Studies on the functionality distribution of hydroxyl-terminated polybutadiene and correlation with mechanical properties

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The functionality distribution of hydroxyl-terminated polybutadiene (HTPB) prepolymer was studied by a combination of preparative and analytical gel permeation chromatography (g.p.c.) and the results correlated with mechanical properties and sol content of the resins cured with diisocyanate. The prepolymers were converted to their ultra-violet-absorbing ester derivatives and fractionated according to their molecular weights. The functionalities of the fractions were determined using dual-detector analytical g.p.c. The functionality distribution was found to depend on the method of polymerization; increasing with molecular weight for free-radically polymerized HTPBs and remaining constant at around two for anionically polymerized HTPB. The different batches of free-radical HTPB were found to contain varying amounts of non- and monofunctional, chain-extending difunctional and crosslinking tri- and polyfunctional species, and their relative amounts have for the first time been quantitatively correlated with the stress–strain properties of the cured resin.

(Keywords: functionality distribution; propellant binder; hydroxyl-terminated polybutadiene; preparative gel permeation chromatography; polymer fractionation; correlation with mechanical properties)

INTRODUCTION

Hydroxyl-terminated polybutadiene (HTPB) prepolymers have gained considerable importance as polymeric fuel binders in modern solid rocket propellants. Functionality, defined as the number of reactive functional groups (hydroxyl in this case) per molecule, is usually expressed as an average in the case of a polymer. However, the determination of average functionality of a prepolymer is not sufficient because it may consist of different proportions of mono-, di-, tri- and polyfunctional moieties. In the curing process the non-functional species does not contribute to the polymer network, the monofunctional species can terminate the growth of the network, the difunctional species contributes to polymer chain extension and hence flexibility, and the tri- and polyfunctional species result in crosslinking and hence rigidity of the cured product. The study of functionality distribution has, therefore, attracted the utmost attention of researchers all over the world in recent years[1–10].

The classical concept of determining the functionality distribution involves two steps—separation of the polymer into fractions of different functionalities and estimation of each fraction in terms of its functionality and quantity. A column chromatographic fractionation method for studying the functionality distribution was first reported by Muenker[2]. Later other workers[3,8–10] used various fractionation techniques like adsorption column chromatography, t.l.c., preparative l.c., etc., involving separations based on the minute polarity difference caused by different amounts of hydroxyl groups in the polymer chain.

Vapour pressure osmometry (v.p.o.) and gel permeation chromatography (g.p.c.) have been employed for the determination of molecular weight of the fractions. For determination of equivalent weights, sensitive spectrophotometric methods (u.v., i.r.) are generally used. In the u.v. method, the hydroxyl group is converted into a u.v.-absorbing derivative. Anderson *et al.*[4,5] used the phenylurethane derivative and evolved a dual-detector (d.r.i. and u.v.) analytical g.p.c. method for the determination of functionality distribution of HTPB without its fractionation. Carver[7] later modified the procedure using the 3,5-dinitrobenzoyl derivative. Both studies showed an increase of functionality with increase in molecular weight for free-radically polymerized HTPB, contrary to the results obtained from adsorption chromatography. This gave the basis for the separation on preparative scale g.p.c. Thus Inagaki *et al.*[9] separated free-radical HTPB into 17 fractions and arbitrarily assigned their functionalities using t.l.c. Pham *et al.*[10] used chemical/n.m.r. and g.p.c./v.p.o. methods to assign the functionalities of the fractions, which were, however, limited in number.

In the present work eight batches of free-radical and one anionic HTPB were each separated into 24 fractions and each fraction analysed by dual-detector analytical g.p.c. (d.d.a.g.p.c.) to obtain the functionality distribution. Although the dependence of mechanical properties of the polymer on its functionality distribution has long been realised, the available literature does not reveal any such quantitative correlation. We also report for the first time a quantitative correlation between functionality distribution and mechanical properties of the HTPB resin cured with diisocyanate.

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Table 1 Important characteristics of free-radical HTPB

Sample no.	Property	Range
1	Hydroxyl value	40 to 50 mg KOH/g
2	Acid value	1 mg KOH/g (max)
3	Volatile matter	0.5% (max)
4	Brookfield viscosity (at 30°C)	4000 to 6500 cP
5	(at 60°C)	800 to 1400 cP
6	Specific gravity	0.90 to 0.92
7	Moisture content (Karl Fisher)	0.1% (max)
8	Molecular weight (v.p.o.)	2450 ± 300
9	Polydispersity	2 ± 0.5
10	Intrinsic viscosity (toluene 30°C)	0.11 to 0.17 dl g^{-1}

EXPERIMENTAL

Materials

Free-radical HTPB was prepared at Vikram Sarabhai Space Centre, India, by free-radical polymerization of butadiene using hydrogen peroxide as initiator and isopropyl alcohol as solvent. (Important characteristics of the resin are given in *Table 1*). Other materials were obtained from the following suppliers: anionic HTPB, Phillips Petroleum Co., USA; 3,5-dinitrobenzoic acid, Spectrochem, India; *N*-methylimidazole, Fluka, Switzerland; thionyl chloride, E. Merck, India; tetrahydrofuran (h.p.l.c. grade), Spectrochem, India. Finally, toluene diisocyanate (2,4:2,6 = 80:20) was employed.

