Modelling the effect of functionality distribution on the crosslinking characteristics of hydroxy-terminated polybutadiene liquid prepolymers[*]

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Network properties like sol content, crosslink density (V_e) and effective chain length (L_X) of polyurethanes based on hydroxy-terminated polybutadiene (HTPB) prepolymers and toluene diisocyanate were calculated using the models of Marsh *et al.* and of Macosko and Miller. The input parameters required are the functionality distribution and equivalent weight of the polymer, extent of reaction (p_A) and density of the cured network. It was found that the functionality distribution of HTPB can be adequately described by di- and trifunctional species estimated from ^{13}C nuclear magnetic resonance spectra and non-functional species obtained from sol content at $r = [NCO]/[OH] = 1.0$. The value of p_A was shown to be nearly 1.0 when $r < 0.9$. Satisfactory correlations were obtained between calculated and observed crosslink densities of HTPB prepolymers of widely varying functionality distribution. These studies were extended to mixed systems containing HTPB, trimethylolpropane and 1,4-butanediol and to propellant systems containing 86% solid loading. Relationships were derived between V_e and tensile strength and modulus, and between L_X and elongation at break (E_b) of gumstocks and propellants. These relationships were used to predict the mechanical properties of several propellant formulations, with very good agreement between observed and predicted properties.

(Keywords: OH-terminated polybutadiene; functionality distribution; modelling)

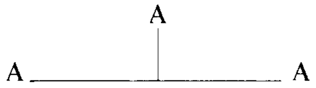
INTRODUCTION

Polyurethane network structures, derived from hydroxy-terminated polybutadiene (HTPB) liquid prepolymers and a diisocyanate, impart three-dimensional stability to a solid composite propellant grain, and the rubbery nature of the network allows the grain to withstand thermal cycling and pressurization[1]. Therefore, an understanding of the relationship between prepolymer properties and the mechanical behaviour of the networks is of crucial importance to the development of solid propellant technology. Such an understanding enables one to design solid propellants with desired properties using a minimum number of formulations.

Considerable attention has been given to the development of models describing post-gel structures of condensation polymers[2–8]. Network characteristics such as crosslink density (V_e), sol–gel content, average length of effective chains, etc., are calculated from a small number of prepolymer characteristics like composition, functionality distribution and extent of reaction (p_A). Good agreement was obtained between experimental and calculated values for simple well defined systems like polyesters[7]. However, the application of these models to the HTPB system is hampered by the fact that no satisfactory method has been reported so far for the determination of the functionality distribution of HTPB[9]. Consequently, judicious assumptions have to be made to arrive at a working model for these systems. In this communication, we report the modelling studies of the polyurethane network derived from HTPB and toluene diisocyanate, and arrive at correlations between prepolymer properties and gumstock and propellant mechanical properties. The predictive capability of the model is demonstrated for certain propellant formulations.

THEORY

Basic concepts regarding the modelling of three-dimensional polymer networks were established by Carothers[10], Flory[11] and Stockmayer[12]. The components of a simple network-forming polycondensation system are a single trifunctional (or branching) component



Trifunctional

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[*] Presented at 'The Polymer Conference', 20–22 July 1993, University of Cambridge, UK

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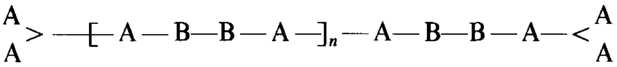
and two difunctional components:

$$\mathrm{A}\text{———}\mathrm{A} \qquad \mathrm{B}\text{———}\mathrm{B}$$

Difunctional

and involves the formation of chains of the type:



$$\begin{matrix}\mathrm{A}\\ \mathrm{A}\end{matrix}\!>\!-\!\!\left[-\mathrm{A}-\mathrm{B}-\mathrm{B}-\mathrm{A}-\right]_n\!-\mathrm{A}-\mathrm{B}-\mathrm{B}-\mathrm{A}-\!<\!\begin{matrix}\mathrm{A}\\ \mathrm{A}\end{matrix}$$

The modelling of such network chains has been approached in two different ways;

(i) α *model*. This model, developed by Flory and extended by Marsh *et al.*, describes the network in terms of branching coefficient (α) defined as the probability that any given one component of a branch unit leads, via a sequence of difunctional units, to another branch. The other network properties are then calculated from this parameter, α. The relevant equations are given in Appendix 1.

