Structure–Property Relationship of HTPB-Based Propellants. III. Optimization Trials with Varying Levels of Diol–Triol Contents

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SYNOPSIS

A systematic study has been conducted on a composite solid propellant formulation using hydroxyl-terminated polybutadiene (HTPB) prepolymer with varying molecular weights and hydroxyl values. Fairly extensive regions of resin parameters have been studied. Contours of important propellant properties have been laid down. In this set of experiments, varying levels of diol and triol contents were used at two different NCO/OH ratios to arrive at the optimum level needed for different grades of HTPB resin. It is seen that different grades of HTPB resin require varying levels of diol–triol contents to give similar properties for the end product. Also, for the best performance, varying the diol–triol ratio at the optimum level of the diol–triol content is necessary.

INTRODUCTION

Composite solid propellants based on hydroxyl-terminated polybutadiene (HTPB) binders have unique advantages of very high performance, good processability, and unsurpassed mechanical properties. At the Vikram Sarabhai Space Centre in India, a study was initiated to investigate the dependence of propellant properties on important resin parameters so as to calculate the formulations to give specific properties with a high degree of confidence. Earlier, we reported the results of a parametric study based on a spectrum of resins in the HTPB series for propellant applications.[1,2] In the first paper, details of HTPB prepolymer preparation and propellant formulation trials with varying ratios of curative to resin were highlighted.[1] The second paper dealt with the influence of varying the ratio of the chain extender to the cross-linker on the resultant propellant properties.[2] Since this study has created interest in the minds of propellant-development scientists, it was decided to carry out further investigations so as to enable the propellant-developing agency to select a suitable formulation for specific application.

The third and the concluding part of this paper was intended to study the remaining possible variables such as use of the chain-extender component alone at a higher NCO/OH ratio, use of the cross-link component alone at a lower NCO/OH ratio, and use of the combination of diol–triol at different levels.

EXPERIMENTAL

The same four batches of HTPB resins that were used in the first two sets of experiments have been used in this study as well. For the sake of completeness, the properties of the four batches of resin are reproduced in Table I together with the properties of the standard HTPB resin.

Propellant Formulation Experiments

The base-line propellant formulation used in the present set of experiments is given in Table II. The variables studied include the following:

(i) Trimethylol propane (TMP) contents of 0.09, 0.06, 0.03, and 0% in the absence of butanediol at the NCO/OH ratio, i.e., *R* value of 0.8.

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Table I Properties of Experimental Batches of HTPB Resin

Properties	Expt Batch No.				
	Standard	E-01	E-02	E-03	E-04
1. Viscosity (30°C CPS)	6,300	6,000	9,070	13,600	41,300
2. OH value (mg KOH/g)	43	40	35	28	20
3. Acid value (mg KOH/g)	0.3	0.3	0.2	0.1	0.2
4. Mol. wt. (M_n-VPO)	2,600	2,900	3,300	3,500	4,500
5. Eq. wt	1,300	1,370	1,600	2,000	2,800
6. Average functionality (M_n/Eq. wt.)	2.0	2.1	2.0	1.75	1.60

(ii) Butanediol contents of 0.09, 0.06, 0.03, and 0% in the absence of TMP at an R value of 0.9.

(iii) Equal combinations of TMP and butanediol at 0.09 and 0.06% at R values of 0.8 and 0.9.

Eight hundred grams of propellant slurry, as per the above formulation, was prepared in a small sigma blade kneader at 40°C. At the end of the mix, apparent viscosity was measured in a Brookfield Visiometer with a helipath stand. The slurry was vacuum-cast into cartons and cured at 60°C for 5 days. The cured propellant block was cut into 5 mm slabs, prepared as dumbbell specimens, and tested in an Instron Universal Testing Machine for mechanical properties such as tensile strength, percentage elongation, and Young's modulus.

