

## Viscometry of Isothermal Urethane Polymerization

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The viscosity values of Indian Space Research Organization's (ISRO) hydroxyl terminated polybutadiene (HTPB) at various temperatures, the isothermal viscosity changes during the curing reaction of ISRO-HTPB with diisocyanatotoluene (TDI) with and without catalyst and with a filler, calcium carbonate have been studied. The effect of temperature on this curing reaction is determined. The viscosity–time profile has shown an anomalous behavior and an explanation is put forward on the basis of polyurethane–HTPB, TDI mixture interaction. The viscosity–time profiles are drawn using normalized coordinates, which is helpful to compare the relative viscosity build up over relative periods.

Urethane polymers have been under active development in industries since inception because of their versatile properties. Urethane elastomers and thermoplastics are two major types of raw materials which are finally fabricated into desired products. Casting is a manufacturing technique for producing the above two classes, from initial liquid reactants to final solid polymer. Before casting, the reactive components have to be precisely metered and mixed. For metering and mixing, from the standpoint of physical handling a precise knowledge of the viscosities of the individual components and also of the mixture, at various conditions of temperature, composition and reaction rate must be known. In addition, rheological considerations are necessary for the design strategies of the mixer type, mixing speed and throughout rate of the mix of the production equipment and for determining mould filling characteristics. There must be a consideration of rheology versus the reaction rate for the length limitation of the hose, which is used for transferring mixed materials from the metering cum mixing machine to the mould for casting.

The purpose of this paper is to characterize the flow behavior of an urethane reacting system involving Indian Space Research Organization's (ISRO) hydroxyl terminated polybutadiene (HTPB) under various conditions.

### Experimental

**Materials.** Uncatalyzed, catalyzed, unfilled and filled Am+Bn liquid urethane reacting systems were used, where Am was hydroxyl terminated polybutadiene (HTPB) developed by the Indian Space Research Organization (a Patented product used for solid rocket propellant binder). Its number average molecular weight ( $\bar{M}_n$ ) was  $3000 \pm 350$  and hydroxyl value was 40. "Bn" was diisocyanatotoluene (TDI) (a mixture of 80:20 2,4 and 2,6 isomers). The catalyst used was tin(II) octanoate. The filler was a fine powder of calcium carbonate with a maximum moisture content of 0.1% and specific surface area of  $0.9255 \text{ m}^2 \text{ ml}^{-1}$ .

**Procedure.** HTPB and TDI were mixed according to the stoichiometry (NCO/OH ratio) equal to one. Three tenth % of the catalyst and 10% of the filler were also added depending on the system selected (unfilled, filled, uncatalyzed and cata-

lyzed). The reactants (also the catalyst and filler wherever necessary) were mixed well at room temperature in a beaker. One ml of the reacting sample was transferred to the plate of the Cone and Plate Brookfield digital viscometer (model DV II) provided with a constant temperature bath and recorder. For the room temperature reaction, the time required for mixing and pouring into the plate were taken into consideration, whereas for the reaction at elevated temperatures this time was neglected. The reactants were allowed to react inside the viscometer. The viscosity was recorded as a function of time at constant shear rates from the initial liquid reactants to the final nearly solid elastomer state.

All the experiments were conducted under isothermal condition using the constant temperature bath. Further because of the small sample size and the longer reaction time, non-isothermal effect due to heat of the reaction could be neglected. To check whether shear thinning was occurring, measurements were periodically made over a range of shear rates, fairly rapidly, so that any viscosity change observed would not be masked by the curing reaction.<sup>1)</sup>

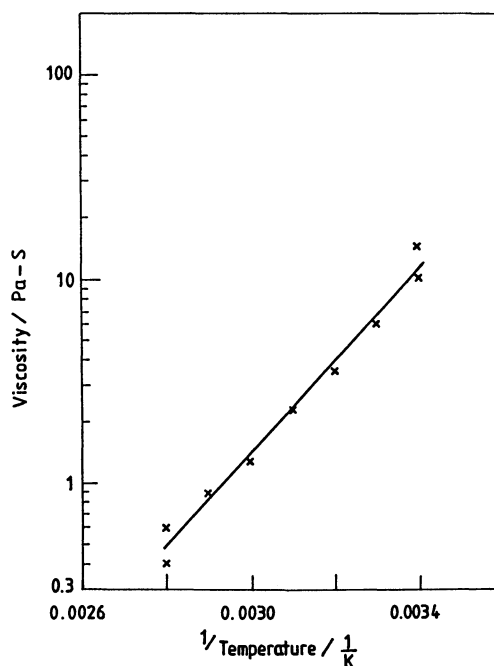


Fig. 1. Effect of temperature on viscosity for HTPB.

### Results and Discussion

Figure 1 shows the effect of temperature on the viscosity of HTPB (non reacting and unfilled). The viscosity data indicate that for shear rates in the range of 1 to 40  $\text{sec}^{-1}$ , the behavior is newtonian. The effect of temperature has been represented by Arrhenius equation,  $\eta = A \exp(E/RT)$ , where  $A = 2.0488 \times 10^{-7}$  Pa s and  $E = 43582$  J  $\text{kg}^{-1} \text{mol}^{-1}$  with  $\eta$  in Pa s and  $T$  in Kelvin.

