Studies on Functionality Distribution of Extractable Sol from HTPB–Isocyanate Gumstock

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SYNOPSIS

Hydroxyl-terminated polybutadiene (HTPB), even when cured with stoichiometric quantities of toluene diisocyanate (TDI), gives some extractable sol from the gumstock and the sol is believed to be predominantly due to the nonfunctional molecules in the HTPB. However, the present work shows that the molecules in the sol contain hydroxyl functional groups whose nature was established by hydrolyzing the urethane present in the sol and by analyzing the functionality distribution of the molecules so generated from the sol. The sol contains chain-extending difunctional and crosslinking tri- and polyfunctional molecules; however, the concentration of the former is more, when compared to the original HTPB. All three types of primary hydroxyl groups of HTPB (G, H, and V) are also present in the sol. While there is a reduction in the G-type hydroxyl in the sol, there is no major difference in the *cis, trans,* and vinyl contents of the backbone of the sol and HTPB. The molecules in the sol have been excluded from the crosslinked network, not only because of the lack of their functionality alone, but also as a result of network imperfections which are an integral part of nonlinear polymerization reactions. © 1995 John Wiley & Sons, Inc.

INTRODUCTION

Polybutadiene prepolymers containing hydroxyl functional groups (hydroxyl terminated polybutadiene, HTPB) are important fuel binders in composite solid propellants. The name HTPB implies that it contains two hydroxyl groups at the ends. However, due to the random reactions occurring during its synthesis by free-radical polymerization, instead of the functionality of two, a mixture of non-, mono-, di-, tri-, and polyfunctional molecules are obtained. The ingredients of the propellant formulations are mixed with HTPB, which is then cured with an isocyanate like toluene diisocyanate (TDI). The mechanical properties of the resultant three-dimensional network depend on the relative amount of the different functional moieties present in the prepolymer.

There have been various attempts to characterize HTPB for its functionality distribution (FD).[1-8] The gumstock properties of HTPB cured with TDI have been correlated to its functionality distribution.[8,9] The sol–gel study of the cured product is an important aspect of the gumstock characterization. The sol content of the gumstock has been postulated to consist mostly of nonfunctional species only, and based on this assumption, attempts have been made to derive functionality distribution and crosslinking characteristics of HTPB.[10] In the present article, we attempted to study the nature of functional groups present, if any, in the sol of cured HTPB. The extracted sol containing urethane groups was hydrolyzed and the functionality distribution of HTPB so recovered was studied using a dual detector analytical GPC (DDAGPC).

EXPERIMENTAL

Materials

The hydroxyl-terminated polybutadiene (HTPB) used was made at NOCIL, Bombay (using the technology developed by VSSC, Trivandrum) by free-radical polymerization of butadiene gas with a H_2O_2 initiator. Toluene diisocyanate (TDI) (2,4 : 2,6 = 80 : 20) was commercial. 3,5-Dinitrobenzoyl chloride (3,5 DNBC) was prepared by refluxing 3,5-dinitro-

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benzoic acid (Spectrochem, India) with excess thionyl chloride (E. Merk, India). After the completion of the reaction, excess thionyl chloride was distilled out. The 3,5-DNBC obtained was recrystallized using carbon tetrachloride (mp 69–71°C). Tetrahydrofuran (THF) was HPLC grade (Spectrochem). All other solvents used were of analytical grade and were dried before use.

Method

The number-average molecular weight and molecular weight distribution (MWD) of the samples were determined using a Waters gel permeation chromatograph (ALC/GPC 244 with R 401 DRI detector, R 440 UV absorbance detector, and M 730 data module). The solvent used was THF at a flow rate of 2 mL/min. Four microstyragel columns of pore sizes 10^4, 10^3, 500, and 100 Å were employed. Universal calibration was done[11] using polystyrene standards of narrow molecular weights.

Hardness measurements were done on a Shore A durometer. FTIR spectra were recorded with Nicolet 510 P FTIR spectrophotometer. ^{1}H-NMR spectra were obtained with a JEOL GSX400 instrument at 400 MHz. The spectra were recorded with a 10% solution in $CDCl_3$ (standard: TMS, no. scans 2000, time of acquisition 2.05 s) at ambient.

