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Natural Rubber-Based Fuel Rich Propellant for Ramjet Rocket

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ABSTRACT

Development of fuel rich propellants for air-breathing propulsion is one of the frontier areas of research. This carries less oxidiser than the normal propellants, uses ram air for complete combustion and is heavily metallised.

Studies were conducted at VSSC for the development of hydroxyl-terminated natural rubber (HTNR)-based *Mg* and *Mg-Al* alloy-filled polyurethane systems. The HTNR prepolymer was modified to make it free of acid functionality so as to avoid reaction with the metals and was then reacted with calculated amount of propylene oxide in the presence of tertiary amine catalyst at room temperature. Various levels of *Mg* and *Mg-Al* alloy were used in different compositions and the effect on propellant characteristics was studied. TMP and butane diol were used for higher crosslinking, chain extension, etc and their effects were evaluated. Propellant compositions using 30-35 per cent by weight of *Mg/Mg-Al* alloy with the modified prepolymer have been developed. They exhibit good processibility and mechanical properties. The feasibility of room temperature curing was attempted. Motors weighing 2 kg with 100 mm OD and 200 mm length were successfully static-tested in the primary mode for performance evaluation.

1. INTRODUCTION

Goddard[1] in 1932 proposed air-breathing propulsion for the atmospheric ascent portion of an earth-to-orbit trajectory. The reasoning was simple. Air-breathing engines can provide about 8-20 times higher effective specific impulse values than the solid or liquid engines at altitudes below 30 km. The idea of a single-stage-to-orbit vehicle has long been considered, which is evident from the number of research papers appearing on studies of air-breathing propulsion in combination with some form of rocket propulsion. Present day multistage launch vehicles consume nearly 80 per cent of their propellant mass before they reach an altitude of about 58 km and a velocity of 2.3 km/s. Large savings on this propellant mass can be effected by using a more efficient air-breathing propulsion system for the lower atmospheric part of the flight. The concept of single-stage-to-orbit mixed mode propulsion for the Space Shuttle was proposed by Salkeld[2] by operating two separate engines in a series. He also introduced the dual-fuel engine concept for reusable one-stage-to-orbit shuttles[3,4]. Martin[5] suggested parallel burn of hydrogen and hydrocarbon engines for a dual-fuel single-stage transport. The theoretical performance of the ramjet propulsion system is found to be much better than either the solid- or the liquid-fueled rocket motors acting alone[7,8].

In Europe in the sixties, work was focused on the development of a solid fuel rocket ramjet (SFRR) engine for developing a multilateral anti-surface ship missile (ASSM). This resulted in the making of Kormoran II, which was later renamed Hydra, with MBB as the principal contractor[10]. The reason for the selection of the SFRR engine over the conventional

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ramjet engine using kerosene as fuel was that when air was passed through it, the afterburner lit automatically and once lit, it could not be extinguished. Thus, it was able to overcome one of the drawbacks of conventional ramjet engine, viz potential flame out at unfavourable aircraft attitudes and the ensuing difficulty of relighting it. Another advantage is that the diameter of the ramjet combustion chamber in the SFRR engine can be made as small as desired and yet be able to maintain a good level of combustion efficiency even while using boron powder as the metallic fuel up to 50 per cent (Thiokol and Hercules pioneered boron propellant development in the US even earlier), the remaining part consisting of polybutadiene and AP in equal proportions. A study carried out in 1977 for a ramjet variant of the Roland surface-to-air missile is reported to have produced a theoretical range increase of 2.7 times the existing value, while maintaining the same engine volumes. Combinations of high performance air-breathing/rocket engines for manned reusable vehicles would find application in Europe in the beginning of the next century[11].

2. RESULTS AND DISCUSSION

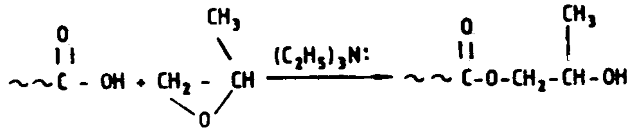
2.1 Work at Vikram Sarabhai Space Centre (VSSC)

Work on fuel rich propellant started in early 1986 using organic fuels, such as HTPB, HTNR, PCPD, naphthalene, etc. High energy propellants based on HTPB and HTNR with *Al* and AP had already been developed[12-14] and were readily available for propellant trials using *Mg-Al* alloy and *Cr*-passivated *Mg* as metallic fuels to start with. HTNR had the advantage over HTPB in its higher *H/C* ratio (1.6 and 1.5, respectively) and lower decomposition temperature (initial 250 and 350 °C and peak 390 and 485 °C, respectively).

