

Rheokinetic Modeling of HTPB–TDI and HTPB–DOA–TDI Systems

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ABSTRACT: A study of the effect of temperature on a mixture of polymer and curative in the processing of rocket propellants is reported. Experimental viscosity of a hydroxyl-terminated polybutadiene–toluene diisocyanate (HTPB–TDI) system was measured using a Brookfield viscometer model DV III. Viscosity showed dependence on temperature as well as time. The viscosity data of the HTPB–TDI system showed a linear relationship with temperature, with a change in slope at 45°C. The time dependence model showed a fourth-order curve fit, which gave better results over the exponential model fit. The activation energy required for flow of the HTPB–TDI system was found to be 15.5 kJ/mol. Experimental viscosity measurements at various temperatures was also carried out on a hydroxyl-terminated polybutadiene–dioctyl adipate–toluene diisocyanate

(HTPB–DOA–TDI) system. The temperature dependence showed a decrease in viscosity with an increase in temperature up to 60 min, beyond which the viscosity increased. Viscosity showed a linear relation with temperature, with a change in the slope at 50°C instead of at 45°C for HTPB–TDI system. Beyond 50°C the data followed a polynomial model similar to that of the HTPB–TDI system, and the results matched well with the experimental data. The activation energy of the HTPB–DOA–TDI system increased with an increase in the binder weight ratio. © 2003 Wiley Periodicals, Inc. *J Appl Polym Sci* 89: 1331–1335, 2003

Key words: rheology; modeling; curing of polymers; polybutadiene

INTRODUCTION

Currently hydroxyl-terminated polybutadiene (HTPB) is considered a workhorse propellant binder and is used all over the globe. Dioctyl adipate (DOA) has been found to be an excellent plasticizer for HTPB. When a plasticizer is added to the polymer, it acts as a lubricant and helps the polymer molecules move freely, thereby reducing the viscosity of the system. The plasticizer helps the easy processing of the propellant mix and also improves low-temperature mechanical properties like tensile strength and elongation of propellant grain. Low viscosity of the binder system helps in achieving more solid loading, which leads to a significant increase in the total thrust or the specific impulse of the propellants.

In propellant formulations curative is added to transform the propellant slurry into a solid grain. The trifunctional curative system in the presence of catalyst builds up a three-dimensional network. Toluene diisocyanate (TDI) is a difunctional curative commonly used for HTPB. A curing catalyst like dibutyl

tin–dilaurate (DBTDL) is employed. For HTPB with a functionality of more than two, toluene diisocyanate (TDI) curative and dibutyl tin dilaurate (DBTDL) are used as curative and cure catalyst, respectively.

Sekkar et al.² studied the effect of catalyst (DBTDL) concentration on the viscosity of HTPB curative systems. They observed that, based on viscosity data, the cure reaction between toluene diisocyanate (TDI) or isophoron diisocyanate (IPDI) with HTPB polymer took place in two stages because of the difference in reactivity between the isocyanate groups present in IPDI and TDI at a lower temperature (30°C), whereas with HMDI it took place in a single stage. This may be because of (1) the reactivity difference of the functional groups of the curatives and (2) high viscosity buildup, decreasing the rate of reaction. The NCO functional group at the para position was more reactive than that at the ortho position because of steric hindrance factor. Yamaguchi et al.^{5,6} studied the effect of crosslinked linear and low-density polyethylene on rheological properties like strain hardening behavior in elongation viscosity and steady shear viscosity, and they also studied the weight fraction effect on the blending of linear and crosslinked polymer gels on elongational viscosity and shear viscosity. They found that the stretching of the chain section between the crosslink points was responsible for the hardening behavior. Eom et al.⁷ proposed a chemorheological