RESULTS AND DISCUSSION

Because the composite solid propellant is viscoelastic in nature, several viscoelastic parameters are needed for completely characterizing it. But, here, we have restricted ourselves to certain minimum properties as listed above. This is because our aim here is not the complete characterization of the propellant for a specific application but that we are interested only in a comparative study of the end product.

Table II Base-line Propellant Formulation

Ingredients	Wt %
HTPB + TDI + TMP + Butanediol	10.90
Plasticizer, antioxidant burn rate modifier	3.50
Aluminum	18.00
Ammonium perchlorate	67.60
Total	100.00

Effect of Trimethylol Propane (TMP) Content

In the first and second parts of this study, TMP was used in combination with butanediol. Here, the effect of TMP alone has been studied at three levels at an R value of 0.8. The results of this set of experiments are depicted in Figures 1 and 2. Whereas Figure 1 shows tensile strength values as a function of the hydroxyl value of the resin with TMP levels as the third parameter, Figure 2 indicates percentage elongation. It is seen that the resin with the lower hydroxyl value, i.e., batch E-04, results in a propellant with high elongation and low tensile strength. Young's modulus values of the propellant with TMP contents of 0.06 and 0.03% are also very low, indicating that these levels of TMP contents are too low for this batch of resin. Even though attempts were made to make propellant slabs with no TMP content at all, none of the batches became cured.

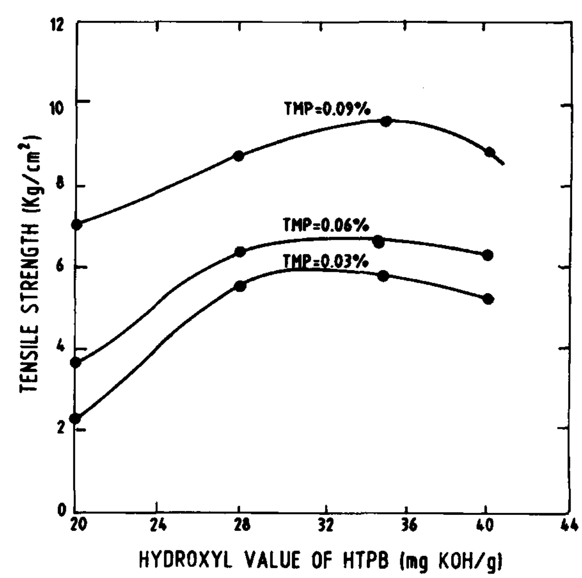

Figure 1 Effect of hydroxyl value of HTPB on tensile strength at three levels of TMP at R = 0.8.

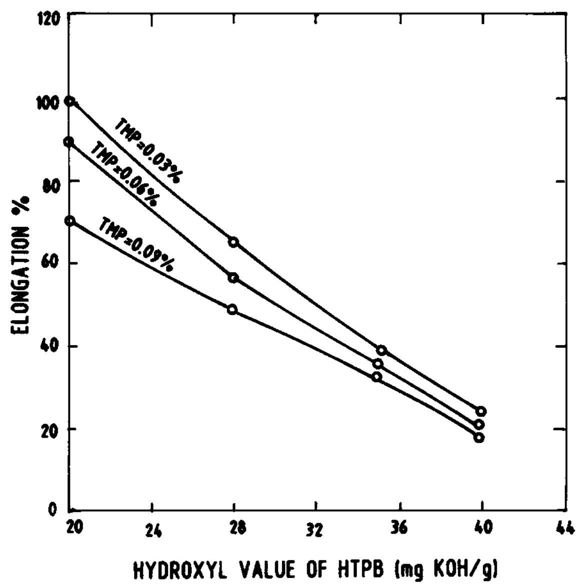

Figure 2 Effect of hydroxyl value of HTPB on elongation at three levels of TMP at R = 0.8.

