

Mathematical Modeling of Rheological Properties of Hydroxyl-Terminated Polybutadiene Binder and Dioctyl Adipate Plasticizer

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ABSTRACT: Solid composite propellants contain 80–90% of a crystalline oxidizer like ammonium perchlorate and powdery metallic fuel like aluminum with 10 to 15% organic binders like HTPB or CTPB, to bind the solids together and maintain the shape under severe stress and strain environment. Also, the propellant must not crack or become brittle at subzero temperatures. Formulating and processing of the highly filled composite propellants are difficult tasks and need a thorough understanding of rheology, even apart from a knowledge of propellant chemistry, particulate technology, manufacturing methods, and safe handling of explosives and hazardous materials. The flow behavior or rheology of the propellant slurry determines the ingredients and some of the abnormalities of the motor during firing. The propellant viscosity and mechanical properties are determined by the binder system, and the unloading viscosity of the propellant slurry is dependent on the initial viscosity of the binder system, solid loading, particle size, and its distribution, shape, temperature, and pressure. In the present report an attempt is made to study the dependency of viscosity of the HTPB binder system on temperature, plasticizer level (composition), and torque (angular velocity of spindle). The viscosity measurements were made using a Brookfield viscometer model DV III at different plasticizer levels (10–50%), temperatures (30–65°C), and torques (50–100%). The data indicate that the viscosity of HTPB, DOA, and their mixture decreases with increasing temperature and is constant with torque. The Arrhenius equation gives the energy for viscous flow to be ≈ 35 kcal/mol for HTPB. The variation of viscosity with temperature of HTPB/DOA and their mixture follows a mathematical model expressed as $\eta_{th} = a_1T^4 + a_2T^3 + a_3T^2 + a_4T + a_5$, where T is the temperature and $a_1, a_2, a_3, a_4,$ and a_5 are the constants. © 2002 Wiley Periodicals, Inc. *J Appl Polym Sci* 85: 1002–1007, 2002

Key words: rheology; modeling; viscosity; HTPB, DOA

INTRODUCTION

Solid composite propellants contain 80–90% of a crystalline oxidizer like ammonium perchlorate,

10–15% powdery metallic fuel like aluminum, and an organic binder like hydroxyl-terminated polybutadiene (HTPB), carboxyl-terminated polybutadiene (CTPB), or polybutadiene acrylic acid acrylonitrile (PBAN), which maintains the shape of the propellant grain under severe stress and strain environments experienced during handling, storage, and transportation. The binder plays two important roles: it acts as a fuel and

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binds the crystalline oxidizer and metallic fuel, thereby contributing to the structural integrity of the propellant; and it determines the mechanical properties.^{1,2} The major requirements of the binders are that it should be a liquid with a workable viscosity, at the mixing temperature ranging from 20–70°C, and it must be capable of conversion to an elastomer on processing, with high tensile and compressive strength and elasticity. In addition, it must have high heat of formation and yield low molecular weight gases. For special applications, it should have low water absorptivity, compatibility with reactive high-energy ingredients, long storage stability, and negligible vaporization or loss in high vacuum. The propellant slurry can be based on binders that may be either thermoplastic or thermosetting. Thermoplastic materials are soft, melting with heat and which can mix with other ingredients and cast. On cooling, it becomes rigid and retains the shape of the mould. Thermosetting materials are liquids or metastable solids at room temperature, but on heating, undergo chemical crosslinking and form insoluble cross-linked rubbery material.

HTPB is one of the prominent binders because of its high solid loading capability (as high as 90%), good processability, improved mechanical properties, low cost, and stability.³ It can take up varying degrees of solid loading, up to 90%, and still exhibits a low viscosity compared to that of CTPB or PBAN binders. It can be cured by a variety of curing agents and is crosslinked with a number of diols and triols.

