

Modelling of Polyurethanes Based on Hydroxyl-Terminated Polybutadiene

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ABSTRACT

Forty formulations based on four different grades of hydroxyl-terminated polybutadiene, HTPB (hydroxyl value 20 - 40 mg KOH/g) at $r = [NCO] / [OH]$ values in the range 0.7 - 1.0 with varying amounts of trimethylol propane and butane diol and containing 86 per cent solid loading were considered to test the applicability of α -model of Marsh, *et al.* for prediction of the mechanical properties of composite solid propellants. Two network parameters, crosslink density (V_e) and effective chain length (LX), were calculated from the model. Tensile strength and modulus were correlated to V_e and elongation at break to LX . Using the correlations obtained from experimental data at $r=0.8$, mechanical properties of the various formulations were predicted. Good agreement between experimental and predicted properties was obtained for formulations with modulus 10 KSC. Probable reasons for deviation observed at stoichiometric ratio $r < 0.8$ and low modulus values are discussed. Improved correlations between mechanical properties and network parameters, applicable over a wide range of formulations, were arrived at. The standard errors of prediction were found to be close to $\pm 1 \sigma$ value of the measurement.

1. INTRODUCTION

Polyurethanes based on hydroxyl-terminated polybutadiene (HTPB) liquid prepolymers serve as work-horse propellant binders for rocket and missile applications due to their easy processibility,

low cost, high solid loading and energetics¹. The networks impart three-dimensional stability to the composite solid propellant grain, and their rubbery nature allows the grain to withstand thermal cycling. Consequently, an understanding of the

dependence of mechanical properties of the propellant grain on the network characteristics of the urethane binder is of crucial importance to the development of solid propellant. Such an understanding enables one to design propellant grains with desired mechanical properties using minimum number of formulations.

Based on statistical considerations, Marsh^{2,3}, *et al.* developed a mathematical model (α -model) to evaluate network characteristics, such as sol content (Ws), crosslink density (Ve) and average length of effective chains (LX). They correlated the parameters to modulus and elongation at break (ϵ_b , %) of the gumstocks. In their earlier study⁴, the model was extended to characterise polyurethane networks based on HTPB and toluene diisocyanate (TDI). Relationships were derived between Ve and LX and the mechanical properties of gumstocks as well as propellants.

In the present study, the validity of these relationships has been further examined by considering propellant formulations at various stoichiometric ratios, $r = [NCO]/[OH]$. Four HTPB polymers having hydroxyl values in the range 20-40 mg KOH/g and containing varying amounts of butanediol (BD) and trimethylol propane (TMP) were used in the propellant formulations. Good agreement was observed between experimental and calculated values for elongation, tensile strength and modulus of the propellants.

2. EXPERIMENTAL DETAILS

2.1 Materials

HTPB polymers I - IV were prepared by free radical polymerisation of butadiene in isopropanol water solvent system at different concentrations of the initiator⁵, H_2O_2 . The polymers were characterised by their Mn (VPO), polydispersity (Mw/Mn , SEC), hydroxyl (OH) value and viscosity. Selected properties of the polymers are given in Table 1.

2.2 Propellant Formulations

The composition of a typical formulation for 100 g of propellant is as follows:

HTPB+ TDI	10.78 g
TMP + BD	0.12 g
Ammonium perchlorate (AP)	67.60 g
Al powder	18.00 g
Other additives	3.50 g

Several formulations (1 - 40) were made using polymers I-IV and varying the amounts of TDI, BD

Table 1. Selected properties of polymers I-IV

Polymer	OH-value (mg KOH/g)	Mn (VPO)	Mw/Mn	Visco (cps at 30°C)	f_n	a_s
I.	40.0	2930	2.8	5740	2.09	0.5649
II.	34.1	3290	2.7	8720	2.00	0.4533
III.	27.4	3510	2.9	12190	1.71	0.3936
IV.	21.1	4480	2.5	37760	1.69	0.2702

and r value ranging 0.7-1.0. Curing was carried out at 60 °C for 5 days. Mechanical properties of the cured samples were evaluated according to ASTM standards. The results taken from the work of Manjari^{6,7}; *et al.* are given in Tables 2 and 3.

3. RESULTS & DISCUSSION

3.1 Evaluation of Input Parameters

Polyurethane networks are characterised by LX and Ve . These parameters were calculated using the α -model. A small number of prepolymer characteristics like composition, functionality distribution and extent of reaction are the required input parameters for this model. They are evaluated as r .

3.1.1 Stoichiometric Ratio

Stoichiometric ratio (r) is equal to the ratio of equivalents of isocyanate curator to the total hydroxyl equivalents

$$r = [NCO] / [OH] = E_{NCO} / (E_{HTPB} + E_{TMP} + E_{BD})$$

where

E_i = Equivalents of the species i .

Table 2. Comparison of experimental[#] and calculated mechanical properties

F.No.	Elong. at break (%)		TS(KSC)		Modulus(KSC)	
	Exptl.	Calc.	Exptl.	Calc.	Exptl	Calc.
	Polymer-I					
1	54	106	3.0	1.7	12	8
2	42	65	4.8	5.9	20	16
3	35	43	7.0	8.0	37	38
4	28	29	8.9	9.3	77	71
5	21	22	11.0	9.9	100	93
6	15	14	11.1	10.7	128	130
7	11	11	11.4	11.0	193	156
Polymer-II						
8.	76	629	2.0	-	6.3	6.5
9.	59	105	3.0	2.7	11.6	8.0
10.	47	69	6.3	6.3	22.0	19.0
11.	34	49	8.0	8.2	43.0	42.0
	28	40	8.6	9.0	65.2	61.0
	25	29	10.6	10.0	88.0	97.0
	19	22	11.0	10.8	124.0	133.0
Polymer-III						
15.	--does not cure-					
16.	133	148	1.2	0	2	7
17.	85	91	3.0	4.8	7	12
18.	65	66	5.7	7.3	20	28
19.	55	55	7.5	8.3	46	43
20.	42	42	9.4	9.5	49	75
21.	34	33	10.5	10.3	85	110
		(40*)		(9.6*)		(82*)
22.	-----does not cure-					
23.	-----does not cure--					
24.	133	139	0.9	-	4	7
25.	105	98	2.4	5.2	16	13
26.	75	82	6.2	6.7	30	22
		(78**)		(7.1**)		(26**)
27.	59	64	8.5	8.4	46	46
28.	36	52	9.6	9.8	76	79