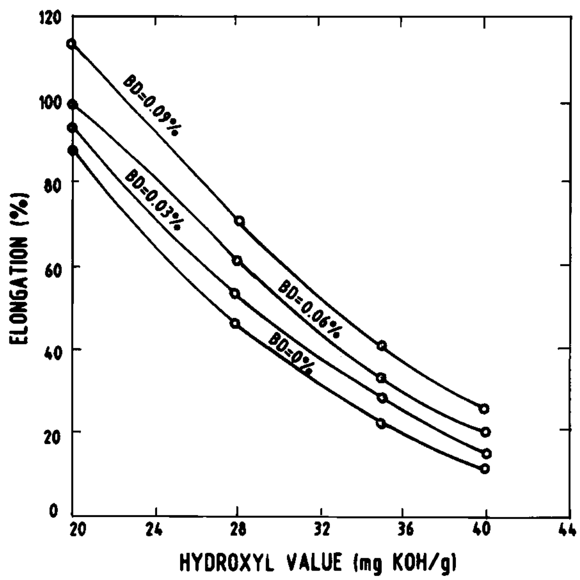

Figure 4 Effect of hydroxyl value of HTPB on elongation at four levels of butanediol at R = 0.9.

Effect of Butanediol Content

Different levels of butanediol were incorporated into the propellant at an R value of 0.9, totally eliminating TMP. The results of these trials are indicated in Figures 3 and 4. At all levels of butanediol, the E-04 batch of the resin gave a propellant with very low tensile strength and modulus. All batches of the resin did cure even at a 0% butanediol content at this R value, i.e., 0.9. Elongation values of the E-01 batch were found to be too low for most of the applications.

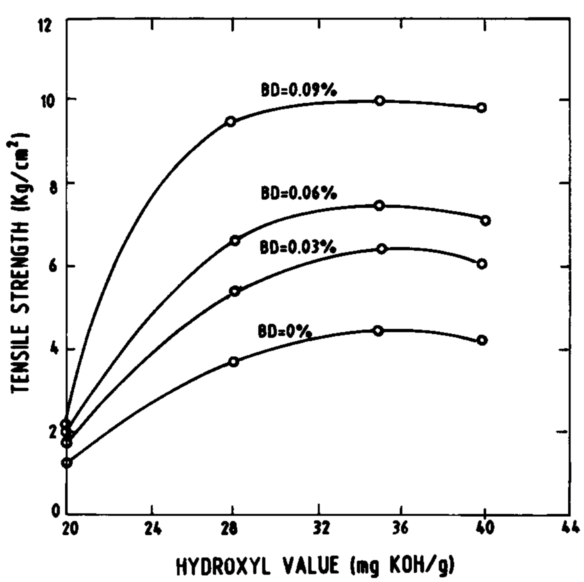

Figure 3 Effect of hydroxyl value of HTPB on tensile strength at four levels of butanediol at R = 0.9.

Another representation of the same data is given in Figure 5, wherein mechanical properties of the propellant for different batches of the resin have been plotted against wt % of TMP and butanediol on the same graph. A V-shaped arrangement of tensile strength contours is obtained as expected, but for the difference in R values. Among the many propellant formulations studied, with different batches of HTPB resins, a narrow band of useful formulations can easily be identified from Figure 5, e.g., formulations giving 6–8 kg/cm^2 tensile strength and 60–80% elongation. Resin E-04 with a triol content of 0.09% at an R value of 0.8 is one such formulation that gives a tensile strength of 7 kg/cm^2 and elongation of 70%.

Effect of TMP–Butanediol Combinations

Four sets of experiments were conducted with 0.045 and 0.03% each of TMP and butanediol. Figure 6 shows the tensile strength of the resultant propellant, and Figure 7, the corresponding elongation at an R value of 0.9. It can be seen that 0.03% each of the TMP and butanediol combination is too low in that it shows lower values of both tensile strength as well as elongation in comparison with those of 0.045%. In case of 0% TMP and butanediol, both tensile strength and elongation have not developed fully.

