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Modelling the Inhibition Cure Behaviour of Unsaturated Polyester Moulding Materials

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ABSTRACT

Much work has been carried out on measuring the curing behaviour of unsaturated polyester moulding compounds [3-12]. However, previous modelling work has usually ignored the effect that cure-preventing inhibitors, which are added for increased storage life, have on the curing behaviour of the material since their effects were considered negligible at moulding temperatures.

An analysis method has been developed for determining the inhibition behaviour of an unsaturated polyester DMC using DMTA and DSC techniques. Results obtained from the analysis have shown that the inhibition reaction is significant at moulding temperatures, and a surprising correlation between surface finish and inhibition has been identified.

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CONTENTS

1. INTRODUCTION

Unsaturated polyester Dough Moulding Compounds (DMCs) are fast curing systems, with the cure process being thermally activated by the formation of catalyst free-radicals [1]. Inhibitors are usually added to unsaturated polyester DMCs to prevent premature cure thereby extending the storage life of the material before use [2]. Inhibitors added to DMCs sacrificially scavenge cure initiating free-radicals, thus preventing cure until there is an insufficient concentration of inhibitor remaining to mop-up the catalyst free-radicals formed. As the temperature is increased the rate of formation of catalyst radicals becomes greater thus resulting in shorter periods of inhibition.

2. MATERIALS

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 desirable end-product properties (eg. high modulus and high operating temperatures over 100°C).

The experimental polyester materials investigated were based on an injection moulding grade of a BIP Plastics Ltd unsaturated polyester dough moulding compound, reference L7049 [1]. The materials differed from the standard L7049 DMC grade 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 (PMCE 379) consisted of approximately:

23 wt% of unsaturated polyester in styrene containing 0.0053 wt% hydroquinol and 0.001 wt% para-tertiary-butyl-catechol inhibitors, 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).

During the investigation three variations of the above base material (PMCE 379) were prepared as follows:

L7049/1. The above base material with a 'standard addition' of 0.13 wt% butylatedhydroxytoluene inhibitor to increase the material's shelf-life to approximately 3 months at room temperature.
PMCE 381. The base material with twice (x2) the 'standard addition' of added inhibitor (0.26 wt% butylatedhydroxytoluene).
L7049/2. The base material with four times (x4) the 'standard addition' of added inhibitor (0.52 wt% butylatedhydroxytoluene).

These materials were compounded in a 'Z' Blade mixer at room temperature. The benzoyl peroxide catalyst and inhibitor, where added, were pre-mixed before the addition of the filler materials to ensure as even a distribution of inhibitor and catalyst as possible.

3. TEST METHODS

3.1 GENERAL

Differential Scanning Calorimetry (DSC) and Dynamic Mechanical Thermal Analysis (DMTA) test methods were used to monitor the cure of unsaturated polyester DMCs. DMTA measurements using a shear deformation test geometry were used to provided information on mechanical property changes, and DSC measurements were made to determine the heat released during cure.

3.2 DMTA

DMTA measurements were carried out using a Polymer Laboratories DMTA. DMTA measurements were used to monitor changes in modulus (G' and G") and the damping behaviour (tan δ) at various isothermal temperatures and during constant heating rate experiments. The equipment was fully automated and controlled via computer software which was used to set the test frequency, strain and temperature profile.

A small sample of the DMC slurry (3-5g) was clamped between two circular 15mm diameter shear plates with a separation of 1mm. Excess material was removed from outside the clamping assembly to prevent errors due to the deformation of this material. A calibrated thermocouple was inserted into the sample through a small hole placed in the outer shear stud to monitor the temperature of the sample, since the sample temperature was known to lag behind the furnace temperature which is measured during testing.

All DMTA experiments were carried out using a frequency of 10 Hz to ensure a sufficient number of data points were collected during each experiment. The peak displacement of the shear deformation was kept to the lowest value of 16µm to minimise any debonding from the shear studs that may have occurred due to the sample deformation.

3.3 DSC

A Perkin-Elmer Power Compensated DSC II was used in the analysis 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 to determine the inhibition kinetics for the cure reaction of the PMCE 381 (x2 inhibitor) and PMCE 379 (no added inhibitor). Isothermal DSC measurements were used to cross-check kinetic data obtained from the constant heating rate experiments and to determine the inhibition kinetics for the standard material, L7049/1. 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.

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

4 RESULTS

4.1 DMTA RESULTS

Constant heating rate DMTA results show that the cure behaviour can be split into three regions, Figure 1. The first region, I, shows the modulus of the material decreasing as the temperature increases, thus indicating that the cure reaction is prevented due to the action of the inhibitor. The second region, II, following the inhibition period displays a slow increase in modulus. Region II is considered to represent the final stages of inhibition where the inhibitor becomes less effective at mopping up the reactive free radicals, thus resulting in partial cure. The final stage, III, represents cure at which point the inhibitor is exhausted and the cure process proceeds unhindered.

Isothermal DMTA measurements carried out on the materials containing differing inhibitor concentrations show that increasing the level of inhibitor results in an increased inhibition period, Figure 2. This result confirms that the inhibition period observed in constant heating rate experiments is not attributable to the slow formation of catalyst radicals at low temperatures but to the action of the inhibitor.

