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THERMOKINETICS AND RHEOLOGICAL PROPERTIES OF POLYURETHANE REACTION INVOLVING A NEW POLYOL

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ABSTRACT

Kinetics and thermal properties of a polyurethane reaction involving a new polyol were obtained by DSC. The reaction was second order and the heat of reaction was 67.38 J g^{-1}. The specific heat of the reaction was not constant throughout the experiment, passing through both a maximum and a minimum. Total heat production at various temperatures, the time required to reach the selected degrees of conversion at various temperatures, adiabatic temperature rise, adiabatic viscosity and isothermal viscosity were all determined.

INTRODUCTION

Mathematical models for reacting systems are usually based on knowledge of the kinetics of the reaction, i.e. the time–temperature dependence of the reaction, thermal properties (which include the specific heat and heat of reaction) and the rheological properties, and their variations with temperature and degree of cure. The kinetics of a reaction constitutes one of the most important outward manifestations of the course of the reaction, because the average molecular weight distribution of the polymer produced, or kinetic observations such as rates and order of the reaction, are a consequence of basic features of the reaction.

Bulk polymerization reactions are usually exothermic, so the reaction exotherm (heat of reaction) is an important parameter for heat transfer characterization of the system. The change in specific heat, which may be considered a measure of the thermal energy storage capacity of a substance, is one of the important physical properties to be considered when describing a reacting system. Reaction viscosity is sensitive to concentration and molecular weight of the polymer formed and to the reaction temperature. An understanding of the rheology of a reacting system, and the parameters influencing it, is necessary before viscous behaviour can be studied and modelled.

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Different experimental techniques have been developed for studying the reaction kinetics. The kinetics of polyurethane cure has been the subject of many recent investigations [1–16]. Differential scanning calorimetry (DSC) has been used by many in both isothermal [17–25] and non-isothermal (dynamic) [22–28] modes to study the cure kinetics and thermal properties of the reacting system. DSC has the advantage of simultaneously yielding kinetic and thermal data.

Isothermal DSC results can be used to derive the heat of reaction and rate of reaction data. Dynamic DSC (non-isothermal) may be used to calculate, in addition, the activation energy of the reaction. Also with dynamic measurements, it is possible to determine the specific heat of the reacting systems as a function of temperature at various levels of cure [23,24]. For these reasons we have selected dynamic measurements. In systems with no autocatalytic effect, the dynamic method is more convenient in the sense that it is more rapid, but there are difficulties in the interpretation of data because time and temperature vary simultaneously. The isothermal method offers the advantage of greater simplicity of data interpretation.

The dynamic DSC method assumes that the reactions follows *n*th order kinetics

$$\mathrm{d}\alpha/\mathrm{d}t = K(T)(1-\alpha)^n \tag{1}$$

where $\mathrm{d}\alpha/\mathrm{d}t$ is the reaction rate (s^{-1}); α is the fractional conversion (dimensionless); $K(T)$ is the specific rate constant at temperature T (s^{-1}) and n is the reaction order (dimensionless).

The temperature dependence of the reaction rate constant, $K(T)$, is assumed to follow the Arrhenius expression

$$K(T) = Z\,\mathrm{e}^{-E/RT} \tag{2}$$

where Z is the pre-exponential factor or Arrhenius frequency factor (s^{-1}); E is the activation energy (J mol^{-1}); R is the gas constant (8.314 J mol^{-1} K^{-1}) and T is the absolute temperature (K).

Substituting eqn. (1) into eqn. (2) and taking logarithms yields:

$$\ln\frac{\mathrm{d}\alpha}{\mathrm{d}t} = \ln Z - E/RT + n\ln(1-\alpha) \tag{3}$$

The above equation is solved with a multiple linear regression of the general formula $Z = a + bx + cy$.