* At $p_A = 0.97$, ** At $p_A = 0.895$

#: Experimental values taken from Ref. 6.

Thus, r is an experimentally set quantity and was varied from 0.7 to 1.0 in the present study.

3.1.2 Equivalent Weight of the System

Equivalent weight of the system (W_{eq}) is obtained from the equation:

Table 3. Effect of variation of hard segments for polymers I-IV at $r = 0.9$ [#]

F.No	TMP	Elong. at break (%)		TS (KSC)		Modulus (KSC)	
		Exptl.	Calc.	Exptl.	Calc.	Exptl.	Calc.
		Polymer-I					
29.	0.06	18	17	11.0	10.2	109	105
30.	0.03	26	26	10.8	9.7	94	85
31.	0.00	31	37	9.8	9.1	65	64
Polymer-II							
32	0.06	32	33	10.8	9.4	79	74
33	0.03	40	45	10.5	8.7	58	53
34.	0.00	47	63	8.5	7.6	39	32
		(56*)		(8.2*)		(42*)	
Polymer-III							
35	0.06	44	45	8.3	8.9	48	57
36	0.03	58	62	6.3	7.8	24	35
37	0.00	80	90	4.2	6.0	12	17
Polymer-IV							
38.	0.06	66	65	8.0	7.8	30	35
39.	0.03	71	95	6.3	5.8	27	16
			(84**)	(6.8**)		(23**)	
40.	0.00	103	229	3.0	0.0	9	7

* At $p_A = 0.898$, ** At $p_A = 0.90$

Experimental values taken from Ref. 7.

$$W_{eq} = (56100 \times E_{HTPB} / (\text{hydroxyl value})_{HTPB}) + (132/3)E_{TMP} + 45 E_{BD} + 87 r.$$

3.1.3 Functionality Distribution

Whereas BD and TMP contribute towards di and tri-functional components, respectively, the HTPB polymer may contain non-, mono-, di- and higher functional components. Therefore, judicious assumptions have to be made to arrive at the functionality distribution of HTPB. It was shown in an earlier study⁸ that HTPB polymers prepared under the present experimental conditions could be approximated to a system containing non-, di- and tri-functional species only with negligible amounts of monofunctionals. Further, it was shown that the mole fraction (a_3) of the hydroxyls from the tri-functional component could be obtained either from ¹³C nuclear magnetic resonance spectroscopy or using the relation

$$a_3 = 206.7 / (\epsilon_b + 165.6)$$

where

ϵ_b is percentage elongation at break of the gumstocks prepared at $r = 1$. The values of a_3 thus obtained for polymers I-IV are also given in Table 1. The mole fraction of the hydroxyls from di-functional component of HTPB is equal to $(1-a_3)$. Therefore, the mole fraction (A_3) of the hydroxyls from the total tri-functional components of the system can be computed from the equation

$$A_3 = (E_{HTPB} \times a_3 + 3 E_{TMP}) / (E_{HTPB} + 3 E_{TMP} + 2E_{BD}), \text{ and}$$

$$A_2 = (E_{HTPB} \times a_2 + 2 E_{BD}) / (E_{HTPB} + 3 E_{TMP} + 2E_{BD}) = 1 - A_3.$$

3.1.4 Extent of Reaction

The formation of polyurethane linkage is very facile and is nearly complete. But determination of the extent of the reaction in a crosslinked system is not quite feasible and it can be arrived at only by comparison of the experimental and calculated properties. An earlier study⁴ had shown that for $r < 0.9$, the reaction could be considered as complete. For values of $r \geq 0.9$, good agreement between experimental and calculated values of properties could be obtained in the present study if it is assumed that the reaction is 99 per cent complete. Since the extent of reaction (p_A) of the hydroxyl functionals and the curator (p_B) are related by the stoichiometric equation

$$p_A / p_B = r$$

we obtain

$$p_A = r \quad \text{if } r < 0.9$$

$$p_A = 0.99 r \quad \text{if } r \geq 0.9$$

3.2 Calculation of Network Parameters

The α -model describes the network in terms of the branching coefficient α defined as the probability that any given component of a branch

unit leads, via sequence of di-functional units, to another branch. The branching coefficient α is related to the input parameters by the equation

$$\alpha = p_A^2 \cdot A_3 / (r - p_A^2 \cdot A_2)$$

The network parameter V_e is computed from α by the equation:

$$V_e \text{ (moles/m}^3\text{)} = [(2\alpha-1)/\alpha]^3 [\rho \cdot A_3 / (2W_{eq})] \times 10^6$$

where

ρ is the density of the cured gumstock and has the value of 0.92 g/cc for HTPB systems.

