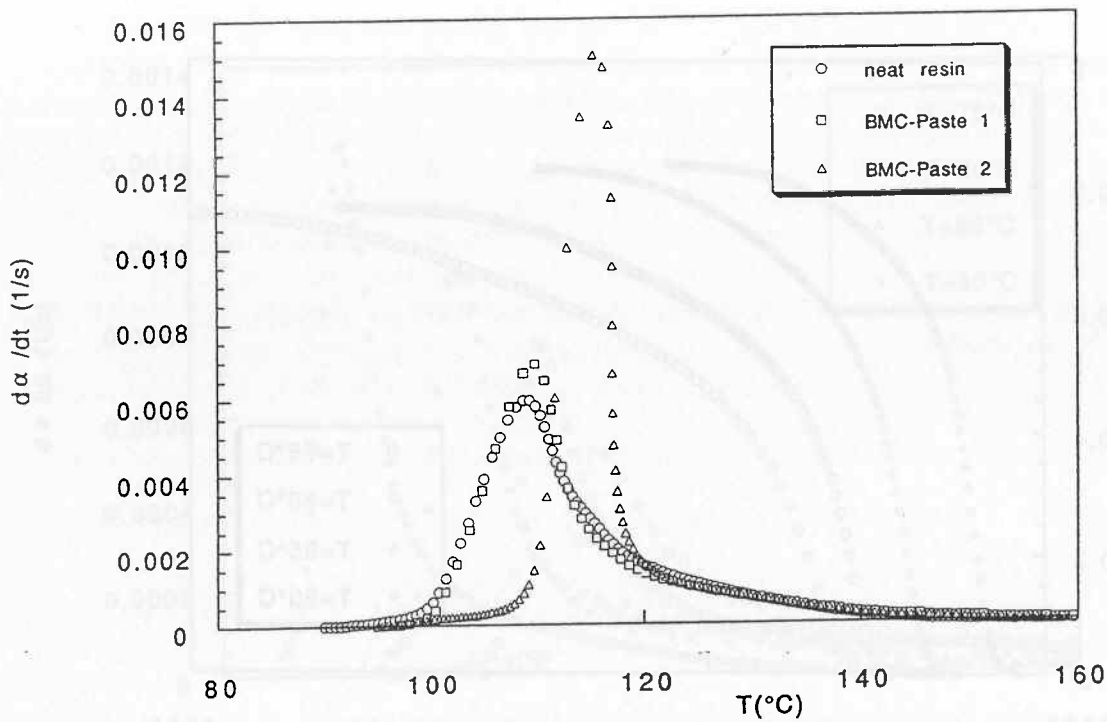Fig.4: Final extent of reaction obtained from isothermal DSC experiments as a function of test temperature.

Fig.5: Rate of reaction as a function of temperature obtained from dynamic DSC experiments at a heating rate of 5°C/min.
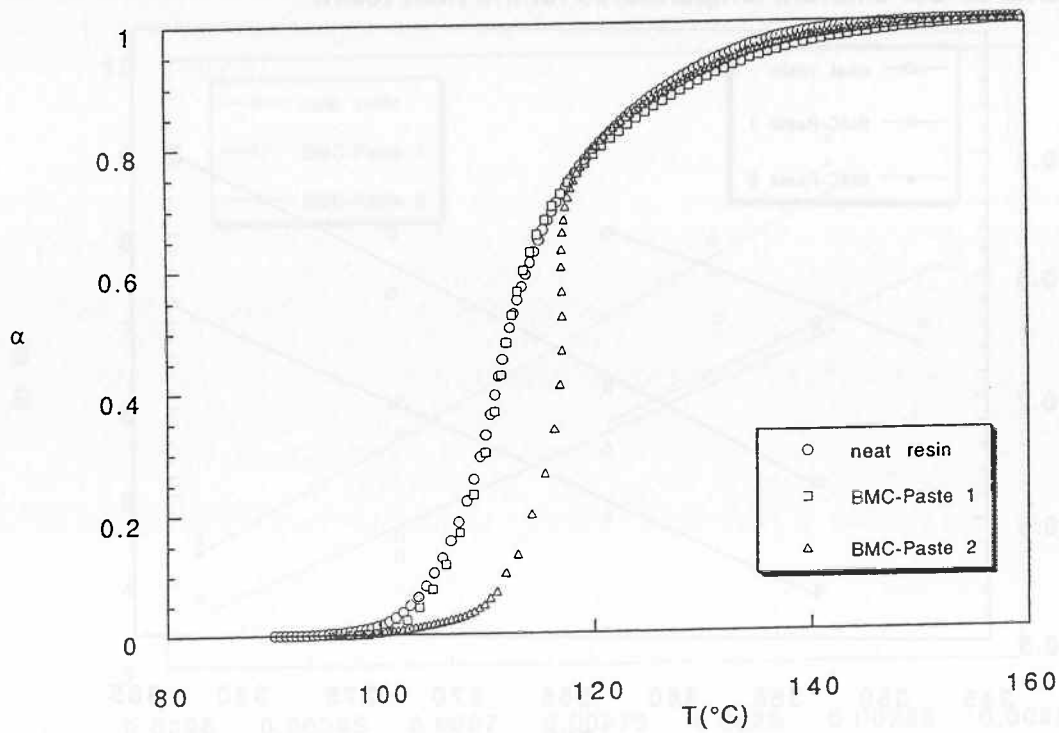
Fig.6: Extent of reaction as a function of temperature obtained from dynamic DSC experiments at a heating rate of 5°C/min.