Both the propellants are being manufactured at VSSC. HTNR is obtained by the depolymerisation of masticated natural rubber in presence of H_2O. The process can be depicted as given below.

During the process of mastication, which is spread out normally for days together, a side reaction creeps in. As is well known, natural rubber is quite sensitive to oxidation in the absence of oxidative inhibitors at low to moderate temperatures[14-18]. Thus, atmospheric oxidation of the masticated rubber is possible and the HTNR produced from this stock is found to have an acid value of about 5 mg *KOH*/g which is prohibitive in polyurethane propellant work. The reason is that the resultant propellant is most likely to be porous due to CO_2 produced by the reaction of *NCO* with *COOH* groups.

To solve this problem a method has been devised to destroy the acid moieties from the prepolymer chains. This method consists of reacting calculated quantity of propylene oxide (E. Merck, Germany) with the acid groups in the presence of triethylamine (SDs) as catalyst at room temperature. The reaction (Fig. 1) is monitored by IR and is over in 3 hr in the laboratory.



$$\sim\sim \overset{O}{\overset{\|}{C}}-OH + CH_2-\overset{CH_3}{CH}\ (\text{-}O\text{-}) \xrightarrow{(C_2H_5)_3N:} \sim\sim \overset{O}{\overset{\|}{C}}-O-CH_2-\overset{CH_3}{CH}-OH$$

Figure 1.

The amine as well as propylene oxide remaining, if any, are driven out during drying of the resin prepolymer at about 100 °C under reduced pressure. By this process it was possible to bring down the acid value of HTNR below 1 mg *KOH*/g from the original value of 5.2 in a 15 kg batch. After 40 numbers of the laboratory scale batches at 250 g capacity, the process was scaled up to 2.5 kg batches without any problem. The process is intended to be incorporated in the manufacturing batches at the Propellant Fuel Complex, VSSC.

BLOCK NATURAI RUBBER (Mooney viscocity 85 ml at 100 °C) $\xrightarrow[\text{20 mm/40 °C}]{\text{MASTICATION}}$ MASTICATED RUBBER – (Mooney viscocity 25-35 ml at 100 °C) TOLUENE

RUBBER SOLUTION $\xrightarrow[\text{3-4 hr/150 °C, 200 psi}]{H_2O_2\text{ (30-40 \%)}}$ HTNR

For the kinetic investigation, IR spectroscopy was used to determine the residual epoxy content; acid concentration was determined by chemical analysis.

The reaction between epoxide and carboxyl groups is usually employed in the preparation of highly crosslinked elastomers and different network-structured polyepoxides[19]. The functional groups present in these reactants can enter into some competing side reactions, such as etherification, condensation, esterification and hydrolysis[20,21]. Generally onium salts, tertiary amines and phosphines are effective catalysts for the acid epoxy reaction which proceeds only at the moderately elevated temperatures[22]. Homopolymerisation is likely to occur in the uncatalysed reaction. Tertiary amines, when used in these types of reactions are found not only to enhance the rate of reaction, but also to suppress largely or completely the undesirable side reactions[20].

2.2 Mechanism

Generally this reaction depends on several factors, such as reactants ratio, type and amount of catalyst and temperature[19]. The high boiling propylene oxide is added 10 per cent in excess of stoichiometry with 0.025 per cent catalyst, and maximum reaction is found to occur in 3 hr at room temperature itself.

The mechanism of the reaction between epoxide and carboxyl groups is complicated and has not yet been fully elucidated[19]. There are different conceptions of the initiation step in the literature[21,23]. Absence of induction period as revealed from acid conversion plots (Fig. 2) and zero order conversion nature of acid conversion (Fig. 3 least square fit regression plot) suggests that the initiation step involves acid amine adduct, where acid acts as the proton donor. The reaction mechanism given in Fig. 4 is found to be consistent with the above facts.

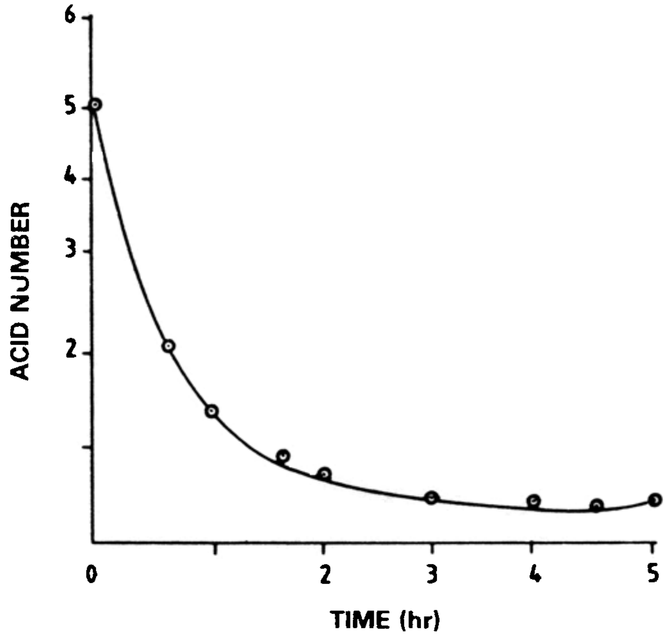


Figure 2. Acid conversion in HTNR-propylene oxide reaction.

