

A Technique to Predict the Curing Behaviour of Unsaturated Polyester Materials

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ABSTRACT

The curing behaviour of a thermosetting unsaturated polyester dough moulding compound (DMC) has been investigated using differential scanning calorimetry (DSC). The cure reaction was found to have two separate distinct regions : an inhibition period where the material was prevented from curing by the action added inhibitors with little or no change occurring in the rheological behaviour of the material, and a cure region where the DMC hardens to produce the final cured article. A kinetic model has been developed for polyester DMCs using a kinetic model containing two rate constants derived from DSC measurements. The first rate constant allows for the inhibition reaction which is followed by a second rate constant which allows for the main cure reaction. The model obtained has been used to estimate fill times and in-mould hardening times during processing. Good agreement has been obtained between moulding practice and the kinetic model indicating that a good model has been obtained.

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CONTENTS

		Page
1	INTRODUCTION	1
2	MATERIALS	2
	2.1 SAMPLE DESCRIPTION	2
	THE CURING OF UNSATURATED POLYESTERS	3
3	DIFFERENTIAL SCANNING CALORIMETRY (DSC)	4
4	DSC RESULTS	4
5	KINETIC MODELLING	4
	5.1 CURE REACTION	4
	INHIBITION AND CURE	6
6	MOULDING PREDICTION USING THE FINAL MODEL	6
	6.1 MOULD FILLING	6
	6.2 MOULD CURE TIME	7
7	CONCLUSIONS	8
8	ACKNOWLEDGEMENTS	8

REFERENCES

FIGURES

1. INTRODUCTION

The processing characteristics and final properties of thermosetting plastics and composites are highly dependent upon the thermal history of the material. If moulding conditions are not chosen carefully the processing characteristics of the material can be greatly affected, for example too high a moulding temperature can result in a poor under-filled scorched moulding, whereas too low a temperature can result in an unnecessarily long in-mould cure time or an under-cured final component.

At present thermosetting polymers and composites are mostly processed on a trial and error basis without detailed knowledge of the curing behaviour. Improvements in processing could be obtained through the use of either kinetic cure models, enabling accurate predictions of the curing behaviour of thermosetting plastics, or by the use of in-line measurement techniques to monitor the state of cure. The benefits of employing these methods for cure determination are numerous including : improved mould design from an improved knowledge of the filling / curing behaviour during mould filling, optimisation of the cure cycle to obtain the best quality mouldings with minimum processing time and hence minimum cost, and for materials design to produce materials with desired cure characteristics.

The main problem associated with the modelling of thermosetting polymers is the complex nature of the curing process, since the cure reaction does not usually follow a simple single reaction route. Complex models can be developed for most thermosetting polymers using NMR and FTIR type techniques. However, industry is often reluctant to use these types of techniques to obtain cure models due to the time, high expense and specialist technical knowledge that is required. There is therefore a need to develop relatively simple, easy to use models to predict the curing behaviour of thermosetting polymers during processing.

The most common method used for following the cure reaction of unsaturated polyesters is by measuring the exothermic heat evolved using differential scanning calorimetry, DSC [1, 2]. Since the rate of reaction is assumed to be proportional to the measured heat release any reaction constant obtained from a kinetic fit of DSC data is an average of all the exothermic reactions occurring within the resin. The exothermic heat evolved in unsaturated polyesters comes from the following reactions [3]:

- (i) The propagation reaction of free-radicals on the polyester-styrene, polyester-polyester and styrene-styrene double bonds.
- (ii) The decomposition reaction of the peroxide initiator.

The heat generated by the initiator breakdown (ii) however is very small compared to (i) and is also further reduced by the free-radical reaction with the inhibitor. The heat evolved from cure can therefore be assumed to be proportional to the number of double bonds reacting per unit mass. The DSC measurement of exothermic heat evolved is therefore an average of the three reactions occurring during propagation, and thus the rate constant obtained is an average for the whole cure reaction. As a consequence of the average rate constant the kinetics obtained from DSC can be expressed simply. Reaction kinetics obtained from DSC experiments are generally of the form [1-13]:

$$\frac{d\alpha}{dt} = K (1 - \alpha)^n \quad (1)$$

Where α is the degree of cure from 0 to 1, t is the reaction time, n is the reaction order which is independent of temperature and K is the rate constant which obeys the Arrhenius relationship :

$$K = A \exp \left[-\frac{E}{RT} \right] \quad (2)$$

Where E is the activation energy, R is the gas constant, T is the temperature in Kelvin and A is the pre-exponential constant.

Of the simple single reaction constant n^{th} order kinetic equations used the most successful and widely used is that proposed by Kamal et al [6,7] :

$$\frac{d\alpha}{dt} = K \alpha^m (1 - \alpha)^n \quad (3)$$

This is a second order type reaction where $m + n = 2$

This type of kinetic equation gives a sigmoidal type cure conversion without the need for a large number of reaction constants. It can be seen that when α equals 0 the rate of conversion is zero and when α is 1 the reaction rate is also zero.

L. J. Lee [5] carried out modelling work on unsaturated polyesters and uncoupled the inhibition reaction from the main cure. Lee stated that inhibitors added to polyesters are highly effective and that an allowance should be made for the consequent inhibition time in mould filling calculations. Inhibition time was measured from the change in base-line of isothermal DSC curves, and the activation energy for cure was derived from the time to peak exotherm. Although the model proposed by Lee included the inhibition stage it was only used to determine a gel time and consequently the final stages of cure were not included in the model.

2. THE MATERIALS

2.1 SAMPLE DESCRIPTION

An unsaturated polyester resin was chosen for investigation as polyesters are probably the most widely used class of thermosetting plastics for the preparation of relatively cheap mouldable composite materials. Unsaturated polyester materials are widely used in the major processing operations of injection, compression, and resin transfer moulding. These materials offer a variety of desired characteristics including: ease of processability, relatively low cost, good surface finish, and high-end product properties (eg. modulus, operating temperatures over 100°C).

The experimental polyester material investigated was based on an injection moulding grade of a BIP Plastics Ltd unsaturated polyester dough moulding compound (DMC), reference L7049 [14]. The materials differed from the standard L7049 DMC material primarily by the absence of the 'E' Type glass-fibres which are usually incorporated into the formulation to provide reinforcement. Glass-fibres were omitted to minimise experimental problems which could have arisen, in part as a consequence of the small reproducible uniform samples that were needed for testing.

The base unsaturated polyester DMC slurry investigated consisted of approximately:
 23 wt% of unsaturated polyester in styrene, containing inhibitor (0.0053 wt% hydroquinol, 0.001 wt% para-tertiary-butyl-catechol and 0.13 wt% butylatedhydroxytoluene), catalyst and mould release agent;
 12 wt% polystyrene which is added as a shrinkage control additive;
 45 wt% chalk;
 20 wt% alumina-trihydrate (flame retardant).