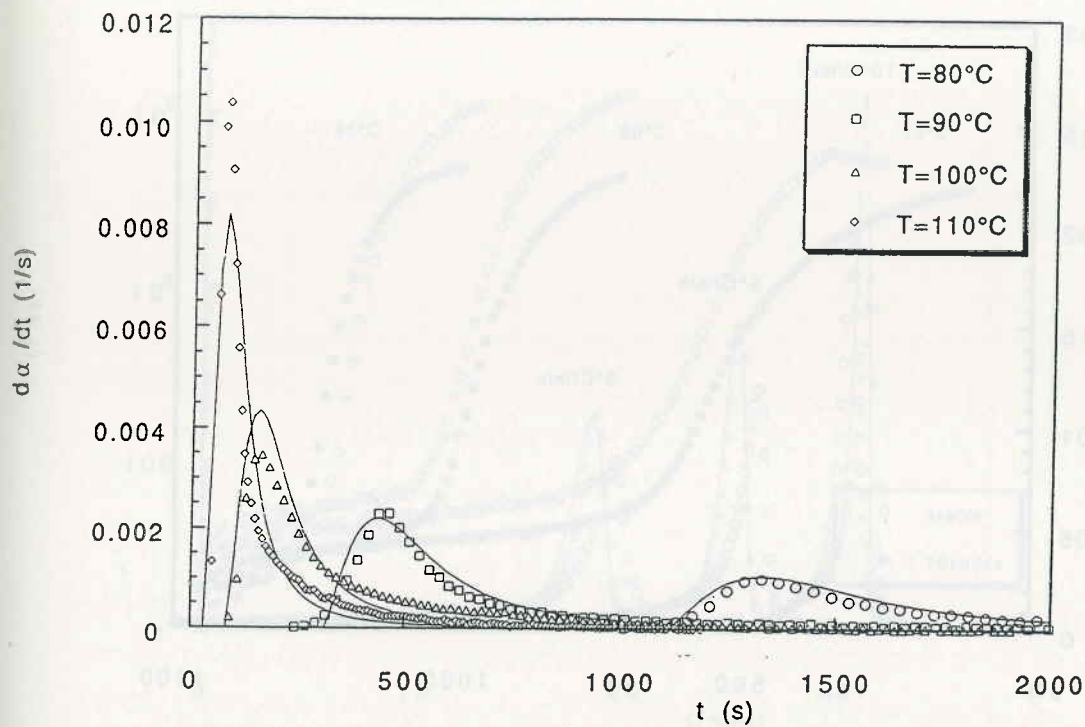
Fig.7: Reaction rate profiles of isothermal DSC experiments for BMC-Paste 1. Full lines correspond to the model data.