Figure 2 shows the effect of temperature on the viscosity of HTPB and TDI reacting system. At higher temperatures, the initial viscosities of the reacting systems are lower, as expected. At 50°C, the reaction effect overtakes the temperature effect on viscosity, at 70 min. At 30 and 50°C, after a gradual increase in viscosity, at a particular time, the viscosity decreases, the decrease continues for some time and then again it increases. At lower temperatures the fall and rise are more. This is believed to be due to the solubility of the solid urethane which is already formed in the reaction

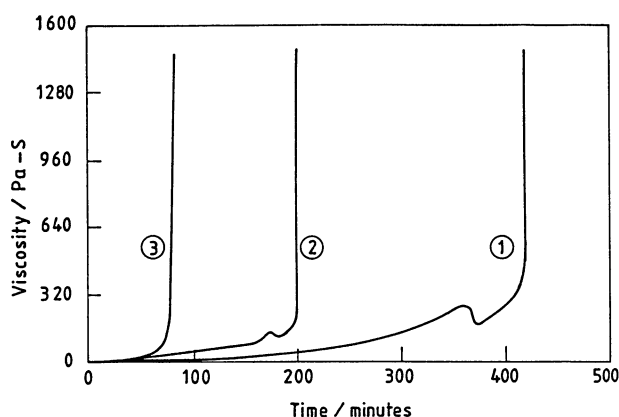


Fig. 2. Viscosity-time profiles for HTPB-TDI reactions at various temperatures; (1) 30°C, (2) 50°C, and (3) 70°C.

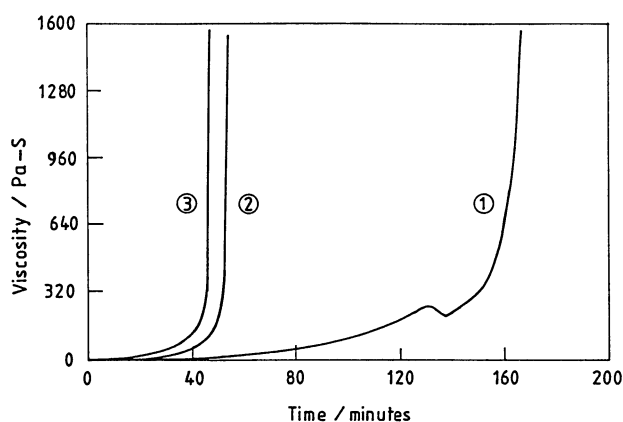


Fig. 3. Viscosity-time profiles for HTPB-TDI reactions in the presence of a catalyst, tin(II) octanoate at various temperatures; (1) 30°C, (2) 50°C, and (3) 70°C.

medium-in the liquid polyol (HTPB)-TDI reacting system. We have separately tested the solubility of the polyurethane in the HTPB-TDI mixture and we have found that this mixture is a very good solvent for polyurethane especially for the initially formed low molecular weight type. We have separated the gel content (low molecular weight polyurethane that is formed) from sol (unreacted polyol, TDI mixture) by solvent extraction technique, using a separating funnel and benzene as a solvent (initially formed low molecular weight polyurethane is soluble in benzene also, but if we allow the reaction to advance before separation, it is possible to separate a good amount of gel from the sol). We have confirmed the mutual solubility of the gel and sol by putting these together back and seen that this sol is a very good solvent for this gel, whereas there is no dissolution when we put a finally formed polyurethane into the same sol. This shows that the dissolution of urethane in the reaction medium is dependent on its molecular weight. Then it is possible to infer that, as the reaction proceeds the dissolution occurs less readily; but because it is the relatively higher molecular weight polyurethane which dissolves, at this time, the net effect will be a decrease in the viscosity of the system; and it is possible that this effect can overtake the viscosity build up due to reaction, so that the viscosity can come down. This suggests that there may be a critical molecular weight build up above which the dissolution stops suddenly (This can be visualized more readily, if we consider the manner in which molecular weight build up takes place, in step addition polymerization, like urethane formation) and this can cause a sudden increase in viscosity. As this molecular weight build up to a critical molecular weight occurs only at the advanced stage of polymerization, and this is essentially preceded by the predominance of dissolution effect over the reaction effect, there is a fall and sudden rise of the reaction viscosity at the advanced stage of the reaction. Moreover we have seen similar observations in the isothermal viscosity changes of another ISRO-Polyol (castor oil based polyol)-TDI system also.<sup>2)</sup> It is also further substantiated from the results of torque rheometry of urethane reacting system<sup>3)</sup> where unreacted isocyanate acted as a plasticizer. The dissolution and reaction have two opposing effects on viscosity, the ultimate viscosity depends on which effect is dominating. At a particular point of time the former dominates over the latter, so that viscosity falls down. As time goes on, the left over HTPB-TDI mixture will react to form polyurethane and as the dissolution decreases and stops, the viscosity suddenly rises up to a large value. This is further evident from the variation of the slope after the peak. We have found that this anomalous behavior is temperature dependent. This is because the dissolution and reaction effects are temperature dependent. At higher temperatures there will be more reaction than dissolution so that the decrease in viscosity is less than that at lower temperatures. We can also