Instruments

Preparative g.p.c. The apparatus was a Waters Deltaprep 3000 equipped with R401 d.r.i. detector, R481 u.v. absorbance detector, ISCO Foxy fraction collector and Waters M730 data module. Styragel columns (122 cm × 20 mm i.d.) of pore sizes 10^3 and 10^4 Å were used with THF as solvent at a flow rate of 10 ml min^{-1}. One gram of the sample was separated into 24 fractions.

Analytical g.p.c. The apparatus was a Waters ALC/GPC 244 equipped with R401 d.r.i. detector, R440 u.v. absorbance detector and M730 data module. Four μ-styragel columns of pore sizes 100, 500, 10^3 and 10^4 Å (30 cm × 0.78 cm i.d.) were used with THF at a flow rate of 2 ml min^{-1}. Universal calibration method was employed to obtain the molecular weight of the eluting species. The number-average molecular weight M_n was determined using a Knauer analogue v.p.o., intrinsic viscosity (toluene, 30°C) using a Cannon Ubbelohde viscometer with Wescan 220 timer of 0.01 s accuracy and melting point using a Mettler FP 80 melting-point apparatus. I.r. spectra were recorded on a Perkin–Elmer model 283 i.r. spectrophotometer. Mechanical properties were determined with Instron UTM model 4201 using dumb-bells conforming to Indian Standards IS 3400.

Chemical modification of HTPB

HTPB resin (20 g) was reacted with excess 3,5-dinitrobenzoyl chloride (DNBC) using *N*-methylimidazole as catalyst[7]. The DNBC was obtained by reacting 3,5-dinitrobenzoic acid with thionyl chloride[11]. The esters prepared were characterized by chemical, physical, chromatographic and spectroscopic methods. They were fractionated into 24 fractions on a preparative g.p.c. at equal time intervals (lesser number of fractions for anionic HTPB due to its narrow dispersity). The individual fractions were run on an analytical g.p.c. to obtain their quantity, molecular-weight averages, dispersity (M_w/M_n) and equivalent weight. Equivalent weights of the fractions were computed from the ratios of the peak areas of their u.v. and d.r.i. signals, which were calibrated against those of unfractionated HTPB ester of known equivalent weight (chemical method):

$$\text{area of the d.r.i. signal} \qquad A_{ri} \propto Q$$

$$\text{area of the u.v. signal} \qquad A_{uv} \propto Q \cdot EV$$

where Q is the quantity of the material present and EV is its ester value, which depends on the OH content. Thus

$$A_{uv}/A_{ri} \propto EV$$

$$A_{uv}/A_{ri} = K \cdot EV$$

K is calculated from the ratio of u.v. and r.i. signal areas of an HTPB ester of known ester value:

$$EV_1/EV_2 = (A_{uv1}/A_{ri1}) \times (A_{ri2}/A_{uv2})$$

$$EV_1 = (A_{uv1}/A_{ri1}) \times (A_{ri2}/A_{uv2}) \times EV_2$$

where subscripts 1 and 2 denote the samples of unknown and known ester values respectively. Finally:

$$\text{equivalent weight of the fraction } (E_i) = 56\,100/\text{ester value}$$

$$\text{functionality } (F_i) = M_i/E_i$$

The calibration was independently confirmed by using 3,5-DNB esters of isopropyl alcohol[4] and ethylene glycol. Independent experiments were carried out to correlate the integral d.r.i. signal with the actual quantity of the sample present in the solutions (obtained by removal of solvent) and good correlation was obtained for the whole range.

Curing of polymer resins

The HTPB samples were cured with stoichiometric quantities of toluene diisocyanate at 70°C for 48 h. The sol content was determined by swelling chopped specimens of the cured samples in toluene at room temperature for 24 h, followed by repeated extractions with toluene at room temperature.