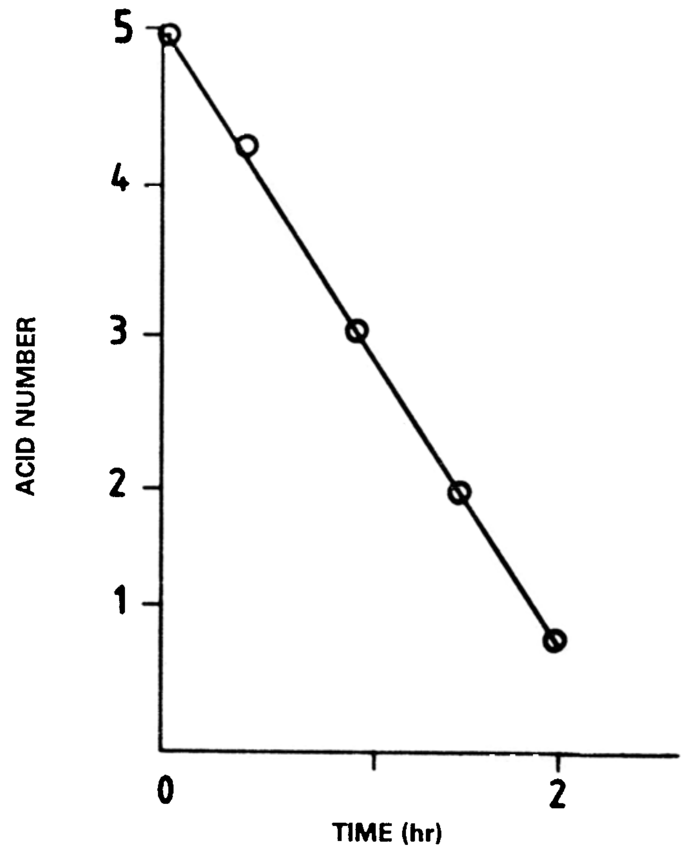


Figure 3. Zeroth order kinetic plot of modified HTNR from acid conversion plot.

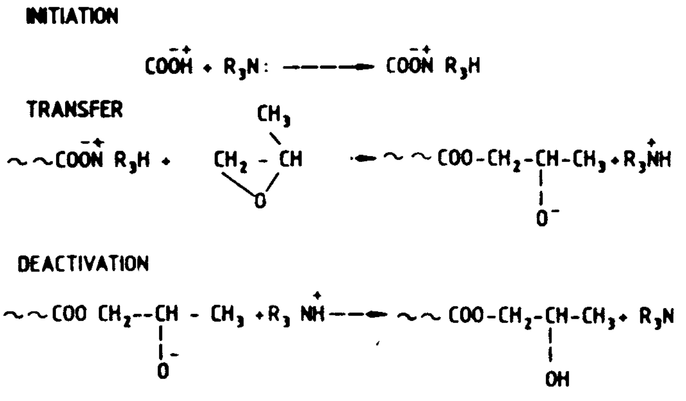


Figure 4. Reaction mechanism between epoxy and carboxyl groups.

The regenerated catalyst in the deactivation step was identified by UV spectrum on acid solution of the product. The acid value of the resin produced on analysis was found to be 0.2 to 0.9 mg *KOH*/g in 36 out of 40 experiments. No appreciable change was noticed in the viscosity of the resin as expected.

2.3 Propellant Formulation and Processing

HTNR thus produced was used in all the propellant experimentations. Fine grade AP (manufactured by ISRO) with an average particle size of 25 μm was used as the oxidiser. Initial experimentations were done with *Mg-Al* alloy powder with a weight ratio of 1:1 and an average particle size of 60 μm. Later experiments were carried out with chromium passivated *Mg* of average particle size 45 μm. The high reactivity of *Mg* with water and acid impurity in the HTNR resin were the major problems encountered in the development phase. These problems were later solved by reacting the acid impurity in the resin by treatment with propylene oxide as described earlier, selecting proper catalyst for the *NCO-OH* reaction, vacuum mixing and low temperature curing of the propellant.