(ii) P_F *model*. In this method, developed by Macosko and Miller, the probability $P(F_A^{out})$ that a particular branch unit will lead exclusively to a finite end (or ends) is evaluated. This probability may be called 'finite chain extension coefficient' and the network properties are derived in terms of this probability using the relationships given in Appendix 2.

Both these methods assume: (a) all functional groups react independently; (b) no inter- and intramolecular side reactions occur; (c) equal reactivities of all functional groups of a given type.

However, unequal reactivity of the functional groups can be readily incorporated into the P_F model. The input parameters for both the methods are: (i) composition of the components; (ii) functionality distribution of the components; (iii) extent of reaction.

Since the extent of reaction is difficult to determine, one of the observed parameters like sol content or crosslink density is used to calculate α or P_F, from which the other parameters can be derived.

EXPERIMENTAL

Materials

HTPB prepolymers were prepared in Vikram Sarabhai Space Centre (VSSC) by H_2O_2-initiated free-radical polymerization of butadiene in 2-propanol and water solvent system. Polymers **I** to **XI** were prepared under nearly similar conditions but inadvertent variations in process parameters resulted in polymers of different properties. Polymers **XII** to **XIV** were prepared using varying amounts of initiator. Some properties of the polymers are given in *Table 1*.

Polyurethane networks

HTPB prepolymers were cured with toluene diisocyanate (TDI) at 60°C for 48 h. The resulting polyurethane networks were characterized by sol content, crosslink density and mechanical properties, and the results obtained (taken from refs. 9 and 13) are reproduced in *Table 2*.

Propellant formulations

A composite solid propellant grain was obtained by curing a mixture of HTPB, trimethylolpropane (TMP), 1,4-butanediol, ammonium perchlorate and other additives with TDI. The total solid loading was 86%.

Table 2 Mechanical properties of polyurethane networks from HTPB polymers **I–XIV**

	$r=0.75$		$r=1.00$		
Polymer	*TS* (KSC)[a]	E_b (%)	*TS* (KSC)	Modulus (KSC)	E_b (%)
I	–	–	7.1	3.0	220
II	4.3	320	7.1	–	107
III	3.5	303	6.6	–	90
IV	3.4	378	7.2	–	139
V	3.5	534	7.4	–	140
VI	3.3	630	6.8	–	170
VII	3.2	712	6.2	–	182
VIII	3.9	725	7.0	–	200
IX	3.5	750	5.8	–	212
X	4.5	1130	6.3	–	323
XI	–	–	7.2	4.5	200
XII	–	–	7.1	3.7	290
XIII	–	–	6.2	3.4	360
XIV	–	–	5.6	2.5	600

[a] *TS*, Tensile strength; KSC, kgf cm^{-2}

Table 1 Properties of HTPB polymers **I–XIV**

Polymer	OH value (mg KOH/g)	$\bar{M}_n$ (v.p.o.)	μ (cP at 30°C)	$\bar{f}_n$	a_3 (^{13}C n.m.r.)
I	45.5	2590	6880	2.10	0.5359
II	44.1	2560	6330	2.01	0.7186
III	47.2	2690	6240	2.26	0.7528
IV	43.7	2700	6460	2.10	0.7273
V	44.6	2660	5820	2.11	0.6923
VI	40.0	2590	5840	1.85	0.6471
VII	41.2	2660	6100	1.95	0.6190
VIII	40.3	2620	6150	1.88	0.5207
IX	41.8	2680	5145	2.00	0.5510
X	39.5	2720	4514	1.95	0.4359
XI	40.0	2930	5740	2.09	0.5649
XII	34.1	3290	8720	2.00	0.4533
XIII	27.4	3510	12190	1.71	0.3936
XIV	21.1	4480	37760	1.69	0.2702

RESULTS AND DISCUSSION

Determination of functionality distribution

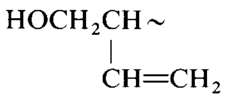
HTPB polymers are likely to contain non- and multi-functional species, and no satisfactory method is reported for an unambiguous determination of its functionality distribution. Consequently, judicious assumptions have to be made to arrive at a working model. In the present study, polymer **I** was considered as typical of the polymers used in propellant formulations and the following approach was adopted to arrive at its funcationality distribution.