4.2 DSC RESULTS

DSC measurements carried out under isothermal and constant heating rate conditions have all shown the period of inhibition followed by cure, as demonstrated in the DMTA results in Figure 3. During inhibition it can be seen that little or no exothermic or endothermic heat is produced as a result of the inhibitor - catalyst reaction, indicating that the energy required to form the phenyl radicals is balanced by the 'mopping-up' reaction of the inhibitor. A comparison of DSC and DMTA results show that the inhibition time obtained from DSC is in agreement with that found in DMTA measurements when using an onset method to determine the end of inhibition (as described in section 5.1), Figure 3. DSC allows faster heating rates and greater temperature control than DMTA. As comparable inhibition times were obtained from the two techniques, DSC was used as the prefered technique for following inhibition.

Good reproducibility was found between DSC experiments when using samples taken from different locations within the main batch, Figure 4. As only 30 mg of material per test was required for DSC this indicated a good homogenous distribution of constituents, showing little disadvantage of using a small sample size.

5. INHIBITION KINETICS

5.1 EXPERIMENTAL DETERMINATION OF INHIBITION TIMES AND TEMPERATURES

Inhibition times from isothermal measurements and the inhibition temperature from constant heating rate experiments were determined using an onset method. The onset method can be applied to both DSC and DMTA data and involves the drawing of two straight lines. The first line is drawn as a best fit to the data from the start of the test during inhibition, and the second straight line is drawn through the steepest gradient of the data during cure, as shown in Figures 5 and 6. The intercept of the two lines was deemed to be the end of the inhibition reaction and the start of cure. The inhibition time is taken from the start of the test to this intercept point. In the case of constant heating rate experiments this intercept point is taken as the inhibition (or onset) temperature. This method simplified the reaction into two separate stages thus neglecting the intermediate phase of a combination of cure and inhibition. However, since the intermediate stage is relatively short lived compared to the inhibition and cure stages the errors involved were considered to be small.

5.2 MODELLING OF INHIBITION KINETICS

The kinetics of the inhibition reaction have been analysed using the following n^{th} order rate equations.

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

where: α is the degree of conversion ($0 \leq \alpha \leq 1$)
n is the order of reaction
t is the time
K_r is the rate constant and is given by

$$K = A \exp -\frac{E_a}{RT} \quad (2)$$

where: A is a pre-exponential factor
E_a is the activation energy
R is the gas constant
T is the temperature (K)

The only available information for the inhibition reaction from DSC and DMTA measurements is the completion point determined using the onset method described earlier. To model such a reaction with a termination a zeroth order model is required, and was therefore used herein. For non-zeroth order reactions which do not exhibit termination but an exponential decay type behaviour, it is necessary to have data on intermediate conversion points to determine the order of the reaction.

For a zeroth order reaction

$$K_r = \frac{\alpha}{t} \quad (3)$$

Therefore when the inhibition reaction is complete, ie. $\alpha = 1$

$$K_r = \frac{1}{t_i} \quad (4)$$

where t_i is the inhibition time

Thus for experiments carried out at different isothermal test temperatures the activation energy E_a and pre-exponential factor A for the zeroth order reaction can be simply obtained from the intercept and gradient of a straight line plot of

$$\ln \frac{1}{t_i} \text{ against } \frac{1}{T}$$

5.3 INHIBITION KINETICS FROM CONSTANT HEATING RATE DSC

The temperatures at which the inhibition reaction finished during constant heating rate experiments were determined from the cure onset method described in section 5.1. The temperatures obtained for the various heating rates were then used to calculate the activation energy E_a and pre-exponential factor A of the inhibition kinetic model (equation 6) by following the procedure set out in ASTM E 698-79 [14], using the onset temperature as opposed to the peak exotherm temperature referred to in the standard.

Zeroth-order kinetics were derived for the base material (PMCE 379) without added inhibitor (but with inhibitor in the resin system) and the material containing twice the standard addition of inhibitor (PMCE 381) usually added to the polyester DMC system investigated.

For the base material without added inhibitor but containing the small amount of inhibitor in the supplied resin the inhibition reaction kinetics were given by :

$$t_i = \frac{1}{A} \exp\left[\frac{E_a}{RT}\right] \qquad (6)$$

where E_a = 124.9 kJ mol^{-1}
A = 8.27 x 10^{15} s^{-1}
t_i = inhibition time, min
R = Gas Constant
T = Temperature, K

For the material containing an addition of inhibitor equal to twice the standard addition (PMCE 381), the inhibition reaction kinetics were given by the same equation but with the differing constants below :

E_a = 145.8 kJ mol^{-1}
A = 4.95 x 10^{18} s^{-1}

These values have been used to calculate cure onset temperatures for constant heating rate DSC tests and have been presented along with experimentally determined values in Table1

Table 1. Comparison of experimental and kinetically determined onset temperatures for constant heating rate DSC

Heating Rate (K / min)	Onset temperature from kinetics for PMCE379: no inhibitor added (K)	Experimental onset temperature for PMCE379 (K)	Onset temperature from kinetics for PMCE381: x2 inhibitor loading (K)	Experimental onset temperature for PMCE381 (K)
2.5	359.0	358.0	-	-
5.0	363.3	363.5	369.7	368.5
10.0	368.5	369.6	373.7	374.0
20.0	376.7	376.7	379.3	379.0
40.0	-	-	385.9	384.4

It can be seen from Table 1 that, as expected, the values of onset temperature are higher in the material containing twice the standard addition of inhibitor compared with the material with only the small amount of inhibitor contained in the resin. The calculated values of onset temperature were close to the experimental values, thus indicating a good fit by the zeroth order equation to the data.

The reaction kinetics obtained with constant heating rate DSC were evaluated by calculating the times for the inhibitor to be consumed (cure onset) under isothermal conditions and comparing the results with experimentally determined onset times for both materials, Table 2. The calculated isothermal reaction times for both materials were found to be in generally good agreement with the experimental evaluations carried out thus demonstrating the degree of reliability of the model for these materials.