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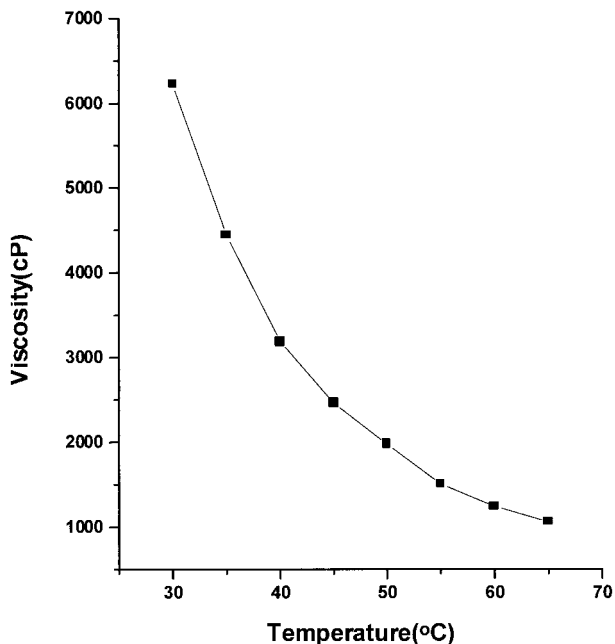


Figure 1 Variation in viscosity of HTPB with temperature.

model to calculate the relaxation modulus of the epoxy resin system with a torsional parallel plate rheometer over the complete range of cure. This new approach for time–cure–temperature superposition, which can be applied to any curing polymer, is useful in analyzing viscoelastic stress buildup following any relevant cure cycle.

In this article, we report on our modeling of the viscosities of HTPB–TDI and HTPB–DOA–TDI systems at various temperatures and times using Brookfield viscometer data.

EXPERIMENTAL

Materials

HTPB was obtained from NOCIL (Mumbai, India). It had a number-average molecular weight of 2200–2600 and an OH value of 42 mg KOH/g. DOA was obtained from Indo-Nippon (Mumbai, India). TDI was procured from M/s Mitsubishi (Kyoto, Japan). They were used as received.

TABLE I
Experimental Viscosity of HTPB at 30° and Different Torques with Corresponding Shear Stress and Shear Rates

Torque (%)	50	60	70	80	90	100
RPM	4.0	4.8	5.7	6.5	7.3	8.0
Viscosity (Cp)	6288	6260	6219	6192	6192	6206
Shear Stress (Pa%)	234	279	330	375	420	462
Shear Rate (S ⁻¹)	3.72	4.46	5.30	6.05	6.79	7.44

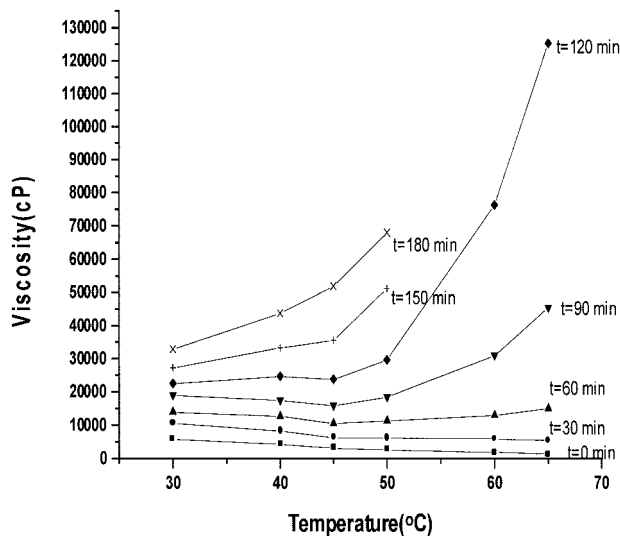


Figure 2 Variation in viscosity of the HTPB–TDI system with temperature.

Viscosity measurements

The viscosity of HTPB was measured in the temperature range of 30°C–65°C at intervals of 5°C. The torque (shear force) was varied from 50% to 100% at intervals of 10%, by using Brookfield viscometer model DV III. A small-scale sample adapter along with spindle no. 21 was used to measure viscosity. To maintain the temperature, a thermostated water bath was used. The viscosity of the HTPB–TDI system was measured at temperatures 30°C, 40°C, 45°C, 50°C, and 60°C. Torque was fixed at 90% for viscosity measurement. The stoichiometric ratio of NCO : OH was 1. Samples of 50 g of HTPB and 3.3 g of TDI were mixed and stirred well, and viscosity was measured. The experimental viscosity of the HTPB–DOA with TDI system was measured at the above-mentioned temperatures with the same stoichiometric ratio. HTPB–DOA in weight ratios of 60 : 40 and 70 : 30 was studied. An average of three experimental data points were considered for modeling.

