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Evaluation of criteria for blending hydroxy terminated polybutadiene (HTPB) polymers based on viscosity build-up and mechanical properties of gumstock

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Abstract

The reaction of HTPB with TDI was studied by bulk viscosity build-up and was found to occur in two stages, the rate constant for the first stage ($K_1 = 2.318–3.448 \times 10^{-2}$ min^{-1}) being greater than for the second stage ($K_2 = 1.040–2.296 \times 10^{-2}$ min^{-1}). The rate constant for blends of polymers was shown to be equal to the weighted average of rate constants of the individual components. The bulk viscosity of the system at the point of intersection (η_i) of the two stages was observed to be independent of r ([NCO]/[OH]), the functionality distribution and temperature for polymers with very close molecular weights whereas the ratio of η_i to the initial viscosity (η_0) was found to be constant for polymers of different molecular weights. Initial modulus and elongation at break of gumstocks of blends of HTPBs were found to be given by the weighted average of the individual components, but tensile strength remained constant. These observations lead to criteria for blending polymers to obtain desired properties. © 2000 Elsevier Science Ltd. All rights reserved.

1. Introduction

Hydroxy terminated polybutadiene (HTPB) liquid polymers play an important role in the manufacture of composite solid propellants for rocket motors on account of their higher specific impulse and desirable mechanical properties of the grain [1]. The urethane copolymers obtained by curing HTPB with a diisocyanate (TDI) serve as fuel and also provide a matrix for inorganic oxidiser, metallic fuel and other dispersed solid components of the propellants. Initially, the ingredients except the curing agent (diisocyanate) are mixed thoroughly to obtain a high degree of homogeneity of the mix. Then the desired quantity of diisocyanate is added and mixed thoroughly just before casting the propellant. During addition of the curing agent, the urethane network formation develops and the viscosity of the slurry increases and the rate of viscosity build-up determines the pot life of the slurry. So an understanding of the factors that contribute to the slurry viscosity build-up and hence the processability of the resin is advantageous to the propellant chemist and was reported earlier by Rao and co-workers [2]. Further, the dependence of network mechanical properties on functionality type and molecular weight distributions is also well understood [3–7]. However, HTPB is usually prepared by a batch process and blended together to manufacture large propellant

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grains. Inadvertent variations of the process parameters during synthesis can lead to batch-to-batch variations in resin properties and the criteria adopted for mixing various individual batches is not well documented. Also the effect of mixing on processability and network mechanical properties is not well understood. So, in this communication, the studies of viscosity build-up and the mechanical properties of gumstock derived from mixtures of HTPB polymers of widely varying functionalities and TDI are reported.

2. Experimental

2.1. Materials

HTPB prepolymers were prepared by H_2O_2-initiated free radical polymerization of 1,3-butadiene in 2-propanol–water solvent system [8]. Polymers I–III were prepared under nearly similar conditions. Polymers IV–VI were produced with varying monomer to initiator ratios [9]. The sample polymers were donated by Propellant Fuel Complex, VSSC. The toluene diisocyanate (TDI, Mitsubishi, Japan) used is an 80:20 mixture of 2,4 and 2,6 isomers and was used as received.

2.2. Polymer characterization

The number average molecular weight ($\bar{M}_n$) of the polymers was determined using a Knauer analog VPO with toluene as solvent at 65°C. Hydroxyl values were determined by standard chemical methods.

2.2.1. Molecular weight distribution

A Waters 515 HPLC/GPC system coupled with a Waters 410 RI detector was used for molecular weight distribution (polydispersity) measurements. Polydispersity was determined using a set of two μstyragel columns with permeabilities of 500 and 100 A° in series. Tetrahydrofuran (THF) was used as eluant at a flow rate of 1.0 ml/min. Millennium 32 software with GPC option was used for computation of molecular weights and polydispersity. Bimodal molecular weight distribution (high molecular weight fraction, Fh) measurements were done on HPLC mode using a reverse phase preparatory column (Shimpack Prep-ODS, Shimadzu). THF was used as the eluant at a flow rate of 5.0 ml/min.

