

Development and Evaluation of a Novel Binder Based on Natural Rubber and High-Energy Polyurethane/Composite Propellants

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Synopsis

Hydroxyl terminated natural rubber (HTNR) was prepared by the depolymerization of masticated natural rubber in the presence of H_2O_2 in toluene. Probable mechanisms leading to the formation of side reaction products are proposed based on the analytical data. A comparative study of some formulation variables was made for their effect in improving the flow characteristics and mechanical properties of an aluminized polyurethane (PU) propellant system based on HTNR. This PU system has also been compared for its theoretical performance characteristics with some other state-of-the-art systems.

Telechelic polymers of saturated and unsaturated, aliphatic hydrocarbon backbone are the current candidate binders for advanced, composite solid propellant technology. Choice of these systems has been the result of intense studies on polymer structure-energy correlations as regards network theory and thermochemistry. The elastically effective, high fuel-value binders based on polybutadiene are the most exploited class of this type. They are amenable for a variety of modifications involving compatibility with special additives like RDX and HMX, advanced oxidizers, etc. Our studies have shown that a closely related system could be obtained from natural rubber. Introduction of OH functional groups during the depolymerization of masticated rubber could yield a hydrocarbon binder which is superior to polybutadiene binders in flow properties and which, in addition, is stereospecific in that it essentially carries an all-*cis* structure. The absence of pendant vinyl groups and the presence of a 1,4-*cis* configuration are capable of conceding a lower viscosity at comparable solid loading¹ and an elastically more effective network. Energetically too, it is a more favorable system both due to a higher fuel value and an all-*cis* configuration. Although the preparation of low molecular weight polymers with *cis*-1,4 structure is well reported in the literature, functionalization of such oligomers has not been studied in detail. Khodzhemirov, Sorokina, and Kosolova² had prepared polymers with increased content of *cis*-1,4 diene units by the degradation of high molecular weight polymers based on conjugated dienes in inert organic solvents, in vacuum, in the presence of catalysts containing Tungsten compounds.² Use of solar energy to depolymerize pale crepe in the presence of acetyl acetonates of Fe and Co and nitrobenzene had been reported by Tilakaretne and Scott.³ Thermal and catalytic depolymerization of natural rubber affected by phenyl hydrazone- $FeCl_2 \cdot O$ had been reported by Mori and Fuji⁴ and by Kempermann.^{5,6} The remarkable efficiency of

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redox couples, comprised of H_2O_2 and p-toluene sulfonic acid in the depolymerization process had been studied by Pautrat and Marteau.⁷ Rabek had observed the sensitizing effect of thiobenzophenone in the photodegradation process of natural rubber and neoprene in benzene solutions.⁸

The works of Reed^{9,10} and Palit¹¹ are the closer ones to the present study in the development of such telechelics. However, Reed's approach differs in starting from the monomers and using free-radical initiated polymerization conditions. According to him, the polymerization temperature significantly affects the molecular weight distribution, the effect being more pronounced in the case of chloroprene than in the case of isoprene or butadiene, on account of its faster polymerization rate. Palit et al.¹¹ have studied some aspects of incorporating COOH terminals in natural rubber after mastication.

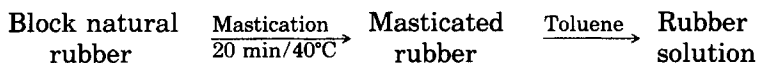
Two more findings of importance to the present study are the following:

(i) The effect of ionic compounds like $TiCl_3$, acids like HCl and HI, and organometallics in the cyclization of natural rubber, in dilute solutions, at relatively low temperature, accompanied by a significant fall in the degree of unsaturation. Cyclization is believed to proceed through the formation of a carbonium ion, as shown in Figure 1.

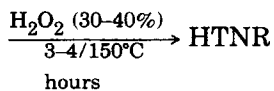
According to Lee and co-workers^{12,13} the cyclorubber contains macrocyclic structures like 1 and to some extent, bicyclics, 2 and polycyclics, 3, all of which are insoluble powders with high softening temperatures (in the vicinity of 370°C). Natural rubber is sensitive to the introduction of air in the presence of $TiCl_3$ too, leading to such changes. Similar effects in the presence of dilute H_2SO_4 have shown that the *cis*-1,4 structures are relatively more resistant to cyclization than the corresponding *trans*-1,4 and *cis*-3,4 structures.¹⁴⁻¹⁷ It is of interest to note here that *cis*-*trans* conversions could also be affected by γ rays in the presence of a sensitizer like butyl mercaptan.¹⁸ Detailed IR and NMR spectral studies of such microstructural changes have been carried out by Agnihotri,¹⁹ and Golub and co-workers,^{20,21} which indicate the presence of mono, bi, tri, and polycyclic structures in these products.