The plasticizer is one of the important ingredients added in the propellant formulation, in the range 20–40% of the binder, to make solid propellant less sensitive to impact, and to improve the processability of the propellant slurry by reducing the viscosity, thus increasing the pot life. It is also added to improve the physical properties of the propellant and the behavior at extreme temperatures. Without the plasticizer, the propellant may crack at low temperatures. It helps the free movement of binder molecules without undergoing chemical reaction. The plasticizers used in propellant formulation are ester-type plasticizers like dioctyl adipate (DOA), isodecyl pelargonate (IDP), trioctyl phosphate (TOF), and hydrocarbon oils like butane and polyisobutylene. For HTPB binder, DOA has been found to be a suitable and compatible plasticizer.

In this study a mathematical model is attempted, to predict the viscosity of the binder/plasticizer system as a prelude to predicting the unloading viscosity of solid propellant slurry.

Studies of this kind have been only scantily reported. Yang et al.⁴ studied the flow characteristics of HTPB and di(ethyl/hexyl)sebacate plasticizer, the prepolymer binder for a propellant system. Their results indicated the existence of a critical temperature (T_c), when $\log \eta$ was plotted against temperature. The viscosity changes rapidly when the temperature is below T_c and changes slower over T_c . In addition, the critical temperature depends on the molecular weight of HTPB. The results obtained from the model compare extremely well with the experimental viscosity of the HTPB–DOA system.

EXPERIMENTAL

Materials

HTPB was obtained from NOCIL (Mumbai, India). It had a number-average molecular weight of 2200–2600. DOA was obtained from Indo-Nippon, Mumbai. Both were used as received.

Methods

The viscosity of HTPB and DOA and their mixtures in the ratios 95/5, 90/10, 80/20, 70/30, 60/40, and 50/50 were measured at temperatures 30, 40, 50, and 60°C each. A Brookfield viscometer model DV III (Brookfield Instruments), with a small-scale sample adapter and spindle no. 21, was used to measure the viscosity of the samples. The accuracy of viscosity measurement was ± 15 cP. A thermostated water bath was used to maintain the temperature of the sample through a water jacket fitted to the small sample adapter. The bath temperature was maintained with an accuracy of $\pm 1^\circ\text{C}$. Before performing the experiments, the samples were deaerated. The viscosity measurements were repeated three times each and the averages of the readings were taken for mathematical analyses of the data. The results are given in Figure 1.

Data Interpretation and Theoretical Modeling

Initially, a parabolic behavior of viscosity with temperature was assumed for curve fitting. The second-order parabolic fit showed that there is variation at higher as well as lower concentrations, as shown in Figure 2. Therefore, for better accuracy, a fourth-order curve was fitted, which gives better results, matching with the experimental.

A curve of the type

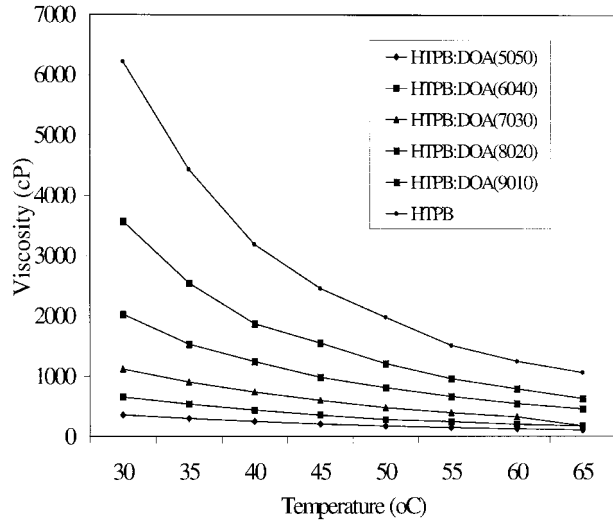


Figure 1 Experimental viscosity plots for HTPB and HTPB/DOA mixtures.

$$\eta_{th} = a_1T^4 + a_2T^3 + a_3T^2 + a_4T + a_5 \quad (1)$$

was fitted for these liquids, where η_{th} is the theoretical viscosity, and a_1, a_2, a_3, a_4, a_5 are constants.