RESULTS AND DISCUSSION

Infra-red spectra of the resins were recorded before and after the esterification reaction. Absorbance at 1740 (ester), 1540, 1350 (nitro), and 1493, 1587 and 1605 cm^{-1} (aromatic) confirmed the introduction of the 3,5-DNB ester group, while the absence of peaks at around 3400 cm^{-1} evidenced conversion of the hydroxyl groups. I.r. spectra also showed the absence of 3,5-DNBC and its hydrolysed product 3,5-DNBA from the absence of their characteristic peaks at 1765 and 1700 cm^{-1} respectively.

A comparison of the more important characteristics of the HTPB resins and their 3,5-DNB esters is given in *Table 2*. The ester values show quantitative conversion of the hydroxyl groups and the negligible acid values confirm the absence of free DNBA. From the M_n (by v.p.o.) and $[\eta]$ results it can be seen that the samples have not undergone any detectable degradation or molecular-weight build-up during the esterification process.

Table 2 Comparison of the important characteristics of HTPB resins and their 3,5-DNB esters

Sample no.[a]	OH/ester value (mg KOH/g)	Acid value (mg KOH/g)	Molecular weight (v.p.o.)	Intrinsic viscosity (dl g^{-1})
1 resin	45.1	0.3	2530	0.141
ester	40.9	0.5	2630	0.141
2 resin	45.5	0.3	2590	0.152
ester	41.8	0.8	2350	0.152
3 resin	43.3	0.3	2610	0.147
ester	40.0	0.7	2800	0.151
4 resin	44.2	0.3	2500	0.152
ester	39.9	0.6	2530	0.159
5 resin	40.2	0.2	2610	0.142
ester	38.0	0.5	2700	0.145
6 resin	43.0	0.5	2020	0.138
resin	36.1	0.9	2040	0.142
7 resin	41.9	0.1	2500	0.146
ester	35.1	0.5	2810	0.143
8 resin	44.2	0.3	2410	0.146
ester	40.8	0.5	2220	0.155
Anionic resin	32.3	0.3	2900	0.155
ester	27.9	0.3	2950	0.156

[a] Sample nos. 1 to 8: free-radical HTPB

A typical d.d.a.g.p.c. curve of resin and its derivative is shown in *Figure 1*. From the d.d.a.g.p.c. data, the functionality distribution of the nine samples was calculated as per the procedure reported by Anderson *et al.*[5]. There is a steady increase in the functionality with increase in molecular weight for all free-radical HTPBs, whereas in the case of anionic HTPB the functionality is steady at around two up to a certain molecular weight and then tapers off to zero. The same observation was made by Anderson. This cannot be expected from the anionic polymerization process, which gives predominantly a difunctional polymer with terminal hydroxyl groups. There is no reason to suspect the preferential formation of non-functional high-molecular-weight species in the process. The g.p.c. signals at the beginning and at the end of the curve are very weak and subject to large errors and therefore the discrepancy can be attributed to measurement errors in that region. In a predominantly difunctional polymer the percentage of hydroxyl decreases with increasing molecular weight. This, coupled with the low mass fraction in the high-molecular-weight region results in very low signal. This problem is solved by the use of preparative g.p.c. in which the fractions can be isolated, concentrated and characterized better.

Thus we have fractionated HTPB into 24 fractions using preparative g.p.c. The 3,5-DNB ester derivatives were used for the fractionation for the following reasons. (i) The equivalent weight of the fractions can be determined directly using the fractionated solutions, without the necessity of complete solvent removal, which leads to gelling in many cases[2]. (ii) The u.v. method is