DSC
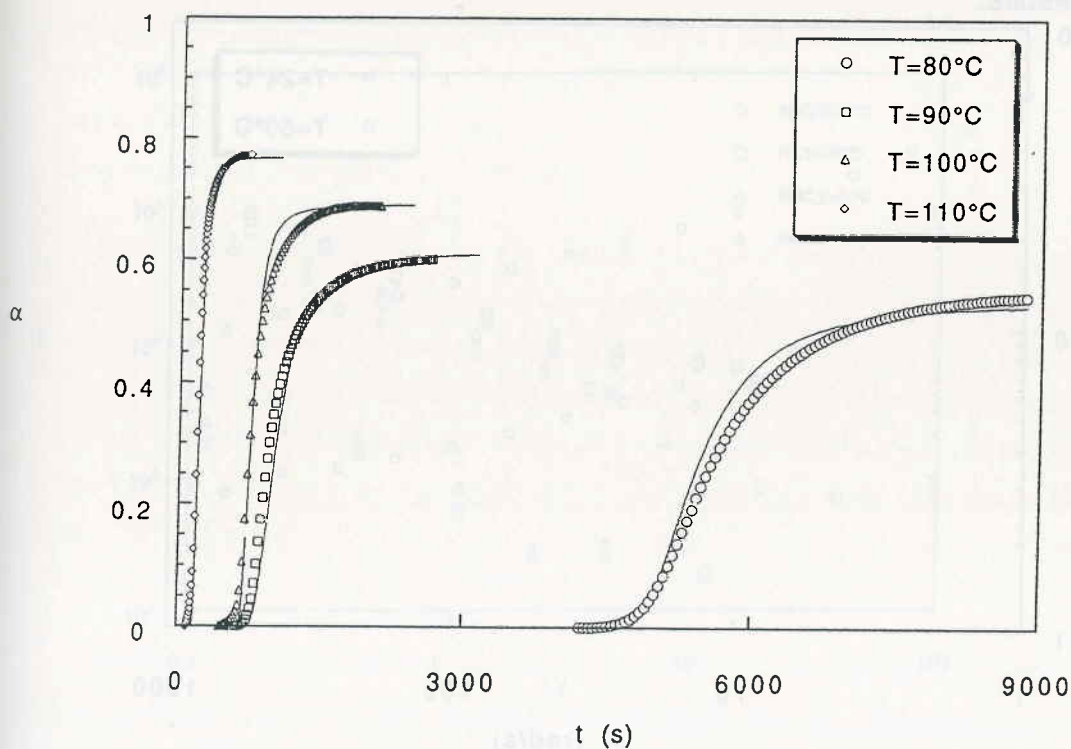
Fig.8: Extent of reaction as a function of time obtained from isothermal DSC experiments for BMC-Paste 2. Full lines correspond to the model data.
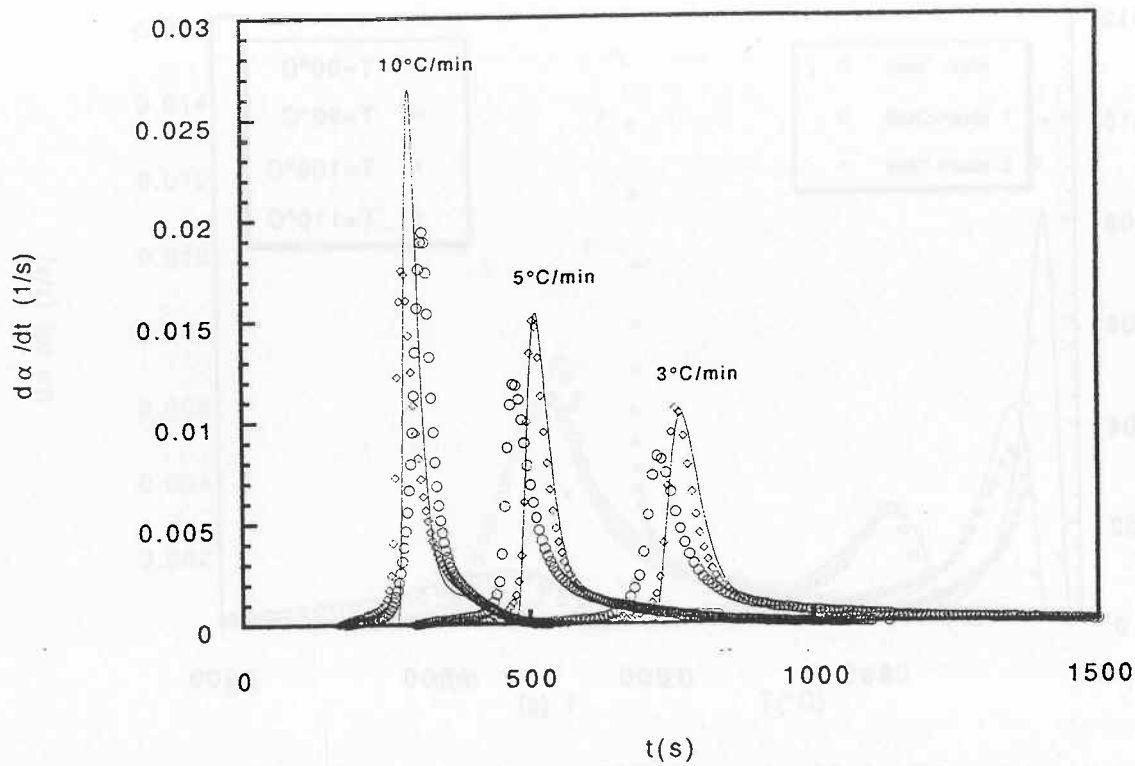
c DSC

Fig.9: Rate of reaction as a function of time obtained from dynamic DSC experiments at three different heating rates for BMC-Paste 2. Full lines correspond to model results.