The nature of the curve for HTPB is

$$\eta_H = 0.0097T^4 - 0.325T^3 + 37.719T^2 - 1904.255T + 37378.023 \quad (2a)$$

and for DOA,

$$\eta_D = 0.000004T^4 - 0.0077T^3 + 0.00582T^2 - 2.129T + 38.109 \quad (2b)$$

The small coefficient, either 10^{-6} or 10^{-3} , in η_D contributes fairly to η because of the higher power in temperature, T^4 or T^3 . Second, uniformity in η_H and η_D for subsequent analyses is essential. This was obtained by least-square analysis of the minimization process. Let E be the error between theory and experiment,

$$E^2 = \sum_{i=1}^n (\eta_{exp}^i - \eta_{th}^i)^2$$

where n is the number of observations in the experiments.

For extremization,

$$\frac{\partial E}{\partial a_i} = 0, \quad i = 1, 2, 3, 4, \dots, 8$$

Thus,

$$\sum_{i=1}^n (a_1T^4 + a_2T^3 + a_3T^2 + a_4T + a_5)T^4 = 0 \quad (3a)$$

$$\sum_{i=1}^n (a_1T^4 + a_2T^3 + a_3T^2 + a_4T + a_5)T^3 = 0 \quad (3b)$$

$$\sum_{i=1}^n (a_1T^4 + a_2T^3 + a_3T^2 + a_4T + a_5)T^2 = 0 \quad (3c)$$

$$\sum_{i=1}^n (a_1T^4 + a_2T^3 + a_3T^2 + a_4T + a_5)T = 0 \quad (3d)$$

$$\sum_{i=1}^n (a_1T^4 + a_2T^3 + a_3T^2 + a_4T + a_5) = 0 \quad (3e)$$

The linear simultaneous equations were solved using the Gauss elimination method. The resulting curve fits are given by eqs. (2a) and (2b). In Figure 1, the experimental viscosity of HTPB and the mixtures of HTPB–DOA at different temperatures is plotted. The experimental data of DOA

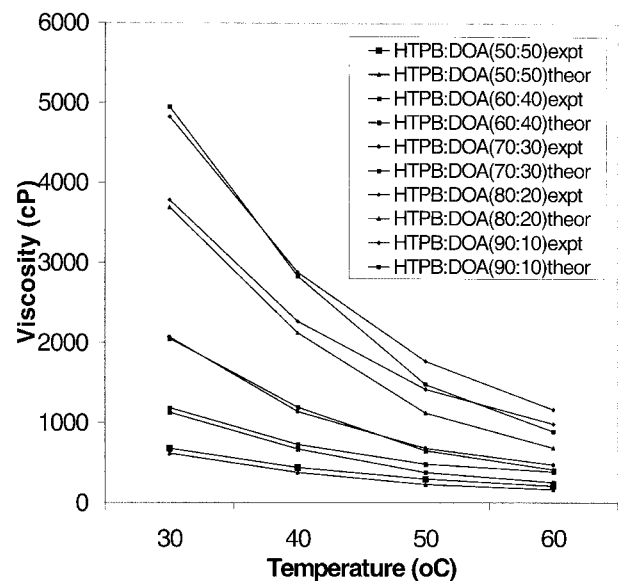


Figure 2 Experimental and theoretical curve fit of second order.

Table I Experimental Viscosity of DOA

Temperature (°C)	Viscosity (cP)
30	9.62
40	7.14
50	5.03
60	4.03

are given in Table I. It is seen that the viscosity of the mixture is lowered as the plasticizer content is increased, but always lies between that of HTPB and DOA. The viscosity of the mixture is assumed to be a linear combination of η_H and η_D in the given temperature range. We write