Table 1. Propellant composition

Ingredient	Percentage	
	Composition 1	Composition 2
HTNR Additives (DOA, TMP, TDI, BD, DBTDL etc)		28.5
Ferric oxide		0
Metal powder	37.5 (*Mg-Al*)	30.0 (*Mg*)
Fine AP	34.5	41.5
Total	100.0	100.0

All the developmental mixing were done in a sigma mixer of 4 kg capacity. The optimised formulations were scaled up to 15 kg capacity mix batches in a vertical mixer. The propellant ingredients were mixed for 3 hr of which 1–1/2 hr mixing was done under vacuum condition (5-8 torr). Both ambient temperature and 50 °C curing were adopted for completion of propellant curing. The propellant slurry was vacuum-cast in polythene cartons and 100 mm dia motor for evaluation. The mechanical properties of the cured propellant were evaluated as per ASTM specifications. Square strands of the size 6 × 6 × 80 mm were used for the acoustic burn rate evaluation.

2.4 Propellant Characterisation

The propellant characteristics of two promising formulations, viz one with 37.5 per cent *Mg-Al* alloy powder and the other with 30 per cent *Mg* powder are listed in Tables 2 and 3. Slurry viscosity build up values are recorded for 3 hr. The cure cycles at ambient temperature as well as at 50 °C were adopted to show the amenability of the propellant curing at varied conditions.

Table 2. Propellant characteristics with 37.5 per cent *Mg-Al*

Propellant property	Curing condition			
	RT (10 d)	RT (30 d)	RT (10 d) +50 °C (2 d)	50 °C (5 d)
TS (KSC)	5.9	6.0	6.2	5.6
Elong (%)	38	38	37	39
I Mod (KSC)	20	25	22	19
SAH	50	50	52	47
Density (g/cc)	1.58	1.58	1.58	.58

RT: room temperature; composition: HTNR binder +additives: 27.0 %, *Mg-Al* powder: 37.5 %, fine AP: 34.5 %; slurry viscosity: EOM viscosity Ps. 50 °C: 11520, viscosity after 3 hr Ps. 50 °C: 25200.

Table 3. Propellant characteristics with *Mg*

Propellant property	Curing condition	
	RT (30 d)	50 °C (5 d)
TS (KSC)	9.4	9.5
Elong (%)	34	35
I Mod (KSC)	54	56
SAH	70	65
Density (g/cc)	.47	1.47
Cured strand BR (mm/s)		
50 KSC	4.5	
70 KSC	5.1	
BR Law	$r_b = 0.09\ p^{0.40}$	

RT : room temperature; composition : HTNR binder + additives 28.5 %, *Mg* powder : 30.0 %, fine AP : 41.5 %; slurry viscosity EOM viscosity Ps. 50 °C : 12800, viscosity after 3 hr Ps. 50 °C : 22400.

The results in Tables 2 and 3 show that the same mechanical properties can be achieved by curing at ambient as well as at 50 °C. The reported mechanical properties are quite comparable or even superior to that of the HTPB-based system. Though both formulations are amenable to sub-scale processing, the large scale processing demands better processibility and pot life, to which attention is being paid. Both formulations can be easily ignited as seen from the cured strand burn rate and motor test results. The faster decomposition characteristics of HTNR over HTPB as evident from the thermogravimetric data given above, are a boon to the easy ignition of HTNR-based fuel rich propellant.

2.5 Motor Performance

Sub-scale motors with 200 mm length and of 100 mm dia using 2 kg propellant were successfully static-tested in the primary mode. The test results are given in Table 4.

Table 4. Ballistic evaluation in sub-scale motors

Parameter	Test results	
Average pressure (KSC)	104.3	97.5
Max pressure (KSC)	158.3	153.3
Effective burn time (s)	3.34	3.29
Throat diameter (mm)	7.66	7.77
Discharge coefficient (s^{-1}	8.14×10^{-3}	7.99×10^{-3}
Burn rate at web average pressure (mm/s)	5.60	5.56

The test results in the primary mode of combustion show the ignitability of HTNR-based fuel rich propellant, which is a prime factor for fuel rich combustion in the air-augmented mode being pursued.

3. CONCLUSION

The development of a fuel rich propellant based on modified HTNR containing 30-37.5 per cent *Mg/Mg-Al* powder has been established in sub-scale mixing. The high reactivity of *Mg* metal with moisture and acid impurity have been controlled and defect-free propellant blocks have been made. The cured propellant has given good mechanical properties. The ignition and sustained combustion of HTNR/*Mg*-based fuel rich propellant has been demonstrated in the sub-scale motor testing in the primary mode.

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