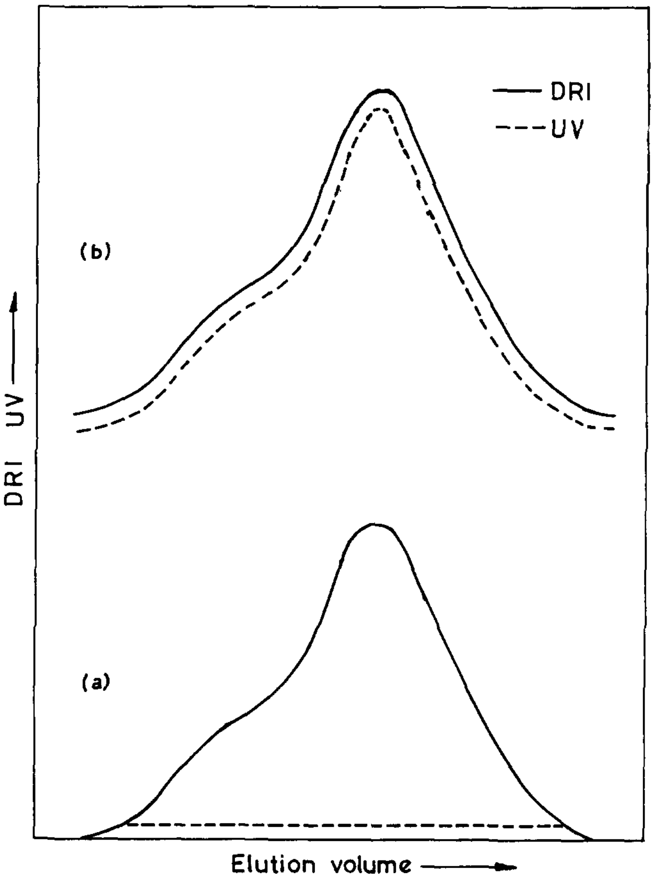

Figure 1 D.d.a.g.p.c. curves of (a) HTPB and (b) DNB ester

extremely sensitive and therefore a larger number of fractions can be studied to obtain a complete picture of the distribution pattern. (iii) Derivatives can be prepared in quantities sufficient for characterization, so that the assumption regarding the completion of derivatization[4] can be avoided.

All the fractions separated by preparative g.p.c. were analysed with d.d.a.g.p.c. to obtain the average molecular weights M_i, quantity Q_i from integral d.r.i. signal and equivalent weight E_i from the integral u.v. signal. Results obtained for a typical free-radical and the anionic HTPB are given in *Tables 3* and *4*. The very large number of fractions collected made it possible to study narrow disperse species with well-defined molecular-weight separation. The dispersity values were close to 1 for the first 10–15 fractions and slightly higher (1.5) for the lower-molecular-weight fractions. The efficiency of separation in a typical case is seen in *Figure 2*, showing the superimposed g.p.c. curves of the fractions.

The functionality F_i of the fractions was calculated from their molecular weight M_n and equivalent weight, and the results of the two samples are given in *Tables 3*

Table 3 Results of a typical free-radical HTPB

Fraction number	Molecular weight, M_n	M_w/M_n	Equivalent weight, E_i	Functionality, $F_i{}^a$	Quantity Q (%)
2	75790	1.2	2170.1	34.92	0.40
3	54910	1.4	2401.0	22.87	0.90
4	43840	1.3	2461.8	17.80	1.50
5	45060	1.2	2393.0	18.83	2.30
6	34170	1.2	2288.8	14.93	3.30
7	23060	1.3	2421.2	9.52	3.90
8	15530	1.5	2288.8	6.79	4.50
9	11610	1.7	2872.2	4.04	5.64
10	9780	1.4	2048.6	4.77	6.80
11	6610	1.4	1979.5	3.34	8.50
12	5135	1.4	1713.3	3.00	9.90
13	3110	1.8	1674.1	1.86	10.70
14	2570	1.4	1257.4	2.04	10.80
15	2630	1.5	1215.6	2.16	9.90
16	1680	1.5	1069.2	1.57	7.70
17	1320	2.0	1024.3	1.29	5.00
18	1500	2.0	1093.1	1.37	3.00
19	1320	2.0	816.1	1.62	2.30
20	1370	1.7	945.0	1.45	1.60
21	1240	1.6	846.7	1.46	0.60
22	1200	2.1	768.9	1.56	0.40
23	1220	2.0	787.5	1.54	0.20

$^a F_n = 2.16$; F_n of unfractionated HTPB from g.p.c. = 2.29

Table 4 Results of anionic HTPB

Fraction number	Molecular weight, M_n	M_w/M_n	Equivalent weight, E_i	Functionality, $F_i{}^a$	Quantity Q (%)
6	17630	1.1	5340	3.18	0.57
7	17550	1.4	4450	3.94	1.58
8	14990	1.3	4660	3.22	3.15
9	11740	1.3	3880	3.03	5.23
10	8680	1.4	3340	2.58	7.73
11	7370	1.4	2730	2.70	9.75
12	6180	1.4	2320	2.66	10.90
13	5250	1.5	2215	2.37	11.33
14	4510	1.6	1820	2.48	11.07
15	3810	1.7	1610	2.36	10.15
16	3350	1.8	1500	2.24	8.66
17	3070	1.7	1490	2.07	6.35
18	2600	1.8	1300	2.00	4.27
19	2540	2.0	1720	1.50	2.97
20	2460	2.0	1490	1.65	2.07
21	2720	1.8	1480	1.84	1.38

