# Structure–Property Relationship of HTPB-Based Propellants. II. Formulation Tailoring for Better Mechanical Properties

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**SYNOPSIS**

There has been a constant endeavor to improve the mechanical properties of hydroxyl-terminated polybutadiene (HTPB)-based composite solid propellants. A systematic study has been conducted on different batches of HTPB resins with varying molecular weights and hydroxyl values. Propellant formulation experiments were conducted wherein the ratio of chain extender to crosslinker was systematically varied, with a view to achieve the maximum possible strain capability and moderately high tensile strength, keeping all other parameters constant. The influence of increasing hydroxyl content from trimethylolpropane at the expense of hydroxyl content from butanediol, on the mechanical properties of the finished propellant, has been depicted on 3-dimensional graphs. The isoproperty lines, plotted as a triangular chart with the percentage hydroxyl contents from the three constituents, can be used to arrive at the suitable formulation for a specified application depending upon the OH value of the resin. HTPB resins with high molecular weight, low functionality, and low hydroxyl value require higher levels of trifunctional curing agent and higher NCO/OH ratios to obtain outstanding mechanical properties, especially elastic properties, compared to low molecular weight, high functionality resins. The impact of *hard* and *soft* segment domain structure on the mechanical behavior of the cured systems is more pronounced in the low molecular weight resin formulations due to the higher *hard* segment content compared to those attainable in high molecular weight resin formulations.


## INTRODUCTION

There has been a constant endeavor to improve the mechanical properties of HTPB-based composite solid propellants. In order to have a better understanding of the influence of resin variabilities like hydroxyl value, molecular weight, functionality, etc. on the resultant propellant properties, a coordinated program was undertaken. Under this scheme, a series of HTPB resins with varying molecular weights and hydroxyl values were produced at Vikram Sarabhai Space Centre.[1] Details of the first set of experiments conducted on these batches of resins by varying the ratio of curing agent to resin, i.e., $R$ values, keeping the chain extender to crosslink ratio the same, have been reported in Part I.[2]

As continuation of the above work, another series of experiments has been conducted, wherein the ratio of chain extender to crosslinker has been systematically varied, with a view to achieving the maximum possible strain capability and moderately high tensile strength for the propellant. The present study investigates the probable correlation between the resin characteristics and matrix structure in HTPB-based systems.

## EXPERIMENTAL

Four grades of HTPB resins with varying hydroxyl values and molecular weights have been used for the present study. Properties of the four experimental batches of resins E-01, E-02, E-03, and E-04 are given in Table I, together with the properties of standard HTPB resins. It can be seen that hydroxyl values cover the range of 20–40 and the number average molecular weight from 2600 to 4500.

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**Table I Properties of Experimental Batches of Resin**

| Properties | Experimental Batch Number | | | | |
|---|---|---|---|---|---|
| | Standard | E-01 | E-02 | E-03 | E-04 |
| 1. Viscosity (30°C, CPS) | 6300 | 6000 | 9070 | 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) | 2600 | 2900 | 3300 | 3500 | 4500 |
| 5. Eq wt | 1300 | 1370 | 1600 | 2000 | 2800 |
| 6. Average functionality ($M_n$/eq wt) | 2 | 2.1 | 2.0 | 1.75 | 1.60 |

### Detailed Characterization of HTPB Resins

The four grades of HTPB resins have been subjected to detailed characterization by gel permeation chromatography (GPC) and spectroscopic analysis.

### Binder Studies

As a prelude to propellant formulation experimentation, gumstock studies were conducted using the four grades of HTPB resins with trimethylolpropane (TMP), 1,4-butanediol combinations using toluene diisocyanate at two different $R$ values.

### Propellant Formulation Experiments

The basic resin matrix is a four-component system with HTPB, trimethylolpropane, 1,4-butanediol, and toluene diisocyanate as the constituents. The propellant trials are conducted with the baseline formulation given in Table II.

### Details of the Investigation

The present investigation involves propellant formulation experiments with the four batches of HTPB resins at the following combinations of triol/diol ratios and $R$ values.

**Table II Baseline Propellant Formulation**

| Ingredients | Wt % |
|---|---|
| HTPB + TDI | 10.78 |
| TMP + butane diol | 0.12 |
| Plasticizer, antioxidant<br>Burn-rate modifier | 3.50 |
| Aluminum | 18.00 |
| Ammonium perchlorate | 67.60 |
| Total | 100.00 |

i. TMP–butane diol ratios of 1 : 0, 3 : 1, and 1 : 1 at an $R$ value of 0.8.
ii. TMP–butane diol ratios of 0 : 1, 1 : 3, and 1 : 1 at an $R$ value of 0.9.

Propellant was mixed in a sigma blade mixer at an 800 gm level at 40°C. Propellant slurry was vacuum-cast and cured at 60°C for 5 days. The cured samples were tested for mechanical properties, i.e., tensile strength, percentage elongation, and modulus.

