Kinetic Studies on Curing of Hydroxy-Terminated Polybutadiene Prepolymer-Based Polyurethane Networks

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ABSTRACT: Hydroxy-terminated polybutadiene (HTPB) prepolymer prepared by free-radical mechanism at Chemical Engineering Complex, Vikram Sarabhai Space Center, Thiruvananthapuram was reacted with toluene diisocyanate (TDI), a curative at varying stoichiometric ratios ($r = $ [NCO]/[OH]) equal to 0.7, 0.8, 0.9, 1.0, and 1.1 at a constant temperature of 70°C. The increased rate of viscosity of polyurethane networks formed was used to calculate the rate constant. Similarly, the rate of change of viscosity of curing networks at different r values (0.7–1.1) and temperature intervals (30–70°C) was used to calculate activation energy. The results of the curing networks showed that the rate constant at $r > 0.9$ is constant and the rate of decrease of activation energy is lower at $r \leq 1$; thereafter, it becomes quite significant. © 2002 Wiley Periodicals, Inc. J Appl Polym Sci 85: 842–846, 2002

Key words: HTPB prepolymer; TDI curative; polyurethane networks; rate constant; activation energy

INTRODUCTION

Polyurethane networks derived from hydroxy-terminated polybutadiene (HTPB) prepolymer and toluene diisocyanate (TDI) curative impart three-dimensional stability to a solid composite propellant grain and the rubbery nature of the network (because of inherent characteristic of butadiene) allows the grain to withstand thermal cycling and pressurization.[1] The ultimate mechanical and thermal properties of the network formed depend on the shelf life of these reaction mixtures. Therefore, an understanding of kinetics of the network formation enables one to design the solid propellants with desired properties with a minimum number of formulations.

Some of the important advantages for consideration of the urethane systems[2] as solid propellants are as follows: (1) the cure reaction takes place between hydroxyl and isocyanate functionalities at relatively low temperature and thus, many side reactions can be effectively avoided[3]; (2) moderate reaction rate allows longer shelf life; thereby, the processing of case bonding type propellants become easier[4]; (3) very low or no shrinkage is generally observed in the case of polyurethane binders during the cure process.[5]

In the present investigation, the effect of temperature and time on the viscosity of the network formed at various stoichiometric ratios, $r = $ [NCO]/[OH], was studied and subsequently, the rate constant (k) and the activation energy (E) of the curing mass were calculated to understand the shelf life of the networks. This will help in the effective formulation of the solid propellants without further loss in material, energy, and time.

Table I   Selected Properties of Standard HTPB Prepolymer

Sample No.	Property	Value
1	Hydroxyl value (mg. of KOH/g)	44.5
2	Viscosity at 30°C (cps)	5510
3	Average molecular weight ($\overline{M}_n$)	2560
4	Average functionality ($\overline{fn}$)	2.031
5	Polydispersity	2.4

Table II   Formulation of Polyurethane Network Formation

Sample No.	r Value	Weight of HTPB Prepolymer (g)	Weight of TDI (g)
1	0.7	100.00	4.80
2	0.8	100.00	5.50
3	0.9	100.00	6.2
4	1.0	100.00	6.9
5	1.1	100.00	7.6

EXPERIMENTAL

Materials Used

HTPB Prepolymer

The HTPB prepolymer was prepared by free-radical polymerization of butadiene (NOCIL, Thane, Maharashtra, India) in isopropanol (Merck) water-solvent system[6] by using hydrogen peroxide (Merck) as the initiator at Chemical Engineering Complex, Vikram Sarabhai Space Center, Thiruvananthapuram (Kerala, India). The prepolymer was characterized by its number-average molecular weight ($\overline{M}_n$, VPO), polydispersity ($\overline{M}_w/\overline{M}_n$, SEC), hydroxyl value (conventional titration method), and viscosity (Brookfield viscometer). Selected properties of HTPB prepolymer are given in Table I.

TDI

A mixture of 80 : 20 of 2,4- and 2,6-isomers of TDI was procured from M/S A.G. Bayer, Germany and was used without further purification as a curative after ascertaining a isocyanate content of >99%.

Preparation of Networks[7–10] and its Viscosity Measurement

Mixing of HTPB prepolymer with TDI curative as per the formulation given in Table II was carried out thoroughly by using a propeller agitator in separate beakers. The beakers were then kept in a temperature-controlled electrically heated water bath at 70°C and Brookfield viscometer was used to measure the viscosity of this curing mass at different time intervals of 10 min (Fig. 1). Similarly, the viscosity of curing mass was measured for the different compositions at varying temperatures in the range of 30–70°C with a uniform heating rate at a temperature interval of 5–10°C.

