

Development of a Polyurethane Binder System Giving a 'Knottable' Composite Solid Propellant

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Abstract. Polyurethane propellants, which constitute one of the 'work-horse' binder systems in modern solid rocketry are easily amenable for tailoring the mechanical properties in terms of variations in the molecular structure of the backbone polyols, the isocyanates and stoichiometry of the reactants. The paper deals with studies in developing an advanced binder system based on poly (oxy propylene glycol) and toluene-di-isocyanate, which is capable of accommodating high solids loading and conceding elongation at maximum stress, of more than 125 per cent. The gum-stock properties of the binder are related with those of a low molecular weight version and the results are explained based on the network theory of condensation polymers.

1. Introduction

The need for a 'low thrust-to-mass level' required of solid rocket motors to put scientific pay-load into planetary orbits, is normally met with by the use of case-bonded end-burning designs which provide low burning surface areas¹. Such designs easily develop a three-dimensional strain during storage and mission operations leading to cracking and failure of the propellant grain. This problem can partially be overcome by reducing the initial modulus and increasing the elongation of the propellant system. While the incorporation of a trimodal blend of the oxidiser in place of the conventional bimodal blend, helps to lower the modulus, a better way of achieving the same and enhancing elongation is in terms of the binder polymer. The introduction of 'telechelic' binder prepolymers may be regarded as a revolutionary approach in this context. In contrast to the back-bone functionalities, telechelics offer elastically more effective polymer networks. Synthesis and tailoring of such networks are relatively easier with polyurethanes on account of simplicity and stoichiometry in their formation and reactions. Flexibility with respect to changes in the molecular make up and functionality of the polyols and di-isocyanates offers

wider possibilities on controlling the mechanical and ballistic properties of the propellant as well as on providing heat-sterilizability for outer-space applications².

Polyurethanes are well-known as products of reactions of polyisocyanates and poly-hydroxy compounds. A propellant-binder grade polyurethane is essentially a cast elastomer system having all the desired qualities of a binder polymer as outlined by Klager³ *et al.* and Smith⁴. In developing case bonded grains, the major property of concern should be a high tensile elongation since the grains are susceptible to high levels of strain during storage and ignition. Tensile strength of such grains can be as low as 50 psi. provided it is capable of preventing creep and grain deformation during storage and under flight-acceleration forces.

The paper deals with studies related to the following formulation variables for their efficiency in building a polymer net-work, capable of yielding a highly rubbery polyurethane-propellant, at a total solids loading of 82 per cent using the prepolymer technique :

- (i) changes in the molecular weight and monofunctional impurity level of the isocyanate-terminated polyurethane prepolymer,
- (ii) Use of two different oxidiser-bonding-agents of varying-NCO active functionalities at different concentration levels,
- (iii) use of a mixed curing agent comprising polyhydroxy compounds of varying molecular make up, and
- (iv) varying the NCO/OH molar ratio of the binder polymer.

In making the above studies, the works of Flory⁵ and Marsh⁶ have been taken as a guideline. Although the prepolymers were not characterised for their molecular weight distribution, useful clues were obtained from the work of Stutchbury⁷ French⁸ *et al.* and Macosko⁹ *et al.*

Symbols

PPG = Poly (oxy-propylene glycol.)

p = Percentage conversion.

\bar{D}_p = Number-average degree of polymerisation.

R = NCO/OH -molar ratio.

α_f = Branching coefficient

ρ_T = Fraction of -OH groups from triols.

ρ_D = Fraction of -OH groups from diols.

$R. T.$ = Room temperature.

2. Materials

The special materials used in this study are the following :

2.1 Prepolymer-A (NCO terminated)

Prepared by the bulk addition reaction of PPG-2000 and a 80/20 mixture of 2, 4/2, 6 toluene-di-isocyanate, using the standard process developed at the VSSC, it is a straw-yellow coloured resin containing free monomeric TDI as a reactive diluent. It has a number average \bar{DP} of 1.32 and a mono-functional content of 12.25 per cent as calculated based on NCO content percentage. It has a viscosity of 70 to 120 poises at 30°C and an average NCO content of 3.5 per cent.

2.2 Prepolymer-B (-NCO terminated)

This is prepared by the same process as used for prepolymer-A, except for an extended holding time given at a reaction temperature to build up the \bar{DP} . The trends in percentage conversion, p and \bar{DP} at different NCO per cent levels in making this prepolymer are shown in Fig. 1. With TDI as reactive diluent, it has a mono-functional content of 21 per cent and an average \bar{DP} of 2.85. Its viscosity ranges from 900 to 1200 poises at 30°C and NCO content, from 3.0 to 3.5 per cent.