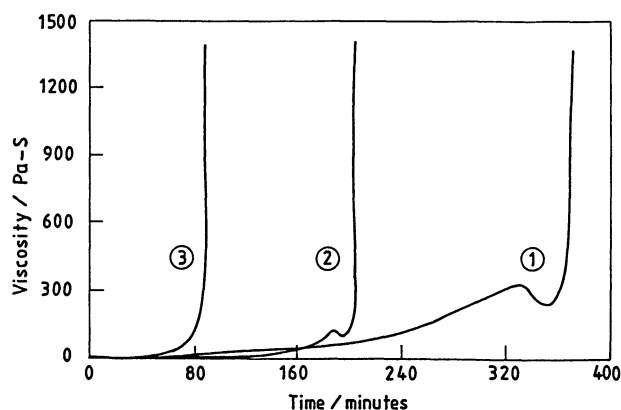


Fig. 4. Viscosity-time profiles for HTPB-TDI reactions in the presence of a catalyst, tin(II) octanoate and a filler, calcium carbonate; at (1) 30°C, (2) 50°C, (3) 70°C.

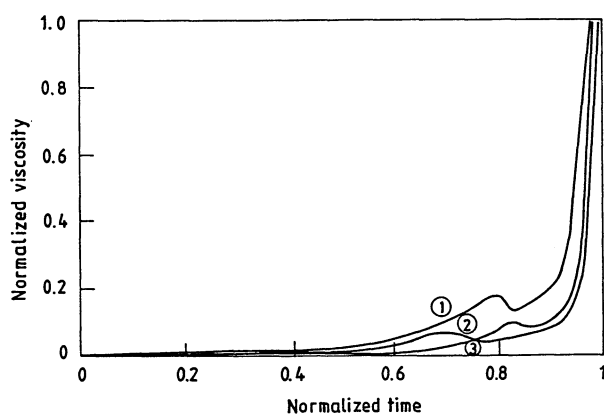


Fig. 5. Normalized viscosity-time profiles for HTPB-TDI reacting systems in the presence of catalyst, tin(II) octanoate; at (1) 30°C, (2) 50°C, (3) 70°C.

obtain a viscosity-time profile where this anomalous behavior is absent, if the reaction rate is always higher than the dissolution effect. That is what happens in the reaction at 70°C in Fig. 2 and in the reaction with catalyst at 50°C and 70°C in Fig. 3 and in chain extended system<sup>4,5)</sup> at all temperatures.

Figure 4 shows that the introduction of filler increases the initial viscosity and in this case we have found that  $\text{CaCO}_3$  is an inert filler, which will not interfere with the polyurethane reaction. So the introduction of a reinforcing type of filler at the reaction stage itself is helpful for better bonding of filler with the urethane matrix, which in turn will increase the mechanical properties of the final urethane polymer formed.

The viscosity data in Fig. 3 are replotted in Fig. 5 using normalized coordinates. The normalized viscos-

ity is defined as  $(\eta - \eta_0)/(\eta_{\max} - \eta_0)$  where  $\eta$  is the viscosity at any time,  $t$ ,  $\eta_0$ , is the viscosity at  $t=t_0$  and  $\eta_{\max}$  is the highest viscosity of this system measured using cone and plate viscometer (it is 1600 Pa s) at  $t=t_{\max}$ , at this condition the material is nearly solid polyurethane. The normalized time is defined as  $(t - t_0)/(t_{\max} - t_0)$ . In these normalized coordinates, the final viscosity is unity. The use of these coordinates helps to compare the relative viscosity build up over relative periods of time. The coordinates are dimensionless. The data for the HTPB-TDI catalyst tin(II) octanoate system in Fig. 5 indicate that at all temperatures the data fall almost on a single curve, till the beginning of the peak, so it is possible to draw a master curve without much deviation from the individual curves in this region and this master curve will be temperature independent.

### Conclusion

The viscosity of the isothermal curing reaction of ISRO-HTPB with TDI is found to show an anomalous behavior which is not reported in literature previously. This behavior can be explained qualitatively, in terms of the opposing effects of dissolution and reaction in the system. A calcium carbonate filler does not have much effect on the curing reaction, other than its increase in initial viscosity, so fillers can be incorporated at polymerization stage itself. As the temperature increases the reaction rate can be expected to increase giving rise to an increase in the viscosity of the system; at the same time a temperature increase has a tendency to decrease the viscosity of the system; as these two effects are opposing each other, it would be interesting to follow the kinetics of the polyurethane reaction and relating the conversion to the viscosity of the system.

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