The above material was compounded in a 'Z' Blade mixer at room temperature. The benzoyl peroxide catalyst and inhibitors were pre-mixed into the resin before the addition of the filler materials to ensure as even a distribution of inhibitor and catalyst as possible was obtained.

2.1 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 [14]. 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 experimental polyester materials investigated herein) is benzoyl peroxide [15]. The benzoyl peroxide breaks down to form two benzoyloxy radicals which then in-turn form two phenyl radicals plus carbon dioxide. Once formed the phenyl radicals react with the carbon-carbon double bonds in the styrene and polyester molecules opening them up to allow polymerisation to occur. Since the open double 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 the cross-linking bridges.

Since benzoyl peroxide is highly reactive the shelf life of an uninhibited unsaturated polyester resins is relatively short at room temperature [15]. 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 [16]. The inhibitor itself is rendered inactive by the inhibitor - free radical reaction. This leads to a phenomena called the induction period as the cure reaction is prevented by the inhibition reaction for a limited period of time only. After the inhibitor molecules are used up the polymerisation, catalysed by the initiator, proceeds in the usual manner.

During polymerisation, as the number of cross-linking bridges increase, 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 [2,3,15]. The gel point therefore represents a processing limit of the polymer. In unsaturated polyester materials the gel point occurs at relatively low polymerisation conversions of approximately 5-10%. Yang and Lee [17] have described the rheological changes occurring and the relatively low gel point of unsaturated polyesters in terms of the formation of micro-gel particle formation.

3 DIFFERENTIAL SCANNING CALORIMETRY (DSC)

A Perkin-Elmer Power Compensated DSC II was used in the investigation of the curing behaviour of the DMC slurries, using both isothermal and constant heating rate experiments. The DSC was calibrated for temperature using a range of metals with known melting points, and the power scale calibrated against a known sapphire reference.

Dynamic DSC experiments using constant heating rates of 2.5, 5, 10, 20, and 40°C/min were used primarily to determine the inhibition kinetics for the cure reaction. However, a constant heating rate of 2.5°C/min was also carried out until the cure exotherm had completed to determine the total enthalpy change for cure reaction.

Isothermal DSC measurements provided the bulk of the DSC experimentation since the specific heat, C_p , of the material changed very little during testing, thus allowing a linear base-line to be drawn to determine the total heat of reaction. All isothermal experiments were initially heated at 160°C/min to raise the temperature as quickly as possible to minimise cure during the heat-up period to the isothermal test temperature. After the initial heating up period the temperature was held constant until the whole cure reaction had completed so that the base-line could be drawn and the heat of reaction calculated for final analysis.

The cure of a polyester material can be greatly affected by the loss of the styrene monomer. To prevent any changes in the curing behaviour of the polyester DMC slurries all DSC experiments were carried out in sealed aluminium sample pans to prevent any styrene loss. As a secondary precaution against styrene loss the sealed aluminium pans were filled to capacity during analysis to prevent styrene escaping to free space at the top of the can. Sample pans were also weighed before and after the experiments to ensure that leakage had not occurred, and where discrepancies were found the results were disregarded.

4 DSC RESULTS

DSC experiments carried out under isothermal and constant heating rate conditions have all shown a period of inhibition followed by cure which can be seen in mechanical testing such as DMTA experiments, Figure 1. During inhibition it can be seen that little or no heat is evolved or absorbed as a result of the inhibitor-catalyst reaction, indicating that the energy required to form the phenyl free radicals is balanced by the 'mopping-up' reaction of the inhibitor. Good agreement of inhibition times can be seen between the DSC and DMTA data (Figure 1) indicating that the DSC data can be correlated with the rheological changes occurring within the DMC sample. It should be noted that the DMTA equipment has insufficient power to fully analyze the cure behaviour of specimens which cure to a final modulus above 2×10^6 Pa. However, it would seem likely that improved agreement would have been obtained for the cure stage by extrapolating DMTA data to 10^9 Pa.

5 KINETIC MODELLING

5.1 CURE REACTION

In a constant heating rate DSC experiment the total area under the exotherm, H , represents 100% conversion of the reaction process, Figure 2. Consequently, by drawing a suitable baseline the degree of conversion that has occurred up to a time, t , can be written in terms of the overall heat of reaction, H .

$$\text{Conversion at time } t, \alpha = \frac{h(t)}{H}$$

However, for an isothermal measurement this is not the case. In a thermosetting material the cure reaction will only continue up to the glass transition temperature (T_g), since diffusion is too slow beyond the T_g to allow further cure. The isothermal test temperature therefore represents a limit on the degree of cure which can occur since the cure temperature is equivalent to the T_g . As a result the total conversion must be derived from dividing the heat of reaction for the isothermal measurement by the total heat of reaction for a fully cured specimen obtained with a constant heating rate DSC experiment. A graph of conversion verses time for the particular isothermal temperature can now be drawn which is representative of the cure that has occurred within a sample, Figure 3 .

The split second-order equation as proposed by Kamal [4], equation 3, has been used to fit the experimental isothermal DSC cure data, for example as presented in Figure 3.

Equation 3 has the solution:

$$\alpha = \frac{[(n-1)Kt]^{\frac{1}{n-1}}}{1 + [(n-1)Kt]^{\frac{1}{n-1}}} \quad (4)$$

Which has a graphical solution of the form $y = mx + c$ as follows

$$\text{Log}(t) = (n-1) \text{Log} \left[\frac{\alpha}{1-\alpha} \right] - \text{Log} [K(n-1)] \quad (5)$$

Therefore, if the data provide a good fit to this model then a plot of $\log [\alpha/(1-\alpha)]$ against $\log$ time should reveal a straight line with a gradient of $(n-1)$ and intercept $-\log [K(n-1)]$.

All data have shown a good fit to the above second-order kinetic model, an example of which is shown in Figure 4, even though as discussed earlier the reaction does not follow one single path. The mean values of the constants m and n obtained from the slopes of the graphs for the different isothermal temperatures were 0.52 and 1.48 respectively ± 0.2 .

The values of the rate constants K obtained from the intercepts of the graphs for each isothermal measurement were used to obtain the kinetics from a plot of $\ln K$ verses $1/T$, Figure 5. The Arrhenius plot obtained was excellent producing the following constants:

$$\begin{array}{ll} \text{Activation energy, } E & = 111.4 \text{ kJ mol}^{-1} \\ \text{Pre-exponential factor, } A & = 4.39 \times 10^{13} \text{ s}^{-1} \end{array}$$

The graph in Figure 6 shows a comparison of the measured and predicted conversions using the derived kinetics for various isothermal tests on the standard material (x1 inhibitor). Results show that a good prediction of the cure behaviour has been obtained when considering the assumptions made to obtain the data fit.