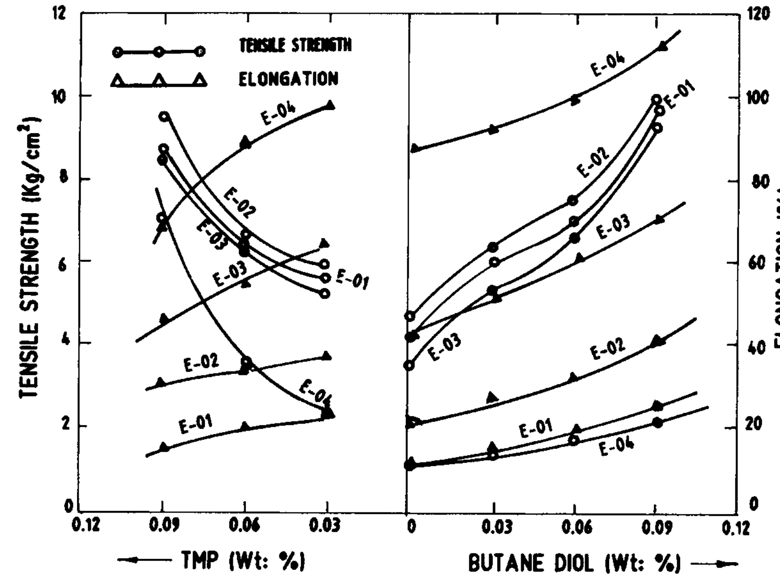

Figure 5 Mechanical properties of propellant with different batches of the resin.

Effect of Hydroxyl Content

Percentage hydroxyl groups available for the cure reaction for each batch of resin at three different levels of TMP content, in the absence of butanediol, are given in Table III. Corresponding mechanical properties are also given side-by-side.

The influence of increasing hydroxyl content from TMP at the expense of hydroxyl content from HTPB, in the absence of butanediol, on the mechanical properties of finished propellant have been plotted on the three-dimensional graph in Figure 8. It is seen that tensile strength traverses a wide range of values starting from 2.2 to 9.6 kg/cm^2 depending upon the relative contribution of hydroxyl contents from HTPB and TMP. Elongation values also show variation from 17 to 99%. The entire spectrum of properties is clearly visible on the three-dimensional

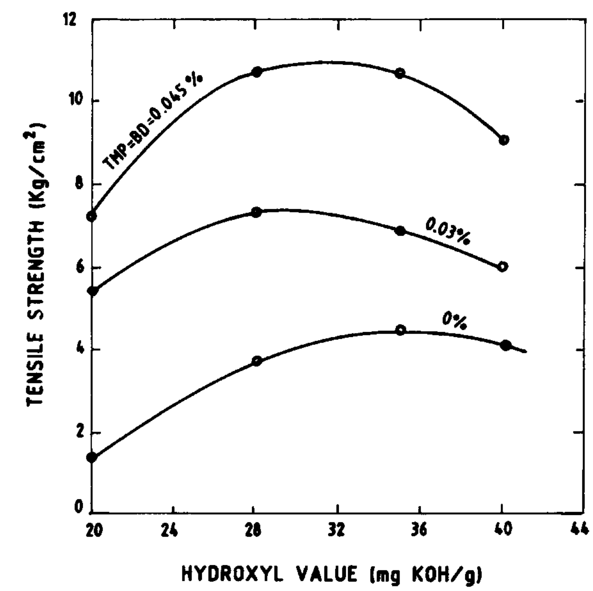

Figure 6 Effect of hydroxyl value of HTPB on tensile strength at different combinations of TMP and butanediol at $R = 0.9$.