2.3 Pedisperse-1

This is a condensate of stearic acid and diethanolamine, reacted in equimolar quantities, prepared at VSSC. This oxidiser-bonding agent is a mixture of

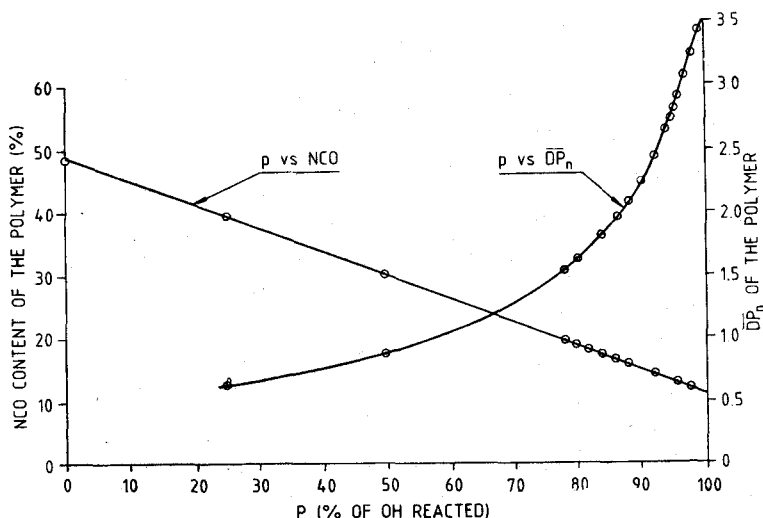


Figure 1. Variation of NCO content and \bar{DP}_n during the formation of Prepolymer-B.

alkanolamide and alkanolamine-ester having an average *NCO*-active functionality of 1.45. It is a waxy solid at *R. T.* with a melting range of 52-55°C.

2.4 Pedospere-2

It is basically the ricinoleic diethanolamide, prepared in a similar way as pedospere-1. It is a viscous liquid at *R. T.* and possesses an average *NCO*-active functionality of 3.0.

In addition to the above materials, the following binder ingredients were used : (i) Castor-oil; (ii) Dioctyl adipate; (iii) Triethanolamine, (iv) Ferric acetyl acetate; (v) Sulfur, and (vi) *N*-Phenyl-2 Naphthyl amine.

In all the propellant compositions, a constant solid loading of 82.5 per cent comprising of 0.5 per cent *HAF* black, 19 per cent aluminium powder (average particle size : 22 microns) and a bimodal blend of ammonium perchlorate was used.

3. Experimental

In all the experiments, involving prepolymer-*A* and prepolymer-*B*, the major objective was to enhance the elongation, keeping the tensile strength of the propellant within tolerable limits (50 psi and above). In the light of the work of Marsh⁶, the binder system was adjusted to yield a near-incipient gelling polymer network. The critical branching coefficient α_f was related to *R*, the molar ratio, *NCO/OH* the fraction of *OH* groups from triols ρ_T and the fraction of *OH* from diols, ρ_d by the equation

$$\alpha_f = \frac{\rho_T}{R - \rho_D} \text{ for } R \geq 1.0$$

or

$$= \frac{R \rho_T}{1 - R \rho_D} \text{ for } R \leq 1.0$$

For the calculation of α_f , castor-oil, which is the basic curing agent, was taken to be a mixture of 74 per cent trifunctional and 26 per cent difunctional polyol. All the propellants were given a cure time of 24 hours at *R.T.* under dry humid conditions followed by 96 hours at 60°C. Mechanical properties were tested from propellants cast as free-grains and cured along with motors. The tensile specimens were conditioned in a desiccator over fused *Ca Cl 2* for 24 hours, before testing. Tensile measurements were performed using the Instron Universal Testing Machine, at a cross-head speed of 5 cm/minute.

4. Results and Discussion

4.1 Experiments with Prepolymer-A

Prepolymer-A comprises the following types of *NCO* functionalities in its structure : Difunctional, polymeric-75.12 per cent Difunctional, monomeric-12.65 per cent and Monofunctional, polymeric-12.23 per cent.