Basic assumption. The functionality $\bar{f}_n$ of HTPB polymer lies in the range 1.85–2.25. Moreover, the functionality increases with increase in molecular weight. Therefore, the contribution of functionalities equal to or higher than 4 can be neglected, and the polymer can be approximated as having tri- and lower functionalities only.

Determination of mole fraction of hydroxyls on trifunctional species (a_3). HTPB contains three types of hydroxyls, **H**, **V** and **G**, with the following structures[14,15]:

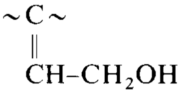
$HOCH_2CH{=}CH\text{-}CH_2\sim$

H



$$\begin{array}{l}HOCH_2CH\sim\\ \quad\;|\\ \quad CH{=}CH_2\end{array}$$

V



$$\begin{array}{l}\sim C\sim\\ \;\;\|\\ CH\text{-}CH_2OH\end{array}$$

G

G-type hydroxyl represents trifunctional (branching) component and the mole fraction of the hydroxyls on trifunctional chain can be readily obtained from ^{13}C n.m.r. as shown in earlier studies[9]. For polymer **I**, the value of a_3 obtained was equal to 0.54.

Estimation of mole fraction of hydroxyls on difunctional species (a_2). **I** was found to give a tack-free cure even at $[NCO]/[OH]=0.7$[13]. Therefore, a minimum value for a_2 can be obtained from equation (2) with $\alpha=0.5$ (condition of gelation). Thus a_2 was found to be 0.35.

Estimation of non-functional species. From the known values of a_3 and a_2, the maximum sol content observed at $[NCO]/[OH]=1.0$ can be calculated by equations (2) and (3) assuming the reaction is complete. The result indicates that the sol content is only 0.8% whereas the observed value is 12.8% (cf. *Table 3*). Therefore, it can be inferred that sol content comprises mostly non-functional species only. This was further confirmed by the absence of absorptions from TDI moiety in ^1H and ^{13}C n.m.r. spectra of the sol.

Estimation of monofunctional species. Let *n*, *m*, *d* and *t* be the mole fractions of non-, mono-, di- and trifunctional species respectively. Then, by definition:

$$n+m+d+t=1$$
$$\bar{f}_n=3t+2d+m$$
$$a_3=3t/(3t+2d+m)$$

From these equations it can be shown that:

$$t=(a_3/3)\bar{f}_n$$

and

$$(d-n)=(1-2a_3/3)\bar{f}_n-1$$

Since a_3, $\bar{f}_n$ and n (from sol content) are known, the mole fractions of di- and monofunctional species can be computed.

The results thus obtained show that the functionality distribution for **I** is as follows:

$$n=0.13, \qquad m=0.02, \qquad d=0.47, \qquad t=0.38$$

Confirmation of functionality distribution. **I** was cured at [NCO]/[OH] ratio varying from 0.7 to 1.2 and the resulting polyurethanes were characterized by their sol content, crosslink density and mechanical properties[13]. From the observed crosslink density, the branching coefficient, extent of reaction, sol content and effective chain length were calculated using equations (1)–(6). The results are shown in *Table 3*. The important points to be noted from these results are:

(i) The calculated sol contents, which include the contribution from non-functional species derived above, agree quite well with the experimental values.

(ii) The extent of reaction is in the acceptable range of 0.95–1.0.

(iii) The extent of reaction decreases with increasing *r* value. This is in accord with the result of mass action of varying levels of excess hydroxyl groups.

(iv) Elongation at break (E_b%) shows excellent linear correlation (correlation coefficient = 0.996) with the calculated parameter 'effective chain length, L_X' (*Figure 1*) as was shown by the model system.