2.2.2. Viscosity measurement

A RVT model Brookfield viscometer was used to measure the viscosity during the cure reaction of HTPB with TDI. The temperature was maintained at 60 ± 0.2°C by means of a large-volume constant-temperature bath. A single spindle with different rotational speeds was used to measure the viscosities. The study was limited to the early stages of reaction.

2.2.3. Preparation of polyurethane networks

The polyurethane network was obtained by curing HTPB polymer samples with TDI at an [NCO]/[OH] equivalence ratio of 0.8 and a stoichiometric ratio of 1.0 at 70°C for 24 h.

2.2.4. Mechanical properties

Tensile strength (TS) and elongation at break (E_b) of the cast polyurethanes were determined using an Instron universal testing machine UTM model 4201 using dumb-bell shaped specimens as described in ASTM D412. Moduli of various specimens were measured at 100% elongation.

2.2.5. Cross-link density and sol content

Cross-link density, defined as moles of effective network chain per cubic meter, was obtained by calculating the volume fraction of the swollen polymer, the experimental details of which is given in the literature [10]. From the volume fraction data under equilibrium swollen condition, the cross-link density (ν_e) was calculated by the Flory–Rhener relation [11]. The sol content of the network was measured by soxhlet extraction with toluene for 48 h.

3. Results and discussion

3.1. Characterization of HTPB polymers

HTPB polymers were characterized by their $\bar{M}_n$

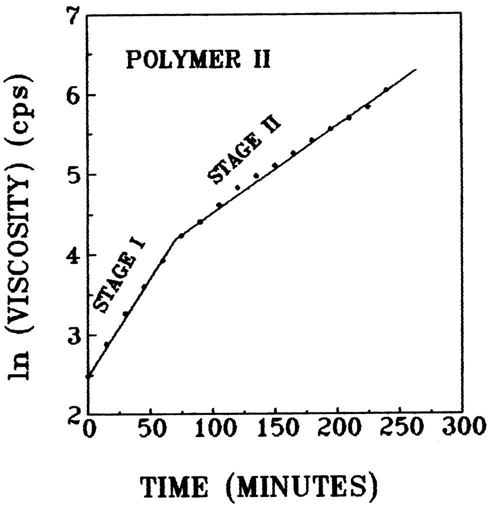

Fig. 1. Plot of ln (viscosity) vs time.

Table 1
Properties of HTPB Polymers

Polymer no.	OH Value (mg KOH/g)	$\bar{M}_n$ (VPO)	Viscosity (30°C) (cps)	$\bar{M}_w/\bar{M}_n$ (GPC)	$\bar{f}_n$	Fh (%)
I	43.3	2670	6350	2.2	2.06	28.4
II	40.8	2560	4920	2.0	1.86	18.4
III	41.5	2640	4900	2.0	1.95	14.5
IV	34.1	3290	8720	2.7	2.00	–
V	27.4	3510	12190	2.9	1.71	–
VI	21.1	4480	37760	2.5	1.69	–

(VPO), OH value (by acetylation), high molecular weight fraction (Fh) by HPLC and polydispersity ($\bar{M}_w/\bar{M}_n$ by GPC) and selected properties of the HTPB polymers employed in the present study are given in Table 1. Polymers I and II differ distinctly in their Fh (high molecular weight fraction) content. Earlier studies [3] have shown that the functionality of HTPB polymers increases with Fh content. So polymers I and II differ considerably in functionality and hence were selected for studying the effect of mixing.