## RESULTS AND DISCUSSION

### Molecular Weight Distribution of HTPB

The number average molecular weight $M_n$, weight average molecular weight $M_w$, and polydispersity calculated from the GPC analysis of the four batches of resins are given in Table III.

The GPC curves indicated a bimodal molecular weight distribution for each batch of HTPB resin. Polydispersities are found to be almost the same for all the samples independent of their hydroxyl values.

### Microstructure of HTPB

IR Spectra of four experimental batches of HTPB resins have been taken. The percentages of different isomers present in the four batches of HTPB resins are given in Table IV. The above results indicate that all the four batches have similar structure. This is in line with the observation that microstructure of the prepolymer is decided by the technique of manufacture, i.e., either by (i) free radical polymerization, (ii) anionic polymerisation, or (iii) degradation of high molecular weight polymers. Here different grades of the prepolymer have been manufactured by the same technique, namely, free radical polymerization, wherein only the process pa-

**Table III Molecular Weight and Polydispersity from GPC**

| Sample | $M_n$ | $M_w$ | Polydispersity | Peak Mol Wt | Mol Wt Range |
|---|---|---|---|---|---|
| E-01 | 5580 | 15,950 | 2.8 | 6565 | 174,300–800 |
| E-02 | 6530 | 18,100 | 2.7 | 7530 | 179,900–660 |
| E-03 | 7200 | 20,920 | 2.9 | 8640 | 206,440–600 |
| E-04 | 12,244 | 31,330 | 2.5 | 18,120 | 283,400–1150 |

rameters have been altered and the microstructure does not vary with these parametric variations.[3] All the hydroxyl groups of the HTPB are primary in nature and are mostly allylic (75%) and very reactive.[4]

## Effect of TMP Content

In our earlier experiments, the ratio of triol to diol was maintained constant with a view to evaluate the influence of $R$ value on mechanical properties.[2] At present, the influence of varying triol/diol ratio has been studied at two different $R$ values. Figures 1 and 2 show the influence of varying triol–diol ratios on tensile strength and elongation at an $R$ value of 0.8. It is seen from Figure 1 that, as the HTPB–OH value is decreased from 40 to 20 and TMP content increased from 1 : 1 to 1 : 0 through 3 : 1, tensile strength traverses a wide range of values starting from 10 to 3 kg/cm$^2$. Similarly, Figure 2 indicates elongation values ranging from 20 to 110%. A similar trend is shown by the second set of experiments conducted at an $R$ value of 0.9, but at triol–diol ratios of 0 : 1, 1 : 3, and 1 : 1, represented in Figures 3 and 4.

HTPB resins with lower hydroxyl values or higher molecular weights require a high triol content to achieve a tensile strength of 6–7 kg/cm$^2$, and moderately high elongation. As the triol content increases, the rate of increase of tensile strength is reduced at higher hydroxyl values of HTPB. This effect is seen at both $R$ values. Another observation made from Figures 1–4 is that triol–diol ratio of 1 : 1 at $R$ = 0.9 is equivalent to triol–diol ratio of 1 : 0 at $R$ = 0.8; 1 : 3 at $R$ = 0.9 is equivalent to 3 : 1 at $R$ = 0.8; and 0 : 1 at $R$ = 0.9 is equivalent to 1 : 1 at $R$ = 0.8.

**Table IV Results of Spectroscopic Analysis**

| Batch No. | *Trans* (%) | *Cis* (%) | Vinyl (%) |
|---|---|---|---|
| E-01 | 58.9 | 18.5 | 22.6 |
| E-02 | 60.0 | 17.9 | 22.1 |
| E-03 | 60.6 | 18.2 | 21.2 |
| E-04 | 61.5 | 16.5 | 23.0 |

## Combined Effect of R Value, TMP Content, and Hydroxyl Value of HTPB Resin

The combined effect of varying all the three parameters i.e., $R$ value, triol/diol ratio, and hydroxyl value, is depicted in Figures 5 and 6. At an $R$ value of 0.8, a triol/diol ratio of 2 : 1 gives lower tensile strength values and higher elongation values. The same triol/diol ratio gives higher tensile strength and lower elongation values at an $R$ value of 0.9. The triol/diol ratio of 2 : 1 may be suitable for resin with OH values in the range of 40–45, but, in the case of lower OH value resins, other combinations, like triol/diol ratios of 3 : 1 at $R$ = 0.8 and 1 : 3 at $R$ = 0.9, are found to give an optimium combination of tensile strength and elongation. In higher OH value resins, the influence of the triol/diol ratio is less significant.