5.2 INHIBITION AND CURE

As previously discussed in section 2.2 the total cure process comprises a period of inhibition which is then followed by the main cure reaction. Previous work by the NPL, details of which can be found in [18], has shown that the inhibition reaction can be predicted using the following equation:

$$t_i = \frac{1}{A_i} \exp \left[\frac{E_i}{RT} \right]$$

where: t_i is the inhibition time, E_i is the activation energy for inhibition and A_i is the pre-exponential factor. To model the complete reaction the inhibition and cure stages described by equations 4 and 6 must be combined. When combined the expression below describes the whole cure process for the unsaturated polyester DMC.

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

where α = conversion from 0 to 1, K = rate constant for cure, t = time from $t = 0$, and is only valid when $(t - t_i) \geq 0$. For $t < t_i$ $\alpha = 0$

Figure 7 compares a predicted cure profile for the L7049 material at 100°C, obtained using the above equation, with the real experimental value. It can be seen that an excellent model for the whole cure process has been obtained and therefore the model is considered reliable for mould process calculations.

6 MOULDING PREDICTION USING THE FINAL KINETIC MODEL

The processing of an unsaturated polyester dough moulding compound consists of two distinct separate steps. The first step involves filling of the mould cavity during which the rheological changes in the material up to and including the gel point are relevant. The second step involves the in-mould cure time after filling to obtain the necessary cure and hence sufficient strength for removal from the mould and achievement of the required final moulding properties.

6.1 MOULD FILLING

Typical injection moulding conditions for standard L7049 DMC mouldings are : fill times up to a maximum of 5.5 seconds and material at 40°C entering the mould which is at a temperature of 140 to 150°C. However, it is found in practice that the best quality mouldings with good surface finish are obtained with injection times under 1 second.

The filling of the moulding cavity requires the modelling of conversion up to the gel point since material flow is severely restricted beyond this limit. As discussed in section 2.2 the gel of unsaturated polyester materials is widely considered to equal a conversion of 5%. From the model, the calculated inhibition times for the moulding temperatures of 140 and 150°C are 0.7 and 0.3 seconds respectively. It can also be calculated that the total time before gel (5% conversion) for the temperatures 140 and 150°C are 2.2 and 0.9 seconds respectively. The

times calculated from the kinetics for inhibition and gel assume that the material reaches the mould temperature instantaneously. Although at the surface this can be assumed a reasonable approximation, at the centre of moulding this is not the case due to the thermal gradients. Therefore, extra time needs to be allowed for the heating of cooler material at the centre of the moulding. To illustrate this calculations have been carried out by Pilkington and the NPL of the temperature-time profiles within DMC sections and the results are summarised in Figure 8. These calculations suggest that the heating up time is of the order of several seconds, depending on geometry and temperature conditions. The heating up time is therefore a significant component of the total time to 'gel' in the centre of the moulding. This time would define a maximum injection time beyond which no flow of material could occur. For accurate determination of the time taken for the material in the centre of the mould channel to reach 'gel' point a more complex numerical model would be required which could take into account the effects of heat transfer and the cure reaction exotherm as well as the material and mould temperatures and the moulding thickness.

Since polyester DMC mouldings are often used for domestic articles such as electrical appliance casings (eg/. electric toasters) the over-riding requirement is for a good surface finish. In practice it is found that although a moulding can be produced with fill times up to 5.5 seconds the best surface finishes are obtained with injection times under 1 second. A possible explanation for this observation is that if the viscosity of the material starts to rise rapidly during processing then a sticking and slipping effect of the material on the surface of the mould could occur. It is suggested that this behaviour causes the matt surface finish with flow marks as seen on the outside of the tray moulding in Figure 10. During inhibition the viscosity of the DMC material remains unchanged (except for viscosity changes due to heating) and therefore surface finish should not be affected due to stick-slip. The centre gated tray moulding (Figure 10) shows that a good surface finish has been obtained in the central region, relating to a fill time of up to 0.6 seconds, after which the surface becomes matt indicating stick-slip flow. Since the inhibition time during which the viscosity of the polyester does not increase was calculated to be 0.7 seconds it is suggested that this effect was due to stick-slip flow. The calculated inhibition time of 0.7 seconds at 140 °C respectively agrees well with the observations for the tray moulding and more generally with injection moulding practice which suggests that fill times under 1 second should be used to obtain good quality surface finish.

6.2 MOULD CURE TIME

The in-mould cure time affects the final properties of a polyester DMC moulding. If the in-mould cure time is too short then at worst the moulding may split and uncured material burst through the surface, as shown in Figure 11, or the moulding distorts due to its low modulus and high internal stresses caused by the formation of 'pockets' of unreacted styrene. If the moulding is only slightly under-cured then the final strength and modulus will be lower than desired. In practice it is found that an in-mould cure time of approximately 45 seconds is required to produce good quality mouldings 3 mm thick at a mould temperature of 150°C.

From the kinetics it can be calculated that for a 90% conversion at 150°C the required cure time including inhibition is approximately 8 seconds assuming that the moulding reaches temperature instantaneously, Figure 9. However, as with the fill-time calculations a 'heating time' should be allowed for in calculations for conduction of heat into the centre of the moulding. From the temperature profile results (Figure 8) it can be seen that the centre of a 3 mm thick moulding reaches 130°C after 7 seconds. Once the temperature in the centre of the moulding has reached 130°C then the time for 90% conversion is found to be approximately 38 seconds, Figure 9. The in-mould cure time from the kinetics is therefore given by the time for the centre of the moulding to cure which is estimated to be

approximately 45 seconds. This result is once again confirmed by moulding practice whereby an in-mould cure time of 45 seconds produces mouldings with the desired characteristics. It should be noted that these calculations are only approximate since no allowance has been made for the cure occurring during the heating up period, or the effect of the heat evolved from the cure exotherm. However, the model shows a good fit to observed results. As was the case for predicting mould filling conditions, more accurate modelling of the cure state of mouldings could be achieved through the incorporation of the kinetic modelling into injection moulding simulation software. This would enable more accurate predictions of in-mould cure times to be made thus enabling processing conditions to be optimised and processing times to be minimised.