$^a F_n = 2.25$; F_n of unfractionated HTPB from g.p.c. = 2.22

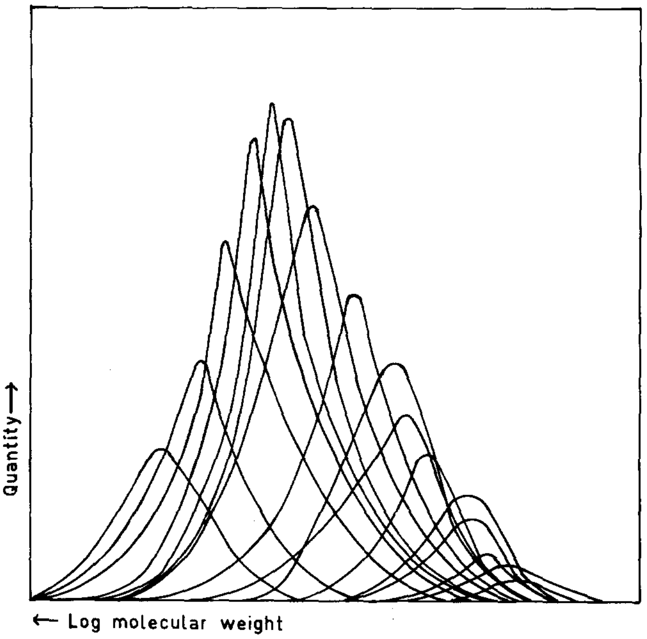

Figure 2 Superimposed g.p.c. curves of fractions

and *4*. The functionality distribution curves for the two samples are shown in *Figures 3* and *4* respectively. From the tables and figures it can be seen that for the free-radical HTPB the functionality distribution is a continuous curve, almost flat up to a certain molecular weight, beyond which the slope increases steadily with increasing molecular weight. Similar observations were made by Anderson *et al.*[5]. Another interesting observation is that for the free-radical HTPB the equivalent weight shows an initial increase and then levels off beyond a certain molecular weight. This agrees well with earlier observation[7]. As the polymer chain grows to larger size in solution containing hydroxyl free radicals, they can get attached to the growing chain at more or less regular intervals in the slow process of chain build-up. In the initial phases, where the propagation and termination are very rapid, this process will be less predominant and low-molecular-weight species will not be multifunctional. In contrast to this, the anionic HTPB gives a functionality distribution curve nearly parallel to the abscissa (*Figure 4*). For p.g.p.c. there is no anomaly of tapering off at high-molecular-weight regions, as seen in the case of d.d.a.g.p.c. *Tables 3* and *4* also give the average functionality ($F_n = \sum N_iF_i/\sum N_i$ where $N_i = Q_i/M_i$) computed from the results of individual fractions. The close agreement of the computed values with those of the unfractionated resin (obtained for all nine samples) indicates the accuracy of the method.

Since the functionality distribution curve is a continuum, it becomes necessary to make a reasonable apportionment in order to postulate a correlation with the end-product properties. In the polymer chain build-up using a difunctional curing agent such as toluene diisocyanate (TDI), moieties with functionality less than 1 do not contribute to polymer networking and therefore we have classified them as non-participating (NP) species with a functionality assignment <1. Likewise the moieties with functionality 3 and above contribute to crosslinking of the network and therefore they can be classified as crosslinker (CR) with functionality assignment >3. The species falling between these two values having functionality assignment >1 to <3 contribute to chain extension in the cure reaction and are classified as chain extender (CE). The cumulative distribution curves of cumulative quantities *vs.* functionality were drawn for all the nine samples. *Figure 5* shows the curves of a typical free-radical HTPB and anionic HTPB. From these curves the quantities of the three types of functionalities, viz. NP, CR and CE, have been derived for all the nine samples of HTPB and are summarized in *Table 5*, which

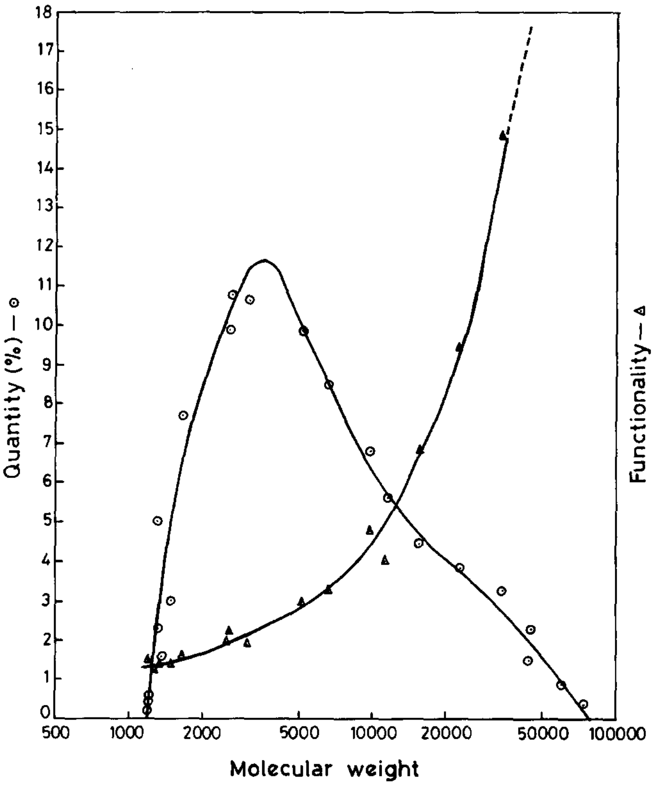

Figure 3 Functionality and molecular-weight distribution of a typical free-radical HTPB (prep. g.p.c.)