Table 2. Comparison of measured and calculated isothermal inhibition times using kinetic modelling based on constant heating rate experiments

Temperature (°C)	PMCE 379 calculated onset time from non-isothermal DSC data	PMCE 379 measured isothermal onset time	PMCE 381 calculated onset time from non-isothermal DSC data	PMCE 381 measured isothermal onset time
21	20.7 days	22 .0 days	5.8 months	
30	4.5 days		29.7 days	
40.6	20.4 hours	19.8 hours	4.2 days	
50	5.1 hours		19.8 hours	
60	75.4 mins	73.5 mins	3.9 hours	
70	20.3 mins	22.0 mins	50.4 mins	
80	5.9 mins	6.1 mins	11.8 mins	12.4 mins
85	3.2 mins		5.9 mins	5.9 mins
90	1.8 mins		3.0 mins	
95	62.0 secs		96.0 secs	106 secs
100	36.0 secs		49.7 secs	59 secs

The kinetics for the material without added inhibitor, PMCE 379, when extrapolated to room temperature were found to show good agreement with the observed shelf-life of the material. The shelf-life of the material was determined experimentally by placing a small pot of the material in a temperature controlled room at 21°C and probing the sample at regular intervals with a rod. The shelf life of the material (cure onset time) was easily identifiable since the viscosity of the material noticeably increased as a result of the early stages of cure. The value for the shelf-life of this material by the use of the probe technique was found to be 22 days which compared with the calculated value of 20.7 days. Since the difference between the experiment and calculated cure onset time was only 6% for this large extrapolation the kinetic model was considered suitable for the prediction of material shelf-life. At the other end of the temperature range, for the determination of inhibition times at moulding temperatures (150°C) a value of 0.3 seconds was obtained using the kinetic model.

This value of 0.3 seconds is considered reasonable since moulding practice for the standard unsaturated polyester DMC requires short injection times of less than 1 second to provide mouldings with good surface finish [16].

The isothermal onset times calculated for the material containing twice the standard addition of inhibitor, PMCE 381, also displayed reasonable agreement with experimental values, Table 2. It is interesting to note that the effect of the added inhibitor is to significantly increase the shelf life of the material whilst not so significantly affecting the onset times at moulding temperatures. This result was once again found in moulding practice where similar processing conditions can be successfully used for materials containing different levels of added inhibitor.

5.4 INHIBITION KINETICS FROM ISOTHERMAL DSC

Isothermal DSC was used to evaluate the inhibition reaction kinetics of the standard (L7049/1) and x4 inhibited (L7049/2) DMC slurry materials. Isothermal DSC was the preferred method since analysis of the results is straight forward compared with that of the non-isothermal method. The inhibition reaction kinetics have been found to be reasonably described by the same zeroth-order type reaction used in constant heating rate DSC, the reaction time for completion being given by equation 6.

For the DMC slurry containing a standard loading of inhibitor (L7049/1) the inhibition kinetics were given by:

$$E = 140.4 \text{ kJmol}^{-1}$$
$$A = 8.52 \times 10^{17} \text{ s}^{-1}$$

For the DMC slurry containing an addition of inhibitor equal to four times the standard addition (L7049/2) the inhibition reaction kinetics were given by:

$$E = 152.0 \text{ kJmol}^{-1}$$
$$A = 3.20 \times 10^{19} \text{ s}^{-1}$$

Table 3. Comparison of experimental and calculated isothermal inhibition times for the standard and x4 inhibitor materials

Temperature (^{o}C)	Standard material x1 inhibitor measured onset time	Standard material x1 inhibitor calculated onset time	x4 inhibitor material measured onset time	x4 inhibitor material calculated onset time
70	37.0 mins	45.5 mins	82.7 mins	80.8 mins
75	18.2 mins	18.2 mins	47.5 mins	37.6 mins
80	12.5 mins	11.3 mins	15.4 mins	17.7 mins
85	6.0 mins	6.0 mins	8.2 mins	8.6 mins
90	2.5 mins	2.7 mins	3.9 mins	4.2 mins
95	-	-	109.3 secs	130 secs
100	-	-	60.0 secs	63.3 secs
105	-	-	29.2 secs	26.0 secs

Table 3 shows that a reasonable fit of the experimental data has been achieved using the zeroth-order reaction kinetic model. Extrapolation of the data to room temperature and moulding temperatures can be seen in the summary table, Table 4, showing calculated inhibition times for all four materials investigated.

The summary table, Table 4, shows very different shelf-life times for each of the materials, with shelf-life increasing with increasing inhibitor addition. However, it can also be seen that the materials display the same inhibition times (within experimental error) at temperatures above approximately 120°C. This observation suggests that the inhibitors in the resin have a dominant effect at high temperatures compared with the inhibitor added to the material to extend shelf-life. Since the high temperature end is unaffected by the addition of shelf-life increasing inhibitor it can be concluded that adding extra inhibitor will not affect the mouldability of the unsaturated polyester DMC. This is indeed the case as it is found in practice that a material containing no added inhibitor can be moulded using the same injection rate and pressures as is used for the standard DMC material, without any detrimental effects on moulding quality. However, it is also found in practice that adding extra inhibitor increases the in-mould cure time. This would indicate that the extra addition of inhibitor consumes some of the benzoyl peroxide catalyst during inhibition and thus less catalyst is available for cure resulting in a slower cure time.