$$\eta_m = C_1\eta_H + C_2\eta_D + C_3 \quad (4)$$

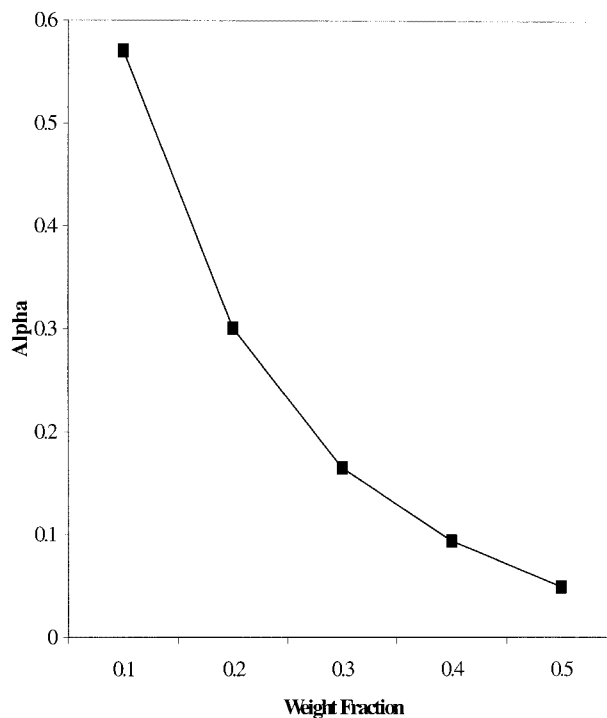
where η_m refers to the viscosity of the mixture. The numbers C_1 , C_2 , and C_3 are constants for a given weight ratio and thereby functions of the weight fraction (w). The values are given in Table II. Again, by least-square analysis of the minimization process, we deduce the linear simultaneous equations of eq. (4), which are as follows:

$$\sum_{i=1}^n (\eta_{\text{exp}} - C_1\eta_H - C_2\eta_D - C_3)\eta_H = 0 \quad (5a)$$

$$\sum_{i=1}^n (\eta_{\text{exp}} - C_1\eta_H - C_2\eta_D - C_3)\eta_D = 0 \quad (5b)$$

$$\sum_{i=1}^n (\eta_{\text{exp}} - C_1\eta_H - C_2\eta_D - C_3) = 0 \quad (5c)$$

The values in Table II indicate a singular characteristic, for $C_1(w)$ and $C_2(w)$; these are the same for a given weight fraction, which clearly indicates that $C_1(w) = C_2(w)$, and it is the thinning


Figure 3 Plot of alpha versus weight fraction.

coefficient in the sum of the viscosities of HTPB and DOA. The plot of $C_1(w)$ (alpha) against the weight fractions is shown in Figure 3, which clearly shows an exponential nature, and works out to be $e^{-5.964w}$. The values of C_3 follow a parabolic type of curve, given by the equation

$$C_3 = (-1884.8724w^2 + 983.9678w + 32.6085) \quad (6)$$

Hence, by substituting for C_3 in eq. (4) and the exponential factor for C_1/C_2 , eq. (4) becomes,

$$\eta_m = e^{-5.964w}(\eta_H + \eta_D) + (-1884.873w^2 + 983.968w + 32.609) \quad (7)$$

Table II Values of the Constants C_1 , C_2 , and C_3

Weight Fraction of Plasticizer	C_1	C_2	C_3
0.5	0.048931	0.049157	69.181984
0.4	0.093796	0.093790	97.137856
0.3	0.1646311	0.164994	145.750641
0.2	0.300405	0.301141	198.030426
0.1	0.579332	0.578791	190.187256

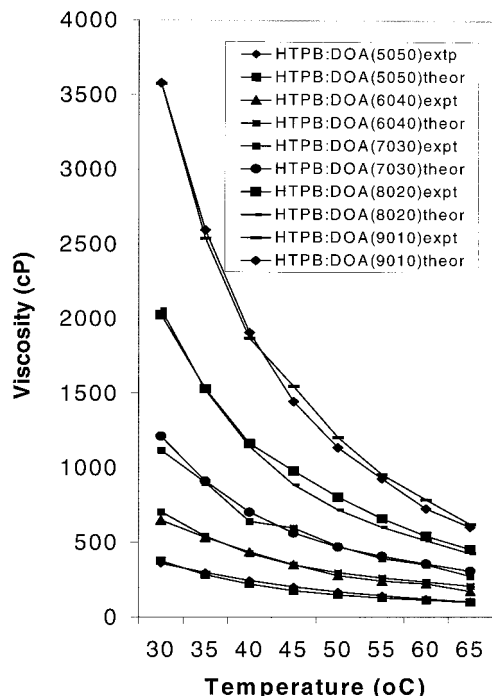


Figure 4 Comparison of experimental and theoretical data.