3.2. Determination of rate constants K_1 and K_2 for viscosity build-up

The viscosity build-up was shown to be a first order reaction in earlier studies [2]. Therefore ln (viscosity) was plotted against time and a typical plot for polymer II is shown in Fig. 1. The plot indicates that the viscosity build-up occurs in two distinct stages. The rate constants K_1 and K_2 for the two stages are evaluated from the slopes of the plots for polymers I and II and their mixes and the results obtained are given in Table 2. It is observed that K_1 is always greater than K_2.

3.3. Effect of mixing on rate constants

The values of K_1 and K_2 for a 1:1 blend of polymers I and II were evaluated and were found to be the averages respectively of the K_1 and K_2 values of the parent resins. For other mixes also, K_1 and K_2 values were found to be the weighted averages of the individual K_1 and K_2 values. This is in accord with earlier observations that the rate constants for viscosity build-up show linear correlation with the mole fraction (a_3) of the hydroxyl groups arising from the trifunctional components of the polymers [2]. Therefore, mixing of two polymers of varying a_3 values would result in a polymer having the weighted average of the individual values if the molecular weights of the polymers are essentially same. Hence, rate constants should show similar behaviour as was observed experimentally (Fig. 2). Therefore, it can be inferred that the viscosity build-up of a mixture of polymers is characterised by weighted averages of the individual components.

3.4. Stage separation during viscosity build-up

A greater insight of the process of viscosity build-up can be obtained by analysing the time (T_i) and viscosity (η_i) at the point of intersection of the two stages. These two parameters, T_i and η_i were evaluated from the linear regression equations obtained from the least square fit of ln (viscosity) vs time data. The values obtained are given in Table 2. The data indicate that although T_i changes from 48 to 79 min, η_i is almost constant (73.6 ± 3.0 ps). This observation suggests very clearly that the second stage in the viscosity build-up is diffusion controlled and is not dependent on the extent of reaction. Further confirmation of these results was obtained by studying the viscosity build-up at different ratios r ($=$[NCO]/[OH]) of the polymer and the curing agent TDI.

Table 2
Viscosity build-up parameters at [NCO]/[OH] = 0.8[a]

Sl. no.	Polymer no.	a_1	$K_1 \times 10^{-2}$ (min^{-1})	a_2	$K_2 \times 10^{-2}$ (min^{-1})	T_i (min)	η_i (ps)
1	I	2.614	3.448	3.166	2.296	47.9	71.3
2	I + II (1:1)	2.584	2.760	3.368	1.478	61.2	71.7
3	I + II (1:3)	2.501	2.840	3.251	1.410	52.5	54.1
4	II	2.532	2.318	3.531	1.040	78.6	77.9

[a] a_1 and a_2 are constants of the rate equations, $\ln \eta = K_1 T + a_1$ (stage I) and $\ln \eta = K_2 T + a_2$ (stage II); T is time in min.

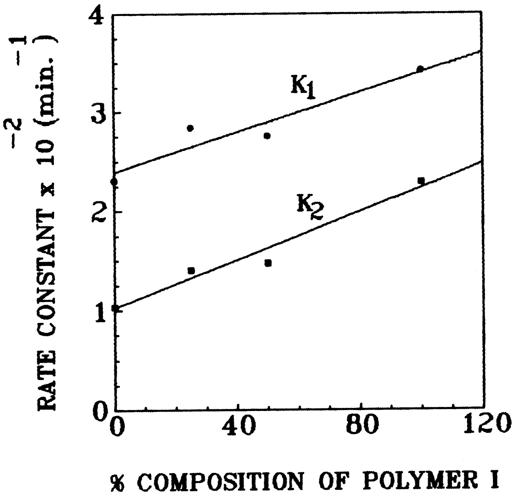

Fig. 2. Plot of polymer rate constant vs composition.