Table 4. Calculated inhibition times for all four test materials and relating to processing stage

Processing region	Temperature (°C)	PMCE 379 no added inhibitor cure onset time	L7049/1 standard material cure onset time	PMCE 381 x2 inhibitor cure onset time	L7049/2 x4 inhibitor cure onset time
Storage	20	24.0 days	4.7 months	7.1 months	14.6 months
	25	10.4 days	53 days	2.6 months	5.1 months
	30	4.5 days	21 days	29.7 days	56.1 days
Barrel	40	22.4 hours	3.5 days	4.7 days	8.2 days
	45	10.5 hours	1.5 days	1.9 days	3.3 days
	50	5.1 hours	16 hours	19.8 hours	1.3 days
	55	2.5 hours	7.2 hours	8.7 hours	13.6 hours
	60	1.2 hours	3.3 hours	3.9 hours	5.9 hours
Nozzle	70	20.3 mins	45.5 mins	50.4 mins	1.2 hours
	80	5.9 mins	11.3 mins	11.8 mins	15.8 mins
	90	1.8 mins	3.0 mins	3.1 mins	3.8 mins
	100	36.0 s	52.2 s	50 s	59 s
	110	12.6 s	16.0 s	14.6 s	16.4 s
	120	4.6 s	5.2 s	4.5 s	4.9 s
Mould	140	0.7 s	0.7 s	0.5 s	0.5 s
	150	0.3 s	0.25 s	0.2 s	0.2 s

5.5 FINAL INHIBITION MODEL

The results presented above have demonstrated that the zeroth order single rate constant models developed for each material are adequate for the prediction of inhibition times of each material where the concentrations and types of inhibitor are not known. The results obtained for the inhibition kinetics, Table 4, show that the inhibitor in the resin, which is different from that added with the catalyst, has a greater effect at high temperatures. For material design purposes a model needs to be developed to split the two inhibitor systems. Splitting the two systems will allow design of materials with both the required shelf life characteristics and the required processing characteristics at mould temperatures.

Since the inhibition kinetics of the resin inhibitor system are known, i.e. from testing the material without added inhibitor (PMCE 379), the only unknown is the kinetic behaviour for the added inhibitor on its own. The activation energy and pre-exponential factor for the added inhibitor have been calculated by subtraction of the inhibition times for the material without added inhibitor (PMCE 379) from the x4 inhibitor material (L7049/2) and plotting $\ln(1/t_d)$ against $1/T$, where t_d is the difference in inhibition times for the two materials. This gave the following constants :

No added inhibitor	$E_1 = 124.8$ kJ/mol	$A_1 = 8.27 \times 10^{15}\ s^{-1}$
x4 inhibitor addition	$E_2 = 163.6$ kJ/mol	$A_2 = 5.37 \times 10^{19}\ s^{-1}$

This assumes that the total inhibition is additive and can be represented by:

$$t_d = \frac{1}{A_1} \exp\left[\frac{E_1}{RT}\right] + \frac{1}{A_2} \exp\left[\frac{E_2}{RT}\right] \qquad (7)$$

where t_d is the total inhibition time.

If the inhibitor concentration is proportional to the inhibition time i.e. doubling the added inhibitor doubles the inhibition time then the total reaction time will be given by :

$$t_d = \frac{X}{A_1} \exp\left[\frac{E_1}{RT}\right] + \frac{Y}{A_2} \exp\left[\frac{E_2}{RT}\right] \qquad (8)$$

where: X is the concentration of inhibitor (hydroquinol and paratertiary-butyl-catechol) added to the resin relative to the investigated material (PMCE 379) .
Y is the fraction of inhibitor (butylatedhydroxytoluene) in the resin relative to the experimental material L7049.2 (ie. in this case the material measured was the x4 inhibitor system therefore if a x2 system is required Y=1/2)

Table 5 shows that the final inhibition model appears to give an adequate prediction of inhibition times at high and low temperatures, with results in the middle temperature range displaying less accuracy. Although less accurate in the mid-temperature range the model is considered to be useful for material design and is considerably more accurate and convenient than a trial and error approach.

Table 5. Inhibition times calculated from the final inhibition model based on the zero and x4 inhibitor systems

Temp. (°C)	Standard material (x1 inhibitor) single rate constant inhibition time	Standard material (x1 inhibitor) inhibition time calculated from final inhibition model (8)	x2 inhibitor material single rate constant inhibition time	x2 inhibitor material inhibition time calculated from final inhibition model (8)
30	21 days	18.6 days	1.0 months	1.0 months
40	3.5 days	2.7 days	4.7 days	4.5 days
50	16.0 h	11.1 h	19.8 h	17.3 h
60	3.3 h	2.2 h	3.9 h	3.2 h
70	45.5 min	30.7 min	50.4 min	41.1 min
80	11.3 min	7.9 min	11.8 min	10.0 min
90	3.0 min	2.2 min	3.1 min	2.7 min
100	52.2 s	42.2 s	50.0 s	48.4 s
110	16.0 s	14.2 s	14.6 s	15.7 s
120	5.2 s	5.1 s	4.5 s	5.5 s
140	0.7 s	0.7 s	0.5 s	0.8 s
150	0.25 s	0.3 s	0.2 s	0.3 s

6. FURTHER DISCUSSION

Since polyester DMC mouldings are often used for domestic articles such as electrical appliance casings (eg. electric toasters) the over-riding requirement is often 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 of the material on the surface of the moulding could occur. It is suggested that this behaviour causes the matt surface with flow marks as seen on the outside of the tray moulding in Figure 7. 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. This effect can be seen in the tray moulding where the surface finish is good in the centre of the tray corresponding to a fill time of up to approximately 0.6 seconds. Outside this region, corresponding to longer fill times, the surface is poorer and it is suggested that this is due to the material no longer being inhibited resulting in an increase in its viscosity. The calculated inhibition time of 0.7 seconds for 140°C therefore agrees well with injection moulding practice indicating that fill times should be under 1 second in order to obtain good quality surface finish mouldings.