(ii) According to Angier,²² Buche,²³ and Brislow,²⁴ mastication is a non-random degradation process in that scission does not occur at random along the chains, but only in those molecules possessing greater than a critical chain length.

In the light of the above data, a modified method of depolymerization of masticated natural rubber has been developed in the presence of H_2O_2 to obtain HTNR. The overall reaction could be depicted as follows:



Mooney vics: 85 ml at 100°C Mooney visc: 25-35 ml at 100°C



200-300 psi

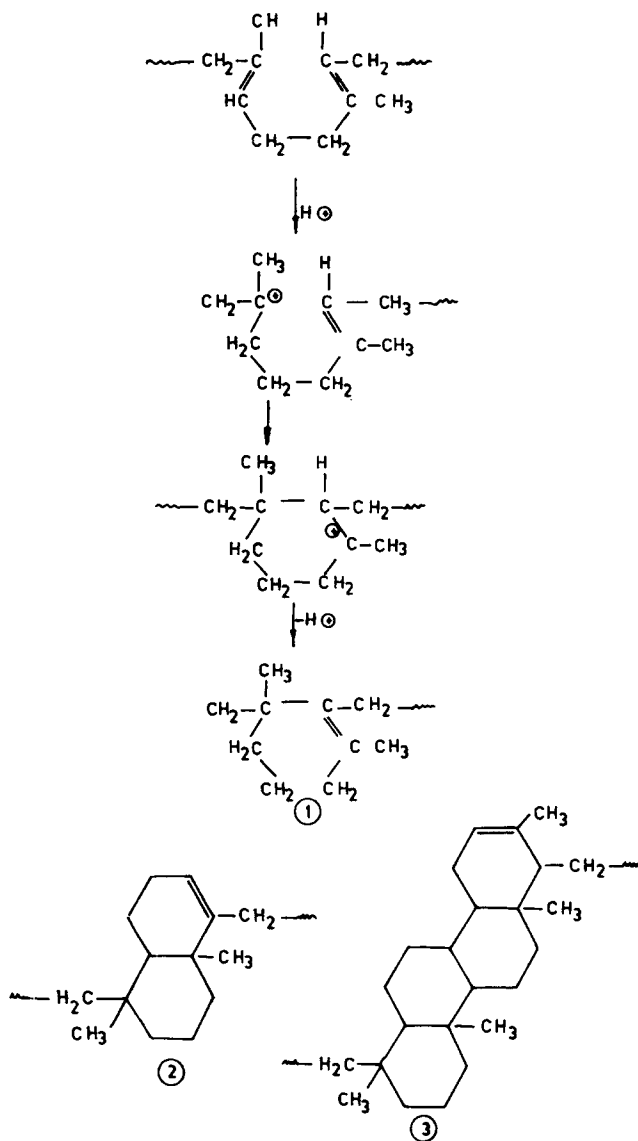


Fig. 1. Formation of cyclorubber.

EXPERIMENTAL

Materials. Block natural rubber IS-NR5, supplied by the Rubber Board of India, was used after mastication. Fifty percent H_2O_2 was obtained from M/s National Peroxide, Bombay and was used as received, after dilution with demineralized water. Toluene and Methanol were CP grade materials, distilled before use. All the propellant binder ingredients were LR grade materials, dried before use.

Apparatus. A Perkin-Elmer Model-283 IR spectrometer was used to record the IR spectra of the HTNR films. Proton NMR of HTNR was recorded from its solution in CCl_4 using a JEOL-JNM 100 spectrometer in the CW

mode. ^{13}C NMR spectrum (proton decoupled) of HTNR was recorded under ambient conditions, from its solution in CDCl_3 , using a JEOL-FX 90Q-FT NMR spectrometer operating at 22.49 MHz. TMS was used as the internal standard and the general experimental conditions were: pulse width, 12 s; data points, 8 K; spectral width, 5000 Hz; and number of pulses, 400. A KNAUER model VPO was used to determine the \bar{M}_n . Mechanical properties of the polyurethane propellants based on HTNR were evaluated using an Instron Universal testing machine, Model 1111. Viscosity of the propellant slurries was checked by a Brookfield viscometer, Model HVT-71179 using the "TD" spindle. A Paar reactor of 7.5 L capacity was used to prepare the HTNR.