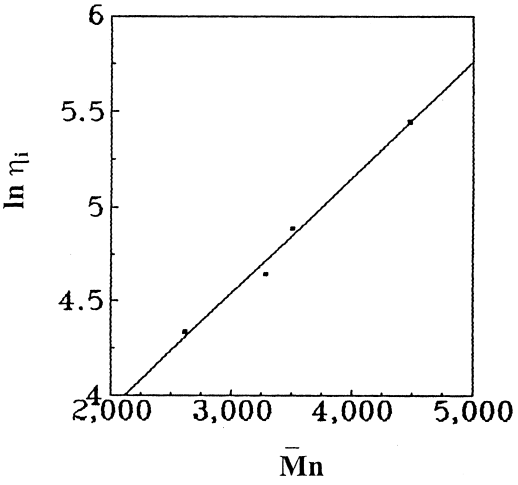

Fig. 3. Plot of ln η_i vs $\bar{M}_n$.

3.5. Effect of r

The HTPB polymer III was cured with TDI at four different values of r (0.7, 0.8, 0.9 and 1.0) at 60°C. The parameters K_1, K_2, T_i and η_i were evaluated as described earlier. The results obtained are given in Table 3 and indicate that:

1. K_1 and K_2 increase with r as expected from the law of mass action;
2. T_i values decrease with r and
3. η_i values remain essentially constant (78.3 ± 3.3 ps) at all values of r and are similar to the values obtained earlier.

3.6. Effect of temperature

Polymer III was reacted with TDI at $r = 0.8$ and 40°C. The values of various parameters obtained are also given in Table 3. Once again, the value of η_i (83.2 ps) is nearly equal to the value obtained earlier.

Therefore, it can be inferred that η_i is independent of r, functionality distribution and temperature for polymers having close molecular weights and their distributions.

3.7. The effect of molecular weight

Since η_i was found to be essentially independent of reaction parameters, the effect of molecular weight on viscosity build-up was studied by considering polymers IV–VI having widely different molecular weights. The polymers were reacted with TDI at $r = 0.8$ and 60°C and the values obtained for K_1, K_2, T_i and η_i are given in Table 4. Interestingly η_i values vary considerably indicating its dependence on the molecular weight of the polymers. Therefore, a plot of ln η_i vs $\bar{M}_n$ was drawn (Fig. 3) and shows a linear correlation. Since the initial viscosities (η_0) of the polymers are different ln (η_i/η_0) values were calculated and are summarised in Table 5. These results clearly indicate that ln (η_i/η_0) is nearly constant (1.84 ± 0.14) except for polymer VI. This discrepancy may arise due to the effect of factors other than $\bar{M}_n$ on the bulk viscosity of the HTPB polymers as was observed earlier [12].

Table 3
Effect of r value on viscosity build-up for polymer III at 60°C

Sl. no.	r	a_1	$K_1 \times 10^{-2}$ (min^{-1})	a_2	$K_2 \times 10^{-2}$ (min^{-1})	T_i (min)	η_i (ps)
1	0.7	2.449	1.964	3.481	0.866	94.0	73.3
2	0.8	2.407	2.179	3.412	1.088	92.1	82.6
3	0.9	2.392	2.262	3.362	1.149	87.2	78.5
4	1.0	2.319	2.604	3.438	1.179	78.5	78.6
5[a]	0.8	3.139	1.642	3.910	0.655	78.1	83.2

[a] At 40°C.

Table 4
Effect of molecular weight on viscosity build-up

Sl. no.	Polymer no.	a_1	$K_1 \times 10^{-2}$ (min^{-1})	a_2	$K_2 \times 10^{-2}$ (min^{-1})	T_i (min)	η_i (ps)	a_3	$\bar{M}_n$ (VPO)	$\bar{M}_w/\bar{M}_n$
1	IV	2.896	2.933	3.694	1.594	59.6	104	0.4533	3290	2.7
2	V	3.156	2.124	4.109	1.206	64.6	133	0.3936	3510	2.9
3	VI	4.600	1.201	5.027	0.598	70.8	233	0.2702	4480	2.5