7. CONCLUSIONS

The curing behaviour of an unsaturated polyester Dough Moulding Compound (DMC) can be kinetically modelled in terms of an inhibition period and a curing period. During inhibition there is no increase in the viscosity of the unsaturated polyester DMC. Changes in the viscosity of DMCs during injection moulding can therefore be modelled in terms of the temperature dependence only, provided that filling occurs within the inhibition stage of cure.

A good kinetic model has been obtained for calculating the inhibition times of unsaturated polyester materials using the cure onset method. The kinetic model shows that the added inhibitor can increase the shelf-life of the DMC whilst not affecting the inhibition time at mould temperatures. This result suggests that the inhibitors present in the resin prior to dough formulation are dominant at moulding temperatures. The kinetic model developed for the two inhibitor system can therefore be used to determine inhibitor additions required to independently control both the low temperature and high temperature cure onset times.

The inhibition period can be related to the surface finish of a DMC moulding. To obtain a good surface finish the mould cavity must be filled during the inhibition stage of cure, since a rapid change in the viscosity of the material during the cross-linking phase of cure results in stick-slip flow.

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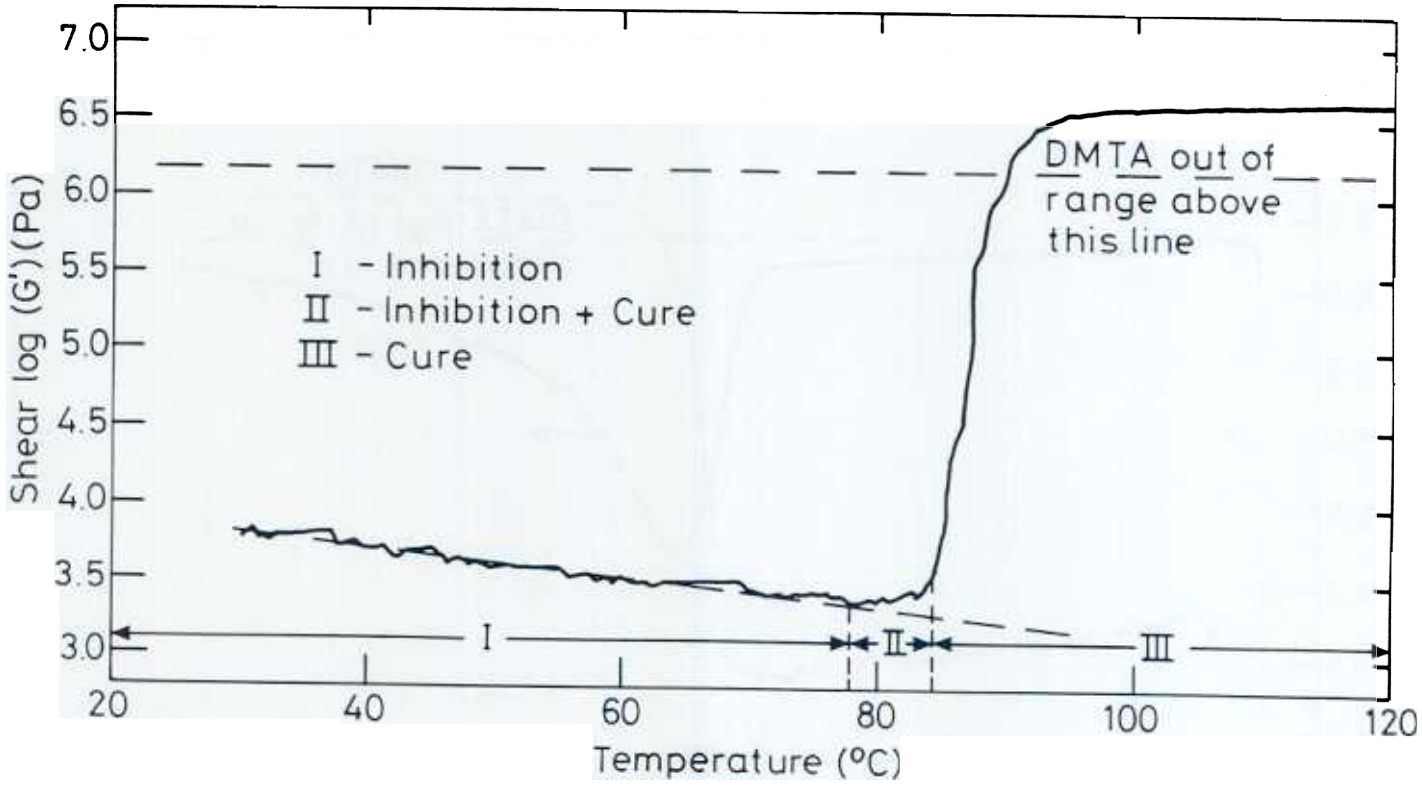