The DSC exotherm is used to measure the basic parameters, $\mathrm{d}\alpha/\mathrm{d}t$ and α, required to solve eqn. (3). The method assumes that the heat evolved in a small time interval is directly proportional to the number of moles reacting during that time. The reaction rate is obtained by dividing the peak height $\mathrm{d}H/\mathrm{d}t$ at temperature T by the total heat of the reaction,

$$\frac{\mathrm{d}\alpha}{\mathrm{d}t} = (\mathrm{d}H/\mathrm{d}t)/\Delta H_0 \tag{4}$$

where ΔH_0 is the total peak area or the theoretical enthalpy.

The fractional conversion is obtained by measuring the ratio of the partial area, ΔH_T at temperature T to the total peak area

$$\alpha = \frac{\Delta H_T}{\Delta H_0} \tag{5}$$

In the numerical procedure used for calculations, the experimental linear scan is approximated by a sequence of equal isothermal steps. This is coupled with the heat balance to calculate the specific heat.

Rheokinetic studies involving isothermal and adiabatic viscosity measurements of a polyurethane reactive system have been reported by many workers [2,4–9,28–32]. However, very little has been reported about the combined analysis of rheological and kinetic data in useful quantitative terms.

The object of this paper is to characterize the kinetics and the thermal and rheological properties of a polyurethane reactive system involving a new polyol (ISRO-polyol) developed by the Indian Space Research Organization.

EXPERIMENTAL

Materials

A catalyzed and chain-extended $A_m + B_n$ type of liquid polyurethane reactive system was used. A_m was a low molecular weight, castor oil based saturated polyester polyol, developed by the Indian Space Research Organization (ISRO) (a patented product used for solid rocket propellent binders). Its hydroxyl plus carboxyl value was 50 and $\overline{M}_n = 2000 \pm 300$. Initial viscosity at 30 °C was 1.4 Pa s and average functionality was 1.7. B_n was toluene diisocyanate (TDI) supplied by Bayer AG and is a mixture of the 2,4- and 2,6-isomers. For synergistic increase in catalytic activity, 0.3 parts of mixed catalyst was used. The ratio of the catalysts used, stannous octanoate and DABCO, was 2 : 1. The chain extender was 1,4 butanediol.

After preliminary trials, and taking into account the inherently low reactivity of secondary hydroxyl groups contained in this polyol and its low functionality, a block ratio of 0.5 : 2.1 : 1.5 reactants were selected for all studies. This made it possible to conduct all the experiments from the liquid reactants to the solid elastomer in a reasonably short period. Identical mixing and sampling were ensured for all experiments.

Procedure

Thermokinetics

An automated Mettler TA 3000 DSC was used to measure the kinetics and thermal properties in the dynamic (non-isothermal) model. A platinum resistance thermometer (Pt 100) was used for temperature and calorimetric calibration. The experimental procedures employed were similar to those described in the literature. Briefly, a drop of the sample of the reactive system (as described above, immediately after mixing) was introduced into the pre-weighed DSC aluminium pan. Hermetic DSC pans were used to minimize losses of volatile materials during the heating of the sample in the DSC cell. The pans were sealed using a hermetic die press. The weight of the sample was determined accurately by differential weighing using a microbalence. The size of the sample ranged from 15 to 20 mg and the temperature was increased linearly at 10 °C min^{-1} from 30 to 300 °C.

At 300 °C, i.e. after 27 min, the reaction was complete since the curve returned to the baseline after a peak. The amount of heat evolved by the reaction was recorded with respect to temperature. For setting the baseline, a DSC curve was recorded using an empty sealed pan instead of the sample. This curve was stored as the baseline reading and retained until the experiment was over. The area under the thermogram (plot of heat flow vs. temperature) was determined by integrating the output signal using an interactive DSC program that was built into the instrument. By this procedure the natural logarithm of the rate constant (ln k), heat production at the start of the reaction (p), reaction time to reach the selected degree of conversion (t), heat of the reaction (ΔH), reaction order (n), activation energy (E_A) and natural logarithm of the frequency factor (Z) are obtained with 95% confidence limits.