7 CONCLUSIONS

This work has demonstrated that the technique of differential scanning calorimetry (DSC) can be successfully used to obtain data for kinetic modelling of the cure behaviour of unsaturated polyester materials. The cure kinetics model presented utilises two rate constants. The first is used to describe the inhibition phase of the curing behaviour and the second the cross-linking phase. A simple analysis indicates that a reasonable prediction of the curing behaviour can be obtained for a commercial moulding situation. The model can be used to estimate the maximum permissible injection time and the minimum desirable in-mould cure time to obtain satisfactory mouldings. However more detailed validation using injection moulding simulation software modified to incorporate the cure modelling would be desirable to assess the accuracy and full usefulness of the kinetic model for predicting the complex behaviour of thermosetting plastics in injection moulding.

8 ACKNOWLEDGEMENTS

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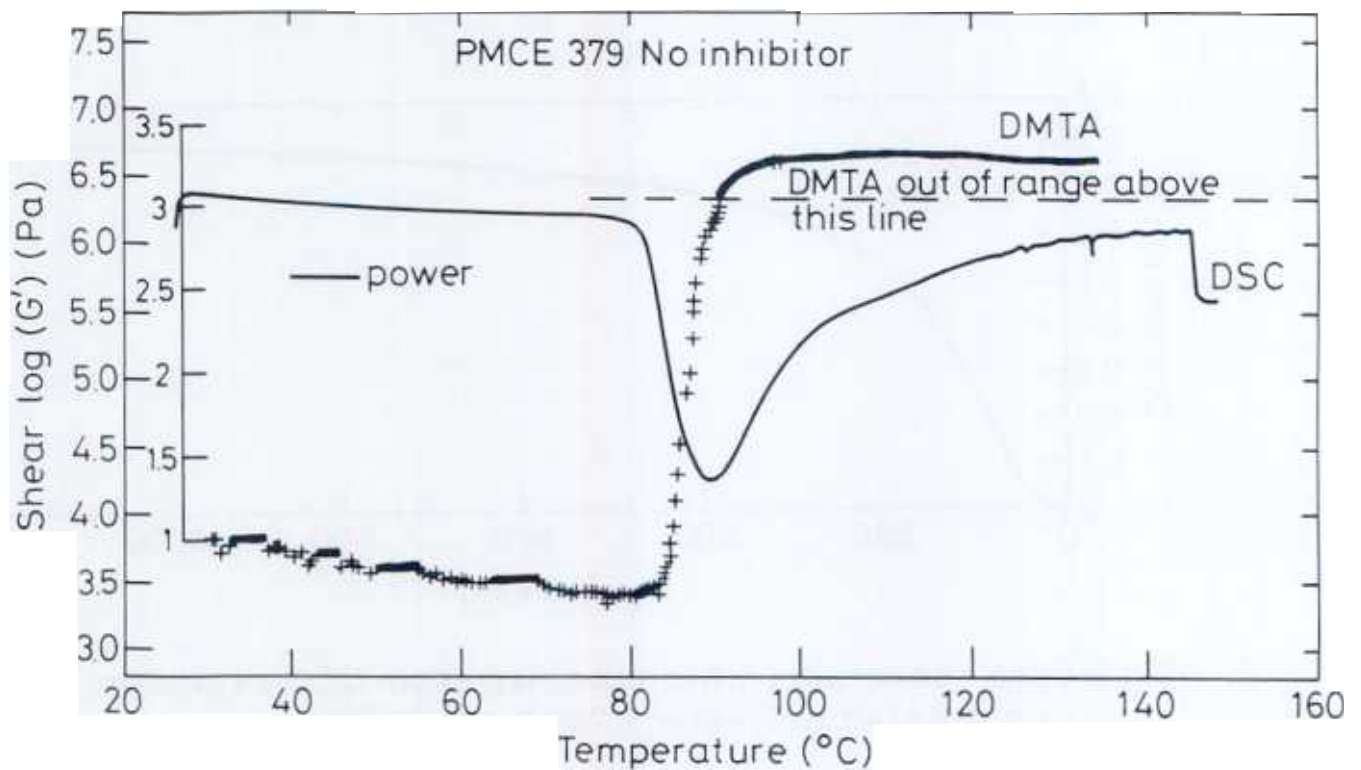


Fig A comparison of DSC and DMTA cure measurements at a constant heating rate of 2°C/min

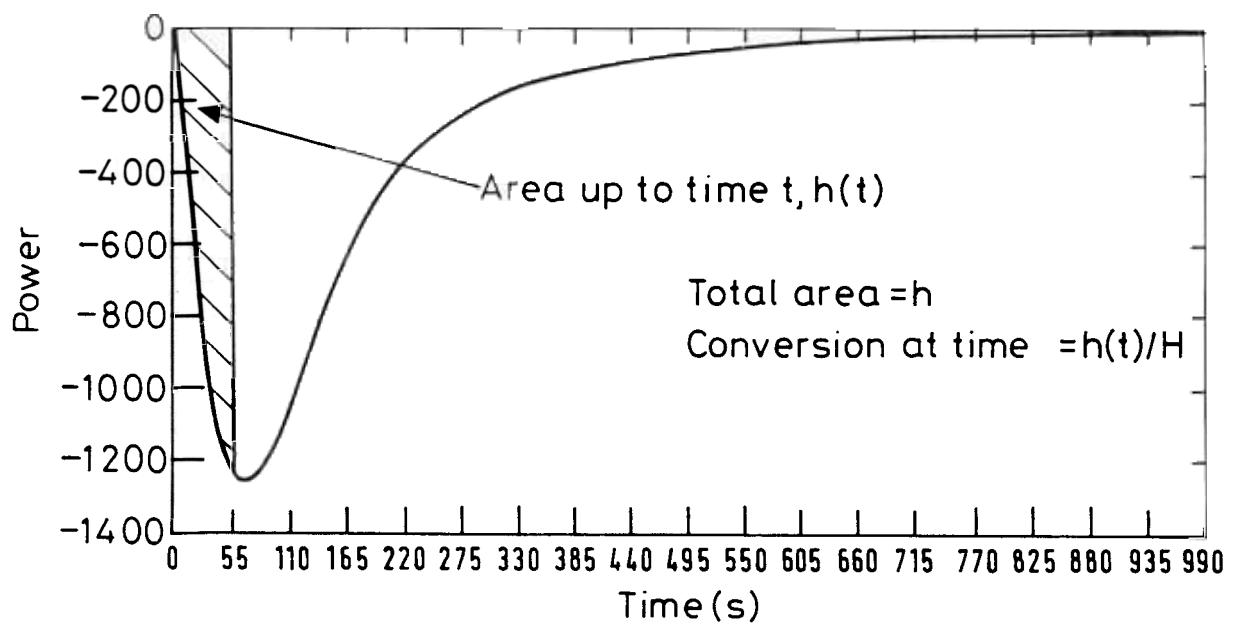


Fig.2 Typical DSC trace showing cure exotherm following the end of the inhibition period for an unsaturated polyester resin at 100°C