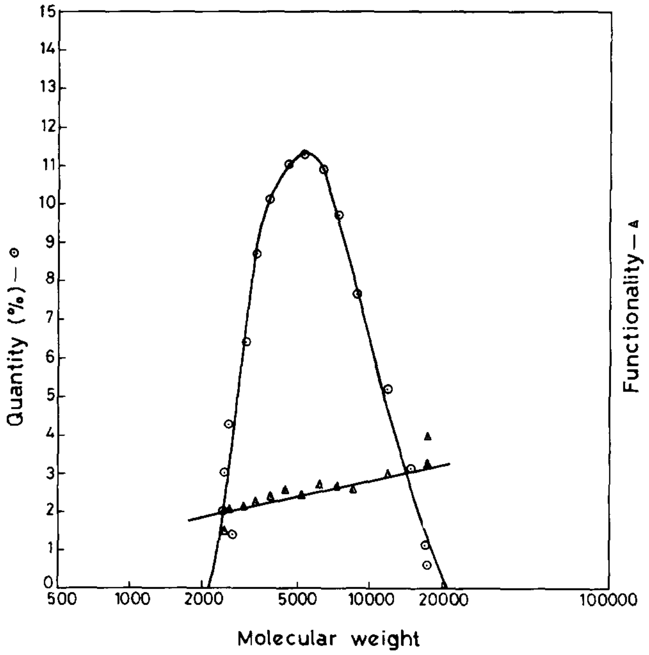

Figure 4 Functionality and molecular-weight distribution of a typical free-radical HTPB (prep. g.p.c.)

shows that (i) anionic HTPB is predominantly (95%) CE only and (ii) free-radical HTPB contains substantial quantities of CR and is, therefore, capable of being cured with TDI alone. Among the eight batches of free-radical HTPB studied, there are some variations in the relative quantities of NP/CE/CR. An assessment of the correctness of our observation is possible by attempting a correlation with the mechanical properties of polymer slabs made from these resins. *Table 6* summarizes the results of tensile strength, elongation, initial modulus and the sol content of the content of the polymer slabs, made by reacting the nine samples of HTPB with stoichiometric quantities of TDI.

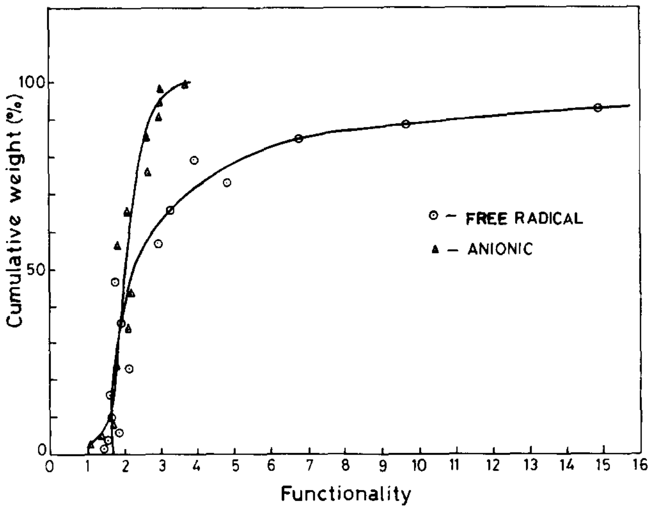

Figure 5 Cumulative distribution curves of free-radical and anionic HTPB

Table 5 Functionality distribution of HTPB samples

	Weight fraction (%) with functionality:		
Sample no.[a]	<1	>1 to <3	>3
1	0	48	52
2	0	56	44
3	0	61	39
4	0	61	39
5	0	67	33
6	0	70	30
7	0	77	23
8	10	52	38
Anionic	0	96	4

[a] Sample nos. 1 to 8: free-radical HTPB

As expected, anionic HTPB resin containing entirely chain extender has not cured with TDI and is extracted completely with toluene. All the eight batches of free-radical HTPB have cured with the difunctional curing agent TDI, giving crosslinked polymer network having tensile strength in the range of 5–8 kgf cm^{-2} and elongation 150–340%.. This corroborates our finding that all the free-radical HTPB samples have got substantial quantities of polyfunctional moieties (CR) present in them. Since there is some variation in the relative amounts of NP, CE and CR in the resin samples, we attempted to correlate their relative quantities with the mechanical properties.