The LX is computed from the following set of equations:

$$W_s = 1 - W_g = (1 - \alpha) / \alpha^3$$

$$L_o = 0.074 \times (W_g \cdot W_{eq} \cdot \alpha^3) / A_3 \cdot (2\alpha - 1)$$

$$R_n = (1 - \alpha) / \alpha$$

$$X_n = 1 / [R_n + 1/R_n]$$

$$R_{n-1} = R_n^2$$

$$L_n = L_o \cdot (1 + 2 X_1) \cdot (1 + 2 X_2) \cdot \dots \cdot (1 + 2 X_n)$$

$$L = L_n \text{ for } X_n \rightarrow 0$$

$$LX = 2 L$$

Therefore, with the knowledge of the input parameters r , W_{eq} , A_3 and p_A , the network properties V_e and LX can be readily computed. The calculated values of V_e and LX thus obtained for polymers I-IV at different values of r are given in Table 4.

3.3 Computation of Mechanical Properties of Propellants

The network parameter V_e can be correlated to tensile strength (TS) and the modulus and LX can be correlated to elongation at break (ϵ_b , %) of the propellants. In an earlier study⁴, the relevant relationships were obtained from a regression analysis of the plots of TS vs V_e , modulus vs V_e and ϵ_b (%) vs LX , based on the experimental values of

TS, modulus and ϵ_b measured at $r = 0.8$ for polymers I - IV . The following correlations were obtained:

$$\epsilon_b (\%) = 0.68 + 0.059 LX - 7.2 \times 10^{-6} LX^2 \quad (1)$$

$$TS (KSC) = 2.65 + 0.245 Ve - 2.9 \times 10^{-4} Ve^2 \quad (2)$$

$$\text{Mod.}(KSC) = 6.5 + 1.26 Ve - 2.3 \times 10^{-3} Ve^2 \quad (3)$$

Using these relationships, the mechanical properties of the propellant formulations 1-28 were calculated and the results are given in Table 2 for polymers I - IV.

3.4 Comparison of Experimental & Predicted Properties

A comparison of the observed mechanical properties of the various formulations with the properties calculated using Eqns 1-3 is shown in Table 2. The important observations that can be made from the results in Tables 2 and 4 are:

- (a) The value of α for formulations 8, 15, 22 and 23 is only 0.5 (Table 2), indicating that the networks are just at the point of gelation and hence cannot be cured properly. This was indeed found experimentally in the case of formulations 15, 22 and 23. This observation validates the assumption regarding the functionality distribution of HTPB polymer. However, formulation 8 gives good cure and the reasons for this deviation are explained here.
- (b) For polymer 1 large deviations were observed between experimental and calculated properties for formulations 1 and 2 at $r = 0.7$ and 0.75 , respectively although satisfactory agreement exists for $r \geq 0.8$, as shown in Fig. 1.
- (c) In the case of polymer-II, calculated ϵ_b values are higher, although modulus values, are comparable to the experimental values as depicted in Fig. 2.
- (d) Good agreement exists between experimental and calculated properties of polymers-III and IV, as shown in Figs 3 and 4, and

- (e) Deviations between experimental and calculated properties are observed for formulations which result in low concentration of elastically effective network chains or crosslink densities and low modulus values.

It can, therefore, be summarised that satisfactory agreement between experimental and predicted properties is observed for formulations with $r \geq 0.8$, implying validity of the correlations (Eqns 1-3) for a wide range of formulations.

Although available experimental data are inadequate to arrive at unambiguous reasons for the deviations cited above, the following factors may be considered as the contributing causes:

3.4.1 Filler-Matrix Interaction

A composite solid propellant grain can be considered as a filled polyurethane system containing ammonium perchlorate (AP), Al powder, and burn rate modifiers as fillers. Since AP is acidic and contains hetero atoms, the H bonding between the filler and the matrix may increase with increase in free OH group concentration in the matrix. Thus, at lower values of r , these interactions enhance the mechanical properties of the matrix and may account for the observed deviations in the experimental and calculated properties at values of $r < 0.8$.

3.4.2 Physical Entanglements

Most of the deviations were observed at low values of the crosslink density ($Ve < 10 \text{ moles/m}^3$). This may be reasonable in view of the fact that at low values of Ve , the molecular weight between crosslinks is quite high. This leads to physical entanglement of chains, causing an enhancement in the values of modulus and a decrease in the values of elongation at break (ϵ_b). This is in accordance with the observation that in all cases where deviations were observed, the calculated ϵ_b values are higher and the moduli values are lower. Attempts are under way to estimate the contribution of physical entanglements to crosslink density of the networks.