Synthesis of HTNR*

Masticated rubber was dissolved in toluene and the solution was charged into the pressure reactor. H_2O_2 was added to this solution with stirring. The reactor was closed airtight and was heated to 150°C with a thorough and constant stirring at 500 rpm. Heating and stirring were maintained for 3 h, when the inside pressure remained in the range of 200–300 psi. After cooling down to ambient temperature, hydroquinone was added to the solution and dispersed. Toluene was removed under reduced pressure and the residual polymer was precipitated with excess methanol. The polymer was dried under vacuum as a honey colored, viscous liquid.

RESULTS AND DISCUSSION

The HTNR prepared as above had its viscosity in the range of 250–400 poises, acid no. less than 2 mg KOH/g, OH no. in the range of 25–33 mg KOH/g and N content, less than 0.2%. \bar{M}_n of the polymer (2500–3000) indicated a No. average functionality of 1.4. It was further characterized by IR and NMR spectra to confirm the functional features shown below:

IR (Neat) (cm^{-1})

3600–3400 (broad, O—H Str), 3040 (m, C—H str.), 2980 (s, C—H asym. str., $-\text{CH}_3$), 2920 (s, C—H asym. str., $-\text{CH}_2-$), 2860 (s, C—H sym. str., $-\text{CH}_3$), 1660 (m, >C=C< , *cis* vinylene), 1450 (s, C—H asym. def., $-\text{CH}_3$), 1375 (s, C—H sym. def., $-\text{CH}_3$), 1310 (m, O—H def., in plane, primary & secondary), 1125 (w, C—O str., saturated aliph. tert. alcohol), 1080 (m, C—O str. aliph. secondary alcohol), 1035 (m, C—O str., aliph. prim. alcohol), 885 (m, $-\text{CH}_3$ deformn), 830 (s, C—H out of plane, def. in $-\text{CHR}=\text{CCR}^1$)

P M R (CCl_4 , 25°C) (δ ppm)†

1.60 (S, $-\text{CH}_2-\text{C}=\text{C}$ 4H), 2.0 (S, CH_3- , 3H) 5.1 (M_{H} , >C=C< 1H)

The spectrum (Fig. 2) also contained minor peaks at 2.5 and 1.20 ppm indicating the probable presence of $\text{CH}_3-\text{C}-\text{CH}_2$ -type of groups, benzylic protons, and stabilizer ingredients.



* Owing to the "classified" nature of the work, exact weights could not be given.

† Resonance absorption due to $-\text{OH}$ protons is masked by the multiplet at 5.1 ppm.