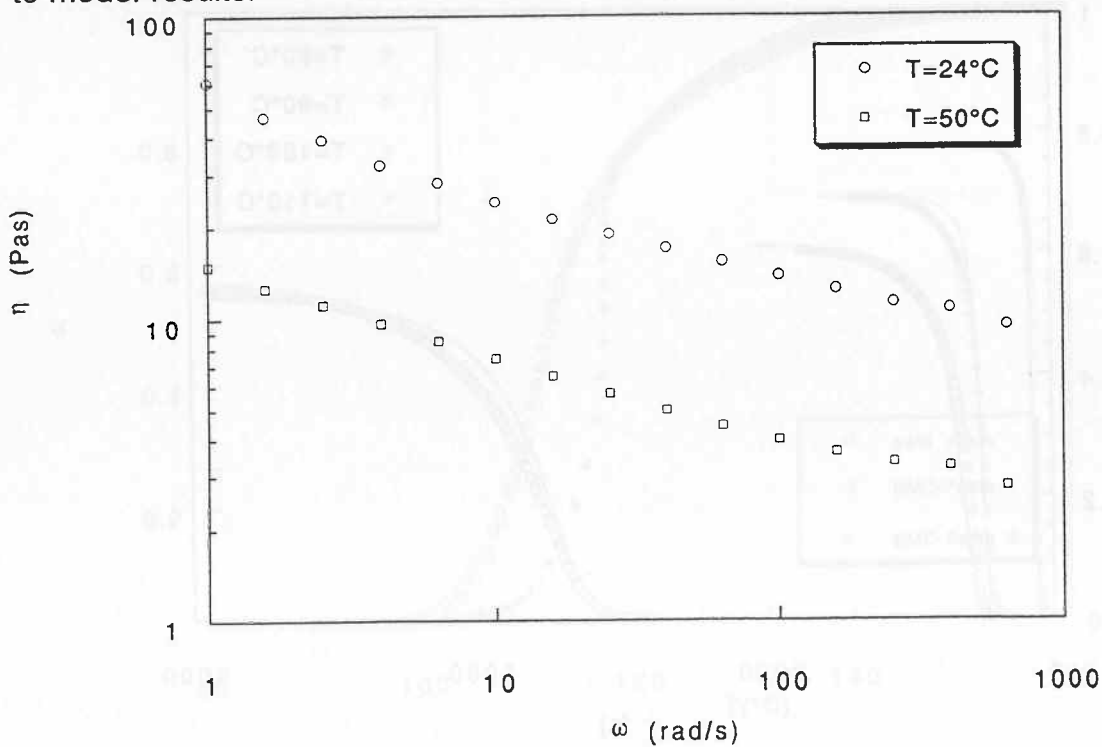
Fig.10: Isothermal complex viscosity as a function of angular frequency measured at two different temperatures for the neat resin.