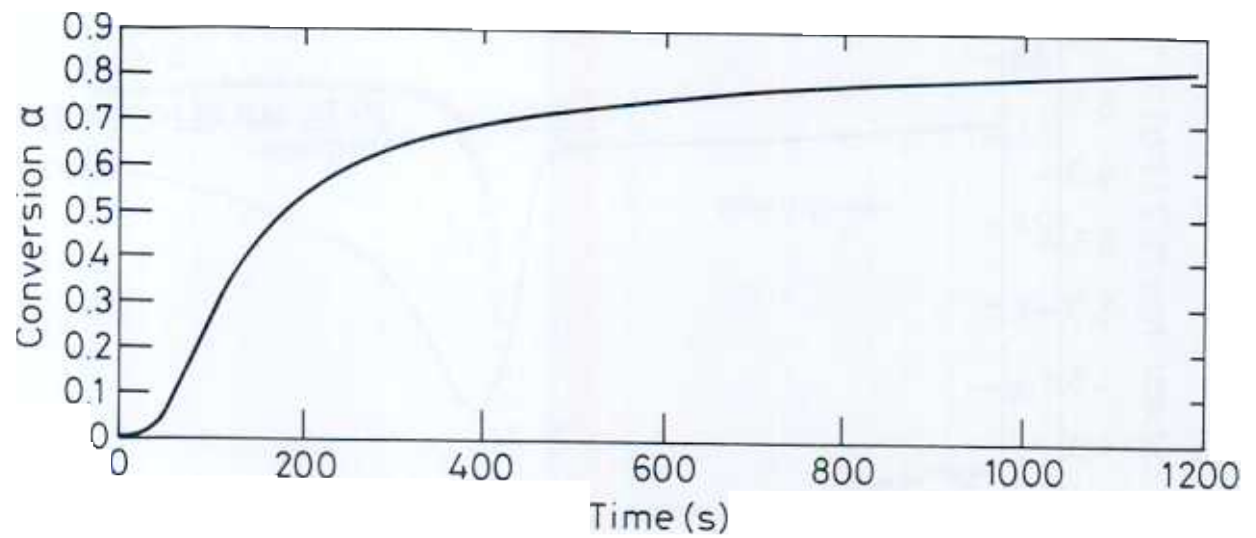


Fig.3 Cure conversion data obtained from DSC exotherm on an unsaturated polyester, L7049, at 100°C