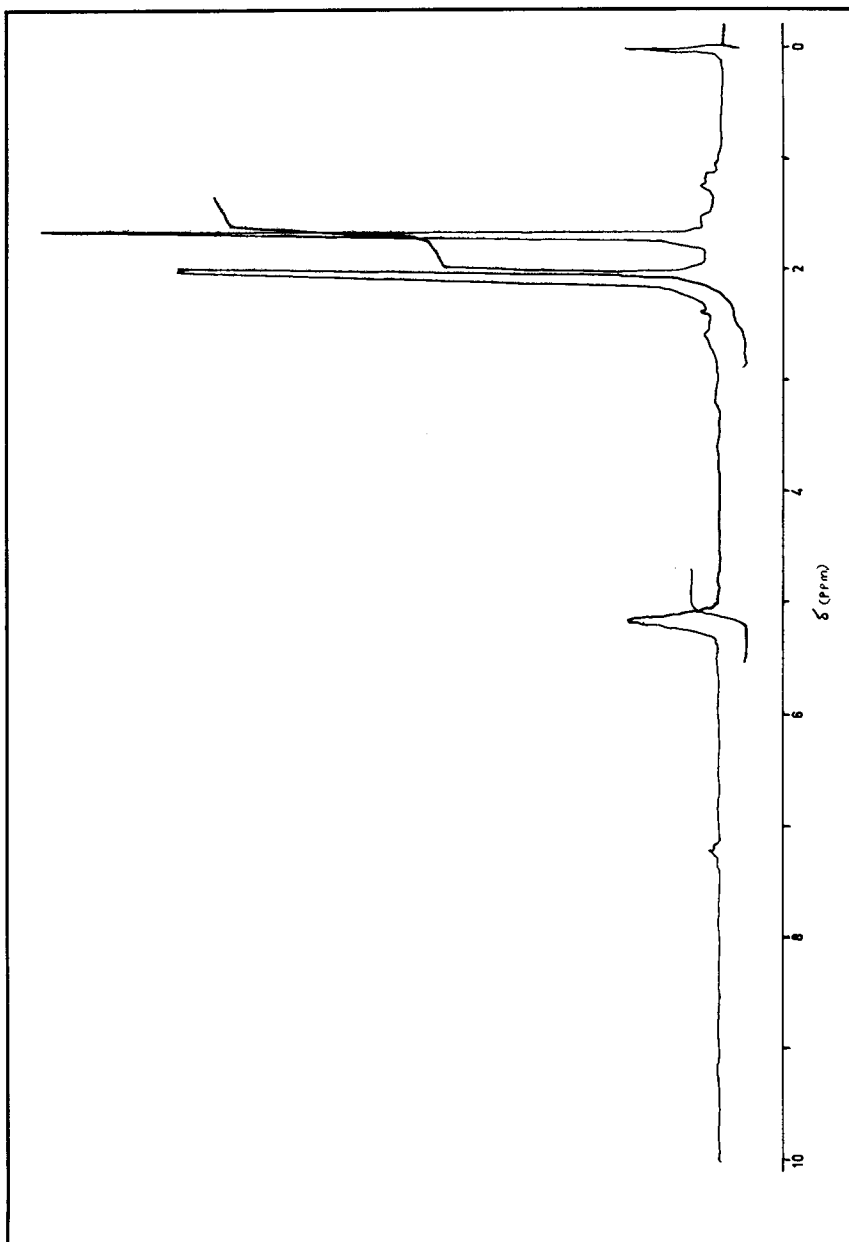
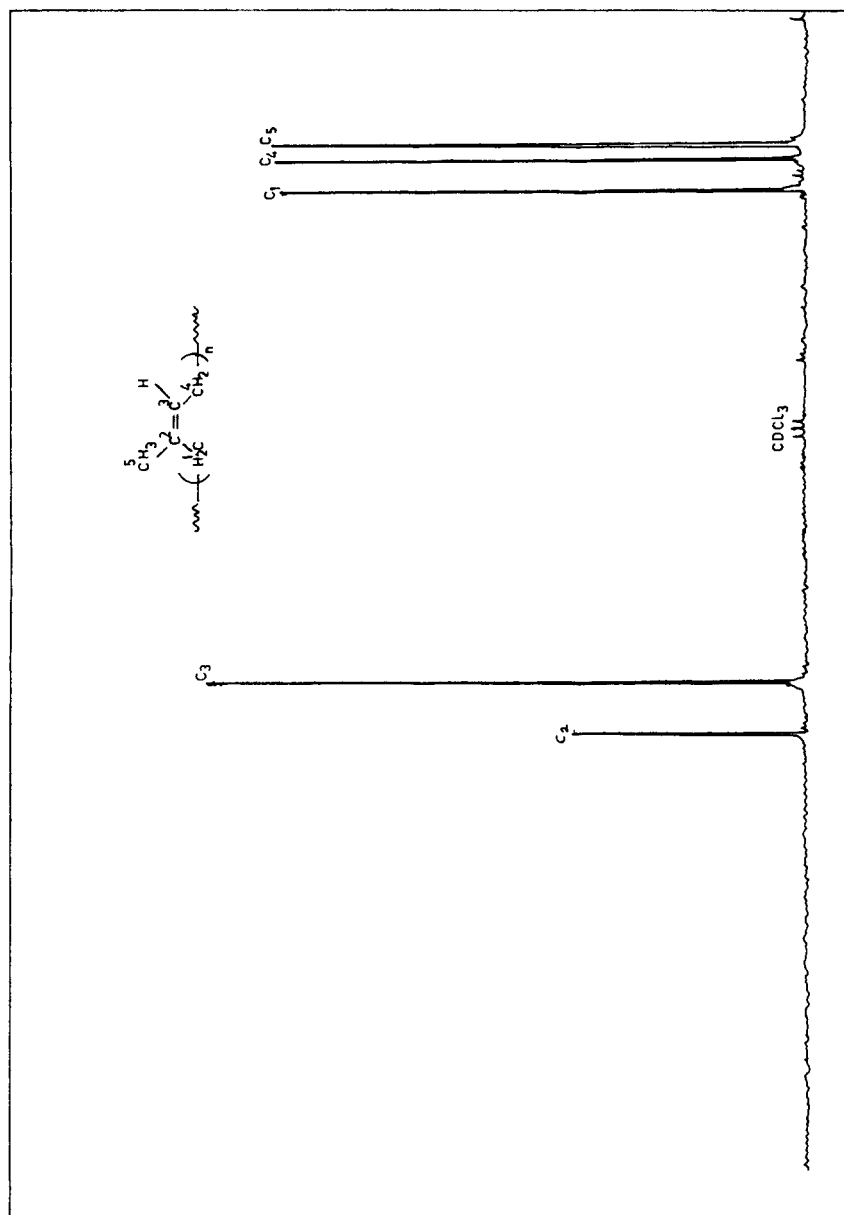
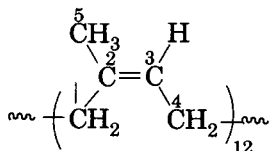


Fig. 2. PMR Spectrum/CC14/25°C of HTNR.