A very important observation made from Figure 5 is that whatever may be the $R$ value and triol/diol ratio, resin with an OH value around 40 does not give a propellant with a very high strain capability, whereas resins with a hydroxyl value less than 30 are very sensitive to changes in curative levels. This leads to the conclusion that a second generation propellant properties can be achieved by making use of HTPB resins with less than 30 hydroxyl values.

## Mechanical Properties of Composite Solid Propellants

Composite solid propellants are used in either case-bonded or in free-standing configurations, depending upon the mission requirements. Although cartridge-loaded solid propellant grains are more suitable for sounding rocket and missile applications, huge case-bonded solid boosters are normally needed in launch vehicles. Solid propellant grains are subjected to a

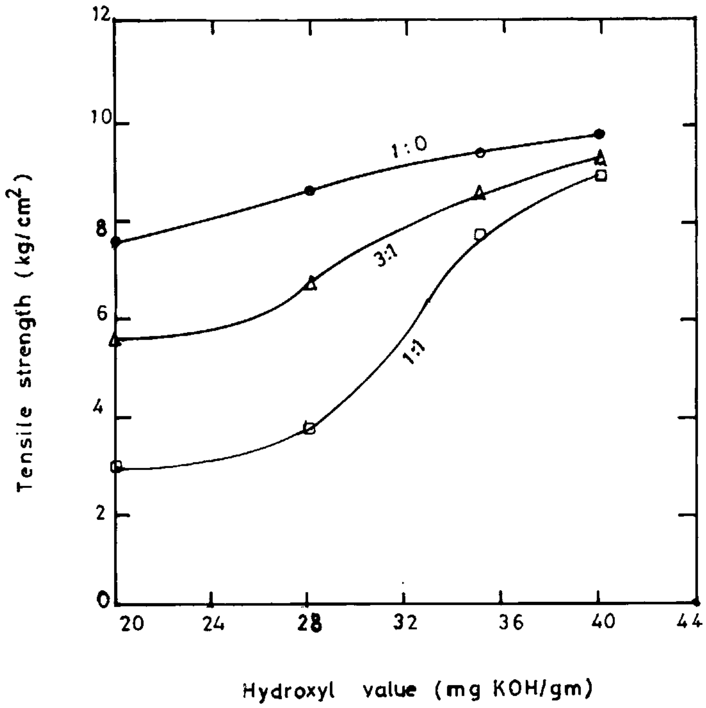


**Figure 1** Effect of hydroxyl value of HTPB on tensile strength at $R = 0.8$.

variety of stresses and strains during manufacture, transportation, storage, and flight. In case-bonded grains, stresses and strains are introduced during curing and cooling of the grains due to differential thermal expansion between the propellant and the case material. Also, thermal stresses arise in the