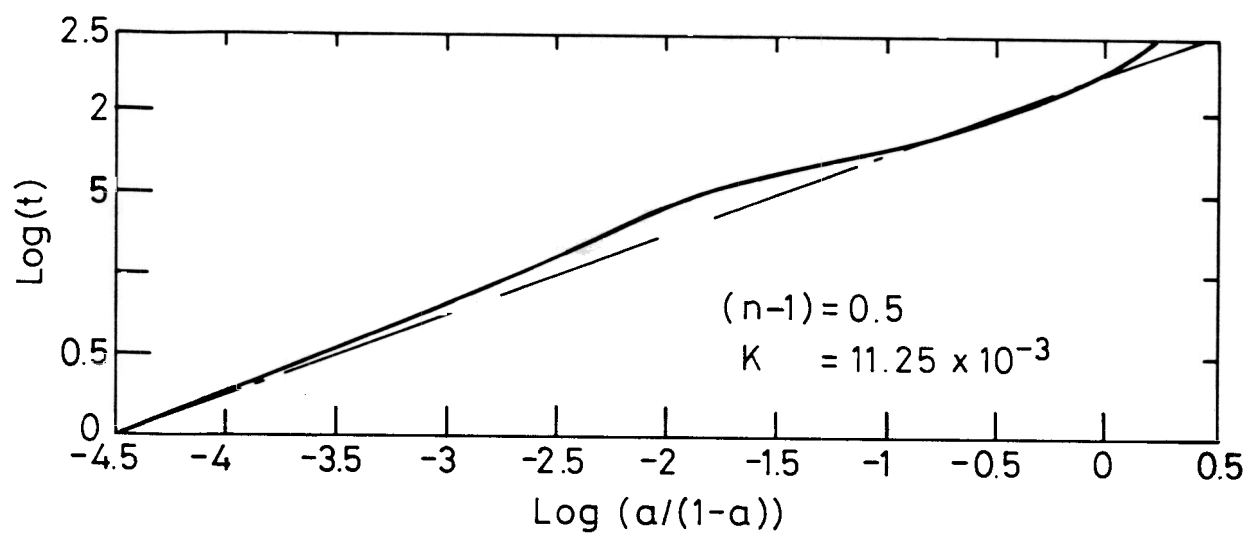


Fig.4 Kinetic analysis of cure data obtained on L7049, at 100°C

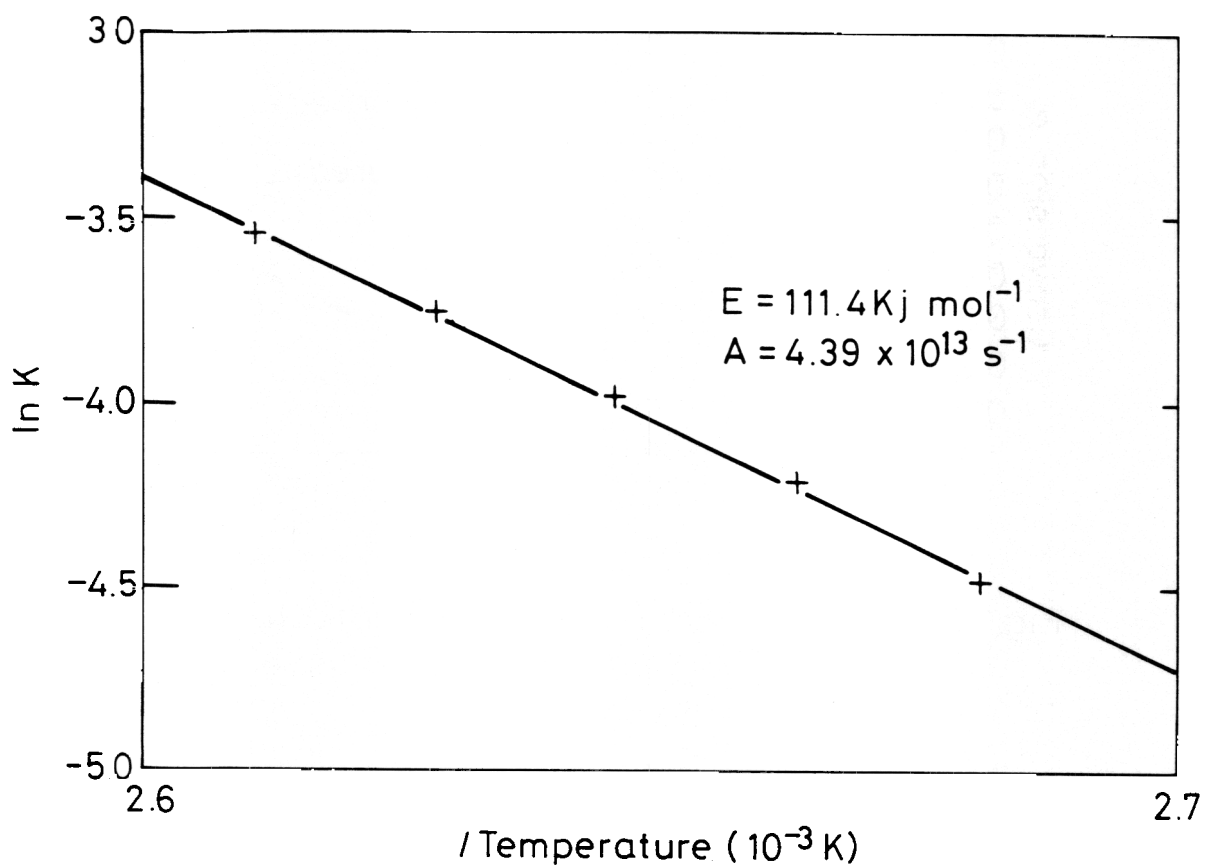


Fig.5 Arrhenius plot to obtain cure kinetics

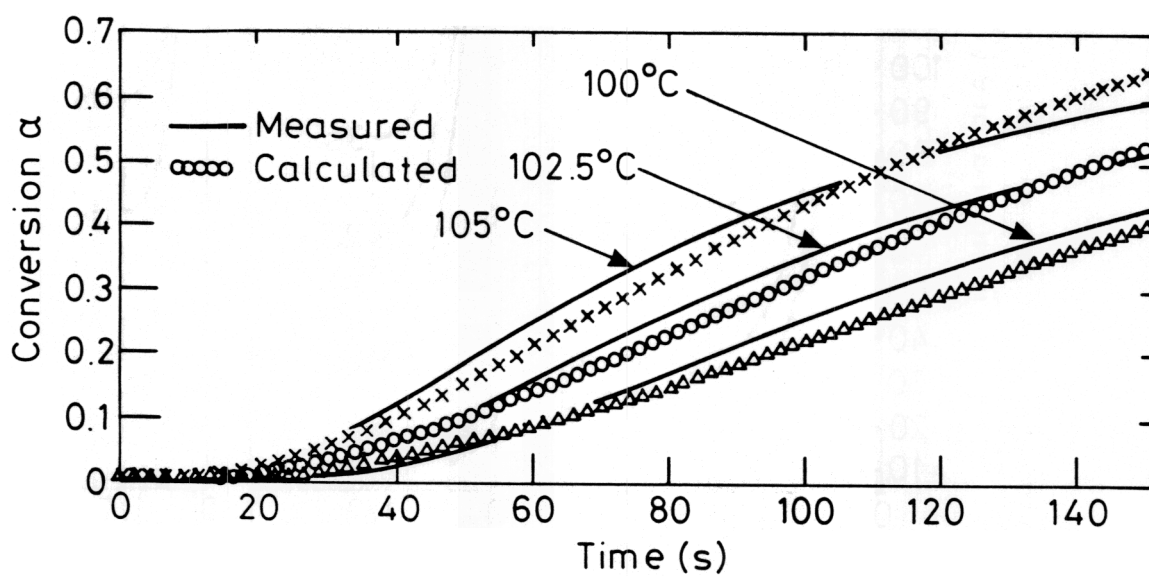


Fig.6. Comparison of measured and calculated cure conversions for L 7049

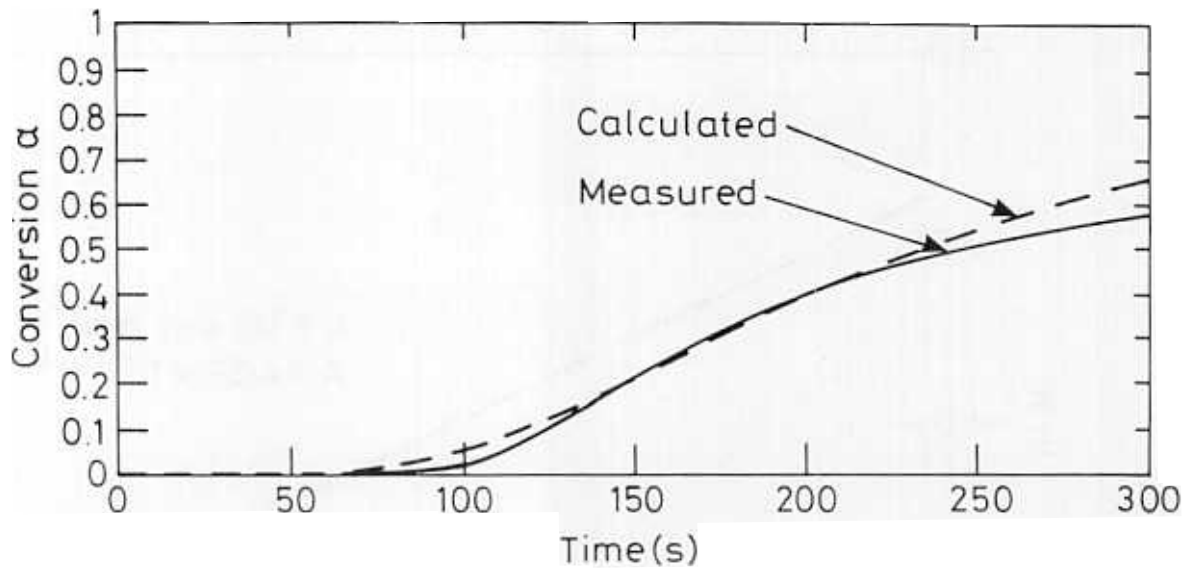


Fig.7 Comparison of measured and calculated cure conversions at 100°C using the full kinetic model which allows for inhibition and cure