Table 3 Calculated network properties of polyurethane from crosslink densities for polymer **I**

No.	r	V_c(obsd) (mol m^{-3})	Sol content (%) Obsd.	Sol content (%) Calcd.	p_A	L_X
1	0.7	2.5	51	57	1.00	2003
2	0.8	14.4	34	32	0.981	1026
3	0.9	42.7	20	19	0.961	654
4	1.0	87.6	13	14	0.944	483
5	1.1	100.1	13	14	0.993	457
6	1.2	101.7	14	14	1.028	454

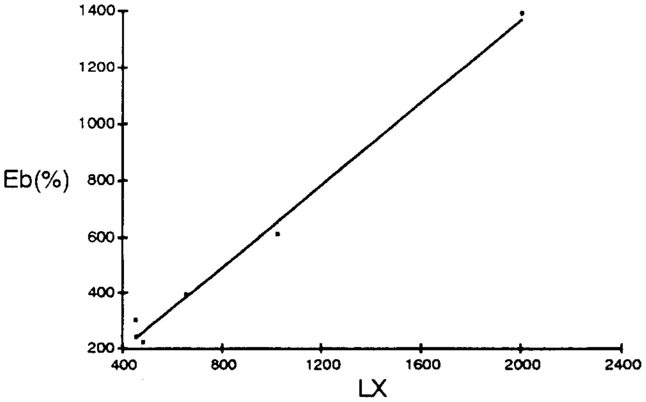


Figure 1 Plot of E_b (%) vs. L_X for polymer **I**

Table 4 Effect if functionality distribution on network properties of polyurethanes from polymers **II-X** at $r = 0.75$

	Sol content (%)			V_e (mol m^{-3})					
		Calcd.			Calcd.		L_X		
Polymer	Obsd.	*a*	*b*	Obsd.	*a*	*b*	*a*	*b*	*c*
II	11.3	10.0	8.0	53	37	41	589	548	297
III	20.5	8.0	7.2	39	47	50	503	474	251
IV	23.1	9.6	7.8	35	39	42	580	541	279
V	20.4	11.2	8.8	44	32	38	631	580	288
VI	18.8	13.7	10.5	39	23	28	814	731	341
VII	26.8	15.6	11.7	27	19	24	879	776	346
VIII	31.4	26.2	18.5	13	7	12	–	–	420
IX	–	22.1	17.9	–	11	15	1175	984	384
X	38.0	44.7	30.5	8	2	5	–	–	512

[a] Calculated at $\rho = 1$
[b] Calculated at $\rho = 5$
[c] Calculated at $r = 1$

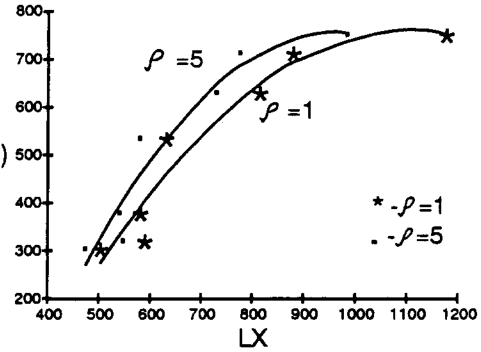


Figure 2 Plots of E_b (%) vs. L_X for polymers **II-X** at $r = 0.75$: (●) $\rho = 1$; ((*) $\rho = 5$

In summary, it can therefore be concluded that HTPB polymers prepared under the present experimental conditions can be treated as containing di- and trifunctional species only and the sol content obtained at $r = 1$ is a measure of the non-functional species.

Effect of functionality distribution

Polymers **II** to **X** have closely similar $\bar{M}_n$, OH value and intrinsic viscosity but show widely differing functionality distribution (*Table 1*, a_3 values) and gumstock properties (*Table 2*). Therefore, these polymers were taken up for modelling studies to evaluate the effect of functionality distribution on network properties. Since the extent of reaction was found to be nearly 1.0 at $r < 0.9$, the polymers were cured at $r = 0.75$. The network properties were then calculated using the α model and assuming $p_A = 1$. The results are shown in *Table 4*. As expected, the calculated values are lower than the observed values for the sol content and the differences can be attributed to the presence of non-functional species, as discussed earlier. The calculated crosslink density values are also observed to be lower by about 40% on average than the observed values. However it was reported by Pham *et al.* that **G**-type hydroxyl is more reactive than *H*- and **V**-type hydroxyls[15]. Hence, the network properties were calculated using the P_F model with a reactivity ratio (ρ) equal to 5. In this calculation, the relationship between P_F and α was used to calculate L_X. The results obtained are also given in *Table 4*. Better agreement ($\sim 20\%$ average error) between observed and calculated crosslink density values is achieved in this way. Similarly, the effective chain lengths L_X were calculated assuming equal and unequal reactivities. The plots E_b vs. L_X are shown in *Figure 2*. It is readily apparent from these plots that:

(i) The assumption of unequal reactivities gives a slightly better fit.

(ii) The observed elongation shows linear dependence on L_X at lower values, but at higher elongations the calculated values are much higher. This may be due to physical entanglement of chains, and consequently lower observed E_b values, at high elongations since the molecular weights between crosslinks (M_c) are higher. This is also in accord with the higher observed crosslink density values as discussed earlier. Further confirmation of these results is obtained from the linearity of the plot of E_b vs. L_X at $r = 1$ (*Figure 3*), wherein physical entanglement of chains is minimized due to decrease in M_c.

Propellant formulations

Composite solid propellants contain an organic fuel binder matrix in which an inorganic solid oxidizer, high-energy metal additive, burning-rate modifier, plasticizer and other additives are uniformly distributed. The binder matrix is obtained by curing varying amounts of HTPB prepolymer, trimethylolpropane and 1,4-butanediol with toluene diisocyanate. Polymers **XI–XIV** with hydroxyl values in the range 45–20 mg KOH/g were chosen for the modelling studies. The polymers were cured at $r = 0.8$. The network properties were computed using the α model with the assumption $p_A = 1$ and the results obtained are shown in *Table 5*. The mechanical properties of the gumstock and the propellant with 86% solid loading are given in *Table 6*[16].

Correlation with mechanical properties

Two of the output parameters from the model are the crosslink density V_e and effective chain length L_X. V_e can be correlated with tensile strength and modulus, and L_X can be correlated to elongation at break (E_b%). The relevant plots are shown in *Figures 4* and *5* for the gumstock studies and *Figures 6, 7* and *8* for propellants. The relationships from these plots are summarized in *Table 7*. In all cases, correlation coefficients greater than 0.9 were observed.

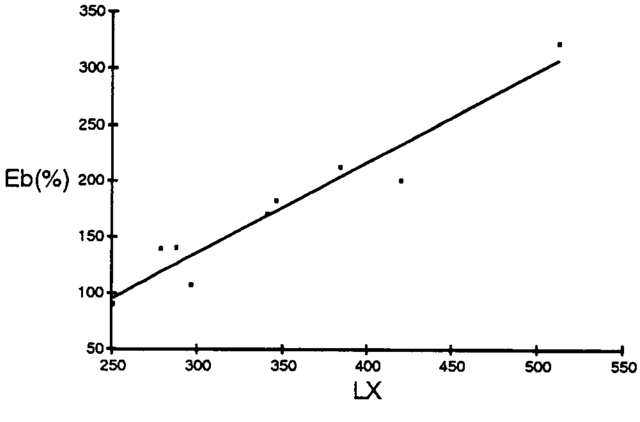


Figure 3 Plot of E_b (%) vs. L_X for polymers **II–X** at $r = 1.0$

Table 5 Calculated network properties of polyurethanes[a] from polymers **XI**–**XIV**

Polymer	Wt of TMP (g)	Sol content (%)	V_e (mol m^{-3})	L_X
	0.12	5.0	77.6	420
	0.09	6.8	57.5	505
XI	0.06	9.5	39.5	632
	0.00	22.1	11.6	1231
	0.12	6.7	52.0	561
XII	0.09	9.9	34.0	722
	0.06	15.4	18.8	1005
	0.00	48.6	1.3	3627
	0.12	7.2	41.9	676
XIII	0.09	11.4	24.6	924
	0.06	19.7	11.0	1431
	0.12	8.7	28.9	901
XIV	0.09	15.8	13.4	1389
	0.06	33.0	3.2	2840