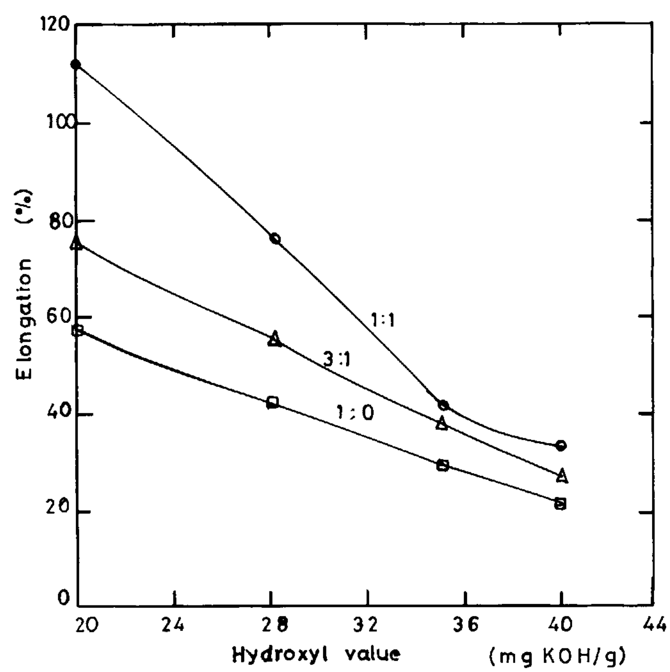


**Figure 2** Effect of hydroxyl value of HTPB on elongation at $R = 0.8$.

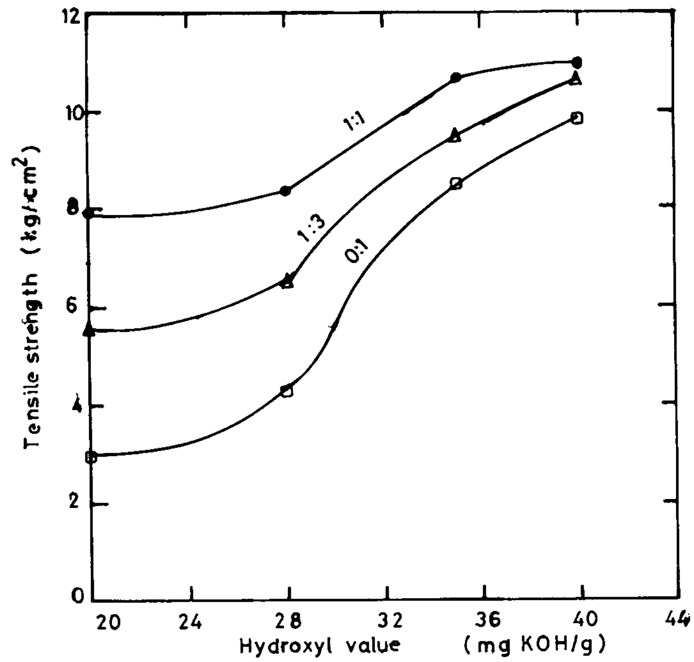


**Figure 3** Effect of hydroxyl value of HTPB on tensile strength at $R = 0.9$.

grain due to temperature gradients during curing and cooling, aerodynamic heating in flight, etc.

A propellant grain should have sufficient tensile strength and elongation to withstand these stresses and strains. Composite propellant exhibits viscoelastic behavior, and several viscoelastic properties are needed to characterize it fully, like relaxation modulus, creep compliance, etc. However, a suitable

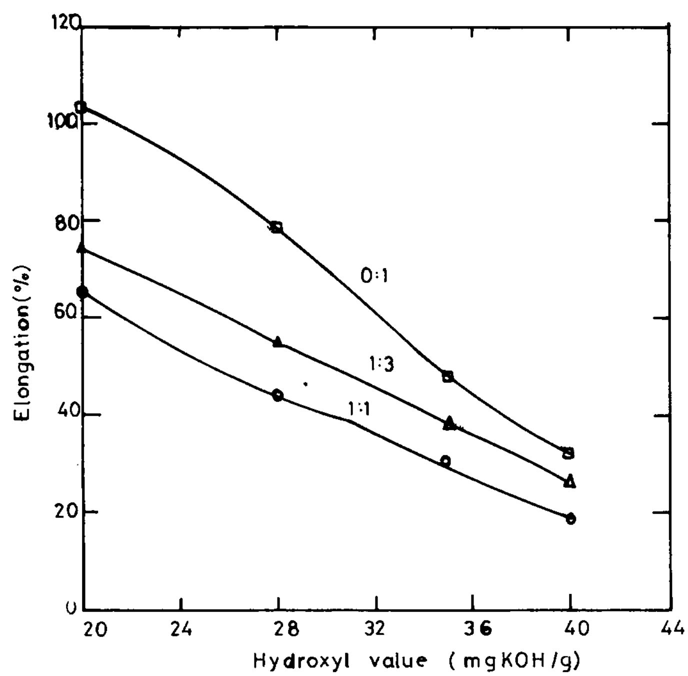


**Figure 4** Effect of hydroxyl value of HTPB on elongation at $R = 0.9$.

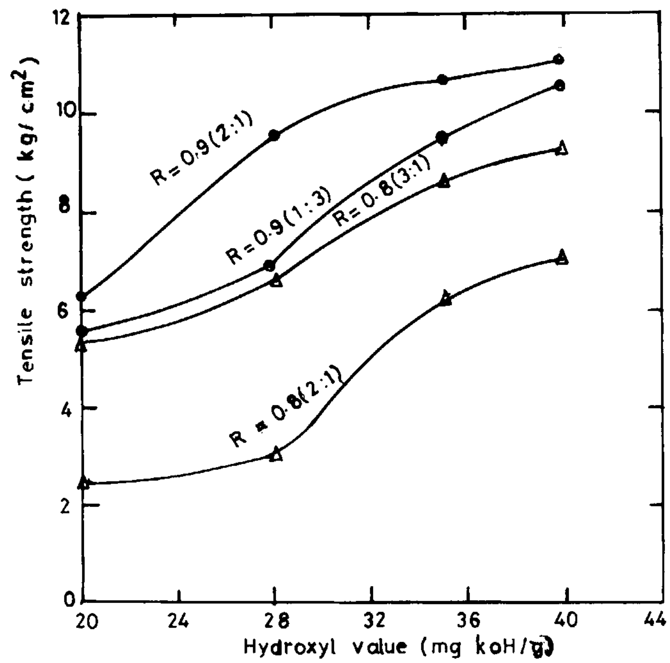


**Figure 5** Combined effect of $R$ value, TMP content, and hydroxyl value of HTPB resin on tensile strength.

combination of tensile strength, elongation, and initial elastic modulus are normally specified to check the adequacy in a particular application. For a typical case bonded upper stage solid rocket motor, suffice it to say that a tensile strength of approximately 8 $kg/cm^2$, an elongation of 40–50%, and an