Preparation of Gumstock

HTPB was thoroughly mixed with TDI in the ratio 1 : 1 (NCO/OH), poured into a mold, and cured for 24 h at room temperature in a desiccator followed by 24 h at 70°C in an oven.

Gel–Sol Experiments

The sol fraction was obtained by repeated extraction of weighed pieces of the cured sample with toluene. Distillation of the extract under vacuum removed toluene. The sol obtained was weighed and characterized. FTIR data revealed the presence of urethane linkage in the sol, showing the possibility of the presence of OH groups in the HTPB forming the sol. To identify the nature of the sol, it was hydrolyzed to break the urethane linkage.

Hydrolysis of the Sol

A known weight of the sol was hydrolyzed with excess 30% methanolic KOH at 175°C in a 2 L pressure reactor for 10 h. The contents were cooled, transferred from the reactor using diethyl ether, and washed several times with 0.1*N* HCl until the ether layer was free of the toluene diamine and K_2CO_3, which are byproducts in the hydrolysis reaction. The solution was then made acid-free by washing with water. The hydrolyzed sol was obtained by evaporating the ether.

Functionality Distribution

The functionality distribution of HTPB and its hydrolyzed sol was determined using a dual detector (UV and DRI) analytical gel permeation chromatograph (DDAGPC) by a method described earlier.[4] The procedure involves derivatization of the hydroxyl groups of HTPB to 3,5-dinitrobenzoyl ester to make them UV-absorbing, followed by analysis on DDAGPC. Since HTPB has no UV-absorbing groups (at 254 nm), the area under the UV absorption curve of the derivatized sample will be proportional to the OH content of HTPB. The functionality at any retention time (related to molecular weight) is obtained by ratioing the calibrated responses of the UV and RI detectors since the former is proportional to the OH content, and the latter, to the quantity.

RESULTS AND DISCUSSION

The characteristics of the HTPB resin used in the study are given in Table I.

Its gumstock, prepared with a 1 : 1 stoichiometric ratio of TDI, was extracted with toluene to obtain 16% sol, whose characteristics are also given in Table I. Figure 1(a) and (b) shows the MWD curves of HTPB and its sol recorded by a dual detector

Table I Characteristics of HTPB and Sol

	HTPB	Der. HTPB	Sol	Hydrolyzed Sol	Der. Hydrolyzed Sol
OH value (mgKOH/g)	41.3	0	0	36.0	0
Acid value (mgKOH/g)	0.4	0.6	0.4	0.7	0.2
M_n (GPC)	2550	2330	7620	2350	2390
Ester value (mgKOH/g)	0	36.1	—	0	33.0

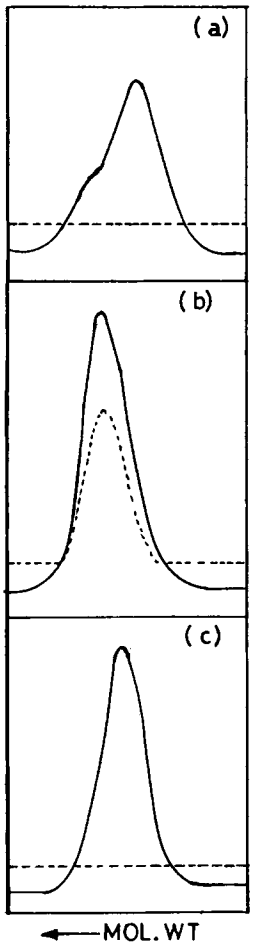


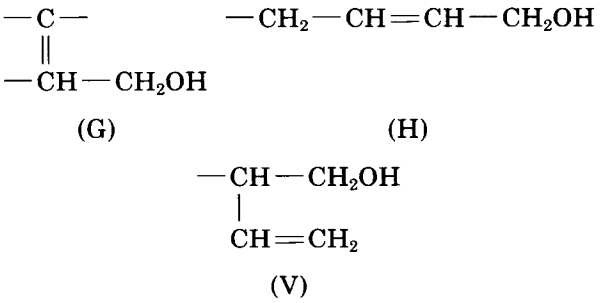
Figure 1 GPC of (a) HTPB, (b) sol, and (c) hydrolyzed sol: (- - -) UV response; (——) DRI response.

analytical GPC. The UV peak in the case of the sol indicates the presence of UV-absorbing aromatic groups of TDI which would have reacted with the HTPB in the sol. The threefold increase in the molecular weight of the sol, which on hydrolysis gives back a product of nearly the same molecular weight as does the parent HTPB, shows that the sol consists of interconnected HTPB molecules.