Fig.1 Typical DMTA test on PMCE 379 heating at 2°C/min

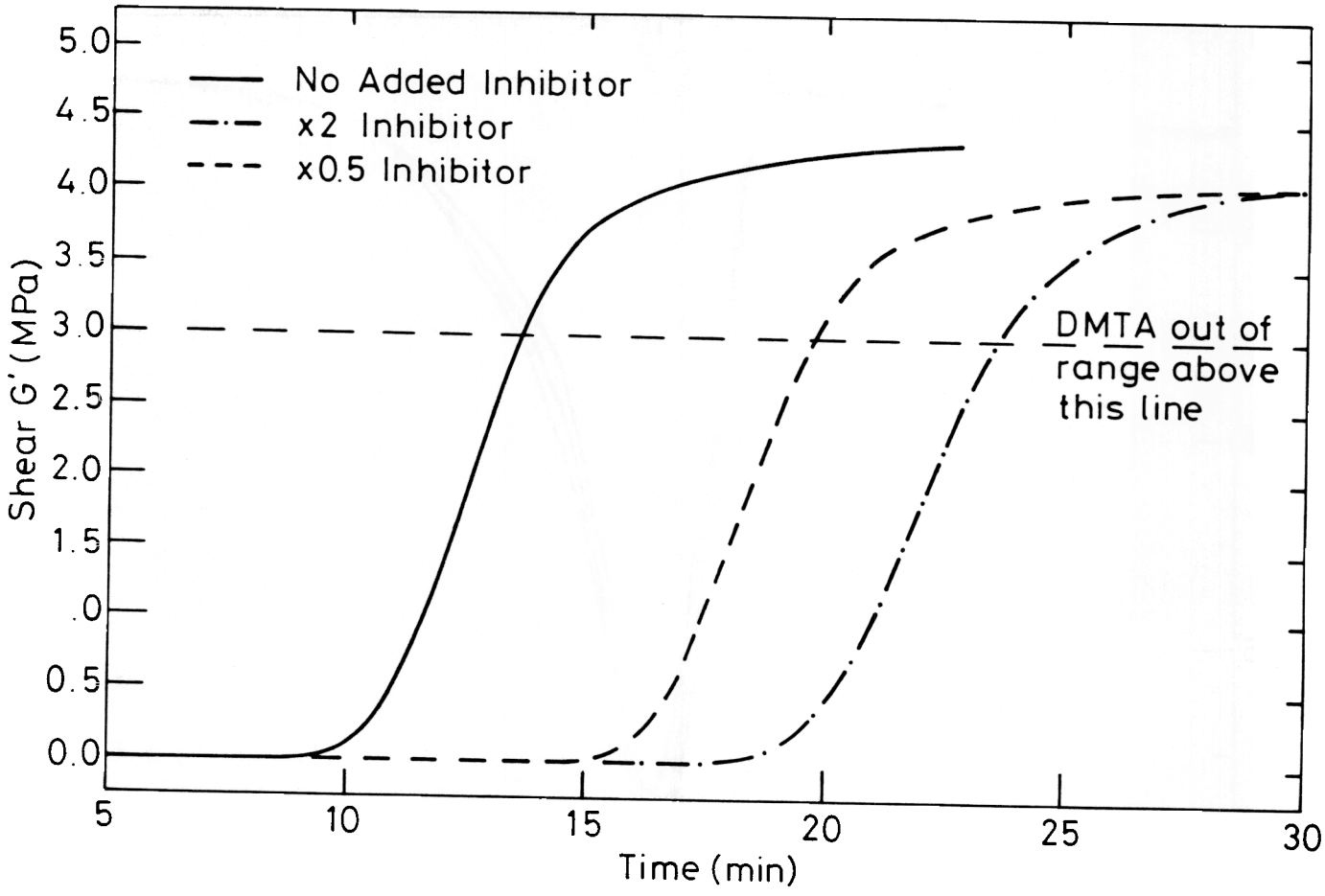

Fig.2 Effect of inhibitor loading on cure behaviour at 80°C

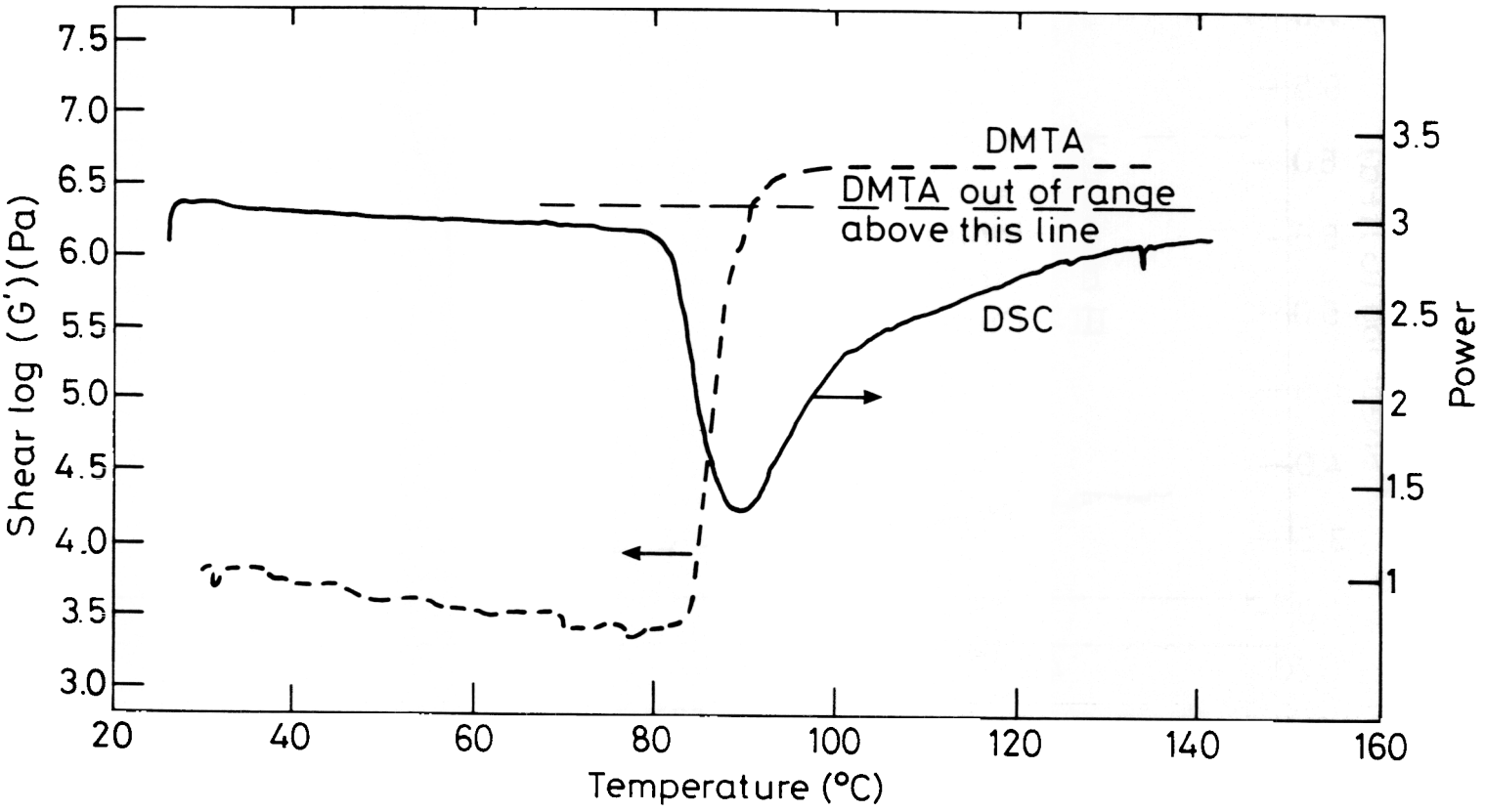