The specific heat at constant pressure (C_p) of the reacting system as a function of time (or cure) is determined by the C_p method using a Mettler TA 3000 DSC instrument. The heat flow to the sample measured at constant heating rate is directly proportional to the specific heat of the substance. In order to obtain precise C_p values, a correction needs to be applied for the additional heat flow arising from the difference between the weights of the sample pan and reference pan. With the help of the preliminary blank experiment the correction is automatically made by the instrument. The weights of both the sample and blank pan enter into the calculation together with the C_p function for aluminium. At the same time the blank correction compensates for any asymmetry in the measuring system.

Rheology

Isothermal

Urethane reacting components as described above were mixed well at room temperature (30 °C). Then about 1 cc of the mixed sample was transferred to the plate of the cone-and-plate Brookfield digital viscometer (Model DV II) fitted with a constant temperature bath and recorder [33]. It was allowed to react inside the viscometer, with the viscosity being recorded as a function of time at constant shear rate from the initial liquid reactant to the final solid elastomer stage. Isothermal conditions were maintained at various temperature levels using the constant temperature bath. Further, the small sample size and the long reaction time ensured that the non-isothermal effect due to the heat of reaction could be neglected. Various shear rates (over the range 0.5–50 rpm of the rotor, corresponding to shear rates of 1–100 s^{-1}) were applied over quick succession before any appreciable change in viscosity could take place due to reaction. It was found that the viscosity was independent of the shear rate, so Newtonian behaviour was assumed.

Adiabatic temperature rise

To determine adiabatic viscosity changes, we first detected the adiabatic temperature increase. The experiment was conducted in a thermos flask (the mouth of which was closed with polyurethane foam with a plastic-coated laboratory stirrer and a Chromel–Alumel thermocouple inserted into the flask through this foam). The formulation used was the same as in the previous experiment. The temperature rise in millivolts was recorded using a calibrated recorder.

Adiabatic viscosity

The profile of temperature vs. adiabatic viscosity change was determined using the above adiabatic temperature rise data. A cone-and-plate Brookfield digital viscometer was employed. The adiabatic viscosity change was determined by measuring a number of isothermal viscosities at various temperatures as follows. Adiabatic temperature at a particular time interval was noted until it levelled off. Then the isothermal viscosity was determined by maintaining the viscometer at each of the above adiabatic temperatures corresponding to a particular time. One cubic centimetre of the reaction mixture was drawn from the thermos flask and placed on the plate of the pre-thermostatted viscometer (while withdrawing the sample, the temperature inside the flask was the same as that of the viscometer). Since time and temperature were varied simultaneously, until the latter levelled off, fresh mixing was done for each viscosity measurement and similar experimental conditions and mixing and sampling procedures were maintained.

RESULTS AND DISCUSSION

Figure 1 shows the thermogram of the DSC kinetic experiment conducted in the dynamic mode, with the sample heated from 30 to 300 °C at 10 °C $\min^{-1}$. Initially one endothermic change was observed. This is common for this type of experiment because of the heat capacity of the sample. By the peak integration technique it was found that ΔH_{endo} for this change was 311.05 mJ at a peak temperature of 44 °C. Thereafter exothermic changes

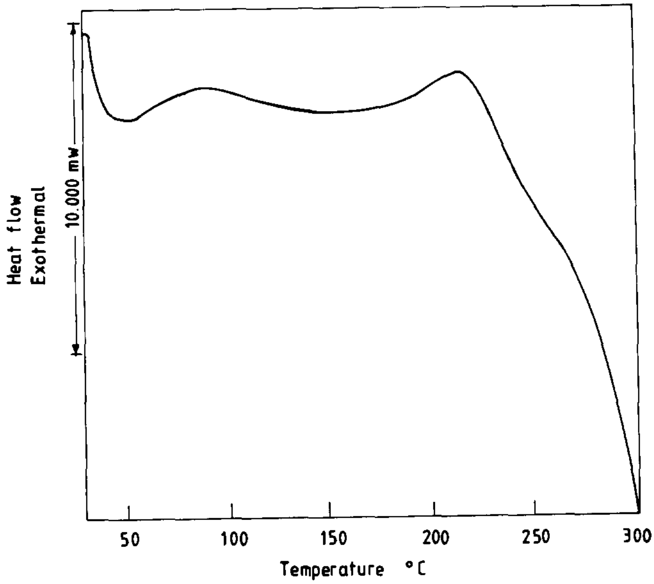

Fig. 1. DSC curve of the polyurethane reaction.