Substituting for η_H and η_D , we finally obtain the mathematical model for the mixture as

$$\eta_m = e^{-5.946w}(-0.00097T^4 - 0.326T^3 + 37.777T^2 - 1906.384T + 37416.132) + (-1884.873w^2 + 983.968w + 32.609) \quad (8)$$

This model gives the viscosity of the mixtures of HTPB and DOA. In the present model, we have considered the effects of both the temperature

and composition of the mixtures. The plot comparing the experimental and theoretical data is shown in Figure 4. It shows that the theoretical result matches well with experimental data at higher concentrations of the plasticizer. The reason for this may be that at lower concentrations the plasticizer occupies the free volume or void in the polymer, thereby contributing to the reduction in viscosity, whereas at higher concentrations of the plasticizer, the polymer may be swelled by the plasticizer.

RESULTS AND DISCUSSION

The experimental viscosities of the DOA and mixtures of HTPB and DOA as a function of temperature are plotted in Figure 1. The viscosity decreases with increase in temperature and vice versa, which may lead one to assume a hyperbolic nature for the viscosity curve, although a mathematical model of this type did not match with the experimental data. It turns out that there is a nonzero limit value for the viscosity when the temperature tends to zero, whereas the viscosity tends to zero asymptotically as the temperature rises.

The experimental data indicate that the viscosity of mixtures of HPTB and DOA depends on the temperature and the mixture weight ratios. The viscosity is independent of the torque of the spindle. The experimental data for the 60 : 40 mixture of HTPB : DOA are given in Table III as a representative example.

The dependency of the viscosity on the temperature of a liquid is numerically related by the Arrhenius and Guzman equation⁵:

Table III Experimental Viscosity of HTPB : DOA (60 : 40) at Different Torques and Temperatures

Temperature (°C)	Torque (%)					
	50	60	70	80	90	100
	Viscosity (cP)					
30	649	646	649	646	646	646
35	533	532	531	530	531	531
40	433	434	433	434	433	433
45	349	349	349	349	350	350
50	275	275	276	276	276	277
55	240	239	239	239	239	239
60	200	199	198	198	198	198
65	171	171	172	171	171	171

Table IV Comparison of Viscosity Data

Temperature (°C)	HTPB			DOA		
	Experimental	Arrhenius Type	Polynomial	Experimental	Arrhenius Type	Polynomial
30	6226.5	6084.48	6206.04	9.0	9.04	8.95
40	3187.3	3515.24	3238.37	6.54	6.49	6.69
50	1975.6	2010.84	1898.18	5.16	4.98	5.14
60	1244.8	1023.40	1285.34	3.81	3.98	3.89

$$\eta = Ae^{B/RT} \quad (9)$$

where A and B are constants for a given liquid. This model gives the energy for viscous flow to be $\cong 35$ kcal/mol for HTPB. The expansion of the exponential function in the Arrhenius equation, up to an accuracy of the order of $1/T^4$, shall be of the form

$$\eta = e + \frac{d}{T} + \frac{c}{T^2} + \frac{b}{T^3} + \frac{a}{T^4} \quad (10)$$

The values of viscosity obtained from eq. (10) are given in Table IV, which also presents a comparison of results from the fourth-order curve, Arrhenius curve, and the experimental data. It is clear that the fourth-order curve provides much higher accuracy compared to that of the Arrhenius curve in the range of temperature studied. The viscosity of the mixture depends on the temperature and decreases with increasing temperature. The numerical equation relating viscosity and the mole fraction of the mixture is expressed by⁵

$$\phi = \phi_A X_A + \phi_B X_B \quad (11)$$

where ϕ is the viscosity of the mixture and ϕ_A and ϕ_B are the values of the pure components whose mole fractions are X_A and X_B . In the present model, we have added a constant term for better results of the viscosity. The same model may be suitable for other types of non-Newtonian liquids

as well. The validation of the model will be done in further studies.

CONCLUSIONS

The experimental viscosities of HTPB, DOA, and their mixtures were measured, the resulting data of which are modeled to fit into a fourth-order equation, which predicts viscosities of mixtures of different weight ratios. The predicted values are in close agreement with experimental data. The model gives the energy for viscous flow as 35 kcal/mol for hydroxyl-terminated polybutadine.

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