Fig.3 Comparison of DSC and DMTA for characterising the curing haviour of polyester materials

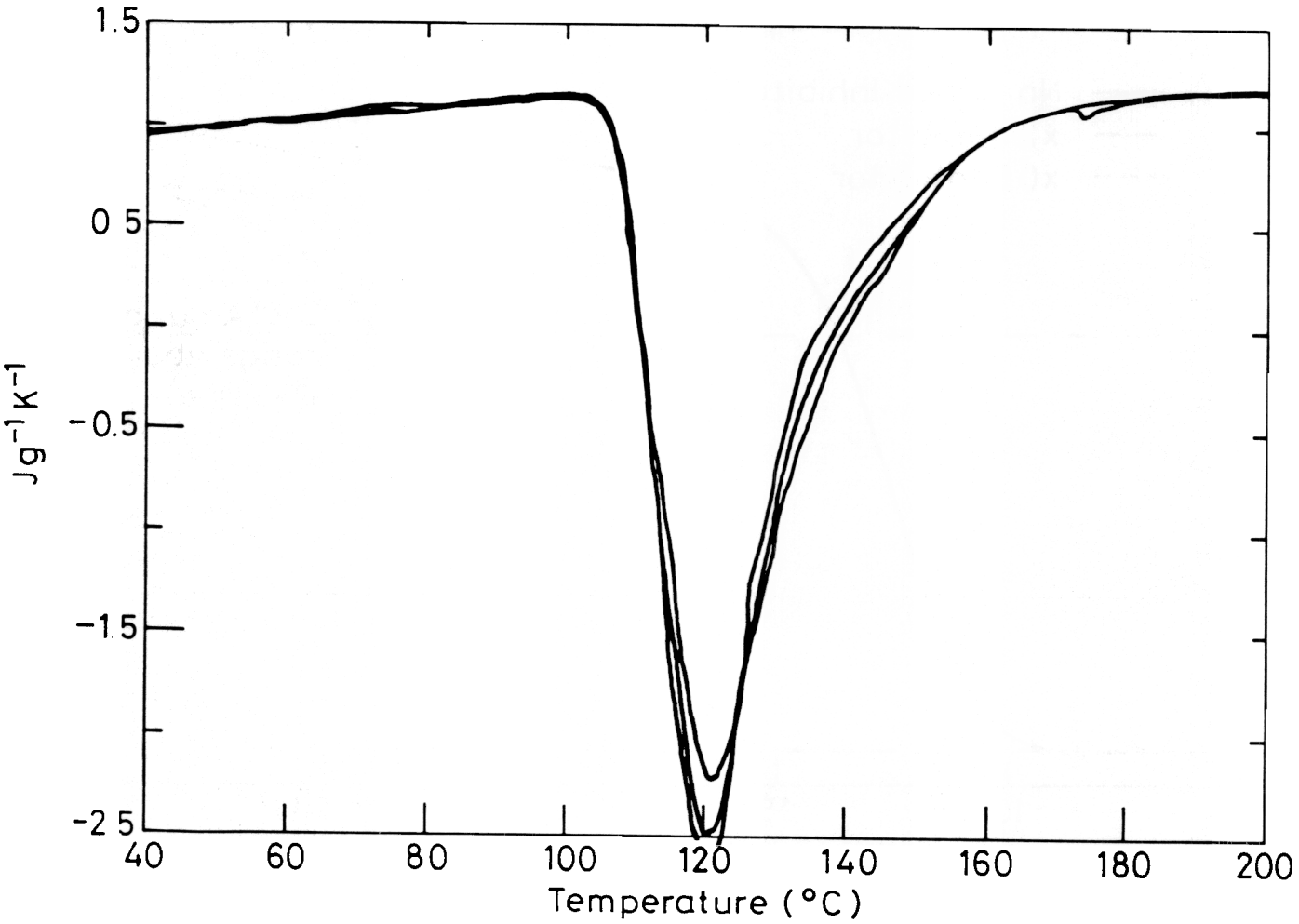

Fig.4 Reproducibility of DSC measurements on standard material (x1 inhibitor)