were observed, with maximum exotherm at 214.7 ° C, where the reaction rate was highest. The peak integration technique showed that ΔH_{exo} at this point was 1188.2 mJ. At 300 ° C, after 27 min, it is seen that the reaction is almost complete, since the curve returned to the baseline. The area under this peak is taken as the total heat of the reaction (ΔH_o). The amount of unreacted material at any time and the fractional conversion can be determined from this peak. The amount of unreacted material is given by the area to the right of the ordinate at any particular time or temperature. Similarly, the ratio of the area to the left of the ordinate at any particular time or temperature to

TABLE 1

Urethane polymerization data

Heat of reaction (ΔH_{exo})	67.38 J g^{-1}
Reaction order (n)	2
Activation energy (E_A)	125.73 kJ mol^{-1}
ln z	23.89 s^{-1}
Natural logarithm of rate constant(ln K)	
at 30 ° C	−26.02 s^{-1}
at 50 ° C	−22.93 s^{-1}
at 70 ° C	−20.20 s^{-1}
at 90 ° C	−17.77 s^{-1}
Specific heats (C_p)	
at 50 ° C	1.42 J g^{-1} K^{-1}
at 70 ° C	1.23 J g^{-1} K^{-1}
at 90 ° C	1.08 J g^{-1} K^{-1}

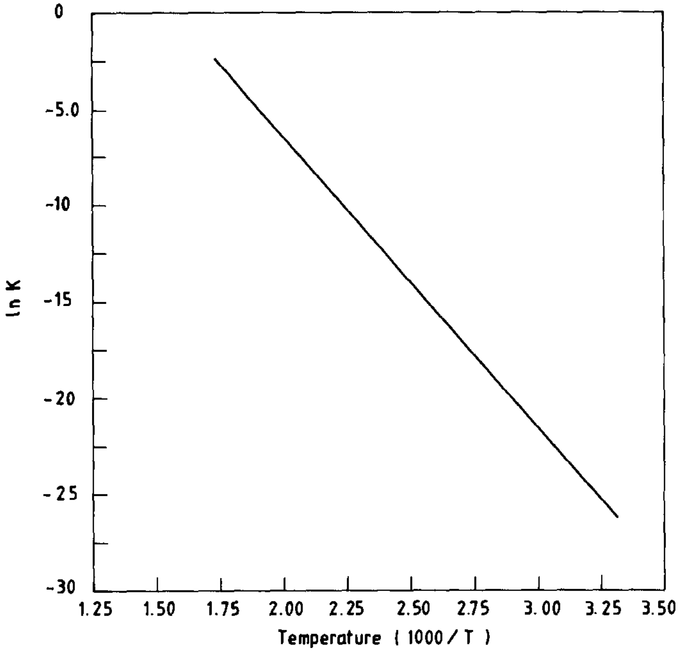

Fig. 2. Arrhenius plot.

the total peak area is the fractional conversion. These are the basic data used to determine the kinetics of the reaction. These kinetic data obtained for the polyurethane having a 0.5 : 2.1. : 1.5 block ratio and involving ISRO-polyol are given in Table 1.

Figure 2 is the Arrhenius plot of the natural logarithm of the rate constant vs. inverse of temperature (K) over the range 30–300 ° C. The slope of this curve is $-E/R$ where E is the activation energy and its intercept is called the reaction rate constant at infinite temperature (or the pre-exponential factor or Arrhenius frequency factor). These kinetics parameters may be used to calculate the course of the reaction at selected isothermal temperatures by using eqns. (1)–(3). Figure 3 is the plot of temperature vs. heat production at the start of the reaction, as well as temperature vs. the reaction time to reach the selected degree of conversion. At higher temperatures, since the reaction rate is higher, the heat production is also higher and the reaction time required to reach the selected degree of conversion is less. This type of analysis suggests use of this system for reactive processing such as reaction injection moulding where mould cycle time is very important. If a process temperature of about 300 ° C is admissible, it can be used in reaction injection moulding because the reaction will be completed at 300 ° C within 1.84 min.