All the samples except sample 8 have only CE and CR. The ratio of chain extender to crosslinker (*Table 6*) should theoretically be correlated to gum stock properties as: (i) increase in sol content and elongation with increase in CE/CR ratio, and (ii) decrease in tensile strength with increase in the CE/CR ratio. The trend of initial modulus would depend on the relative values of stress and strain; however it should also show a systematic dependence.

Resin samples 1 to 4 have given relatively low sol content of 11–12% and these samples also have relatively low ratio of CE/CR (0.9–1.6) and hence better crosslinked network. The exception is sample 8; even though its ratio is on the lower side (1.4), it has given high sol content of 20%. This is due to the presence of 10% NP in the sample; as NP does not take part in the network structure, it is totally extractable and adds to the sol content. Resin samples 5, 6 and 7, having high sol content of 20%, have relatively high ratio of CE/CR (2.0–3.3). Anionic resin with negligible CR gives 99% sol content.

The data in *Table 6* show a decrease in tensile strength and initial modulus and an increase in elongation with the increase in CE/CR ratios (except in sample 8 containing 10% NP). *Figure 6* shows the curves of mechanical properties *versus* CE/CR of these samples. This regular trend of mechanical properties with respect to the ratio of CE/CR makes the data amenable to statistical treatment. Using computer, different curve fittings were worked out with the data and it was found that the ratio (R) *versus* tensile strength (TS), elongation at break (E) and initial modulus (M) can be best fitted as second-degree curves following the equations:

$$TS = 9.321 - 1.762R + 0.1716R^2$$

$$E = 470.2 - 446.5/R + 152.8/R^2$$

$$M = -0.6340 + 10.96/R - 4.908/R^2$$

Table 6 CE/CR and mechanical properties of free-radical HTPB

		Mechanical properties			
Sample no.	CE/CR	Tensile strength (kgf cm^{-2})	Elongation (%)	Initial modulus (kgf cm^{-2})	Sol content (%)
1	0.92	7.0	155	5.4	12
2	1.22	8.2	226	5.1	12
3	1.56	7.2	210	4.7	11
4	1.56	7.6	230	4.5	11
5	2.03	6.3	307	3.3	19
6	2.33	5.3	320	2.6	22
7	3.34	5.6	340	2.6	19
8	1.37	5.0	213	3.1	20

The correlation coefficients for the curves are 0.789, 0.951 and 0.958 respectively. The r values are reasonably good, confirming the validity of our assumption regarding the correlation between the ratio of CE/CR and the mechanical properties. The reliability of the curve fitting was evaluated by the F test[12]. The Fisher constants for the three curves work out to be 3.31, 16.77 and 22.58 respectively. The critical value of F for the system at a confidence level of 95% is 6.94. Since the computed values of F are above this for the curves of elongation and modulus the confidence level of their correlations is above 95%. A probable explanation for the relatively lower confidence level of the TS correlation can be that the presence of defects like blowholes in the sample have a more pronounced effect on TS than on elongation. The effect of such defects may be less manifested in the initial portion of the stress–strain curve.