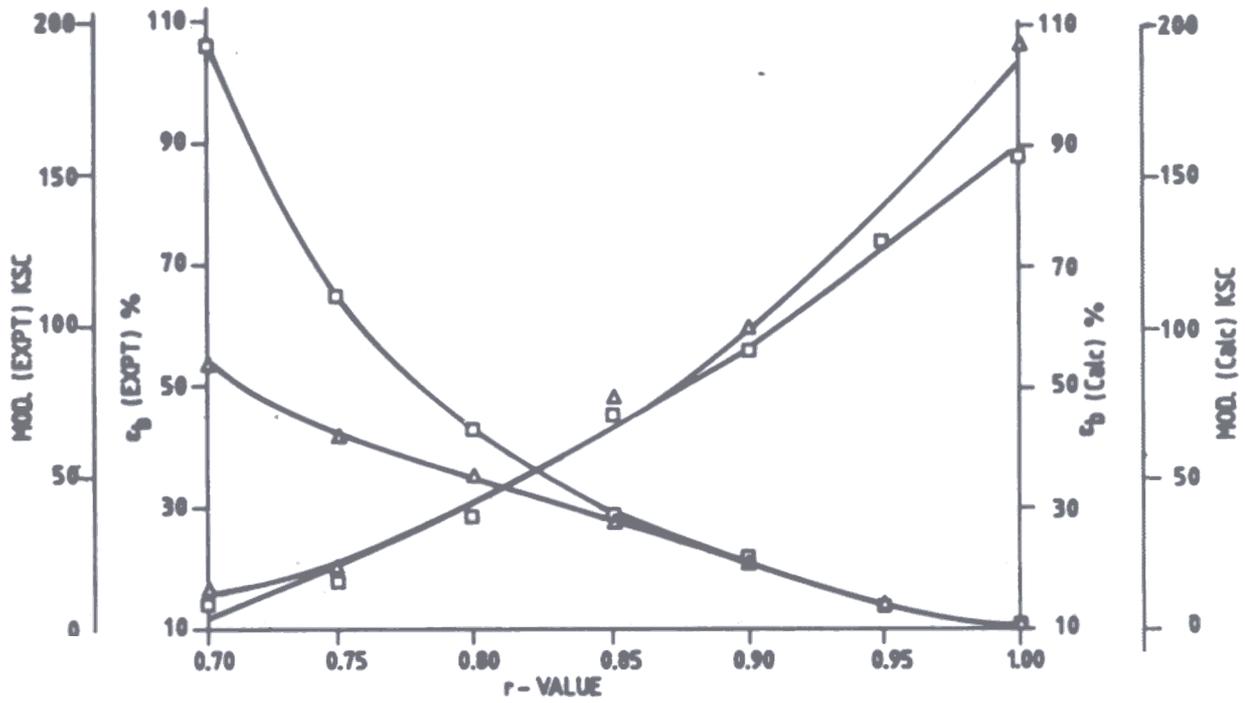


Figure 1. Comparison of calculated ϵ_b (%) and modulus (KSC) with experimental values at varying r values for polymer-I (Δ , Exptl ; \square Calc.)

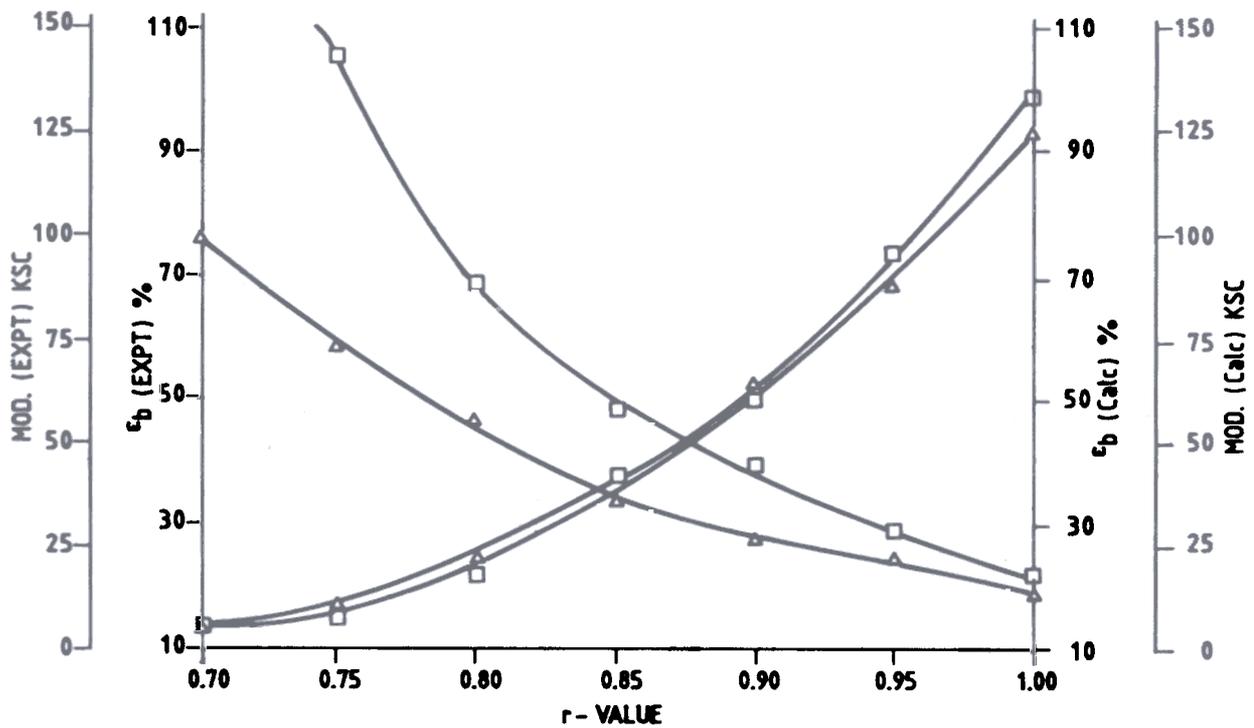


Figure 2. Comparison of calculated ϵ_b (%) and modulus (KSC) with experimental values at varying r values for polymer-II (Δ , Exptl ; \square , Calc.)