3.8. Correlation of mechanical properties

Polymers I and II and their blends were cured by reacting with TDI at 70°C for 24 h to obtain crosslinked polyurethane networks. The cure reaction was carried out at an [NCO]/[OH] equivalence ratio of 0.8. The cured polymers were characterized by their sol content, crosslink density and mechanical properties (tensile strength, modulus and elongation at break E_b). The measured mechanical properties are given in Table 6. Plots of E_b and modulus against composition of polymers (Fig. 4) show linear correlation, indicating the mechanical properties of the system also exhibit properties which are weighted averages of the individual components. Interestingly, the tensile strength of the gumstocks shows no apparent variation with the composition. This trend was further confirmed by preparing gumstocks of polymers I and II at $r = 1.0$ and their mechanical properties are also shown in Table 6. Once again, it is observed that the tensile strength of the two samples (Table 6) differ only marginally.

3.9. Correlation of network properties

Earlier studies [4] showed that HTPB systems could be approximated to a system containing non-, di- and tri-functional species with only negligible amounts of mono functional species. Further, it was shown that **G** type hydroxyls $\sim\sim CH_2{-}C\ (=CH{=}CH_2OH) \sim\sim$ could be considered as branching points and the mole fraction (a_3) of the hydroxyl groups arising from the trifunctional components could be obtained either from ^{13}C nmr spectroscopy or using the relation

$$a_3 = 206.7/(E_b + 165.6)$$

Where E_b = percentage elongation at break of gumstock prepared at $r = 1.0$. The values of a_3 thus obtained for polymers IV–VI are given in Table 4. Network properties like crosslink density (ν_e) and sol content were also calculated using the relationships [4]:

$$\nu_e = \left[\frac{rp^2(1+a_3)-1}{rp^2 a_3}\right]^3 \frac{a_3\, d}{2W_{eq}} \times 10^6 \text{ moles m}^{-3}$$

$$\%\ \text{sol} = [(rp^2-1)/rp^2 a_3]^3 \times 100 + \%\ \text{non-functionals}$$

where a_3 is mole fraction of the trifunctional component; r is [NCO]/[OH]; p is extent of reaction; d is density of the gumstock (0.92 g/cc) and W_{eq} is equivalent weight of the system.

Table 5
Variation of η_i with $\bar{M}_n$ and η_0

Sl. no.	Polymer	r	$\bar{M}_n$	η_0 (ps)	η_i (ps)	ln η_i/η_0
1	I	0.8	2670	13.7	71.3	1.65
2	I+II (1:1)	0.8	2610	13.3	71.7	1.69
3	I+II (1:3)	0.8	2590	–	–	–
4	II	0.8	2560	12.6	77.9	1.82
5	III	0.7	2640	11.6	73.3	1.85
6	III	0.8	2640	11.1	82.6	2.00
7	III	0.9	2640	10.9	78.5	1.97
8	III	1.0	2640	10.2	78.6	2.05
9	IV	0.8	3290	18.1	104	1.75
10	V	0.8	3510	23.5	133	1.74
11	VI	0.8	4480	99.5	233	0.85

Based on the previous experience on the prediction of mechanical properties of gumstocks and propellants, the extent of reaction (p) was assumed to be 0.975.

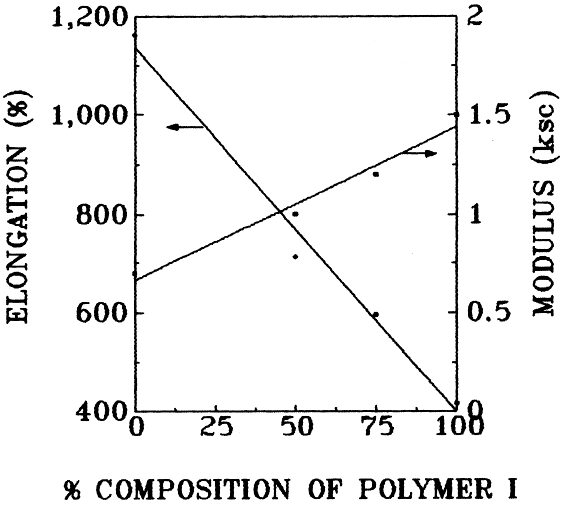

Fig. 4. Plot of elongation, modulus vs composition.