TABLE II
Values of Slopes and Constants for Linear Curve Temperature Model of HTPB–TDI System

Time (min)	Slope up to 45°C (degree) Slope	Slope after 45°C (degree) Slope
0	-174.864	-80.89
30	-279.35	-37.01
60	-213.828	212.84
90	-203.836	1437.42
120	106.285	4990.595
150	561.5	—
180	1245.59	—

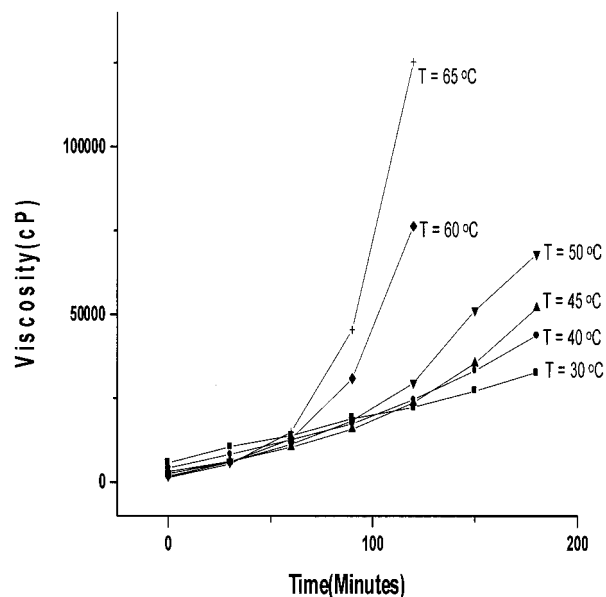


Figure 3 Variation in viscosity of the HTPB-TDI system with time.

Data analysis and modeling

Temperature modeling of HTPB

The experimental viscosity data for HTPB is plotted in Figure 1, which shows its major dependence on temperature. Because of instrumental error, the independence of the torque (shear force) is assumed to be less. The experimental data at various toques and shear rates are given in Table I. The data was modeled by a fourth-order curve with temperature of the type

$$\eta_{th} = a_1T^4 + a_2T^3 + a_3T^2 + a_4T + a_5$$

where η_{th} is the theoretical viscosity, T is temperature; and a_1 , a_2 , a_3 , a_4 , and a_5 are constants. The linear equations were obtained with the error minimization method. They were solved by the Gauss elimination method, from which the coefficients were obtained. The resulting model data matched the experimental data well. We also compared this model with the Arrhenius model¹ for the temperature range of 30°C–

TABLE III
Values of Constant (η_0) and Rate Constant (k) of Exponential Time Model

Temperature (°C)	η_0	k
30	6944.60	0.01016
40	5255.34	0.01242
45	3716.73	0.01518
50	3249.479	0.01801
60	2047.142	0.03039
65	1574.0339	0.03696

70°C. The polynomial model was more accurate than the Arrhenius model for that particular range of temperatures.

Temperature modeling for HTPB-TDI

When TDI was added to HTPB, the characteristic nature of the mixture changed to the opposite of that of HTPB, a result of the curing action of TDI. As temperature increased, viscosity built up with time. The resulting data for temperatures at specified times are shown in Figure 2. It was observed that viscosity decreased with an increase in temperature, as expected, but not at the same rate as for HTPB. This is because the effect of temperature on viscosity matches the effect of the curing reaction rate. Viscosity decreased slowly with time at 0, 30, 60, and 90 min, but above 90 min viscosity increased slowly up to 45°C. Beyond 45°C, viscosity built up fast with time because of the increase in reaction rate with temperature.

A sharp change was observed in the neighborhood of a particular temperature. Therefore, a linear relation of the data with temperature was assumed. The slopes up to 45°C and above 45°C are given in Table II. It can be seen that up to 45°C the slope decreased over time up to 90 min and increased for times longer than 90 min. For temperatures above 45°C the slope increases at all times. By plotting $\ln(\text{viscosity})$ versus $1/T$ (K), the activation energy of the HTPB-TDI system at 30 min after the addition of TDI was found to be 15.5 k J/mol.