More details were obtained from the FTIR spectra. Figures 2 and 3 show IR spectra of HTPB resin and its sol fraction. In the case of the sol, the additional carbonyl peaks at 1740 cm^{-1}, N—H str. vibration at 3100–3300 cm^{-1}, and C—N str. vibration at 1530 cm^{-1} reveal the presence of urethane linkage. Absence of the —NCO peak at 2270 cm^{-1} indicates that there is no free isocyanate group. The presence of urethane linkage and the absence of free —NCO in the sol suggests that the molecules in the sol do contain OH groups. The urethane linkage can arise from the termination OH—NCO reaction with monofunctional polymer or the formation of cyclized products with di- and polyfunctional molecules during network formation. It has been mentioned elsewhere[12] that, in a nonlinear polymerization, synthesis of a perfect network is virtually inaccessible experimentally even if we take a stoichiometric ratio of the reactants. The imperfections are due mainly to the inelastic loops formed in postgel intramolecular reactions.[13] Literature available concerning the formation of elastically inactive cycles in a polyurethane network using triol and diol model compounds[12,13] suggests that the sol is composed mainly of cyclic products. Some workers experimentally proved[12] the presence of cyclic molecules by comparing the sol fraction and equilibrium modulus of the networks.

The sol on hydrolysis gives back the HTPB, nonfunctional or functional; the former will be present as such and the latter as urethane in the sol. During hydrolysis with 30% methanolic KOH, urethane linkages present in the sol undergo scission and become converted to the corresponding amine (toluene diamine), alcohol (HTPB), and potassium carbonate. Figure 4 shows the FTIR spectra of the hydrolyzed product before washing, wherein the peaks at 1620, 1590, and 1550 cm^{-1} show the formation of aromatic amine. Absence of the peaks corresponding to the urethane group suggests the completion of hydrolysis. Removal of toluene diamine and alkali from the resin was achieved by washing with dilute HCl and water. The hydroxyl value of the hydrolyzed sol (Table I) shows that the HTPB that had gone into the sol has nearly the same functional group concentration as that of the parent HTPB.

The nature of the hydroxyl groups in the hydrolyzed sol was established from its NMR spectra. Three types of primary hydroxyl groups have been identified[14] in free-radical HTPB: (i) geraniol type (G), (ii) 2-hexene-1-ol type (H), and vinyl type (V), appearing in the NMR spectra at 4.1, 4.0, and 3.5 ppm, respectively. The structure of these carbon-bonded protons of primary alcohols are given below:



It was suggested earlier[15] that the G type corresponds to tri- and polyfunctional molecules which