Table 6
Mechanical properties

Sl. no.	Polymer no.	r	a_3	Eq. wt.	Modulus (ksc)		Elongation (E_b) (%)	Tensile strength (ksc)	Crosslink density (moles m^{-3})		Sol content (%)	
					Obs.	Calcd.			Obs.	Calcd.	Obs.	Calcd.
1	I	0.8	0.6252	1107	1.5	–	417	4.3	30	32	28.0	25.0
2	I+II (3:1)	0.8	0.5920	1123	1.2	1.3	596	4.3	25	25	26.6	27.0
3	I+II (1:1)	0.8	0.5589	1139	1.0	1.1	713	4.3	20	19	30.0	30.0
4	II	0.8	0.4926	1170	0.7	–	1162	4.2	9	9	35.0	32.0
5	I	1.0	0.6252	1107	4.8	–	165	6.6	352	–	10.0	13.0
6	II	1.0	0.4926	1170	3.4	–	254	6.0	–	–	–	–

The sol content measured at $r = 1.0$ is assumed to be equal to the amount of non-functional species. With these assumptions, the value of crosslink density (ν_e) and % sol were calculated and compared with the observed values in Table 6. A satisfactory agreement between the two sets validates the assumptions and show that the network properties are also weighted averages of the values of the individual components.

The modulus of the gumstock can be correlated with crosslink density, ν_e. Thus a plot of modulus vs ν_e (Fig. 5) is linear and the relationship is given by the equation

$$\text{Modulus} = 0.03678\,\nu_e + 0.3277$$

However, tensile strength is least sensitive to the number of crosslinks. This shows that tensile strength is dictated more by the nature of the backbone of the network and is much less sensitive to the number of crosslinks.

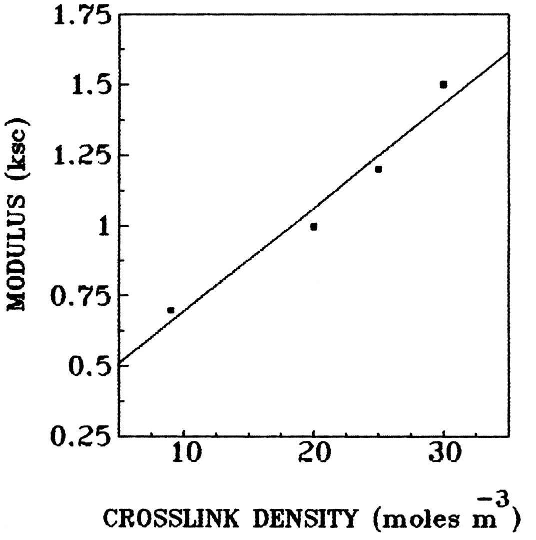

Fig. 5. Plot of modulus vs crosslink density.

4. Conclusions

The important conclusions that can be drawn from the present study are:

1. the reaction of HTPB and TDI occurs in two stages, with the first order rate constant for the viscosity build-up being greater for the first stage;
2. the viscosity build-up for mixture of HTPB polymers is characterized by the weighted average of the rate constants for the individual components;
3. the bulk viscosity of the system (HTPB + TDI) at the point of intersection of the two stages is independent of r, functionality and temperature for HTPB polymers of very close molecular weights ($\eta_i = 73.6 \pm 3.0$ ps);
4. for HTPB polymers of different molecular weights, η_i/η_0 is essentially constant ($\ln \eta_i/\eta_0 = 1.84 \pm 0.14$) and
5. the preceding observations lead to the criteria for blending HTPB polymers to obtain desired properties.

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