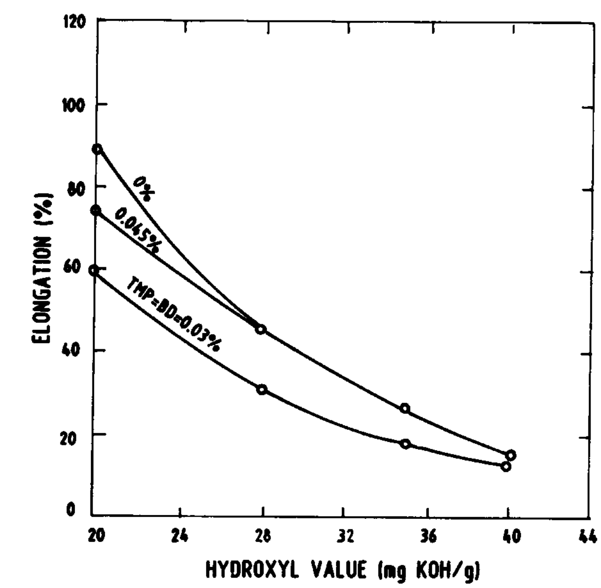

Figure 7 Effect of hydroxyl value of HTPB on elongation at different combinations of TMP and butanediol at $R = 0.9$.

Table III Hydroxyl Contents at R = 0.8

Wt % TMP	Batch No.	%OH Content			Properties		
		HTPB	TMP	BD	TS (kg/cm^2)	Elongation (%)	Modulus (kg/cm^2)
0.09	E-01	78.6	21.4	0	8.8	17	81
	E-02	76.0	24.0	0	9.6	34	57
	E-03	72.0	28.0	0	8.6	48	43
	E-04	65.0	35.0	0	7.0	69	25
0.06	E-01	85.0	15.0	0	6.2	20	58
	E-02	82.6	17.4	0	6.7	35	44
	E-03	79.6	20.4	0	6.3	55	24
	E-04	73.8	26.2	0	3.6	90	9
0.03	E-01	92.0	8.0	0	5.2	23	43
	E-02	90.6	9.4	0	5.7	38	33
	E-03	88.7	11.3	0	5.6	66	20
	E-04	85.0	15.0	0	2.2	99	6