TABLE IV
Comparison of Predicted Model Results with Experimental Data of HTPB-TDI System

Temperature (°C)	30			50			
	Time (min)	Experimental	Polynomial	Exponential	Experimental	Polynomial	Exponential
30		10540.5	10495.43	9419.33	6076.5	7378.64	5577.80
60		13887.5	13971.48	12775.94	11242.0	9540.89	9574.416
90		18958.5	18864.93	17328.70	18363.5	18520.26	16434.69
120		22400.0	22462.11	23503.85	29569.5	30835.83	28210.51
150		27191.5	27176.46	31879.53	51194.5	50140.93	48423.96
180		32821.5	32822.77	43239.92	67914.5	68179.41	83120.77

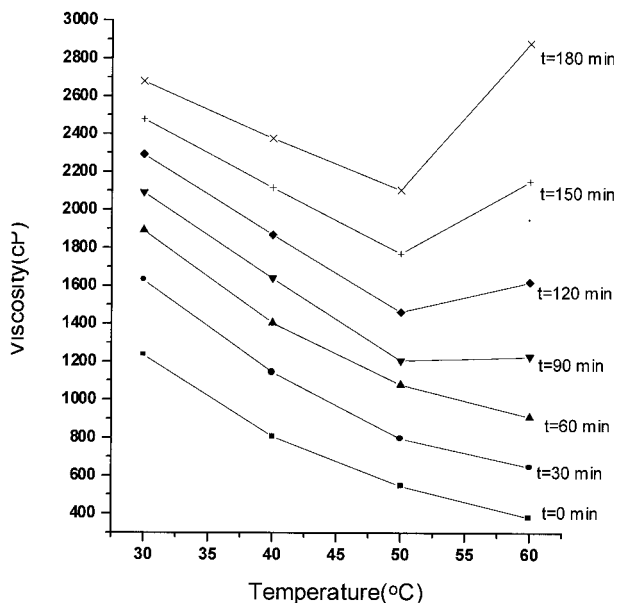


Figure 4 Variation in viscosity of the HTPB-DOA (70:30)-TDI system with temperature.

Time modeling of HTPB-TDI system

The experimental data of viscosity with time for different temperatures is given in Figure 3. The data were modeled to a fourth-order equation of the type

$$\eta_{th} = a_1t^4 + a_2t^3 + a_3t^2 + a_4t + a_5$$

where η_{th} is the theoretical viscosity; t is time; and $a_1, a_2, a_3, a_4,$ and a_5 are constants. The same procedure was used to obtain the coefficients, as explained above. The model results matched the experimental data well.

Similar results were reported by Sekkar et al.^{2,4} They studied HTPB with different curatives such as TDI, IPDI, and HMDI at 25°C, 30°C, 50°C, and 70°C and at different stoichiometric ratios of NCO:OH. The viscosity data was plotted as $\log(\eta)$ with time. They found that the data at 30°C showed a two-stage separation of viscosity buildup for the HTPB-TDI system, but at higher temperatures stage separation was not observed. Analysis was carried out through an exponential modeling of

$$\eta = \eta_0 e^{kt}$$

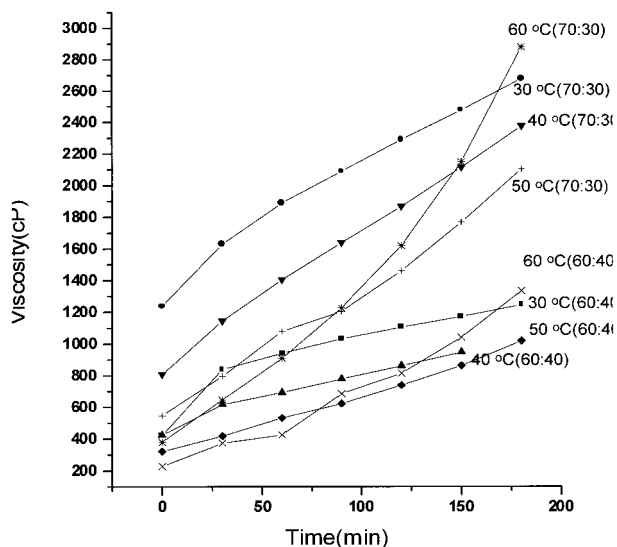


Figure 5 Variation in viscosity of the HTPB-DOA-TDI system with time.

and the values of η_0 and k were determined. Our results of η_0 and k are shown in Table III. The polynomial model results were compared with those from the exponential model. It was found that the results of the polynomial model were more accurate than those of the exponential model over the given range of time. The comparative data from these two models along with the experimental data are given in Table IV. It is proposed that the exponential model does not satisfy the boundary states at $t = 0$ and as t increases to infinity; instead, the polynomial fit provides a better description of the results in a finite temperature range.