[a] Polyurethane formulations:
Wt of HTPB + TDI = 10.78 g
TMP + butanediol = 0.12 g
$r = [NCO]/[OH] = 0.80$

Table 6 Mechanical properties of gumstocks and propellants from polymers **XI** to **XIV**

		Gumstocks[a]		Propellants[b]		
Polymer	Wt of TMP (g)	TS (KSC)[c]	E_b (%)	TS (KSC)	Modulus (KSC)	E_b (%)
	0.12	7.10	255	9.7	77	23
	0.09	7.03	332	9.2	71	28
XI	0.06	5.50	387	8.8	54	34
	0.00	3.10	541	8.2	24	48
	0.12	6.8	328	9.1	68	30
	0.09	4.0	211	8.5	68	38
XII	0.06	5.9	595	7.6	40	42
	0.00	3.9	1147	3.7	13	70
	0.12	7.4	357	8.5	42	45
XIII	0.09	7.3	520	6.6	29	55
	0.06	7.4	703	3.5	11	78
	0.12	8.4	452	9.3	42	57
XIV	0.09	7.4	658	6.6	22	75
	0.06	8.5	1048	2.8	7	111

[a] Gumstock formulations as given in *Table 5*
[b] Propellant formulations:
86% solid loading + 3% plasticizer
[c] Tensile strength