Figure 4 is the plot of time vs. degree of conversion at three different temperatures, 50, 70 and 90 ° C. If we know the rheological properties of the

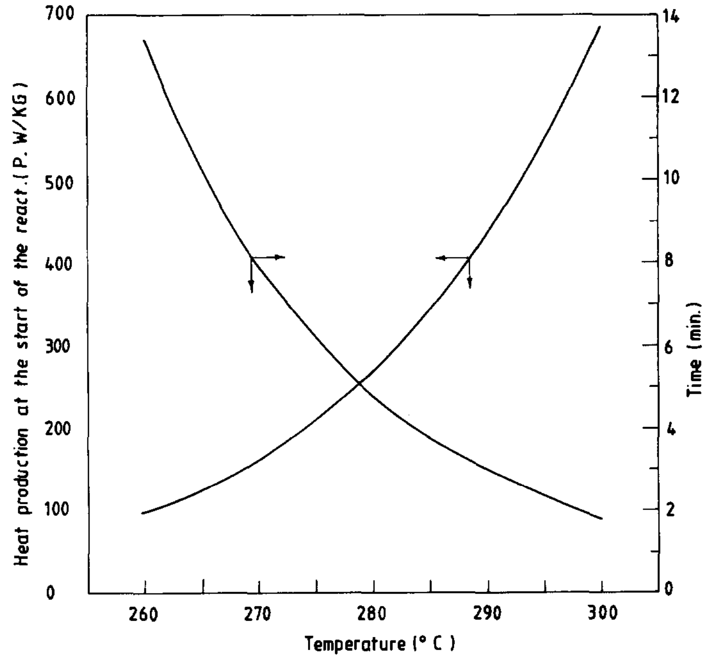

Fig. 3. Plot of temperature vs. heat production and the reaction time taken to reach the selected degree of conversion.

reacting system and the kinetic data over the same temperature range, then it is possible to correlate these two to obtain rheokinetic data. Such a combined analysis is essential for reactor design.

The change of specific heat with respect to temperature or time (they are interchangeable) is shown in Fig. 5. It is seen that the specific heat is not constant during the curing reaction. The maxima and minima that appear in the curve might result from the competition between two factors: one is that the specific heat may rise with temperature and the other that it may fall as the extent of curing rises. These peaks can be associated with transitions like gelation and glass transition which may occur during the reaction.

It may be possible to compute the adiabatic course of the reaction based on the numerical integration of the following equation

$$-\frac{\mathrm{d}T}{\mathrm{d}t} = K_0 \exp(-E_A/RT)(1-\alpha)^n(\Delta H_{\mathrm{spec}}/C_p) \tag{6}$$

where $K_0 \exp(-E_A/RT)(1-\alpha)^n = \mathrm{d}\alpha/\mathrm{d}t$; $(\Delta H_{\mathrm{spec}}/C_p)$ is the total adiabatic temperature rise, and C_p is the mean specific heat during the reaction. As an approximation, a C_p value measured before the onset of the reaction is sufficient.

Viscosity–time profiles of isothermal reaction of the polyurethane system at various temperature levels are shown in Fig. 6. Owing to the low functionality and secondary nature of the hydroxyl groups contained in the