Fig. 3. ^{13}C NMR- $\{^1\text{H}\}$ FT/CDC13/25°C of HTNR.

^{13}C NMR {H}/ $\text{CDCl}_3/25^\circ\text{C}$

The FT NMR spectrum (shown in Fig. 3) indicated ^{13}C shieldings, typical of *cis*-1,4 polyisoprene at the following ppm positions: (δ , ppm, with respect to the TMS position):



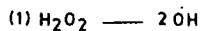
C_1 , 32.2; C_2 , 135.5; C_3 , 125.3; C_4 , 26.4; and C_5 , 23.4. These positions are in good agreement with those reported by Duch and Grant.²⁵ Apart from these major peaks, the spectrum also contained minor peaks due to CDCl_3 (77 ppm).

The analytical data indicate the capability of the present method in functionalizing masticated natural rubber during depolymerization. Comparison of the molecular weight (\bar{M}_n) data with the hydroxyl no. of the polymer shows, however, that the efficiency of functionalization is low. Thus the average —OH functionality of the HTNR was 1.4. This could have been brought about by side reactions, shown in Figures 5 and 6 along with the desired mode of attack, shown in Figure 4. Of these, the reactions shown in Figures 4 and 6 do not affect the double bonds. Reactions shown in Figure 5 lead to the loss of one OH and formation of a —CHO group. However, the PMR spectrum did not show any resonance peak in the 9.9 ppm region, characteristic of the aldehydes. Reactions shown in Figure 6 which lead to the formation of a vicinal glycol are based upon the relatively longer life of the benzyl radical and could be favored under the reaction conditions in the presence of excess peroxide + toluene. However, the glycol contains a tertiary and a secondary OH group which differ considerably in their reactivity to form urethane groups and, not being telechelic, they cannot contribute in forming elastically effective polyurethane (PU) networks.

The presence of minor NMR signals at 1.5 and 2.3 ppm in the PMR spectrum support the formation of such products (less than 10% of the total). Simplicity of the ^{13}C NMR spectrum confirms (in terms of the C_1 and C_5 shieldings) that the depolymerization and functionalization processes do not affect the stereoregularity. It also complements the PMR spectral data in concluding that the proposed side reaction products (except cyclized rubber, which is insoluble in the medium) are formed only in negligible quantities.

Propellant Studies with HTNR

Although depolymerized natural rubber had been studied in solid propellant formulations earlier,²⁶⁻²⁸ the use of HTNR in such applications is not well reported. A preliminary study in this regard has been made by



(2) :

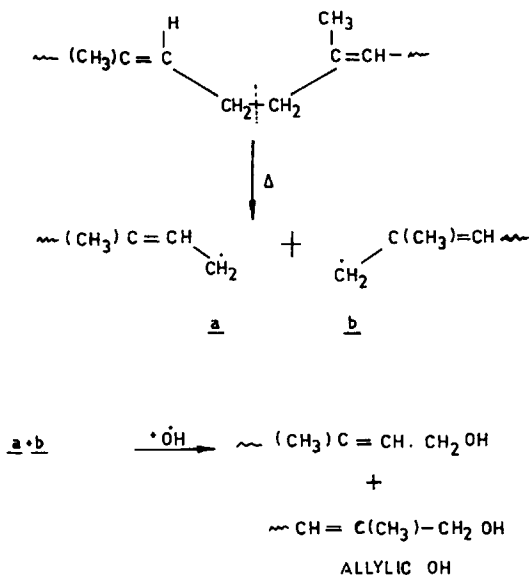


Fig. 4. Desired reaction.

Gupta, Kurup, and Baby.²⁹ In the present study, polyurethane propellants were made based on the binder system, consisting, essentially of HTNR, toluene diisocyanate and trimethylol propane. Binder additives included plasticizers like dioctyladipate, trioctylphosphate, rubber oil, etc. and processing aids like voltalef-35 oil, Pedobond (a stoichiometric condensate of 12-hydroxy-stearic acid and diethanolamine), MT-4 [a condensate of *tris*-(methyl aziridinyl)phosphene oxide (MAPO) and tartaric acid], etc. The following formulation variables were studied for their relative effect in improving the mechanical properties, the propellant mixings being done at 4 kg batch levels, at 50°C and curing of the propellants (in plastic cartons), at 60°C for five days, unless stated otherwise.