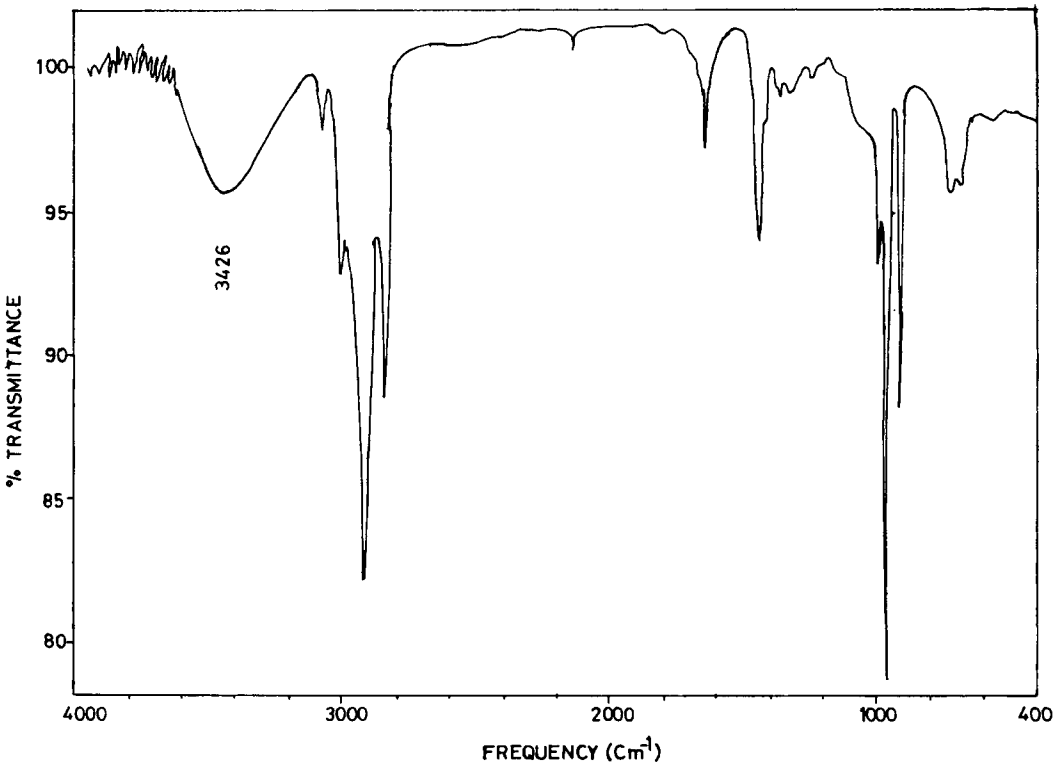


Figure 2 IR spectrum of HTPB.

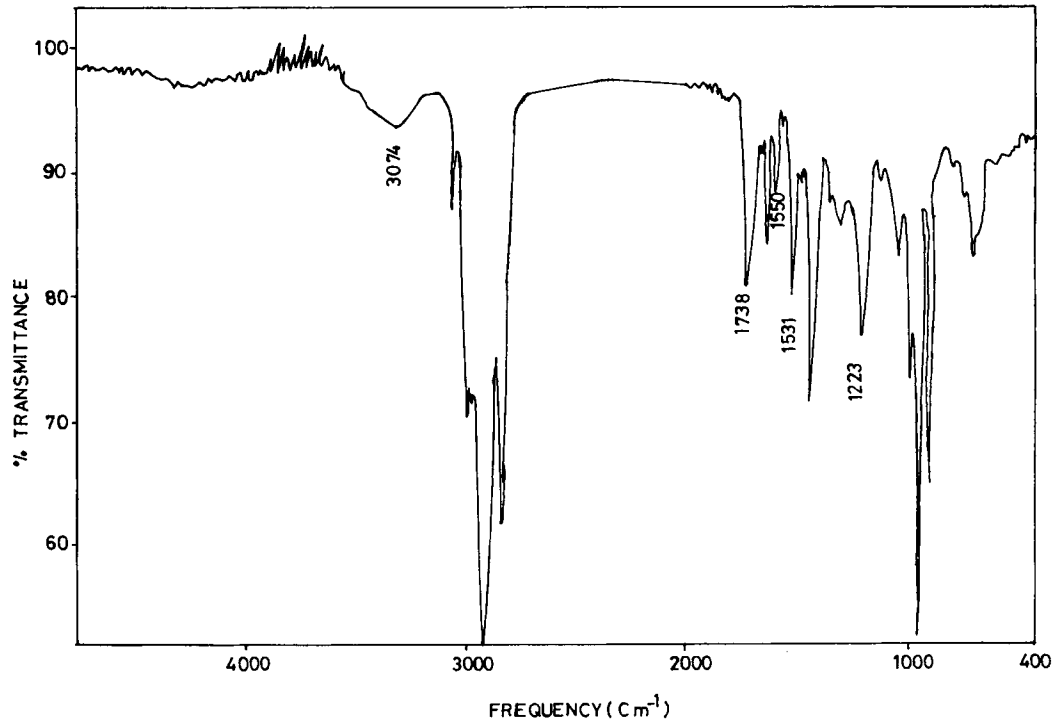


Figure 3 IR spectrum of sol.