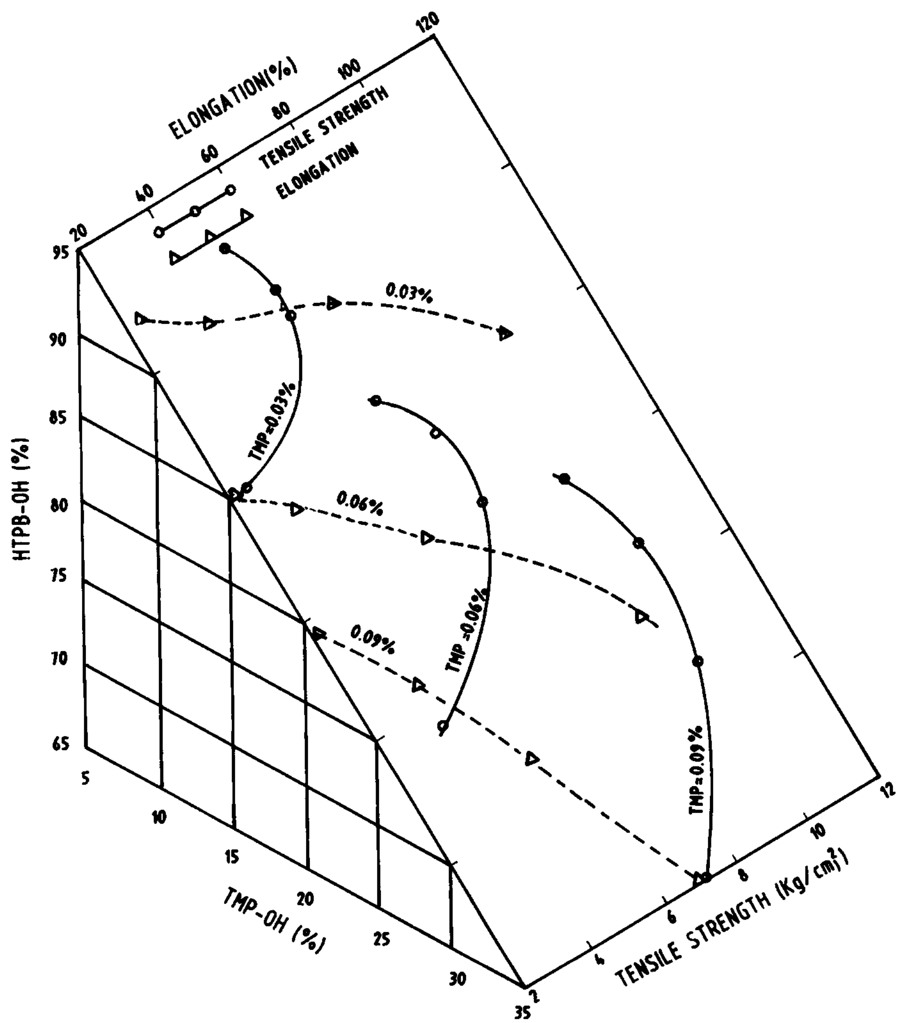

Figure 8 Variation of tensile strength and elongation at three levels of TMP content at R = 0.8.

Table IV Hydroxyl Contents at $R = 0.9$

Wt % BD	Batch No.	%OH Content			Properties		
		HTPB	TMP	BD	TS (kg/cm²)	Elongation (%)	Modulus (kg/cm²)
0.09	E-01	78.6	0	21.4	9.7	26	78
	E-02	76.0	0	24.0	10.0	41	58
	E-03	72.0	0	28.0	9.4	70	50
	E-04	65.0	0	35.0	2.1	113	5
0.06	E-01	85.0	0	15.0	7.0	20	86
	E-02	82.6	0	17.4	7.5	32	59
	E-03	79.6	0	20.4	6.5	62	60
	E-04	73.8	0	26.2	1.9	99	14
0.03	E-01	92.0	0	8.0	6.0	15	78
	E-02	90.6	0	9.4	6.4	29	44
	E-03	88.7	0	11.3	5.3	52	24
	E-04	85.0	0	15.0	1.7	94	15