Effect of Oxidizer

Two types of experiments were carried out, *viz.*:

(i) Changing the coarse/fine blend ratio (BR) of the NH_4ClO_4 oxidizer at a constant loading level of 70% in an 18% aluminized composition (average particle size: coarse, 310 μm ; fine 50 μm).

(ii) Changing the percentage level of the oxidizer with a constant coarse/fine blend ratio (BR) (3.0) in a propellant formulation with 18% Al. The binder was formulated with excess —OH, i.e., with an *R* value (NCO/OH molar) of less than 1.0. Results of these experiments shown in Tables Ia

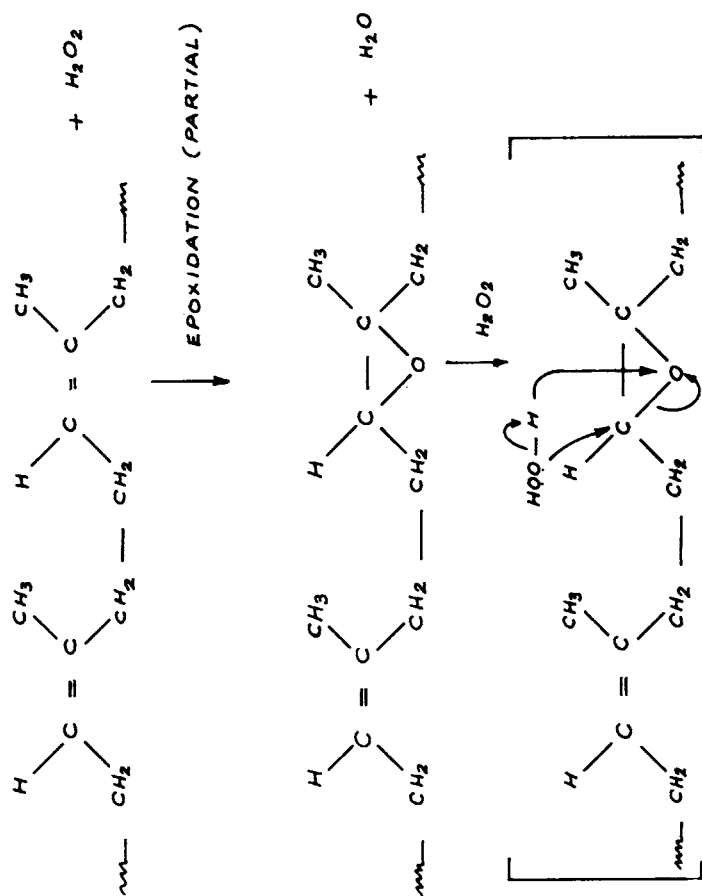


Fig. 6. Side reaction, involving solvent participation and double bonds.

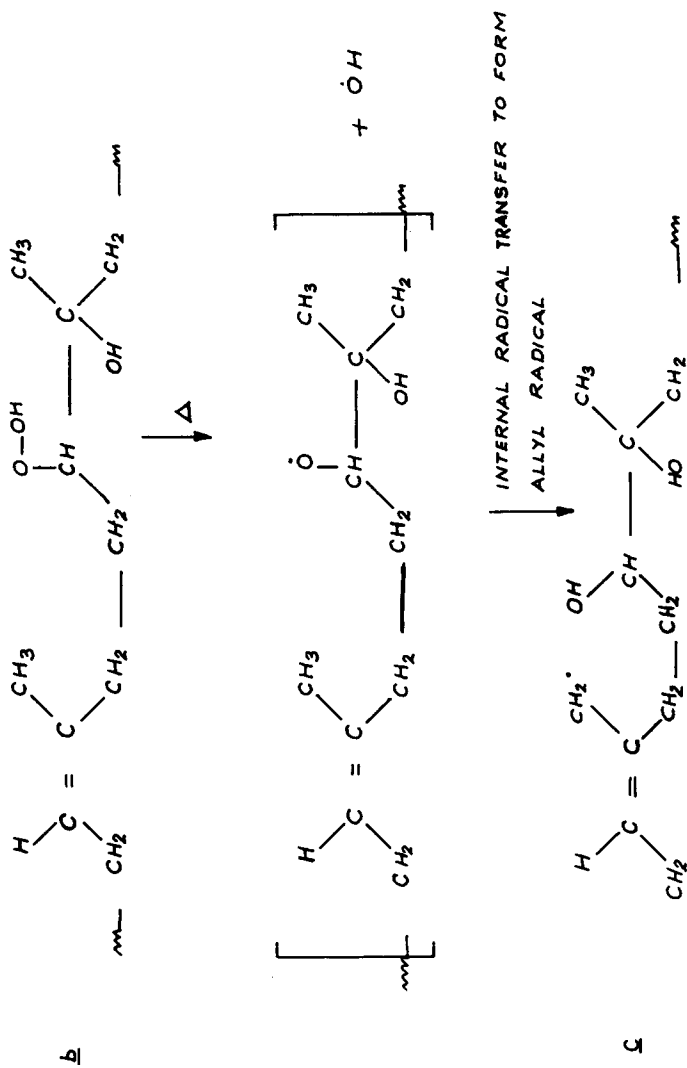


Fig. 6. (Continued from the previous page.)