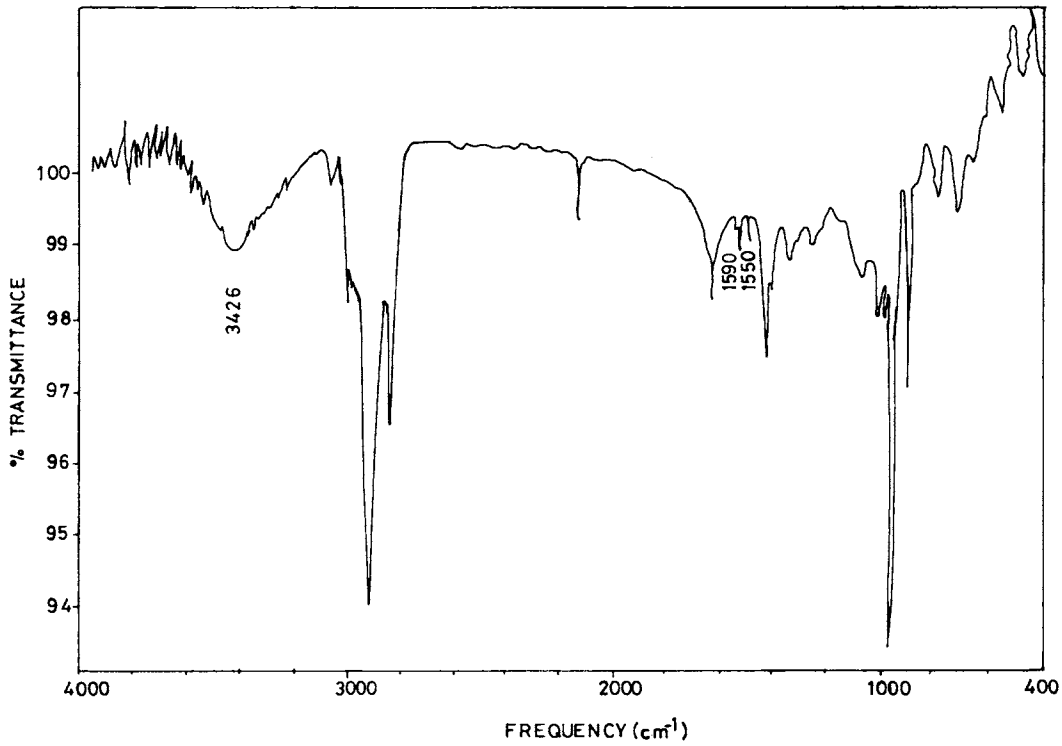


Figure 4 IR spectrum of hydrolyzed sol.

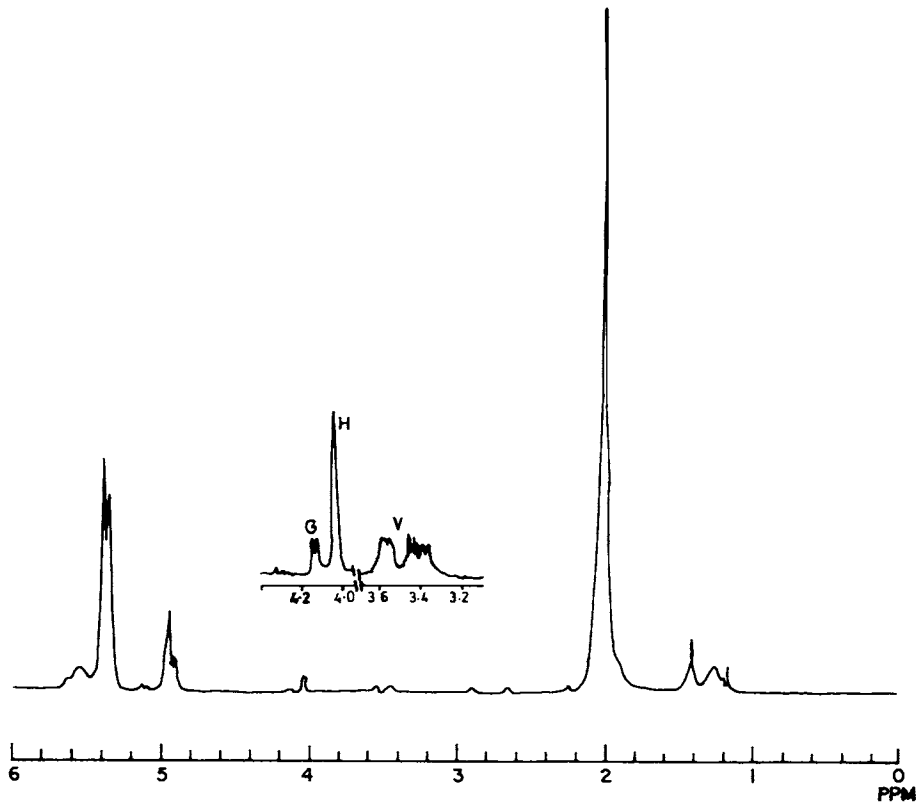


Figure 5 ^{1}H-NMR spectrum of free-radical HTPB.