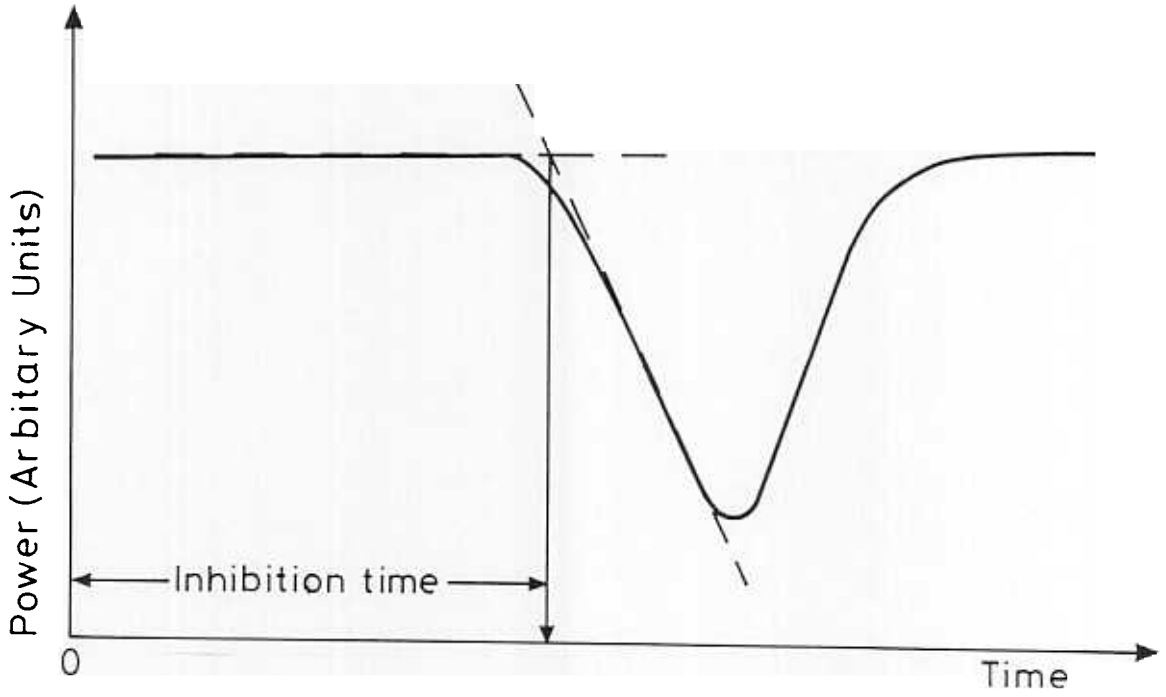

Fig.5 Schematic representation of isothermal DSC data showing the onset method to determine the inhibition time

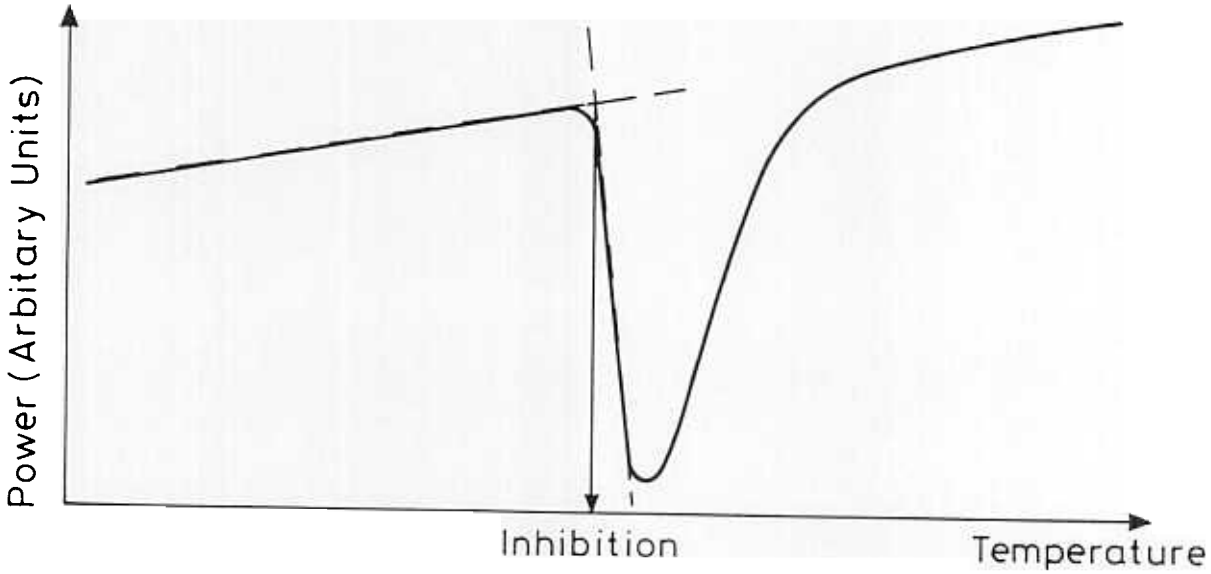

Fig.6 Schematic representation of constant heating rate DSC data showing the onset method to determine the inhibition (cure onset) temperature

Fig 7 Photograph of centre gated tray moulding showing glossy surface finish the central region near to the gate and a poor matt surface finish at the edge due stick-slip flow caused by cure the end of inhibition