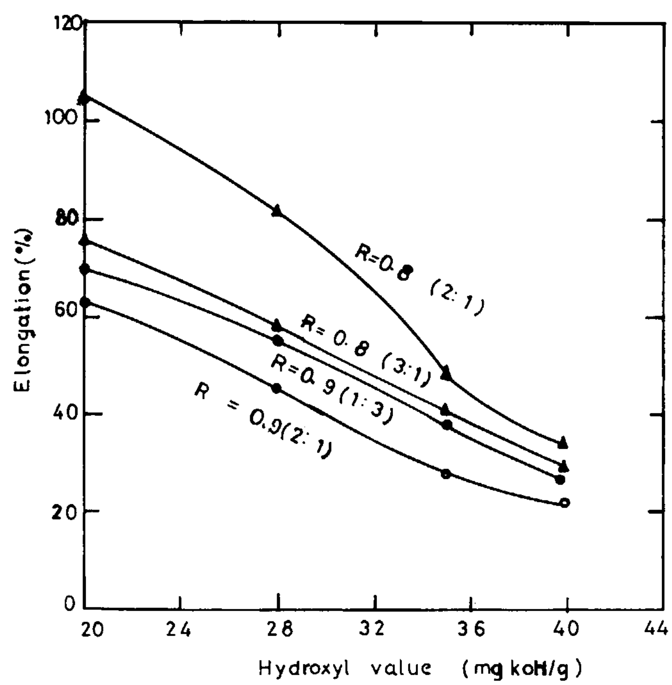


**Figure 6** Combined effect of $R$ value, TMP content, and hydroxyl value of HTPB on elongation.

**Table V Hydroxyl Contents at $R$ = 0.8**

| Batch No. | TMP (wt %) | % OH Content | | | Properties | |
|---|---|---|---|---|---|---|
| | | HTPB | TMP | BD | TS (kg/cm$^2$) | Elongation (%) |
| E-01 | 0.12 | 73 | 27 | 0 | 9.7 | 23 |
| E-02 | | 70 | 30 | 0 | 9.1 | 30 |
| E-03 | | 66 | 34 | 0 | 8.5 | 45 |
| E-04 | | 58 | 42 | 0 | 7.3 | 57 |
| E-01 | 0.09 | 73 | 20 | 7 | 9.2 | 28 |
| E-02 | | 70 | 22 | 8 | 8.5 | 40 |
| E-03 | | 66 | 26 | 8 | 6.6 | 58 |
| E-04 | | 58 | 32 | 10 | 5.6 | 75 |
| E-01 | 0.06 | 73 | 14 | 14 | 8.8 | 34 |
| E-02 | | 70 | 15 | 15 | 7.6 | 42 |
| E-03 | | 66 | 17 | 17 | 3.5 | 78 |
| E-04 | | 58 | 21 | 21 | 2.8 | 111 |

initial modulus of 40–50 kg/cm$^2$ are reasonable. A modulus that is too high will reduce the strain levels introduced in the grain by a particular stress level, but at the same time strain capability of the propellant also comes down. Similarly, a modulus that is too low will give rise to excessive deformation due to creep during storage. Hence it is the usual practice to specify the minimum and the maximum values for the initial modulus of the propellant.

Although the foregoing discussion is based only on the mechanical property requirement, energetics of the propellant are mainly decided by the composition of ingredients other than the binder, like oxidizer, metallic fuel, burn-rate modifier, etc. The binder has only a minor influence on ballistics. Here, we are concerned with a suitable combination of HTPB resin, curing agent, crosslinking agent, and chain extender component, which can be used so as to result in a propellant with mechanical properties suitable for case-bonded applications.

## Effect of Hydroxyl Content

A detailed analysis of the contribution of percentage hydroxyl groups from the three ingredients, namely, HTPB resin, TMP, and butane diol, on the me-

**Table VI Hydroxyl Contents at $R$ = 0.9**

| Batch No. | TMP (wt %) | % OH Content | | | Properties | |
|---|---|---|---|---|---|---|
| | | HTPB | TMP | BD | TS (kg/cm$^2$) | Elongation (%) |
| E-01 | 0.06 | 73 | 14 | 14 | 11.0 | 20 |
| E-02 | | 70 | 15 | 15 | 10.8 | 32 |
| E-03 | | 66 | 17 | 17 | 8.3 | 44 |
| E-04 | | 58 | 21 | 21 | 8.0 | 66 |
| E-01 | 0.03 | 73 | 7 | 20 | 10.8 | 26 |
| E-02 | | 70 | 8 | 22 | 9.5 | 38 |
| E-03 | | 66 | 8 | 26 | 6.6 | 55 |
| E-04 | | 58 | 10 | 32 | 5.6 | 71 |
| E-01 | 0 | 73 | 0 | 27 | 9.8 | 31 |
| E-02 | | 70 | 0 | 30 | 8.5 | 47 |
| E-03 | | 66 | 0 | 34 | 4.2 | 80 |
| E-04 | | 58 | 0 | 42 | 3.0 | 103 |