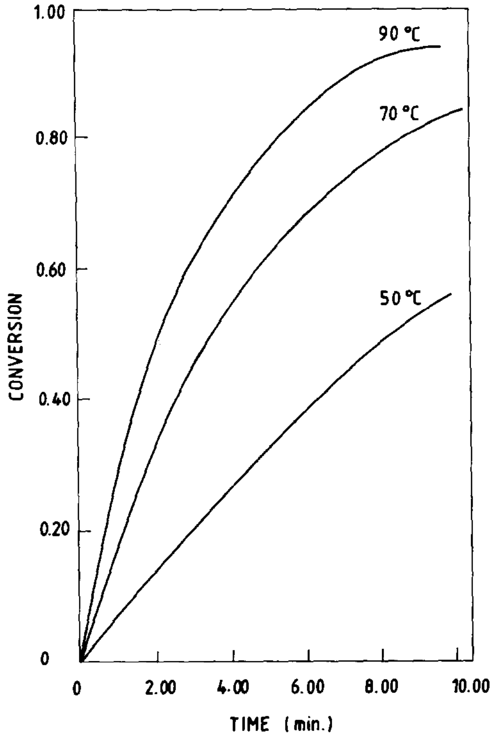

Fig. 4. Plot of time vs. degrees of conversion at various temperatures, calculated from the heat of the reaction.

ISRO-polyol, the reaction is very slow. The viscosity build-up is also very slow until polymerisation is well advanced. This is very typical for polycondensation reactions. In the case of a reacting system which contains only polyol and TDI, the viscosity–time curve shows anomalous behaviour with sudden fall and rise of viscosity at higher degrees of conversion. This effect is found to be temperature dependent but the reason for it is not clear. To check for any shear-thinning effect, various shear rates were applied by changing the rotor speed. It is seen that the viscosity is almost independent of shear rates (Fig. 7).

Figure 8 shows the adiabatic temperature rise and adiabatic viscosity changes of a 0.5 : 2.1 : 1.5 block ratio urethane reactive system. The total adiabatic temperature rise was 87.5 ° C and the reaction was complete within 90 min. For the first 15 min the rate of temperature rise was high; within 15 min a temperature of 77 ° C was reached (from 30 ° C). Thereafter the rate of temperature rise was very low until about 90 min, after which levelled off at 87.5 ° C. The adiabatic viscosity remained low until near the completion of the reaction and then rose rapidly to infinity. This is due to the opposing effects of temperature on the viscosity and reaction rate; after a certain time the latter is dominating so that the viscosity shoots up.

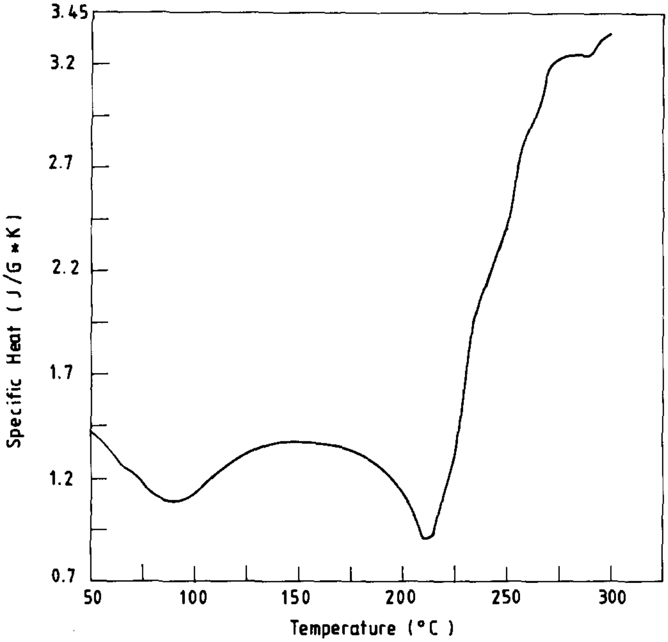

Fig. 5. Changes of specific heat of the reacting system with temperature.

In any actual polymer processing technique, neither isothermal nor adiabatic conditions prevail completely. Since the material must be heated from some ambient temperature to the processing temperature, it may undergo a