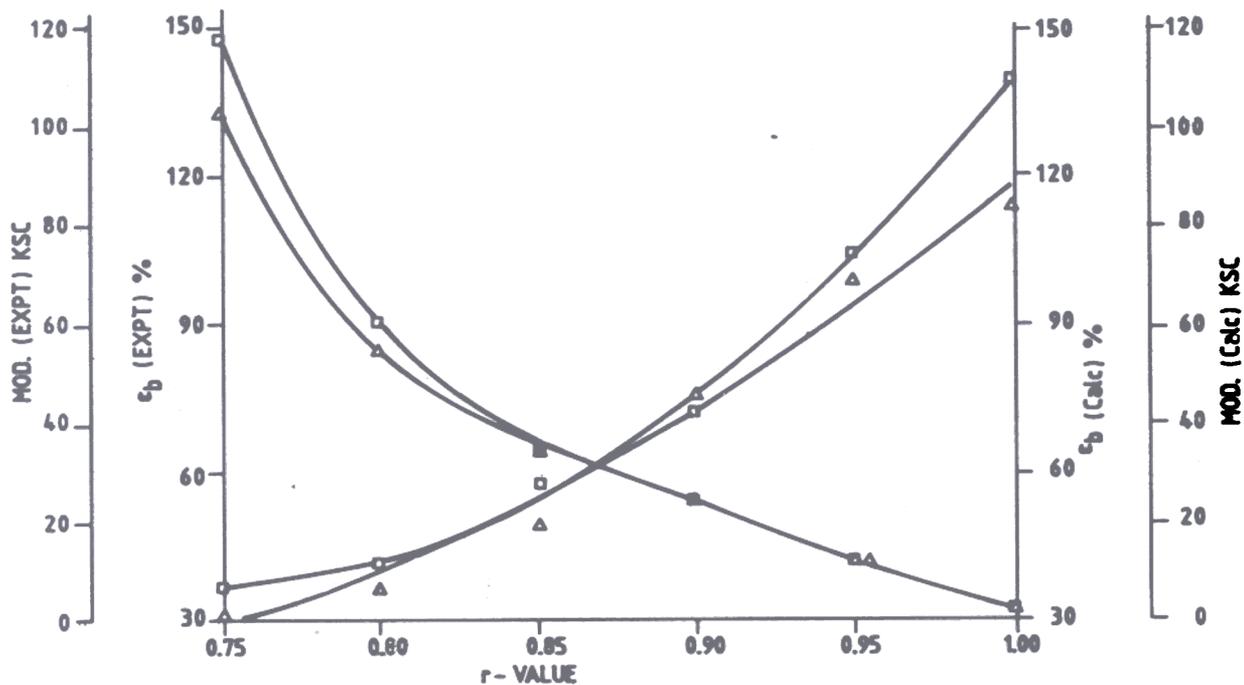


Figure 3. Comparison of calculated ϵ_b (%) and modulus (KSC) with experimental values at varying r values for polymer-III (Δ , Exptl; \square , Calc.)

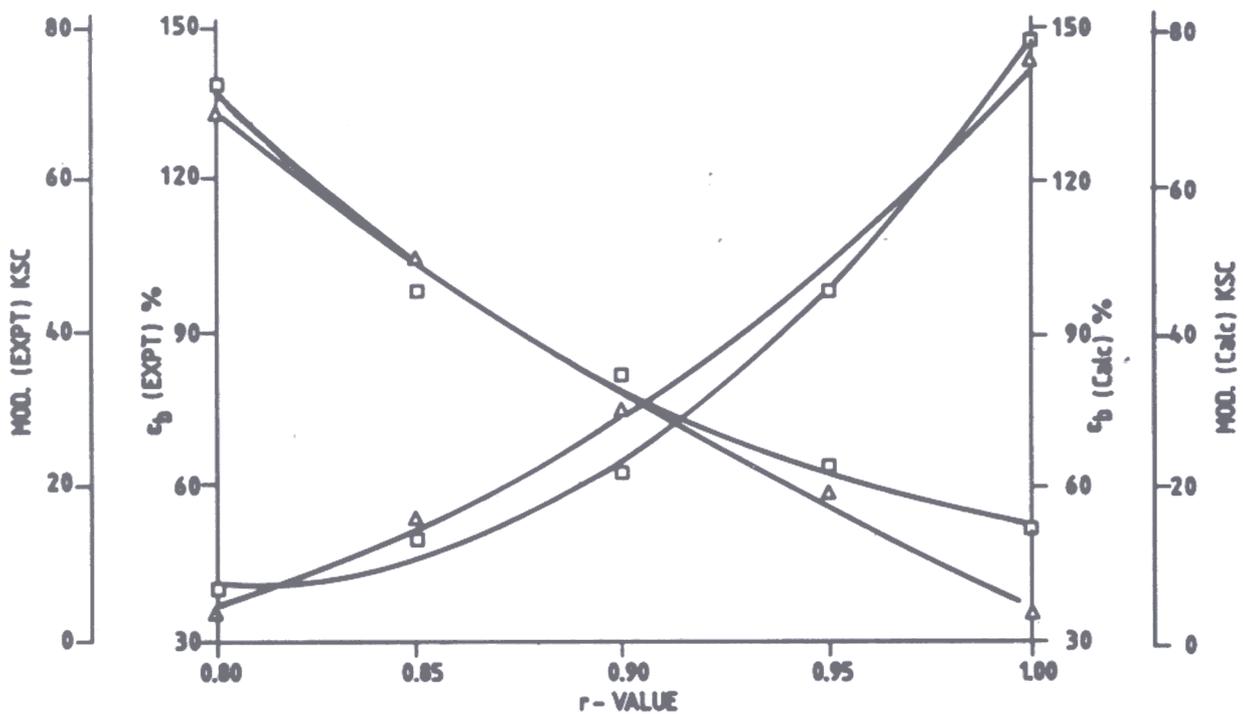


Figure 4. Comparison of calculated ϵ_b (%) and modulus (KSC) with experimental values at varying r values for polymer-IV (Δ , Exptl; \square , Calc.)