TABLE Ia
Effect of the Coarse/Fine Ratio (BR) of NH₄ClO₄^a

BR	Unloading viscosity at 55°C(ps)	T.S. (psi)	Elongation at break (%)	Modulus (psi)	Hardness (shore A)
4	14,700	71	22	395	74
3	19,200	85.1	20	497	74
2	Difficult to cast				

^a Al = 18%, solids = 88%, $R = 0.7$.

TABLE Ib
Effect of the Loading Level of NH₄ClO₄^a

Loading level (%)	Unloading viscosity at 55°C (ps)	T.S. (psi)	Elongation at break (%)	Modulus (psi)	Hardness (shore A)
80	4800	81	43	350	61
82	6700	90	35	532	66
84	9600	100	32	574	68
86	14,700	118	23	920	75
88	20,800	214	15	2030	88

^a BR = 3, Al = 18%, $R = 0.9$.

tion of both binder reactive and surface-active substances. Thus a system of such processing aids, selected from TMP (trimethylol propane), MT-4, Pedobond, Voltalef-3s oil, butyl ferrocene, and carbon black were studied for their overall efficiency in improving the slurry viscosity and mechanical properties of the cured propellant in an 86% loaded composition with 18% Al (BR = 3.0 and $R = 0.70$). All these compositions contained DOA as the plasticizer at 3.4% by weight of the propellant. The results shown in Table III, indicate that MT-4 and Pedobond perform well under these conditions.

Effect of R in the Binder System

The HTNR-PU system was capable of curing at room temperature. This is a major advantage of this propellant system, with considerable energy saving potentials. Effect of the variable R was studied, in both NCO-rich and OH-rich recipes. The NCO-rich formulations were difficult to cast. These propellants had an 86% solids loading with Al = 18%, BR = 3.0, and rubber oil at 3.8% by weight (as the plasticizer) and were cured for 10 days at 30°C. The results are shown in Table IV.

Development of a High Tensile Strength Propellant Based on HTNR-PU

The need for developing free-standing solid propellant grains with good grain integrity and thermal cycling characteristics could be met successfully with the HTNR-PU system. Development of such systems with tensile strength in the range of 260 psi was essentially based on a study involving

TABLE II
Effect of Plasticizers at a Constant Concentration Level^a

Plasticizer	Unloading viscosity at 55°C (ps)	T.S. (psi)	Elongation at break (%)	Modulus (psi)	Hardness (shore A)
DOA	8960	78	25	596	78
Rubber oil	17,250	113	20	1050	82
TOF	5800	72	13	880	75
DOA/Rubber oil (9:5)	12,000	99	22	752	74

^a Solids = 86%, BR = 3, $R = 0.7$, plasticizer at 3.4% by wt of the propellant.

changes in the polyol components at $R = 1.0$. Removal of Pedobond and decreasing the HTNR/TMP ratio showed improvements in this regard, as summarized in Table V.

Variation of the Mechanical Properties with Temperature

Case bonded propellant systems are generally required to retain a good percentage of the "ambient-temperature" mechanical properties at extremes of global temperatures. It is known that in the case of natural rubber, stiffness gradually increases as temperature is lowered below -20°C and that at -40°C it is twice as stiff as at $+20^{\circ}\text{C}$.³⁰ At -60°C , the elastomer becomes glassy and brittle. The relative changes in the mechanical properties of the HTNR-PU propellant, when exposed to temperatures in the range of -60°C to $+60^{\circ}\text{C}$ were studied with cured specimens, soaked at these temperatures, immediately before testing. The trends are shown in Table VI.