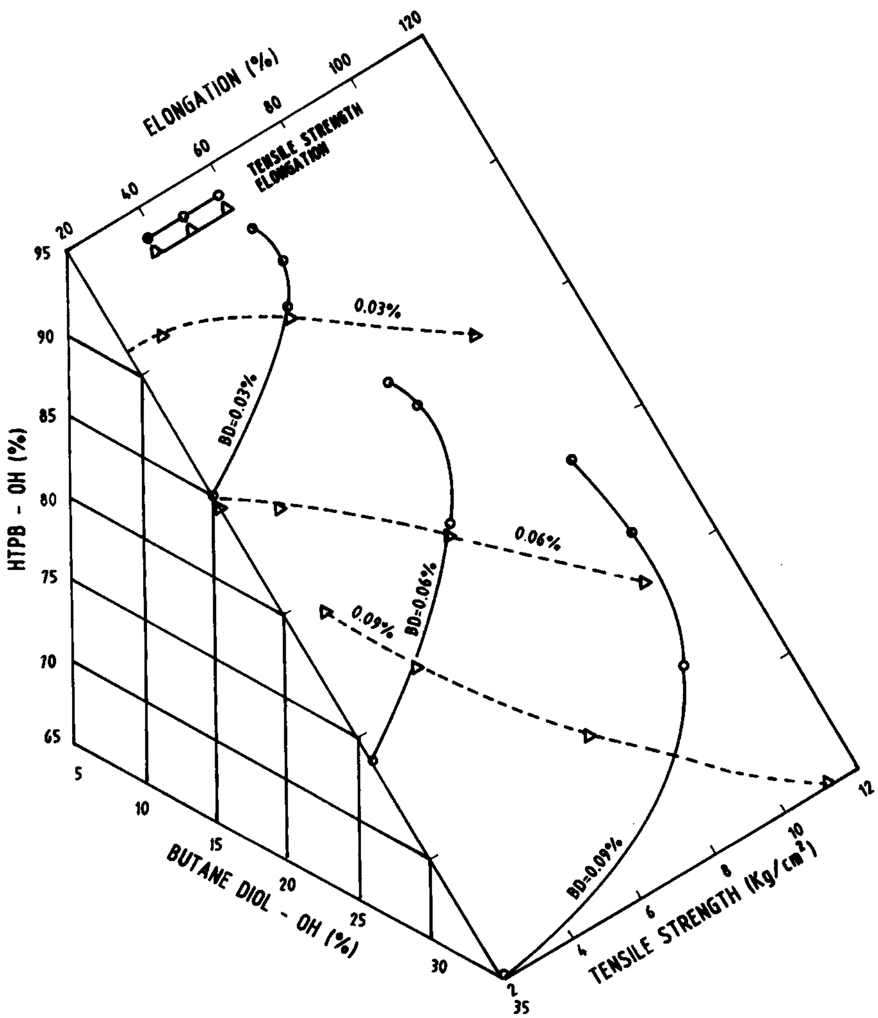

Figure 9 Variation of tensile strength and elongation at three levels of butanediol content at $R = 0.9$.

Table V Mechanical Properties of Propellants with TMP and Butanediol

Wt %			Mechanical Properties					
			R = 0.8			R = 0.9		
TMP	BD	Batch No.	TS (kg/cm^2)	Elongation (%)	Modulus (kg/cm^2)	TS (kg/cm^2)	Elongation (%)	Modulus (kg/cm^2)
0.045	0.045	E-01	8.9	30	59	9.0	14	107
		E-02	7.9	45	35	10.7	25	64
		E-03	6.0	76	13	10.6	44	62
		E-04	2.0	117	5	7.1	76	25
0.03	0.03	E-01	5.3	29	51	6.0	12	100
		E-02	5.6	23	29	6.8	18	70
		E-03	4.1	75	12	7.3	30	44
		E-04	1.2	129	3	5.3	61	17