RESULTS AND DISCUSSION

Determination of Rate Constant[11]

Variation of viscosity with time for HTPB prepolymer curing at 70°C and various r values (0.7–1.1) is shown in Figure 1. It was observed that the viscosity of the curing polyurethane increased as the extent of urethane formation advanced with time. A mathematical relationship between viscosity and time was obtained by fitting the data to an exponential function by the least-squares method. The general form of the relationship used is given by $\eta = ae^{bt}$, where a and b are empirical
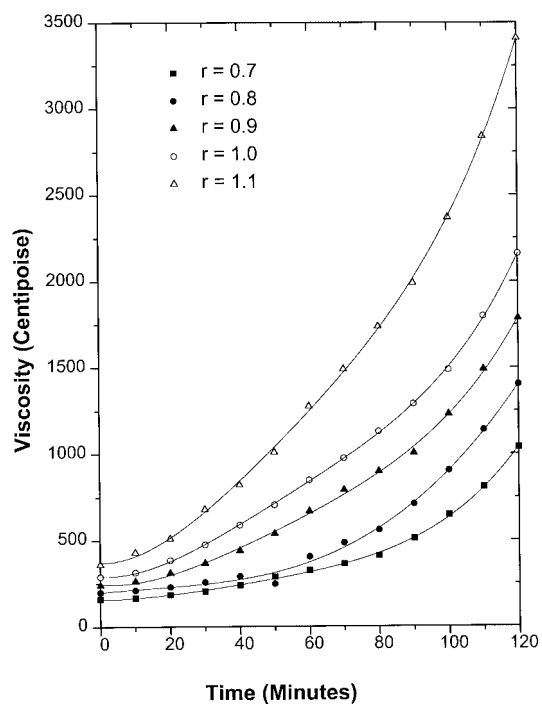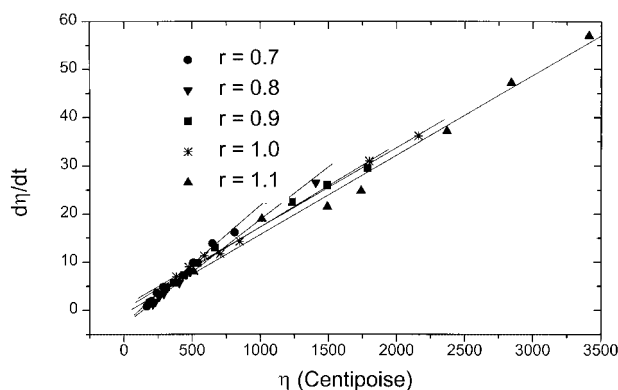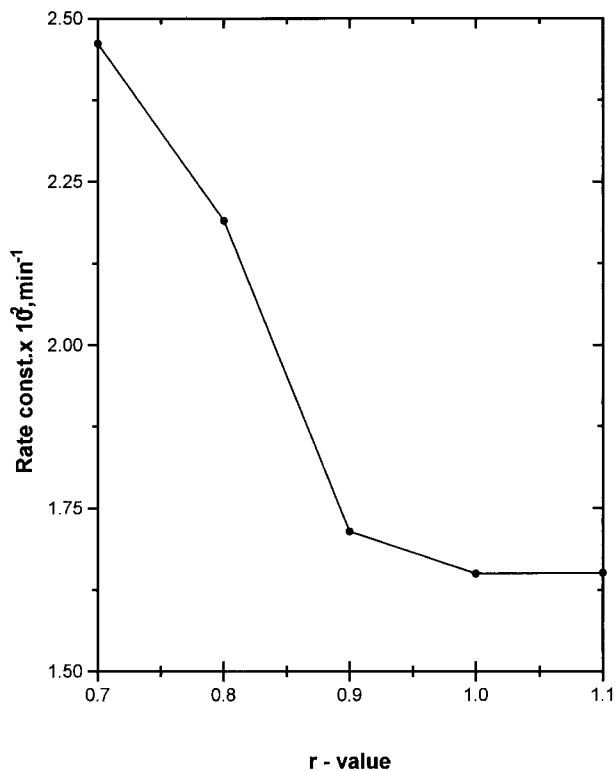

Figure 1   Change of viscosity with time for prepolymer curing at 70°C and various r values.