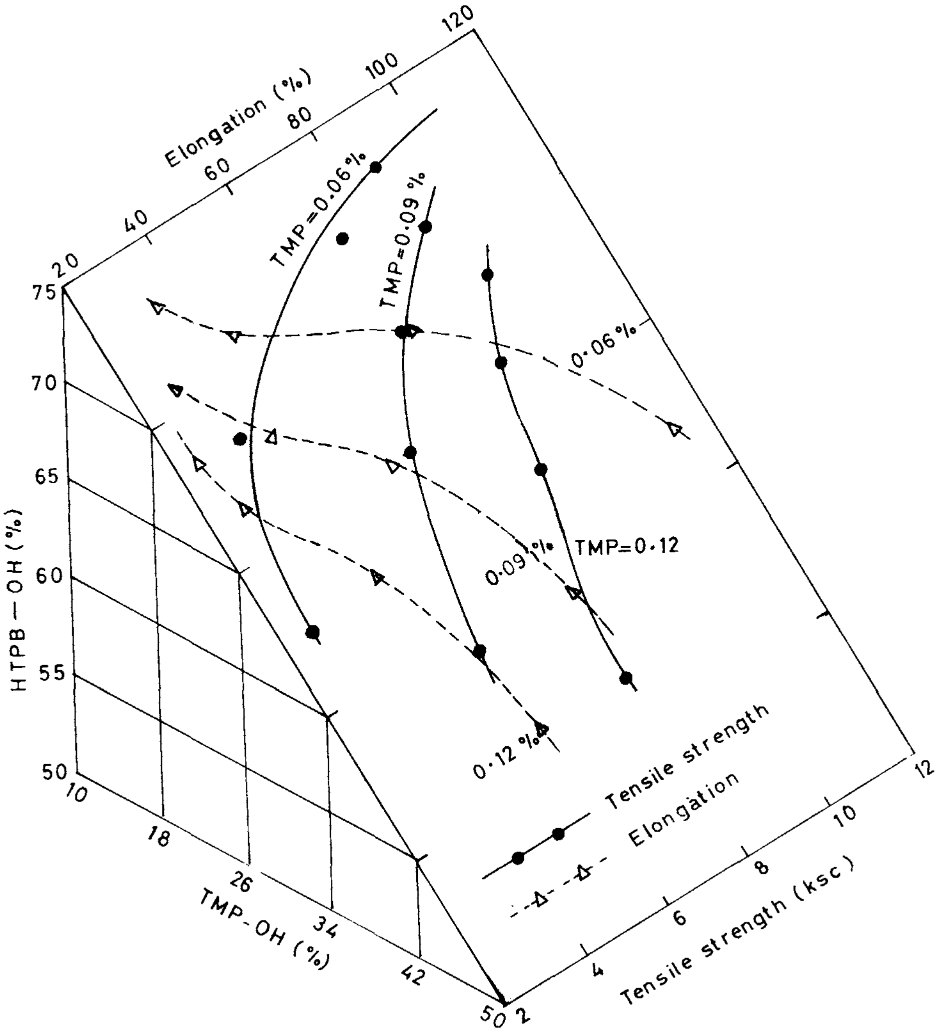


**Figure 7** Variation of tensile strength and elongation at three levels of TMP content at $R = 0.8$.

chanical properties of the finished propellant, has been carried out. Table V gives the values of percentage of hydroxyl groups available for cure reaction for each batch of resin at three different levels of TMP contents, i.e. 0.12, 0.09, and 0.06% in propellant formulation, corresponding to an $R$ value of 0.8. Corresponding mechanical properties are also given side-by-side. Similar values for an $R$ value of 0.9 are given in Table VI. The influence of increasing hydroxyl content from TMP at the expense of hydroxyl content from butane diol, on the mechanical properties of the finished propellant, has been depicted on the 3-dimensional graphs in Figures 7 and 8. HTPB—OH (%) is taken on the $Y$-axis, and TMP OH (%) on the $X$-axis, which is at 120° to the $Y$-axis. Tensile strength and elongation values at different combination of HTPB OH and TMP-OH are taken on the $Z$-axis, which is perpendicular to the $X$-$Y$ plane. The graphs are plotted on a plane which cuts the $X$-$Y$ plane at 45°.