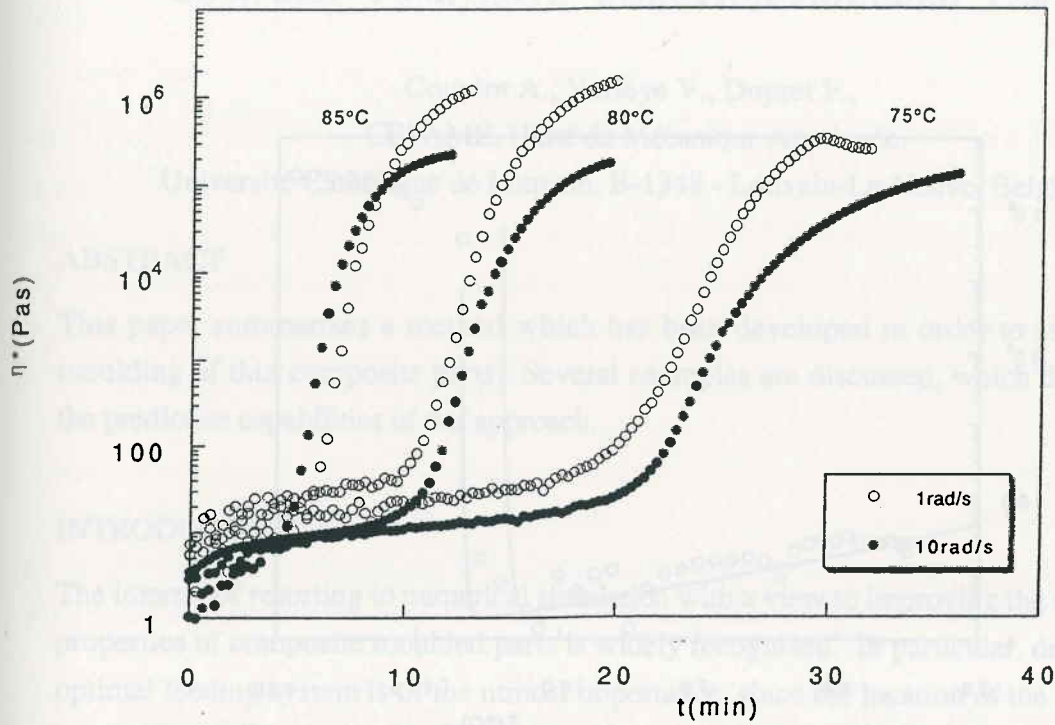
Fig.11: Isothermal complex viscosity as a function of time measured at three different temperatures and two different angular frequencies for the neat resin.
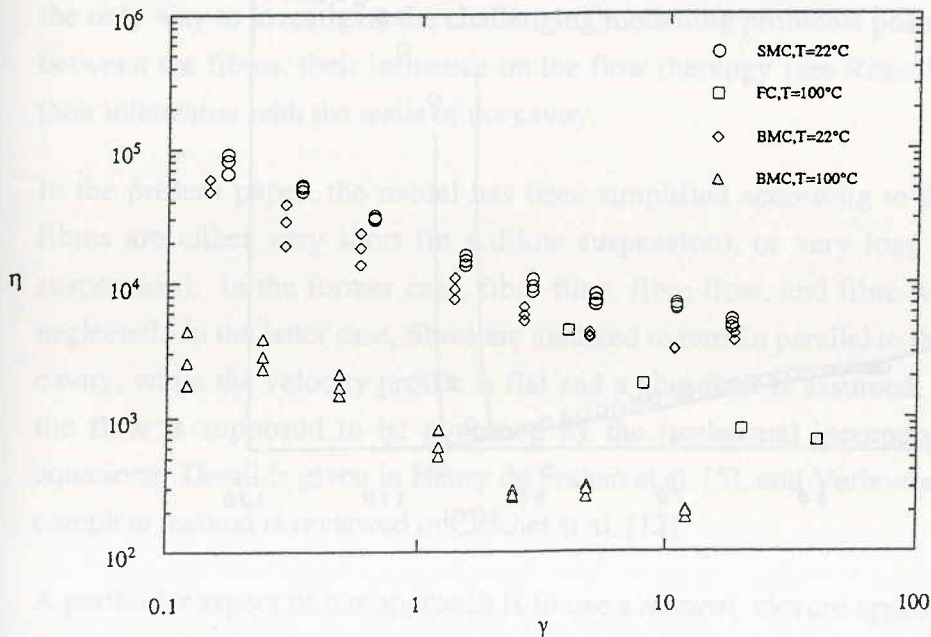

Fig. 12: Capillary rheometer results for the viscosity of the two compounds studied at two different temperatures: (BMC and SMC=BMC-paste 1, FC=BMC-Paste 2)