Table 4. Polyurethane network properties for polymers I-IV

F.No*	Input parameters			Network properties		
	r	A_r	W_{r_e}	α	V_e moles/m ³	LX
Polymer-I						
1.	0.70	0.5029	1103	0.5399	0.7	3057
2.	0.75	0.5027	1106	0.6013	8.0	1222
3.	0.80	0.5026	1110	0.6678	26.4	758
4.	0.85	0.5024	1113	0.7400	56.7	552
5.	0.90	0.5022	1116	0.7879	80.8	476
6.	0.95	0.5020	1120	0.8706	127.3	395
7.	1.00	0.5018	1123	0.9611	181.6	346
Polymer-II						
8.	0.70	0.4172	1232	0.5000	0	3.4x10 ⁸
9.	0.75	0.4171	1235	0.5558	1.3	2957
10.	0.80	0.4170	1238	0.6252	10.0	1344
11.	0.85	0.4169	1241	0.7026	29.6	860
12.	0.90	0.4168	1244	0.7549	47.5	706
13.	0.95	0.4167	1248	0.8481	85.0	554
14.	1.00	0.4166	1251	0.9535	131.9	468
Polymer-III						
15.	0.70	0.3723	1423	0.4999	0	1.0x10 ⁹
16.	0.75	0.3723	1426	0.5276	0.14	7706
17.	0.80	0.3723	1429	0.5982	4.2	2196
18.	0.85	0.3722	1432	0.6784	17.4	1248
19.	0.90	0.3722	1435	0.7322	30.7	984
20.	0.95	0.3721	1438	0.8329	60.8	739
21.	1.00	0.3721	1440	0.9483	104.0	608
Polymer-IV						
22.	0.70	0.2948	1670	0.5000	0	5.0x10 ⁹
23.	0.75	0.2949	1672	0.5000	0	6.0x10 ⁹
24.	0.80	0.2950	1675	0.5412	0.3	7664
25.	0.85	0.2950	1678	0.6257	5.2	2565
26.	0.90	0.2950	1680	0.6849	12.7	1788
27.	0.95	0.2950	1683	0.7979	33.6	31188
28.	1.00	0.2957	1686	0.9356	65.0	912

* Formulation No.

3.4.3 Reactivities of OH-Functional Groups

The basic assumption made in α -model is that the reactivities of given type of functional groups are same. However, the present system contains different hydroxyl-bearing components, namely, HTPB, TMP and BD. It is likely that the reactivity of OH groups of the low molecular weight molecules TMP and BD could be higher than that of the OH groups in HTPB. In fact, all the OH groups even in HTPB do not have the same reactivity. A

consequence of the higher reactivity of TMP and BD would be an increase in the relative proportion of the 'hard segments' (comprising TMP + TDI and BD + TDI) to the soft segments (HTPB + TDI) in the network when compared with equal reactivities. This effect should be predominant at lower values of r when OH groups are in excess. Consequently, enhancement in mechanical properties would occur at lower values of r with lowering in ϵ_s values and increase in modulus. However, it may be noted that this effect is taken into consideration since the correlations (Eqns 1-3) were derived using the experimental data at $r = 0.8$. This could be a probable reason for good agreement of calculated and experimental properties at $r \geq 0.8$. To confirm this point further, propellant formulations containing different amounts of TMP and BD were cast at $r = 0.9$.

3.5 Effect of Hard Segments

In the propellant formulations considered so far, the amount of TMP and BD were kept constant at 0.04 and 0.08 per cent, respectively. To elucidate the effect of variation in hard segments on the network properties, formulations with varying amounts of TMP and BD, but keeping their sum constant, were prepared. The properties of these propellants were calculated using Eqns 1-3 and were compared with the experimental values given in Table 3. The experimental data were taken from the work of Manjari,⁷ *et al.* The extent of reaction (p_A) was slightly varied in the case of formulations and to obtain better agreement with the measured properties. These results confirm that Eqns 1-3 derived at $r = 0.8$ hold good at $r = 0.9$ as well, and that the effect of the hard segments is incorporated into the correlations between network parameters and mechanical properties.

3.6 Modified Correlations

The correlations (Eqns 1-3) between the network properties and the mechanical properties of the propellant were derived using limited data at $r = 0.8$. The present study shows that these correlations could be extended to a wide range of formulations with $r = 0.7$ to 1.0 and varying amounts of the hard segments. Thus, the correlations could be refined by using the large

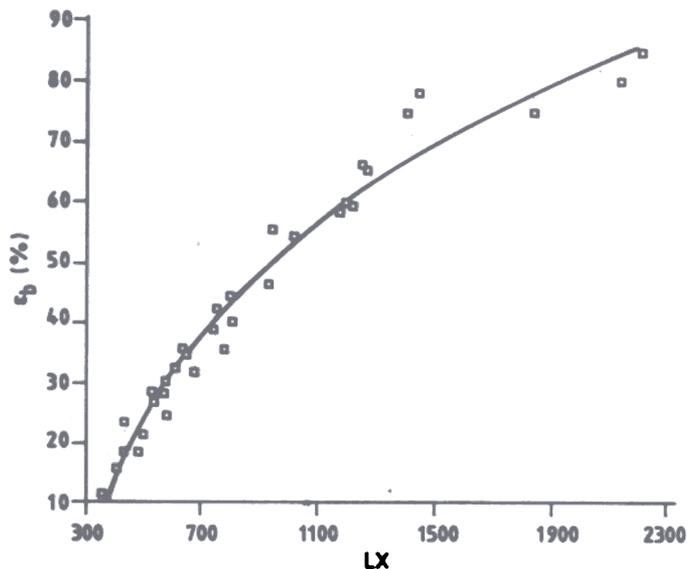


Figure 5. Plot of ϵ_b (%) vs LX for various propellant formulations.

amount of available experimental data. Different functional forms were considered to fit the data and the best fits obtained are shown in Figs 5-7. The modified correlations thus obtained are given in Eqns. (4)-(6).

$$\epsilon_b(\%) = 41.88 \log(LX) - 235.8 \quad (4)$$

$$TS \text{ (KSC)} = 2.079 \log(Ve) + 1.0697 \quad (5)$$

$$\text{Mod. (KSC)} = 9.174 + 1.263 Ve - 0.0025 Ve^2 \quad (6)$$

The mechanical properties of various formulations were calculated using Eqns (4)-(6) and the results are given in Table 5.