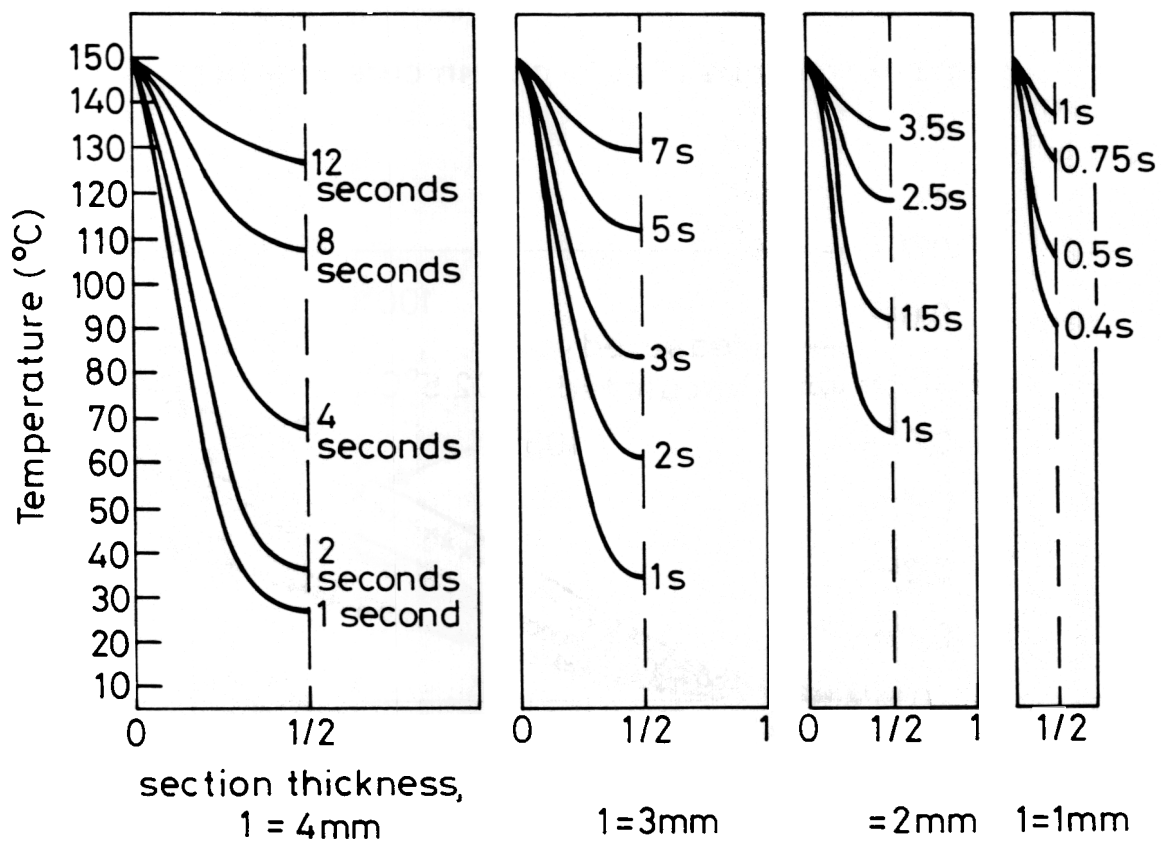


Fig.8 Calculated temperature profiles through unsaturated polyester DMC section after different periods of time, based on material at 20°C entering a mould at 150°C

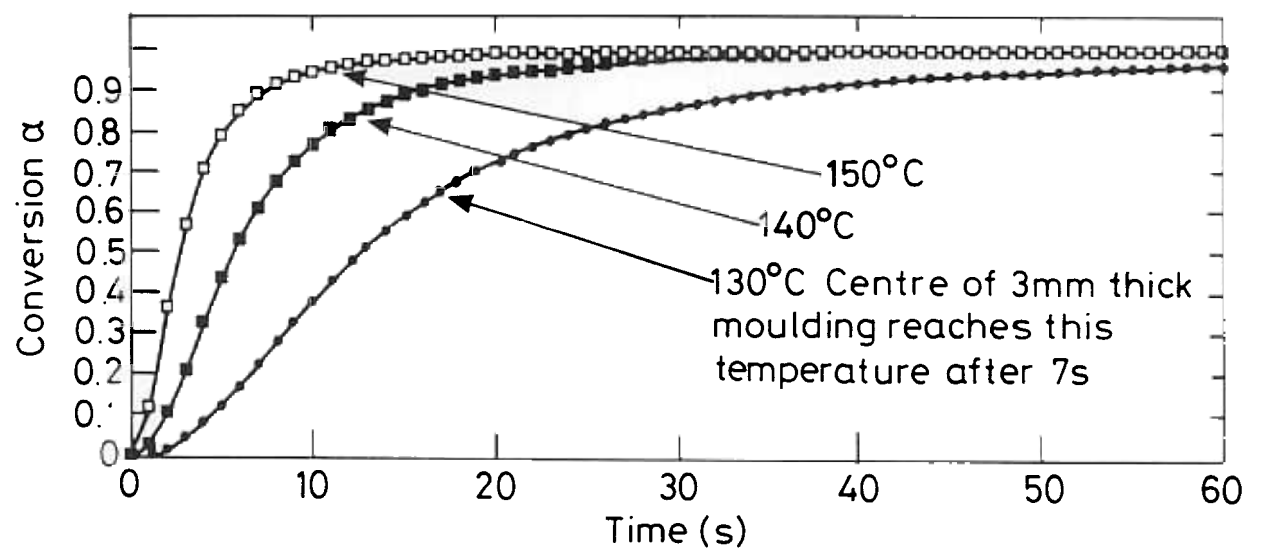


Fig.9 Calculated cure conversion data for the DMC materia at moulding temperatures