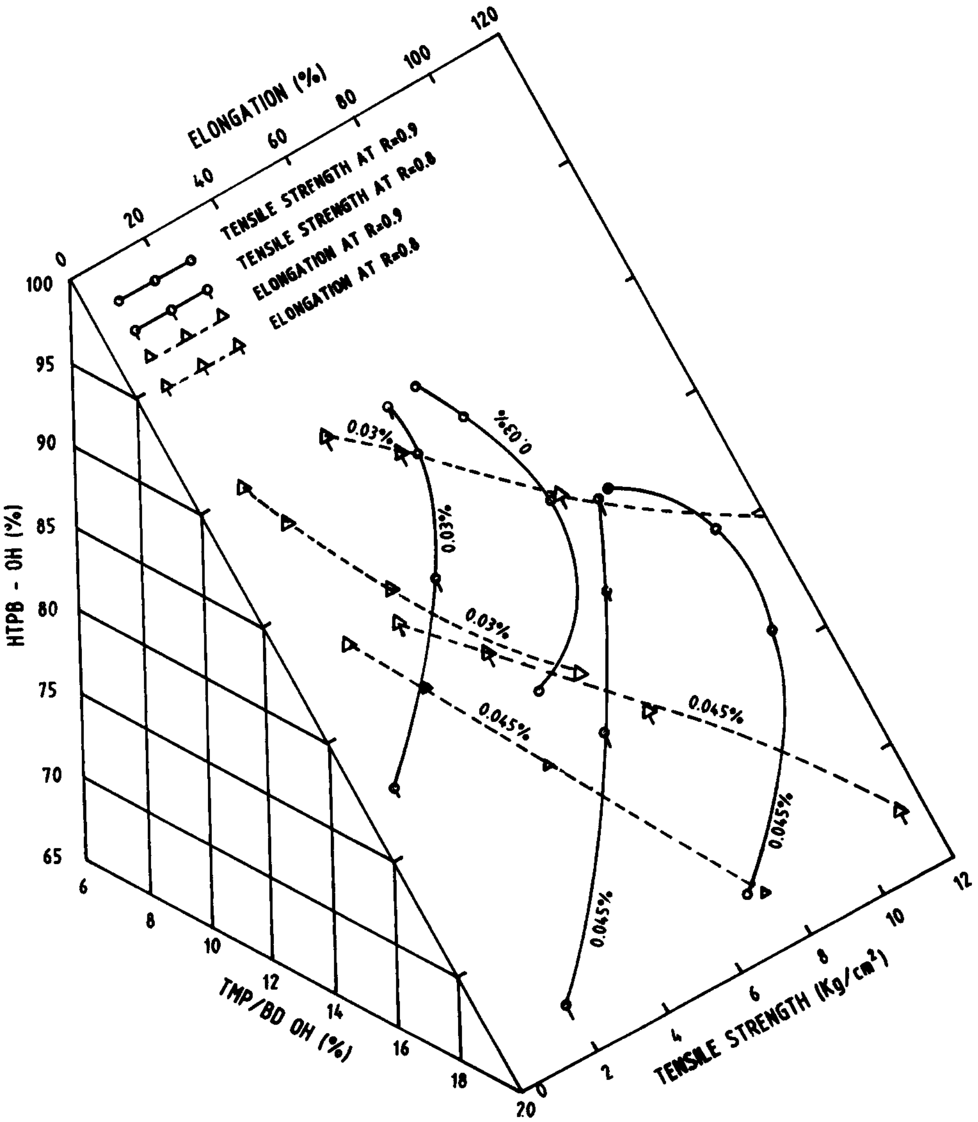

Figure 10 Variation of tensile strength and elongation at different combinations of TMP and butanediol.

plot of Figure 8. The percentage of hydroxyl groups available in the next set of experiments, where butanediol alone was used, is given in Table IV.

The mechanical properties of the propellant with various combinations of HTPB and butanediol for different batches of resin have been pictorially represented in Figure 9.

A comparison of Figures 8 and 9 shows that a somewhat identical performance is given by similar amounts of butanediol in the place of TMP, but at a different *R* value, i.e., 0.9 instead of 0.8. This indicates that when the chain extender alone is used in the absence of a cross-linker, higher amounts of basic curator is needed. Mechanical properties of the propellants with combinations of TMP and butanediol are given in Table V.

An attempt has been made to represent the results of the combination trials with TMP and butanediol at two different *R* values in Figure 10. It is seen that 0.03% each of TMP and butanediol at an *R* value of 0.8 is found to give a propellant with less than 6 kg/cm^2 tensile strength for all the batches of the resin, which is not very desirable for many applications. But trials with 0.045% each of TMP and butanediol at an *R* value of 0.9 give an excellent property for the propellant with the E-03 and E-04 batches of resin.

Apparent Viscosity

The apparent viscosity of the propellant slurry at the end of the mix ranges from 8,000 to 11,000 *p* for the E-01, E-02, and E-03 batches of the resin and 17,000–20,000 *p* for E-04.

CONCLUSION

Although tensile strength of the composite propellant is decided by many factors such as properties of the matrix resin, particle size, shape, distribution, and concentration of the solid ingredients, and binder–filler interaction, elongation capability is very sensitive to changes in the resin parameters. The diol–triol ratio and their level constitutes a useful tool for control of physical and/or mechanical properties of HTPB-based propellants in addition to the NCO/OH ratio. The best properties can be achieved with high molecular weight HTPB resin by using a cross-link component alone at a lower NCO/OH ratio, a chain-extender component alone at a higher NCO/OH ratio, or a combination of diol–triol at a higher NCO/OH ratio.

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