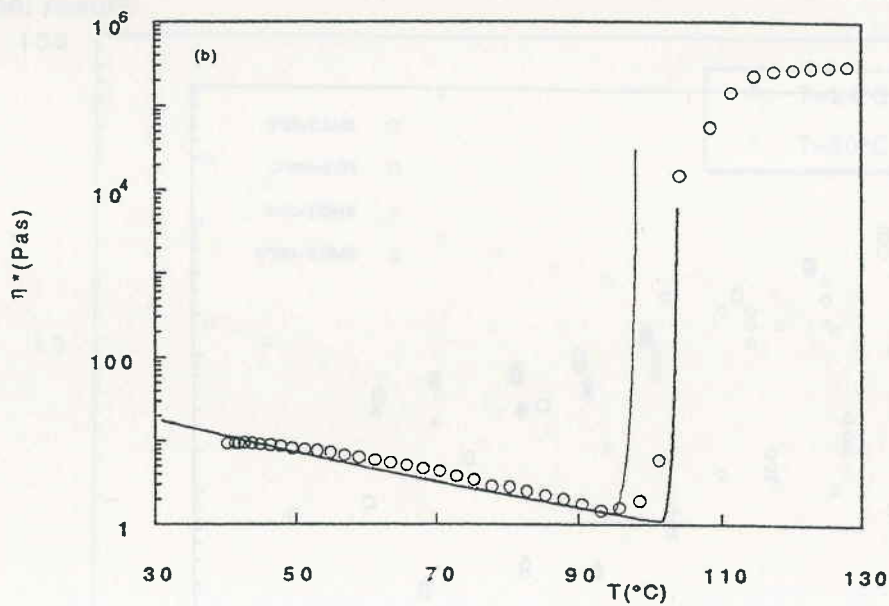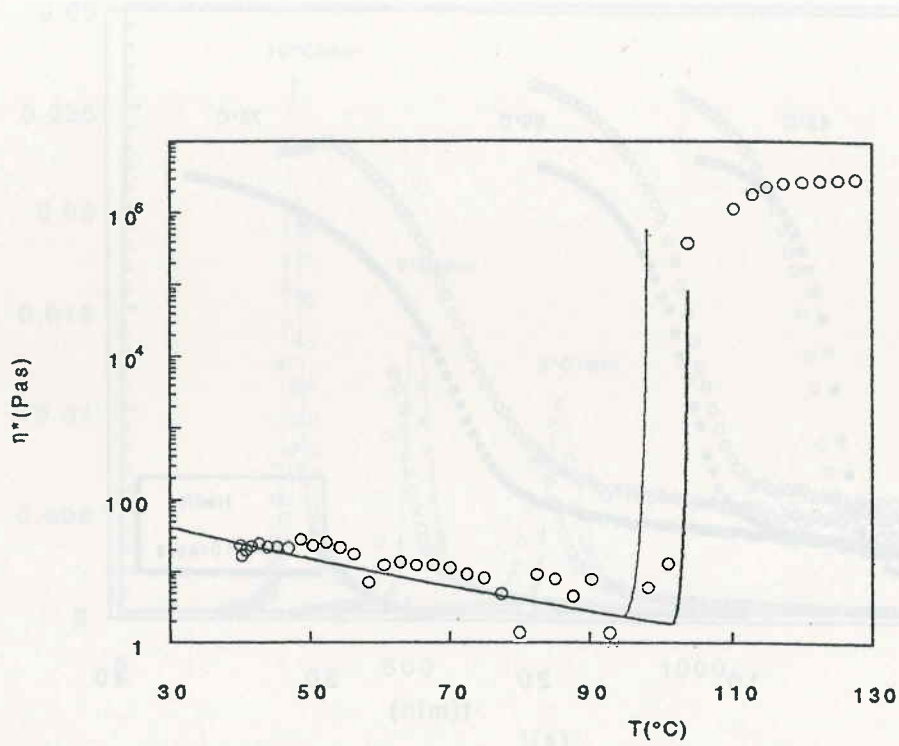
Fig.13: Complex viscosity as a function of temperature obtained at a heating rate of 7.8°C/min for the neat resin. Angular frequency: (a) 1rad/s; (b) 10 rad/s.
Full lines correspond to the model data. Induction period calculated by means of: DSC data (___), rheological data (___).