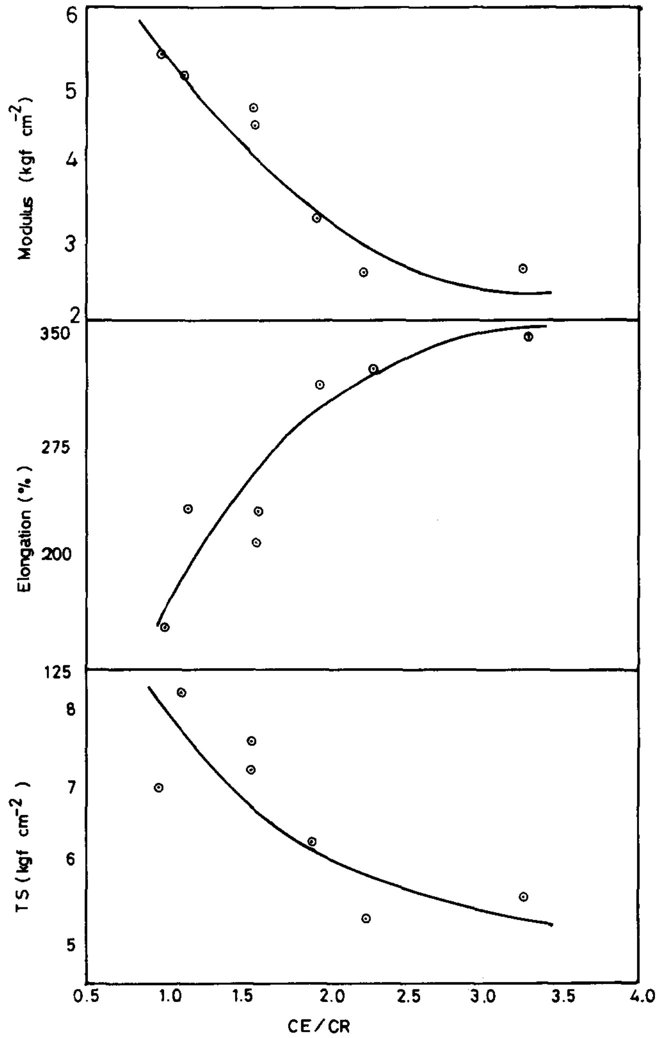

Figure 6 Mechanical properties *vs.* functionality distribution of free-radical HTPB

A search through the available literature has not shown any earlier reported quantitative correlation between the measured functionality distribution and the observed mechanical properties. In *Table 7* we have listed the free-radical HTPB resins in the order of their observed mechanical properties (except sample 8). All the usual properties of the resin as well as the newly measured functionality distribution are also given in the table. It can be observed from this table that the parameter showing the most pronounced dependence on the mechanical properties of the gum stock is the functionality distribution. The study is being continued with different types of binders in our laboratory. It is hoped that a better understanding of functionality distribution of the binders will go a long way in formulating solid propellants of desired end properties.

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REFERENCES

1 Muenker, A. H. and Hudson, B. E. *J. Macromol. Sci. Chem.* 1969, 3, 1465

2 Muenker, A. H. 'Determination of prepolymer functionality and its relationship to binder properties', AFRPL-TR-69-214, 3 Feb.–31 Aug. 1969

Table 7 Comparison of the properties of cured and uncured free-radical HTPBs

	Sample no.							
Properties	1	2	3	4	5	6	7	8
Modulus (kgf cm^{-2})	5.4	5.1	4.7	4.5	3.3	2.6	2.6	3.1
Elongation (%)	155	226	210	230	307	320	340	213
Tensile strength (kgf cm^{-2})	7.0	8.2	7.2	7.6	6.3	5.3	5.6	5.0
Sol content (%)	12	12	11	11	19	22	19	20
Hydroxyl value (mg KOH/g)	45.1	45.5	43.3	44.2	40.2	43.0	41.9	44.2
Acid value (mg KOH/g)	0.3	0.3	0.3	0.3	0.2	0.5	0.1	0.3
Volatile matter (%)	0.3	0.2	0.2	0.7	0.5	0.4	0.3	0.3
Viscosity at 30°C	5370	6880	6240	6160	5150	5200	5600	5250
Specific gravity	0.90	0.90	0.90	0.90	0.90	0.90	0.90	0.90
Molecular weight (v.p.o.)	2530	2590	2610	2500	2610	2060	2500	2410
Dispersity, M_w/M_n	2.1	2.0	1.7	2.0	2.0	1.9	1.9	2.2
Intrinsic viscosity (dl g^{-1})	0.14	0.15	0.15	0.15	0.14	0.14	0.15	0.16
CE/CR	0.92	1.22	1.56	1.56	2.03	2.33	3.34	1.37

3 Law, R. D. *J. Polym. Sci. (A-1)* 1971, **9**, 589

4 Anderson, J. N. and Baczek, S. K. *J. Appl. Polym. Sci.* 1975, **19**, 2255

5 Anderson, J. N. and Baczek, S. K. *J. Appl. Polym. Sci.* 1975, **19**, 2269

6 Regan, P. R., Teo, H. H. and Booth, C. *Br. Polym. J.* 1985, **17**, 22

7 Carver, J. C. 'Improved specifications for composite propellant binders for army weapon systems', TR-RK-81-5, June 1981

8 Min, T. I., Miyamato, T. and Inagaki, H. *Rubber Chem. Technol.* 1977, **50**, 63

9 Inagaki, H., Donkai, N., Saitoh, A. and Zenitani, Y. *J. Appl. Polym. Sci.* 1984, **29**, 3741

10 Descheres, I., Paisse, O., Ceccaldi, J. N. C. and Pham, Q. T. *Makromol. Chem.* 1987, **188**, 583

11 Vogel, A. I. 'Text Book of Practical Organic Chemistry', 3rd Edn., ELBS and Longman, London, 1970, p. 262

12 Mack, C. 'Essentials of Statistics', Plenum Press, New York, 1967, p. 157