Temperature modeling for HTPB-DOA-TDI system

These studies were carried out at three temperatures. They showed a critical change in the neighborhood of a particular point. Therefore, viscosity buildup with temperature was considered to be linear with change in slope. Viscosity growth up to 60 min for all temperatures showed a straight-line fit. For times of 60 min or longer, a critical temperature existed beyond which the slope of the curve changed rapidly. This is shown by a straight line with a change in slopes at a particular temperature. It was observed that beyond

TABLE V
Values of Slopes and Constants for Viscosity of Binder Curative System with Time for Two Binder Weight Ratio

Temperature (°C)	30		40		50	
	Slope (deg.)	constant	Slope (deg.)	constant	Slope (deg.)	constant
HTPB-DOA (60:40)-TDI	2.6809	775.0	3.286	473.57	3.8011	303.32
HTPB-DOA (70:30)-TDI	7.659	1352.53	10.673	1203.75	8.399	529.54

TABLE VI
Comparison of Experimental and Polynomial Model Results for Two Binder Weight Ratios for HTPB-DOA-TDI System

Time (min)	Viscosity (cP) (60:40)		Viscosity (cP) (70:30)	
	Experimental	Polynomial	Experimental	Polynomial
30	692	685.32	958	953.52
60	841	847.77	1343	1345.09
90	999	1003.21	1752	1761.42
120	1195	1181.89	2260	2243.75
150	1381	1390.23	2787	2797.18
180	1613	1610.79	3393	3390.69

50°C the effect of plasticizer did not show much effect on the reaction rate. The experimental data of viscosity at different temperatures is shown in Figure 4. The activation energy for the HTPB-DOA (60:40)-TDI system was 21.2 kJ/mol and for the HTPB-DOA (70:30)-TDI system 25.6 kJ/mol. This shows that as the binder weight ratio increased, the activation energy increased.

Time modeling for HTPB-DOA-TDI system

The experimental viscosity data of the HTPB-DOA-TDI system at different temperatures for the 60:40 and 70:30 weight ratios are shown in Figure 5. For these mixtures viscosity increased monotonically at a slow rate with time for different temperatures. In this system the plasticizer affected the reaction rate of the curative in a limited temperature range, that is, up to 50°C; beyond it, the system behaved like the HTPB-TDI system and followed the polynomial model. The slopes and constants were obtained by fitting a linear curve of viscosity with time up to 50°C are given in Table V. The polynomial results match the experimental data well. The results of the polynomial model are given in Table VI. These show the values of the slope and the constant increased with an increase in temperature and satisfied the model.

CONCLUSIONS

The viscosity of the polymer decreased with temperature. The polymer admitted a fourth-order polynomial model and showed good results compared to the Arrhenius temperature dependence model.

The addition of a curative to the polymer reversed the viscosity dependence on temperature. The viscosity slowly decreased up to 45°C and 90 min, beyond which viscosity buildup increased sharply as temperature increased. It followed a linear model with temperature. Two linear curves were obtained, with a change in slope at 45°C. The time modeling of the HTPB-TDI data followed a fourth-order polynomial

curve. The results were good compared to the exponential time-dependent model.

The temperature modeling of the HTPB-DOA-TDI system showed a linear relation for temperature up to 60 min; beyond that time, it showed two linear fits, with a change in slope at 50°C instead of at 45°C for the HTPB-TDI system. This shift in slope from 45°C to 50°C shows the effect of DOA on the reaction rate of TDI.

The time modeling of the HTPB-DOA-TDI system was compared to a polynomial model for the HTPB-TDI system. The model was linear with time up to 50°C; beyond 50°C, the model was polynomial like that of the HTPB-TDI system. This may be because of the effects of plasticizer on the reaction rate of curative in a limited temperature range, that is, up to 50°C; beyond that it behaved like the HTPB-TDI system and followed the polynomial model, which produced better results. Thus, it may be concluded that a temperature in the range of 40°C–50°C is good for the processing of rocket propellant slurry.

The activation energy for flow of the HTPB-DOA-TDI system increased with a decrease in the plasticizer weight ratio.

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