3.7 Accuracy of Prediction

Propellant formulations with low modulus values show considerable deviation between experimental and predicted properties for reasons discussed earlier and therefore, were not considered further. Most of the remaining data were subjected to least square analysis and the plots of predicted values vs experimental values are shown in Figs 7-9 for ϵ_b , TS and modulus. A perfect fit for such a plot should show a slope of 1.0 and an intercept 0 with correlation coefficient 1.0. The values of these

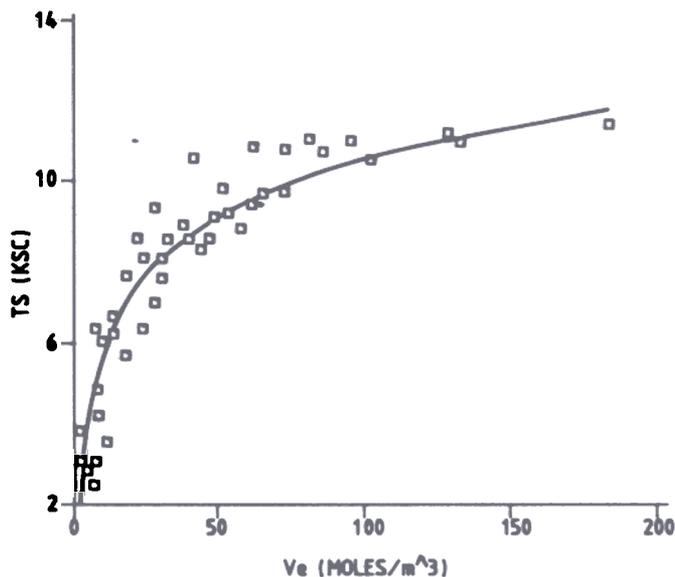


Figure 6. Plot of TS (KSC) vs LX for various propellant formulations.

parameters, as shown in Figs 8-10, are very close to the theoretical values, indicating an excellent agreement between predicted and experimental values. Moreover, in a typical measurement of the mechanical properties the following values were obtained:

$$\epsilon_b(\%) = 41 \pm 3.0 ; TS \text{ (KSC)} = 6.3 \pm 0.6 \text{ and Mod (KSC)} = 39 \pm 4.4$$

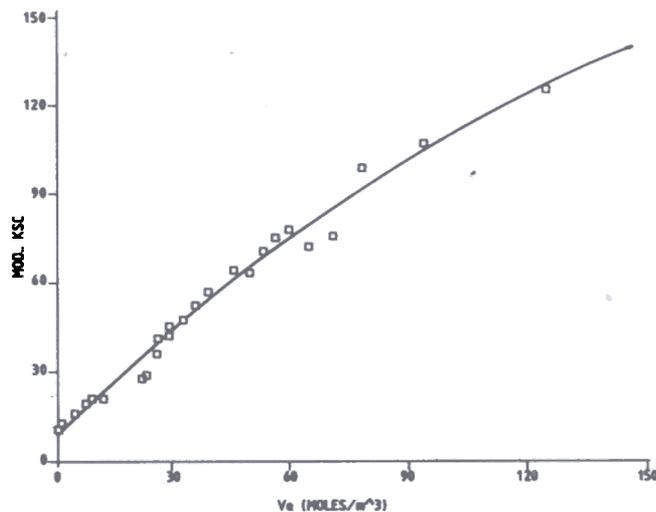


Figure 7. Plot of modulus (KSC) vs Ve (moles/m³) for various propellant formulations.

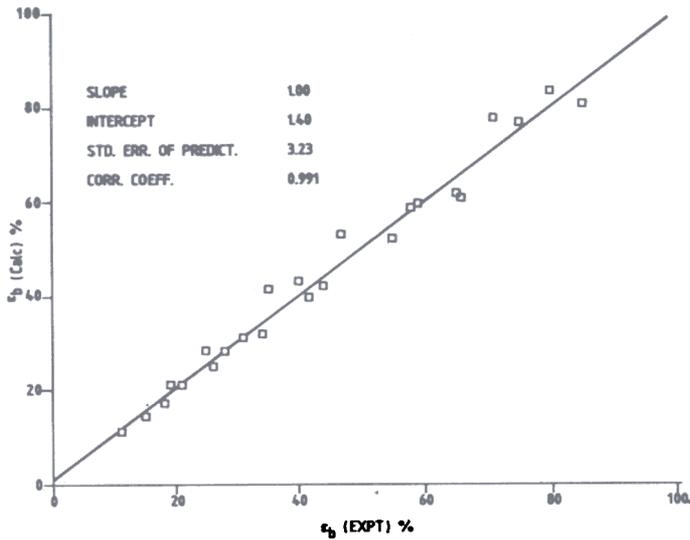


Figure 8. Plot of ϵ_b (Calc.),% vs ϵ_b (Exptl.), % for various propellant formulations.

The standard errors of prediction derived from the analysis (Figs 8-10) are very close to the standard deviations observed in the measurements. Therefore, it can be concluded that the predicted values lie close to the experimental values and the deviations are close to $\pm 1 \sigma$ value of the measurements.

4. CONCLUSIONS

The following important conclusions can be drawn from the present study:

- The assumptions made regarding the functionality distribution of HTPB and the extent of reaction are reasonable
- The α - model of Marsh, *et al.* can be used to predict the mechanical properties of the composite solid propellants

Mechanical properties of the propellants can be correlated to the network parameters V_e and LX

- Propellants with low modulus (< 10 KSC) show deviation from the predicted values and
- The standard errors of prediction are close to $\pm 1 \sigma$ value of the measurements.