From Figures 7 and 8, it is evident that TMP contents of 0.12% at an $R$-value of 0.8 and 0.06% at an $R$-value of 0.9 give rise to values of tensile strength which are too high and values of elongation which are too low for resins with higher OH values, whereas, for lower OH value resins, these combinations give moderate values of tensile strength and elongation. As the hydroxyl contribution from the resin increases, hydroxyl contribution from TMP and butane diol should be so adjusted that cross-linking is reduced. It is observed that TMP content of 0.09% is the most suitable for lower OH value resins at an $R$ value of 0.8. Similarly, TMP content of 0.03% is the most suitable for lower OH value

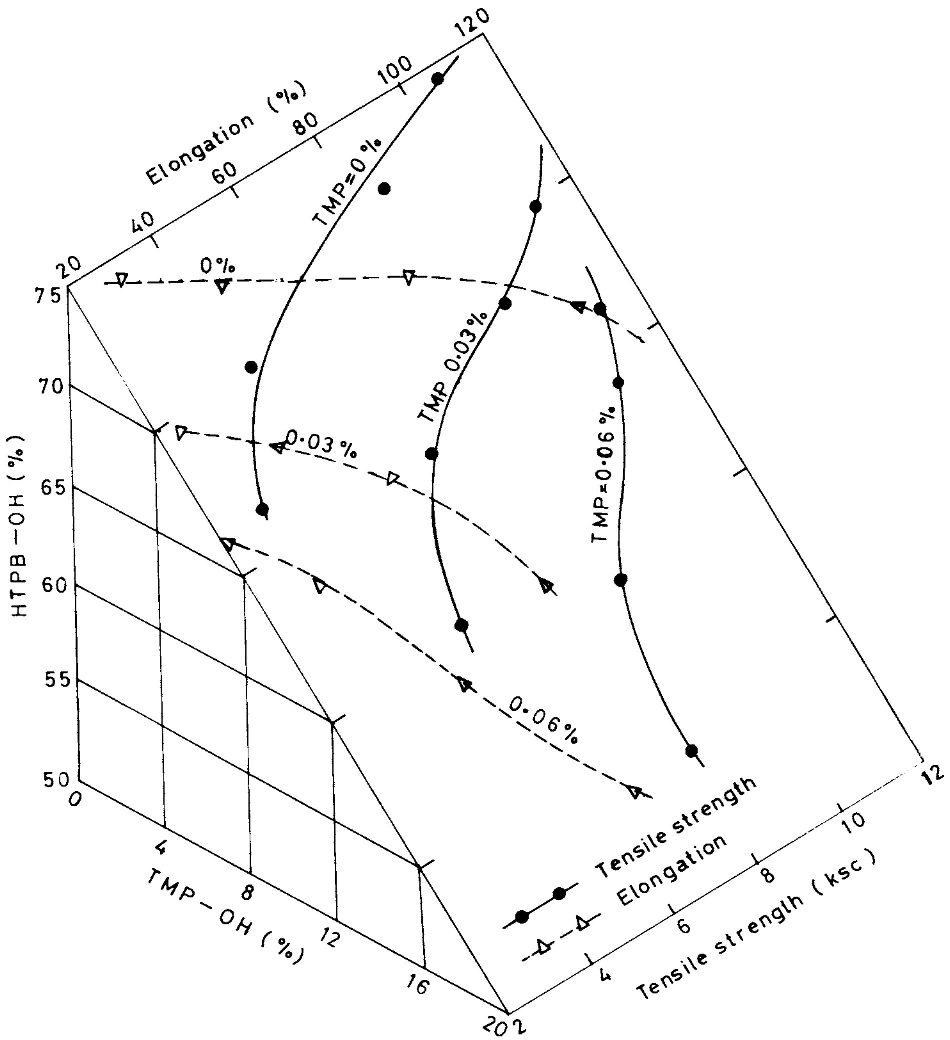


**Figure 8** Variation of tensile strength and elongation at three levels of TMP content at $R = 0.9$.

resins at an $R$ value of 0.9. Other combinations can be used for specific applications.

A triangular chart with the percentage hydroxyl contents from the three constituents has been plotted in Figure 9. Compositions giving elongation values of 30, 50, 75%, etc. and associated tensile strength values have been joined together to get a constant property line. This isoproperty line can be used to arrive at the suitable formulation depending upon the OH value of the resin.

## Propellant Processability

The apparent viscosity of the propellant slurry at the end of the mix ranges from 8000 to 12,000 P for E-01, E-02, and E-03 batches of resin and 18,000–21,000 P for E-04. Three sets are well within the processability range by the vacuum casting technique whereas the E-04 slurry lies at the marginal case, in which case pressure casting techniques may have to be adopted to obtain flawless propellant grains.