Table III   Empirical Constants of Curing Reaction Mixtures at Different r Values

Sample No.	r Value	Empirical Constants	
		a	b
1	0.7	135.944	0.0155
2	0.8	165.069	0.0166
3	0.9	227.360	0.01707
4	1.0	286.975	0.0169
5	1.1	375.058	0.01878

constants; their values are given in Table III. From this relation, the rates of viscosity buildup ($d\eta/dt$) were computed at various time intervals for all the r values and are plotted against the corresponding viscosity (Fig. 2). Good linearity of these plots indicate that the viscosity buildup is a first-order process. Since the rate of viscosity buildup depends on the extent of cure reaction taken place at time t, it could be regarded as a measure of the concentration of the species responsible for the cure reaction at the corresponding time. Thus, the slopes of the rates of viscosity buildup ($d\eta/dt$) versus viscosity (η) plots could be considered as a measure of the rate constant (k) of viscosity buildup. A similar procedure was adopted by Abraham et al.[12] The plot of calculated rate constants versus r values is shown in Figure 3, which indicates that rate constant falls sharply at lower r values (i.e., at r = 0.7, 0.8, and 0.9); after that, it remains almost constant. It is because at r = 0.7, excess [OH] remains unreacted, causing less conversion, less branching and crosslinking, and consequently, less viscosity buildup. However, with an increase in r (up to r

Figure 3   Effect of r value on rate constant for curing networks at 70°C.

= 0.9), conversion increases, resulting in more branching and crosslinking and higher viscosity buildup. This increase in viscosity reduces the interaction between reacting molecules, thereby reducing the rate constant of network formation. At r > 0.9, the viscosity buildup becomes so high that no further reaction continues to an appreciable extent, therefore showing the trend of rate constant almost unchanged. A similar study was reported by Abraham et al.[12]

Determination of Activation Energy[4,12–16]

It is well known that the temperature dependence of viscosity follows the Arrhenius exponential relationship given as

$$\eta = Ae^{E/RT}$$

$$\ln \eta = \ln A + E/RT$$

and

E = Activation Energy of viscous reaction mixture

Figure 2   Effect of viscosity of curing networks on the rate of viscosity buildup at 70°C and various r values.

A = Empirical constant
T = Temperature of reaction mixture
R = Universal gas constant.

The exponential relationship of Arrhenius is applicable to this system as the used HTPB is a prepolymer of low molecular weight and low viscosity (Table I); a similar relationship for such a prepolymer has also been reported[4,12] earlier. The plots of ln η versus $1/T$ for HTPB prepolymer (i.e., virgin prepolymer) and curing reaction mixtures at varying r values are shown in Figure 4. The slope of each plot is a measure of its E/R. For example, the value of E/R for virgin HTPB prepolymer alone is 4.640. By taking R = 8.31447 KJ/kg mol K, the value of E becomes $38.579 \approx 39$ KJ, which is similar to that reported by Descheres et al.[17] and Abraham et al.[12] The plot of calculated values of activation energy E for virgin HTPB prepolymer alone and its reaction mixtures (i.e., polyurethane networks at varying r values) are shown in Figure 5. Here, it was observed that the rate of decrease in E for curing networks is lower at $r \leq 1$; thereafter, it becomes quite significant.
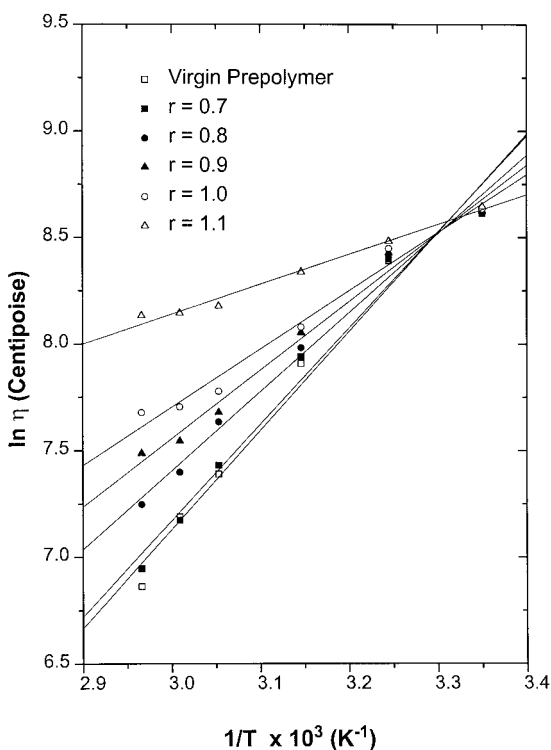

Figure 5 Variation of activation energy with r value for prepolymer and polyurethane networks.

Figure 4 Effect of temperature on viscosity of virgin prepolymer and polyurethane networks at various r values.

CONCLUSION

It was observed that the rate constants of the polyurethane network formation at $r > 0.9$ do not vary much, meaning thereby that the shelf life of these reaction mixtures is not much affected thereafter. The rate of decrease of activation energy for such reaction mixtures (polyurethane networks) also becomes quite significant at $r > 1$.

Determination of the rate constant and the activation energy of the polyurethane networks at varying r values help in understanding the reaction mechanism, which could further be interpreted in its application in the propellant casting system.

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