Table II Quantity (%) of Different Hydroxyl Groups and Backbone Microstructure of HTPB and Hydrolyzed Sol

	Original Resin (HTPB)	Hydrolyzed Sol
Peak and type of OH group		
3.5 ppm (vinyl type)	40	46
4.0 ppm (hexenol type)	45	47
4.1 ppm (geraniol type)	15	7
Microstructure		
cis-	25	27
trans-	52	51
Vinyl-	23	22

contribute to crosslinking in the reaction with TDI and the H and V types act as chain extenders. Both HTPB and the hydrolyzed sol give similar ^{1}H-NMR spectra showing the presence of all the three hydroxyl groups in the hydrolyzed product. A typical spectrum is shown in Figure 5. This confirms the presence of multifunctional molecules in the sol. However, the quantity of the different OH groups present in the resin and the hydrolyzed sol as estimated from the ^{1}H-NMR data is different. Table II gives their concentrations, which shows that there is less G type in the sol.

More of the G type, which is responsible for crosslinking, has gone into the gel; however, its presence in the sol, although to a smaller extent, shows that the sol consist of molecules of even tri- or polyfunctionality. The microstructure (*cis, trans,* and vinyl contents) of HTPB and the hydrolyzed sol were determined from FTIR data[16] and the results are also given in Table II. The microstructure of the two samples does not differ much.

A detailed analysis of the MWD of the HTPB, its sol, and the hydrolyzed sol was done by dividing the MWD curves into four regions (A, B, C, and D). The results of the relative percentage of the regions (region content) are given in Table III.

It can be seen from the table that the percentage of high molecular weight species is more in the case of sol. This is due to the interconnection of HTPB molecules through urethanes linkages in the sol, as discussed earlier. However, the quantity of the high molecular weight species in the hydrolyzed product is less when compared to that in the HTPB before its reaction with TDI. This is also clear from the MWD curves [Fig. 1(a) and (c)], wherein the shoulder present for the high molecular weight species is absent in the case of the hydrolyzed product. The concentration of the low molecular weight species is higher in the hydrolyzed sol. In an earlier study, it was established that the functionality of free-radical HTPB increases with increase in molecular weight above a certain range and higher molecular weight species are virtually polyfunctional.[8] The inclusion of polyfunctional molecules in the gel has therefore resulted in a decrease in higher molecular weight fraction in the sol. This is also seen in the reduction in G-type OH in the hydrolyzed sol.

The functionality distribution of the HTPB prepolymer and the hydrolyzed sol containing the molecules which are expelled from the network was studied by a method developed by Anderson and Baczek.[4] The two samples were first derivatized using 3,5-dinitrobenzoyl chloride. Completion of esterification was confirmed by determining the ester value. The characteristics of the esters prepared are given in Table I. Figure 6 represents the functionality distribution of HTPB and its hydrolyzed sol. In the polymer chain buildup, using a difunctional curing agent such as toluene diisocyanate (TDI), molecules with functionality less than 1 do not contribute to the polymer networking and have therefore been classified[8] as nonparticipating (NP) species. Likewise, molecules with functionality 3 and above contribute to crosslinking of the network and therefore they have been classified as crosslinkers (CR). The species falling between these two, having functionality > 1 to < 3, contribute to chain exten-

Table III Region Content Results

	Mol Wt Range			
	A (%) $> 25{,}000$	B (%) 25,000–5000	C (%) 5000–1500	D (%) < 1500
HTPB	12	40	39	9
Sol	22	53	20	5
Hydrolyzed sol	1	23	51	25