## Results of Binder Studies

The gumstock studies showed mechanical properties which are parallel to those of the corresponding propellant samples. All the gumstocks cured with 1,4-butane diol alone at an $R$ value of 0.9 show better than expected properties, even though the cross-linking levels are low. This is basically due to the *hard* and *soft* segments when the soft rubbery bu-

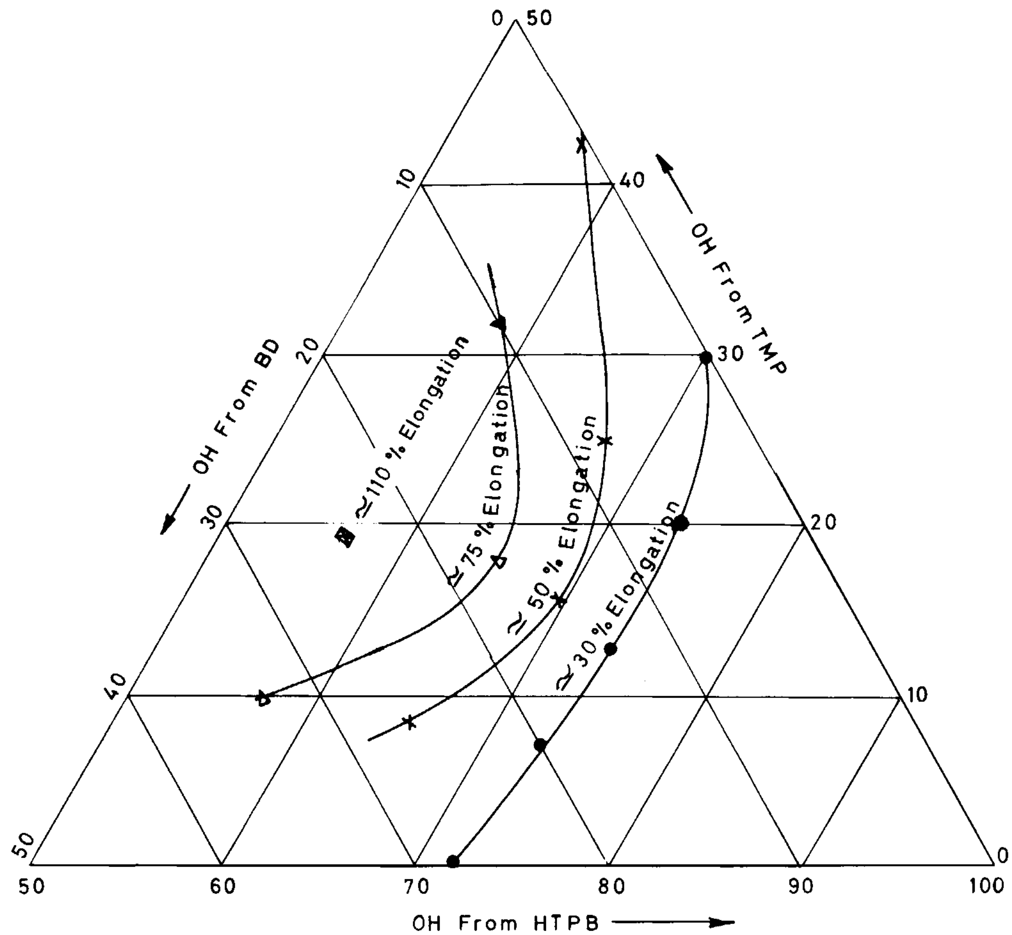


**Figure 9** Triangular chart showing constant mechanical property lines.

tadiene is cured at higher isocyanate levels with 1,4-butanediol. TDI/1,4-butane diol portion acts as the *hard* segment and HTPB chain acts as the *soft* segment.[5-7] This indicates that butane diol added to the propellant and gumstock does not act as a chain extender alone, but, in combination with isocynates, it changes the morphology of the network favorably or otherwise, depending on the formulation.[8]

### Molecular Structure–Mechanical Property Correlation

HTPB-based polyurethane formulations containing 1,4-butane diol TMP and TDI shows interesting mechanical behavior in both filled and unfilled systems. The impact of *hard* and *soft* segment domain structure on the mechanical behavior of the cured systems is more pronounced in the low molecular weight resin formulations due to the higher *hard* segment content compared to those attainable in high molecular weight resin formulations.

## CONCLUSION

HTPB resins with high molecular weight, low functionality, and low hydroxyl value require higher levels of trifunctional curing agent and higher $R$ values to obtain outstanding mechanical properties, especially elastic properties, compared to low molecular weight, high functionality resins. The triol/diol ratio of 2 : 1 is suitable for resin with OH values in the range of 40–50, but, in the case of lower OH-value resins, other combinations, like triol/diol ratios of 3 : 1 at $R = 0.8$ and 1 : 3 at $R = 0.9$, are found to give optimum combinations of tensile strength and elongation. In higher OH value resins, the influence of the triol/diol ratio is less significant.

A very important observation made from the present study is that whatever may be the $R$ value and triol/diol ratio, resin with an OH value around 40 does not give propellant with very high strain capability, whereas resin with hydroxyl value less than 30 is very sensitive to changes in curative levels.

This leads to the conclusion that second generation propellant properties can be achieved by making use of HTPB resins with hydroxyl values less than 30 mg KOH/g.

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