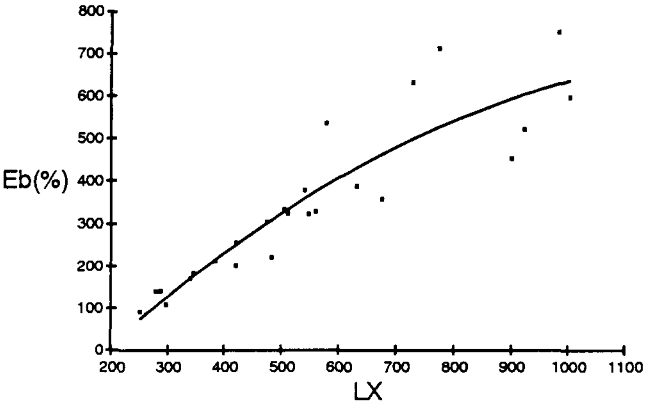


Figure 4 Plot of E_b (%) vs L_X for gumstocks

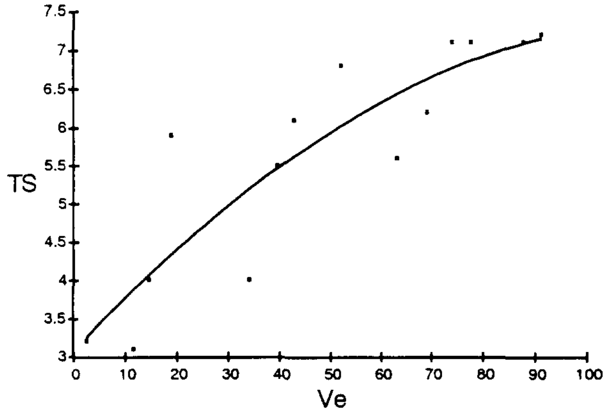


Figure 5 Plot of TS vs. V_e for gumstocks

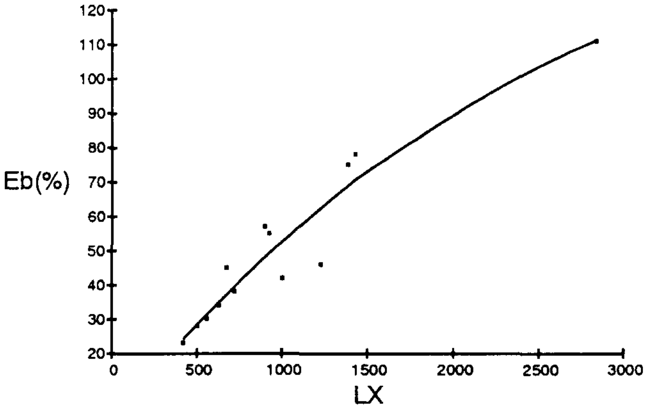


Figure 6 Plot of E_b (%) vs. L_X for propellants

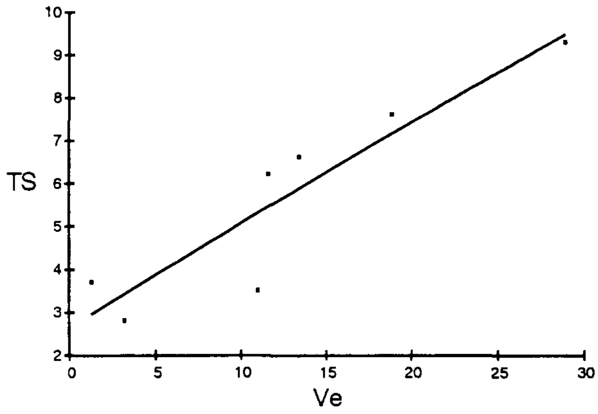


Figure 7 Plot of TS vs. V_e for propellants

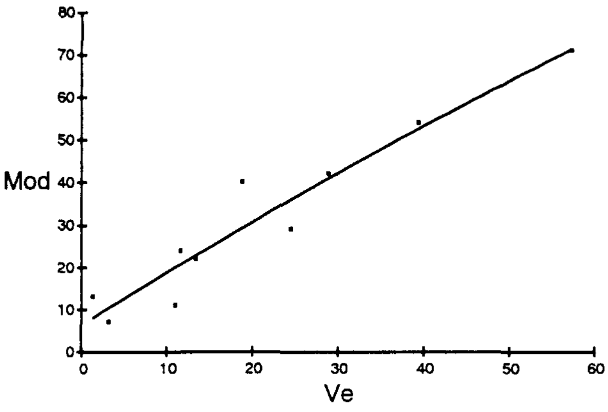


Figure 8 Plot of modulus vs. V_e for propellants

Table 7 Correlation of network parameters with mechanical properties of gumstocks and propellants

No.	Parameter	Property	Relationship
Gumstocks			
1	L_X	Elongation at break, E_b (%)	$E_b = -243.6 + 1.39 \times L_X - 5.1 \times 10^{-4} \times L_X^2$
2	V_e	Tensile strength, *TS* (KSC)	$TS = 3.1 + 0.073 \times V_e - 3.1 \times 10^{-4} \times V_e^2$
Propellants			
3	L_X	E_b (%)	$E_b = 0.68 + 0.059 \times L_X - 7.2 \times 10^{-6} \times L_X^2$
4	V_e	*TS* (KSC)	$TS = 2.65 + 0.245 \times V_e - 2.9 \times 10^{-4} \times V_e^2$
5	V_e	Modulus (KSC)	$\text{Mod.} = 6.5 + 1.26 \times V_e - 2.3 \times 10^{-3} \times V_e^2$

Table 8 Comparison of observed and calculated mechanical properties of propellants

	E_b (%)		*TS* (KSC)^a		Modulus (KSC)	
No.	Obsd.	Calcd.	Obsd.	Calcd.	Obsd.	Calcd.
1	51	49	6.6	7.7	35	32
2	59	54	5.4	6.5	23	26
3	66	60	5.1	5.5	21	21
4	68	67	4.3	4.7	20	17
5	71	76	3.7	4.0	16	13
6	84	100	2.7	3.1	11	9
7	41	43	7.0	7.4	38	31
8	48	44	6.8	9.7	39	42
9	47	53	7.2	6.5	31	26
10	41	38	7.4	10.5	45	45
11	40	42	6.6	7.0	37	30

^{a}Tensile strength

Prediction of propellant properties

The proposed model and the relationships derived therefrom were further tested by predicting the properties of several propellant formulations. These formulations were obtained by varying the amounts of HTPB and TDI and keeping all other ingredients constant. The observed and predicted properties of the propellants are given in *Table 8*. Excellent agreement between the two sets of data validates the assumptions made in arriving at the proposed model.

CONCLUSIONS

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

For modelling purposes, HTPB prepolymers prepared in-house can be treated as containing tri-, di- and non-functional species with negligible amounts of monofunctional species.

The α model of Marsh *et al.* can adequately describe the network properties of HTPB-based polyurethanes.