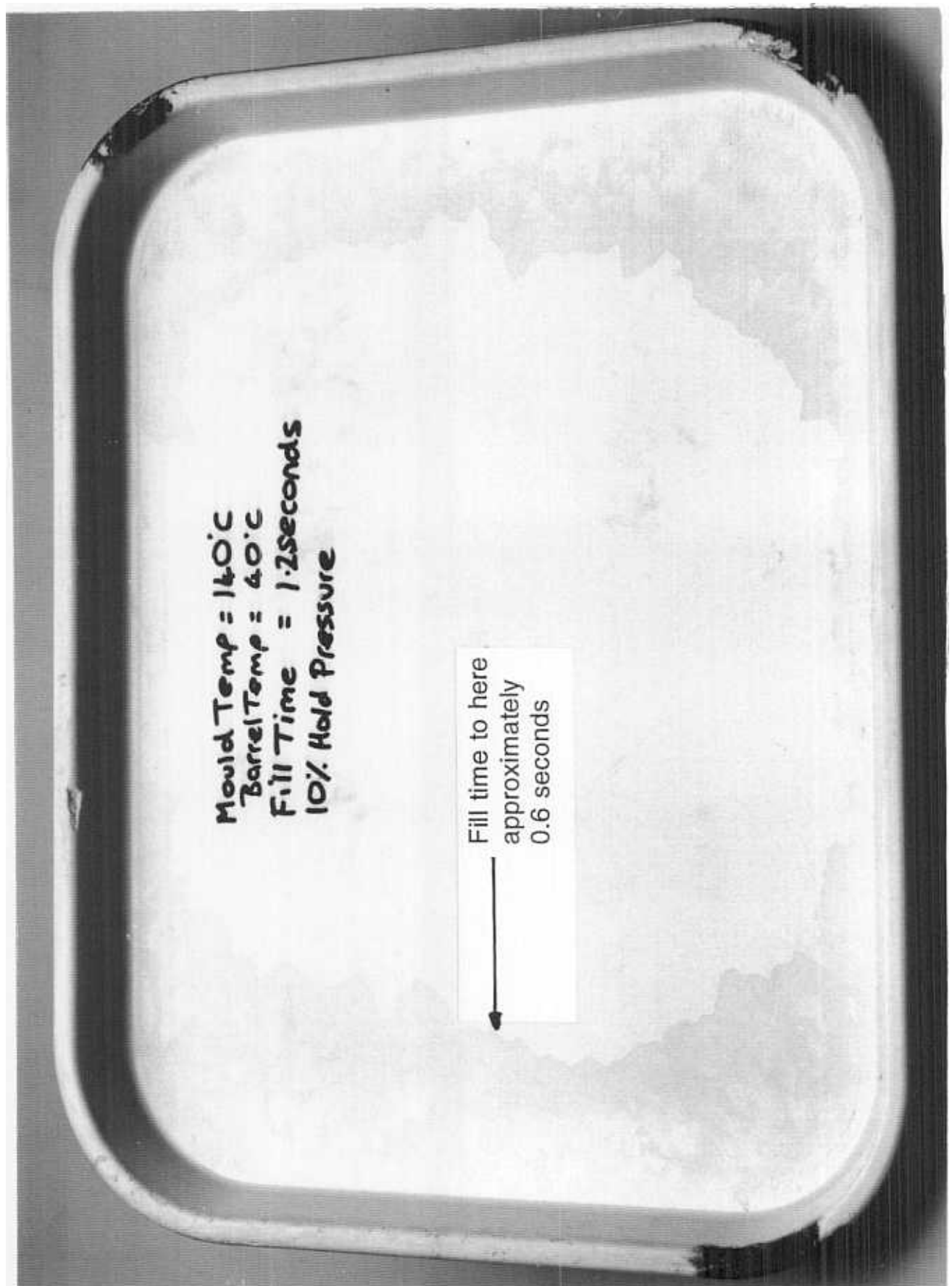


Fig.10 Photograph of centre gated tray moulding showing glossy surface finish in the central region near to the gate and a poor matt surface finish at the edge due to stick-slip flow caused by cure at the end of inhibition.

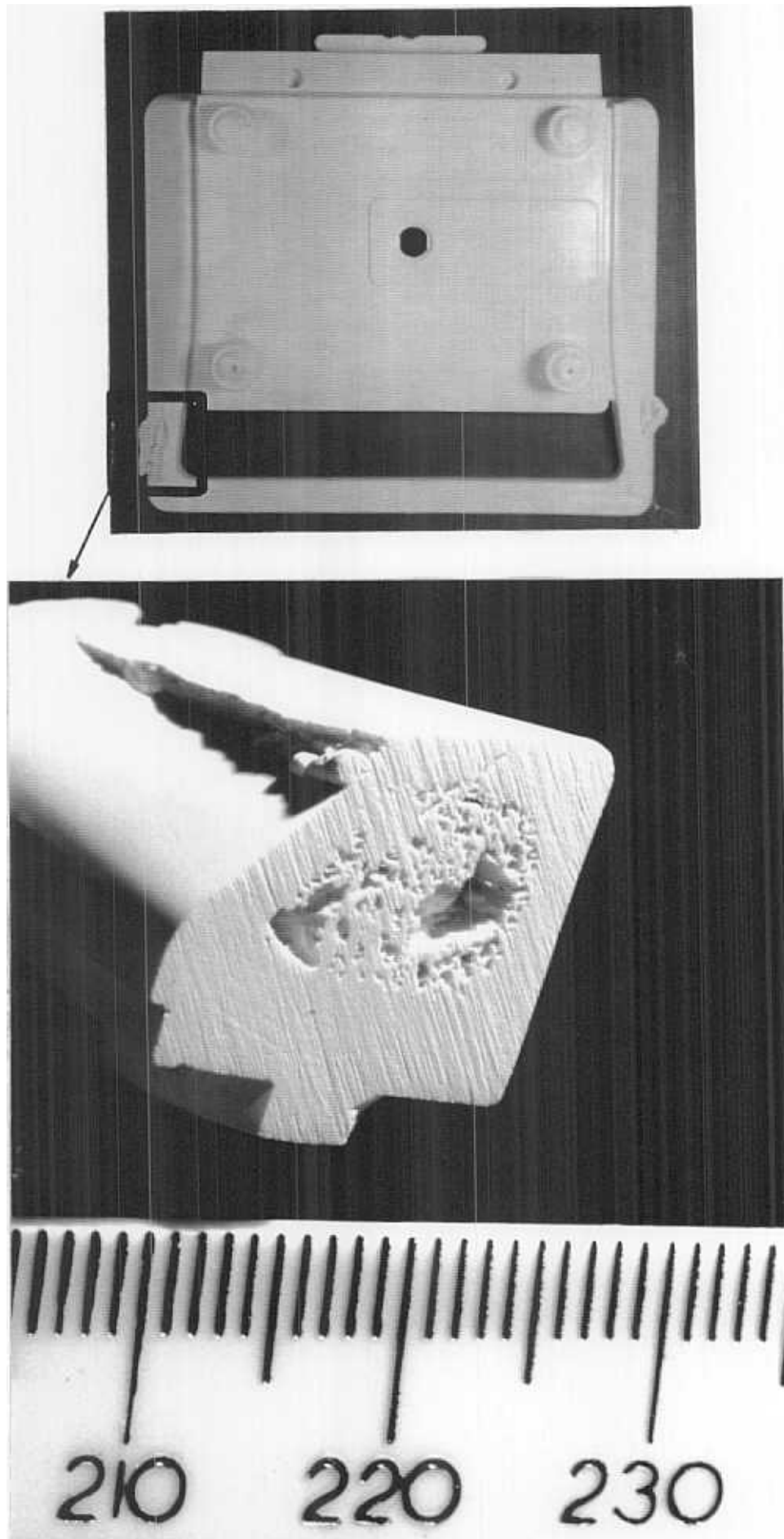


Fig.11 Sandwich toaster moulding showing surface rupture and resulting internal porosity due to short in-mould cure time and consequent under-cure