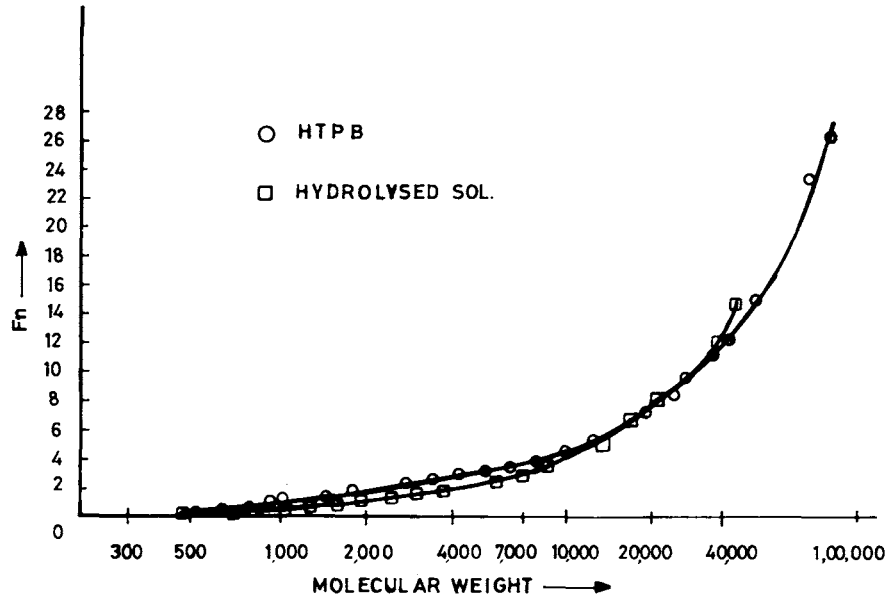


Figure 6 Functionality distribution of HTPB and hydrolyzed sol.

sion in the cure reaction and are classified as chain extenders (CE).

The percentage of NP, CE, and CR present in the samples was determined from the cumulative functionality distribution curves (Fig. 7). The results are given in Table IV.

The CE/CR ratio is 0.83 in HTPB, while it is 4.4 in the hydrolyzed sol. The percentage of polyfunctional (high molecular weight) molecules is less in the sol fraction, as they become easily included in the network forming the gel. Similarly, the concentration of the molecules with functionality below 1 which do not contribute to the network is higher in the sol. Nevertheless, the sol is not nonfunctional, as thought earlier.[10] More than 80% of the sol consists of functional molecules, di-, tri-, and poly-, which could not form a part of the gel due to network imperfections.

The presence of multifunctional molecules in the sol was further confirmed by reacting the hydrolyzed sol with TDI. A rubbery crosslinked product with relatively high sol content (30%) was obtained. The hardness of the product was lower (20 Shore-A against 30 Shore-A for HTPB gumstock). The lower hardness and the higher sol content of the gumstock prepared from the hydrolyzed sol can be attributed to its higher CE/CR ratio and higher NP content.

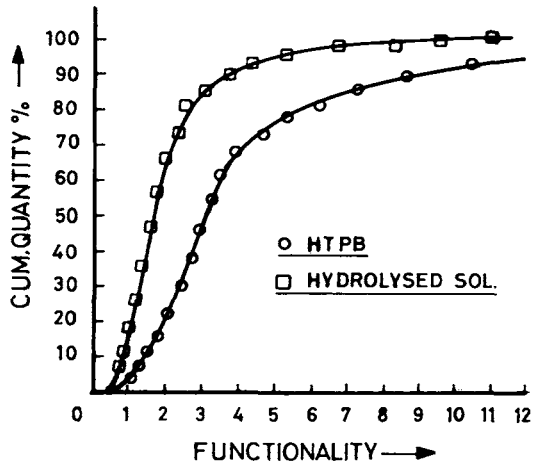


Figure 7 Cumulative functionality distribution of HTPB and hydrolyzed sol.

CONCLUSION

1. In the crosslinking reaction of HTPB with TDI, more than 80% of the sol extracted comprises molecules with functionality 2 and above. These molecules are expelled from the network, not due to the lack of their functionality but as a result of network imperfections in the system.

Table IV Functionality Distribution Results

	Weight Fraction (%) with Functionality		
Sample	< 1	> 1 to < 3	> 3
HTPB	3	44	53
Hydrolyzed sol	19	66	15

2. The functionality distribution of HTPB and its sol is found to be somewhat similar. However, the concentration of low molecular weight species with functionality below 1 is more in the sol. The chain extender-to-cross-linker ratio is higher in the sol, since the poly functional high molecular weight species are preferentially included in the network. This is also seen from the NMR data, which shows a reduction in G-type hydroxyls in the sol. The backbone microstructure is same for hydrolyzed sol and HTPB.

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