The extent of reaction between HTPB and TDI depends on their stoichiometric ratio (r) and is nearly equal to 1 when $r < 0.9$.

Better correlation between observed and calculated parameters is obtained when unequal reactivities of the hydroxyl groups of HTPB are assumed.

Crosslink density and effective chain length calculated from the model can be used to predict the mechanical properties of the gumstocks and the propellants.

ACKNOWLEDGEMENTS

We thank Mr U. I. Somasundaram and Mrs K. Ambikadevi for providing us with some of their experimental results to check the model proposed. We also thank Dr K. J. Scariah and Mr C. R. Dhaveji for analytical support and editorial assistance. We are also thankful to the Director, Vikram Sarabhai Space Centre, and the Chairman, Indian Space Research Organisation, for all the encouragement given to carry out this work and the kind permission accorded for presentation at 'The Polymer Conference'.

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APPENDIX 1

The following equations for the α model, derived by Marsh *et al.*, are applicable to the formation of polyurethanes from a polyol (component A) containing tri-, di- and monofunctional species and a difunctional curing agent (component B):

$$r = [B]/[A] = p_A/p_B \tag{1}$$

$$\alpha = p_A p_B a_3/(1 - p_A p_B a_2) \tag{2}$$

$$W_S = [(1-\alpha)/\alpha]^3 \tag{3}$$

$$V_e = [(2\alpha - 1)/\alpha]^3 (d a_3/2W_{eq}) \times 10^6 \tag{4}$$

$$L_0 = W_G W_{eq} L_{sp} \alpha^3/a_3(2\alpha - 1) \tag{5}$$

$$R_n = (1-\alpha)/\alpha \tag{6a}$$

$$X_n = 1/(R_n + 1/R_n) \tag{6b}$$

$$R_{n+1} = R_n^2 \tag{6c}$$

$$L_n = L_0(1+2X_1)(1+2X_2)\ldots(1+2X_n) \tag{6d}$$

$$L = L_n \qquad \text{for } X_n \rightarrow 0 \tag{6e}$$

$$L_X = 2L \tag{6f}$$

where

a_3 = mole fraction of hydroxyls on trifunctional component of A

a_2 = mole fraction of hydroxyls on difunctional component of A
p_i = fraction of component i reacted
$W_G = 1 - W_S$ = weight fraction of gel
W_{eq} = equivalent weight of the polymer system
L_{sp} = number of chain atoms per gram
d = density of the polyurethane (g cm^{-3})
V_e = crosslink density (mol m^{-3})
L_X = effective chain length

APPENDIX 2

The equations for the P_F model are:

$$P(\mathrm{F}_{\mathrm{A}i}^{\mathrm{out}}) = 1 - q_i + q_i P(\mathrm{F}_{\mathrm{B}}^{\mathrm{in}}) \qquad i = 1, 2, 3$$

$$P(\mathrm{F}_{\mathrm{B}}^{\mathrm{in}}) = P(\mathrm{F}_{\mathrm{B}}^{\mathrm{out}})$$

$$P(\mathrm{F}_{\mathrm{B}}^{\mathrm{out}}) = \frac{(1 - p_{\mathrm{B}}) + p_{\mathrm{B}}[(a_f/f)\sum_{i=1}^{3} h_i q_i P(F_{\mathrm{A}fi}^{\mathrm{in}}) + (1 - a_f) q_1 (F_{\mathrm{A}2}^{\mathrm{in}})]}{(a_f/f)\sum_{i=1}^{3} h_i q_i + (1 - a_f) q_0}$$

$$P(\mathrm{F}_{\mathrm{a}}^{\mathrm{out}}) = 1 - q_i + q_i P(\mathrm{F}_{\mathrm{B}}^{\mathrm{out}})$$

$$V_e = \left(\prod_{i=1}^{3} [1 - P(\mathrm{F}_{\mathrm{A}i}^{\mathrm{out}})]^{h_i}\right) a_3 d \times 10^6 / 2W_{eq}$$

where

h_i = number of units of A_i functionality
q_i = fraction of A_i species reacted
a_f (or b_f) = mole fraction of A (or B) with $f = 2$, 3 functional groups