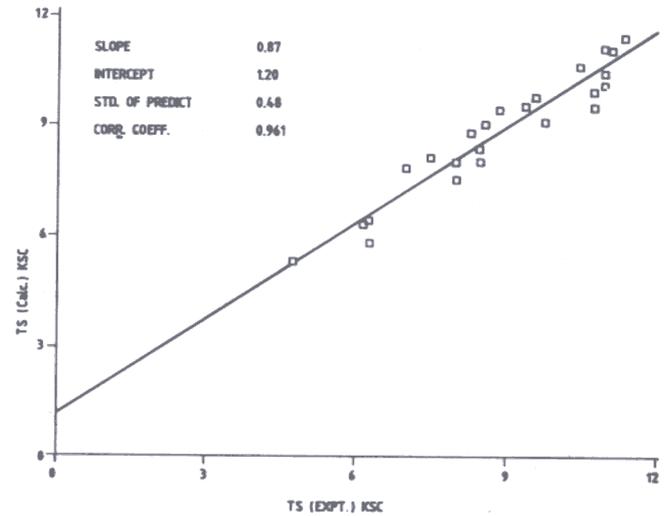


Figure 9. Plot of TS (KSC) (Calc.), vs TS (KSC) (Exptl.) for various propellant formulations.

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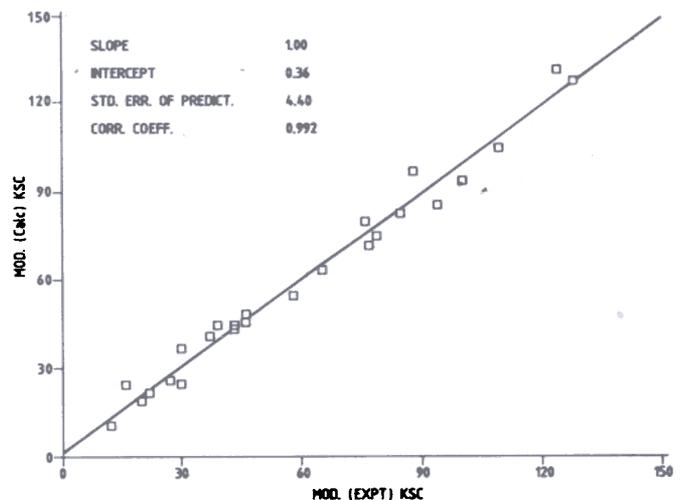


Figure 10. Plot of modulus (KSC) (Calc.) vs modulus(KSC) (Exptl.) for various propellant formulations.

Table 5. Summary of mechanical properties of propellants of different formulations

F. No	Elong. at break (%)		Tensile strength (KSC)		Modulus (KSC)	
	Exptl.	Calc.*	Exptl.	Calc. \$	Exptl.	Calc.*
2.		62		5.4		
3.		42		7.9		
4.		29		9.5		
5.		22		10.2		
6.		15		11.2		
7.		12		11.5		
9.		99		1.6		
10.		66		5.9		
11.		47		8.1		
12.		39		9.1		
13.		29		10.3		
14.		22		11.2		
16.		139		0		
17.		82		4.1		
18.		63		7.0		
19.		53		8.2		
20.		41		9.6		
21.		33		10.7		
25.		93		4.5		
26.		78		6.4		
28.		50		9.8		
29.		18		10.5		
30.		26		10.0		
31.		36		9.2		
32.		32		9.6		
33.		44		8.7		
34.		54		8.1		
35.		43		8.9		
36.		60		6		
37.		85		5.4		
38.		62		7.6		
39.		79		6.5		
40.		214		0		

* Using Eqn (4), \$ Using Eqn (5),

Using Eqn (6).

REFERENCES

1. Mastrolia, E.J. & Kluger, K. Propellants manufacture, hazards and testing, edited by

R.F.Gould. Advances in Chemistry, Series 88, American Chemical Society, Washington, DC, 1969.

2. Marsh, H.E; Cheng, S.Y; Hsu, G.C. & Wallace, C.J. *In Chemistry & properties of crosslinked polymers*, edited by S.S.Labana. Academic Press Inc.,1977. pp. 341-74.

3. Marsh, H.E. Modelling of polymer networks for application to solid propellant formulating; NASA, Washington, DC, 1979. NASA-CR-158788.

4. Sastri, K.S.; Rama Rao, M. & Manohar Singh. Modelling the effect of functionality distribution on the crosslinking characteristics of hydroxyl-terminated polybutadiene liquid prepolymers. *Polymer*, 1994, 35 (21), 4555 - 561.

5. Alwan, S.; Shanmugham, K. & Sastri, K. S. Synthesis and characterisation of different grades of HTPB resin.. Vikram Sarabhai Space Centre, Thiruvananthapuram. VSSC-TR-108-90.

6. Manjari, R.; Joseph, V.C.; Pandureng, L.P. & Sriram, T. Structure-property relationship of HTPB-based propellants, III. Optimisation trials with varying levels of diol - triol contents. *J. Appl. Polym. Sci.*, 1993, 48, 271-78 .

7. Manjari, R.; Somasundaran, U.I.; Joseph, V.C.; & Sriram, T. Structure-property relationship of HTPB-based propellants, II. Formulating tailoring for better mechanical properties. *J. Appl. Polym. Sci.*, 1993, 48, 279-89 .

8. Rama Rao, M.; Scariah, K.J.; Ravindran, P.V.; Chandrasekharan, G.; Alwan, S. & Sastri, K.S. Correlation of binder mechanical properties with functionality type and molecular weight distribution for hydroxyl-terminated polybutadienes : ¹³C - NMR and SEC studies. *J. Appl. Polym. Sci.*, 1993, 49, 435-44.