Comparison of the Mechanical and Ballistic Properties of HTNR-PU with Those of Some Other Candidate Propellants

Polyurethanes are the state-of-the-art propellant binders and basic changes in the physical, environmental, and ballistic properties in these

TABLE III
Effect of Additives/Processing Aids^a

Additive	Unloading viscosity at 55°C (ps)	T.S. (psi)	Elongation at break (%)	Modulus (psi)	Hardness (shore A)
Base formulation	15,700	75	15	539	72
TMP	8,960	85	19	497	78
MT 4	10,800	106	20	851	78
Pedobond	11,200	109	22	851	72
Pedobond + TMP (0.1)	17,200	114	20	1050	78
Pedobond + TMP (0.1) + Voltalef 3S (0.1)	12,700	116.4	19	1050	76

^a Additive = 0.5%, solids = 86%, Al = 18%, DOA = 3.4%, BR = 3.0, $R = 0.7\%$.

TABLE IV
Effect of *R* (NCO/OH) of the Binder (OH Contribution from HTNR, TMP, and Pedobond)^a

<i>R</i>	T.S. (psi)	Elongation at break (%)	Modulus (psi)
0.55	44	32	284
0.65	58	31	355
0.70	71	30	440
1.00	146	23	1150

^a These propellants were cured at 30°C for 10 days. Solids = 86%, Al = 18%, rubber oil = 3.8%, BR = 3.0.

TABLE V
Effect of Varying the HTNR/TMP Ratio of the Binder in the Absence of Pedobond^a

HTNR/ TMP (%)	Unloading viscosity at 55°C (PS)	T.S. (psi)	Elongation at break (%)	Modulus (psi)
95:5	8960	85	19	496
90:10	7850	168	15	1080
80:20	6400	248	12	3457
75:25	5000	262	10	3690

^a Solids = 84%, Al = 18%, DOA = 3.4%, BR = 3.0.

are brought about in terms of the nature of the polymeric polyol and isocyanate. Table VII compares the HTNR-PU system with two other types of PU, *viz.* SSM-2, based on HTPB and IPDI (Isoporone di-isocyanate) and IP-PEDESTER, based on ISRO polyol and TDI. A PBAN propellant (RCN-01) is also included for relative comparison.

CONCLUSION

The above studies indicate that the HTNR resin prepared as per this study, is stereo-regular and is capable of yielding a high-energy composite solid propellant of the PU type, similar to HTPB-PU system in its mechanical and ballistic properties. It exhibits a good environmental resistance

TABLE VI
Variation of the Mechanical Properties with Temperature

Temp. (°C)	T.S. (psi)	Elongation (%)		Modulus (psi)
		At max. load	At break	
-60	647	2	—	—
-50	498	13	16	12,983
-40	416	33	34	6527
-20	224	40	43	1390
0	162	34	36	865
+10	133	31	32	738
+30	118	23	28	710
+40	105	25	26	667
+60	82	25	25	525

TABLE VII
A Comparison of the Mechanical and Ballistic Properties of HTNR Based Propellant with some other Propellants used in Space Vehicles

Polymer	HTNR based propellant	SSM 2 propellant ^a	Polyol ^b propellant	RCN OI propellant
	HTNR	HTPB	IP PEDE ester	PBAN
Solids (%)	86	86	83	84
Aluminium (%)	18	—	18	12
Curator	TDI	IPDI ^c	TDI	Epoxy/Aziridine
Cure temp.	R.T. (25°C)	65°C	60°C	75°C
Cure time (day)	10	6	5	8
Mechanical properties				
Tensile strength, (min) (psi)	99.3	113.5	56.8	56.8
Elongation (%)	25-30	20-30	25-30	25-30
Hardness, shore A (min)	60	60	60	60
Density (gm/cc)	1.76	1.70	1.74	1.73
Modulus (psi)	425-565	—	425-500	425-565
Ballistic properties				
Burning rate at 1000 psi, (mm/s)	6.1	11	6	6
Specific impulse (theoretical), s	262	254	250	258

^a Developed by Jet Propulsion Laboratory, Pasadena, CA.

^b Castor oil based, developed at VSSC.

^c IDPI = isophorone di-isocyanate.

to temperature changes. It is amenable to modifications in the binder composition and is compatible with a variety of binder additives. In addition, this binder system is unique as regards the following aspects:

(i) Room temperature curing characteristics with resultant energy savings in the curing of larger propellant grains is feasible.

(ii) An all-*cis* configuration, capable of yielding a low viscosity to the propellant.

(iii) A higher calorific value compared with HTPB and hence, better ballistic performance.

(iv) Ease of availability of the starting material, viz. natural rubber and ease of depolymerization.

(v) Absence of pendant vinyl groups as occurring in the case of HTPB and hence, formation of a more uniform polymer network.

There is, however, further scope for improving the functionality of the polymer and narrowing its molecular weight distribution. The humid aging characteristics of the propellant also needs to be investigated further. Deproteination of the masticated rubber before depolymerization could also bring about improvements in the mechanical properties. Further work is under way on these lines.

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