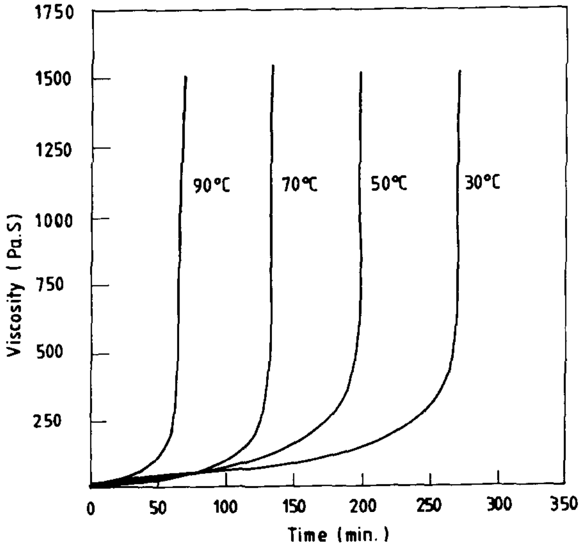

Fig. 6. Isothermal viscosity changes of the polyurethane reactive system.

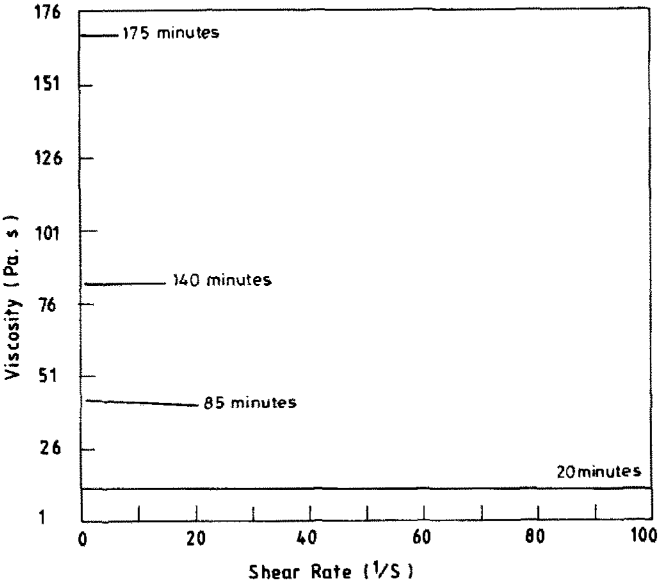

Fig. 7. Viscosity vs. shear rates plot at various levels of cure.

dynamic mode of transformation. It is therefore useful to see what can occur at a high heating rate prior to the attainment of the isothermal processing condition. With a dynamic experiment mode, as described above, it is possible to follow the reaction and determine whether such heating to the

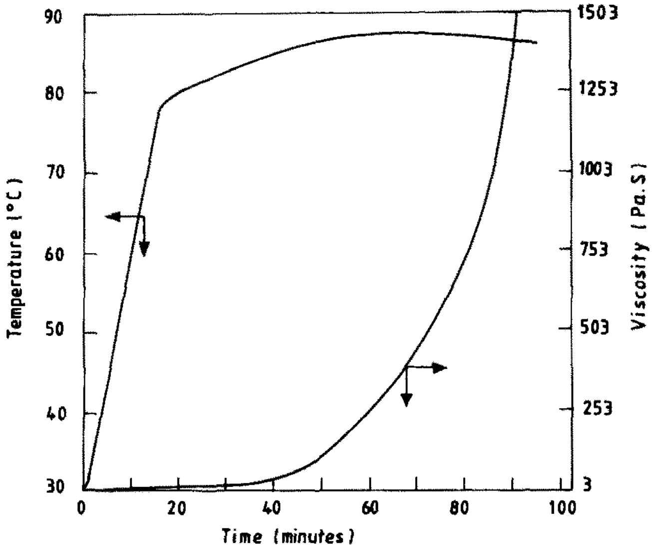

Fig. 8. Adiabatic temperature rise and adiabatic viscosity changes with time.

operational temperature is desirable before the isothermal conditions of processing are reached.

CONCLUSION

The polyurethane reaction involving ISRO-polyol follows a second-order reaction. The heat evolved during the scanning experiment was 67.38 J g^{-1} and the specific heat of the system was not constant throughout the experiment. The linear scan experiment by DSC is useful for studying the kinetics and thermal behaviour simultaneously. Anomalous behaviour was observed in the isothermal viscosity changes of the reacting system in the absence of a chain extender. A cone-and-plate viscometer was used for determining adiabatic viscosity.

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