Since the isocyanate groups are highly susceptible to spurious reactions with the moisture content of the propellant ingredients and of the environment, the polyurethane propellant system is normally immunized against such reaction by keeping the isocyanate-index well above 100. With one such system, where the index is 125, the binder characterised by $\rho_T = 0.3290$ and $\alpha_f = 0.5085$, yields the following mechanical properties* in the gum-stock and in the propellant thereof :

System	<i>T. S.</i> (psi)	Elongation at break (%)	Modulus (psi)	Shore-A hardness
Gum-stock	67	400	80	30
Propellant	90	25	1150	80

Keeping the above propellant as the base, the system was studied for its amenability for improving the tensile elongation with the incorporation of pedosperse and triethanolamine at different percentage levels.

The basic binder system was first evaluated (without the addition of plasticiser) for its useful range of α_f using a mixed curatur consisting of a 80 : 10 : 10 mixture of castor oil, pedosperse-1 and triethanolamine. As shown in Table 1, the system remains useful only in a narrow range of *R* viz. between 1.1 and 1.30.

Table 1. Effect of *R* on gum-stock properties : with prepolymer-A

<i>R</i>	ρ_T	α_f	<i>T. S.</i> (psi)	Elonga- tion at break (%)	Modulus (psi)	Hard- ness (Shore-A)
1.00	0.3460	0.7955	Sticky mass			
1.10	0.3625	0.7197	48.5	600	45	20
1.20	0.3750	0.6599	75.0	325	80	25
1.30	0.3911	0.5915	125.0	280	90	25-30
1.40	0.4037	0.5190	150.0	200	97	35
1.50	0.4152	0.4165	Blisters on surface-Bottom remains soft			

*The propellant consists of Binder-15.08%, *DOA*-2.683%, *Fe* (*AA*)₃-0.017%, Sulphur-0.11% Nonox-*D*-0.11% plus solids.

In the light of the above data, an isocyanate index of 125 was chosen and effects of using Pedosperse-1 alone and in combination with triethanolamine were studied for improvements in tensile elongation. α_f was adjusted to be nearer to 0.5 in order to observe maximum sensitivity. As shown in Tables 2 & 3, use of pedosperse-1, (which contributes 45 per cent to ρ_D and none to ρ_T) alone shows a negative trend in that it causes a decrease in elongation at higher levels, and a over-all decrease in tensile strength with respect to the base system. Triethanolamine on the other hand is effective in improving the elongation and lowering the modulus. Propellants prepared according to the formulations of Table 3 were observed to possess good storage stability under ambient conditions up to six months as regards their mechanical properties.

Table 2. Effect of varying pedosperse-1 concentration on propellant elongation a constant R (prepolymer-A).

Pedosperse-1 (% of curator)	ρ_T	α_f	T. S. (psi)	Elonga- tion at break (%)	Modulus (psi)	Hardness (Shore-A)
2.5	0.3206	0.4909	60	50	515	70
3.0	0.3191	0.4886	60	45	450	75
5.0	0.3124	0.4798	55	30	368	70
7.5	0.3040	0.4685	50	30	368	60
10.0	0.2960	0.4578	44	25	368	60

$R = 1.25$, $Al = 19.5\%$, Solids = 82%.

Table 3. Effect of varying Triethanolamine concentration on propellant elongation (prepolymer-A) (at a constant concentration of pedosperse-1 and $R = 1.25$).

Pedos- perse-1 (% of curator)	Trietha- nolamine (% of curator)	ρ_T	α_f	T.S. (psi)	Elonga- gation at break (%)	Modulus (psi)	Hard- ness (Shore-A)
5.0	5.0	0.3182	0.4847	52.5	20	950	80
5.0	10.0	0.3240	0.4895	97.5	45	450	70
5.0	20.0	0.3354	0.4987	88.2	52	390	70
5.0	30.0	0.3471	0.5124	51.5	78	295	65

$R = 1.25$ $Al = 19.5$ Solids = 82%.

An alternate approach, incorporating equal concentrations of both pedosperse-1 and triethanolamine was also good in getting better elongation. However, at higher concentration levels, the propellant slurry was difficult to cast. The system also showed substantial post-curing effects causing a decrease in elongation after six months of storage under ambient conditions. The results are summarised in Table 4.

Table 4. Effect of equimolar concentrations of pedosperse-1 and triethanolamine on elongation improvement (prepolymer-A).

Pedosperse-1 (% of curator)	Triethanolamine (% of curator)	ρ_T	α_f	T. S. (psi)	Elongation (%)	Modulus (psi)	Hardness (Shore-A)
5	5	0.3182	0.4907	38 (51.5)	40 (45)	808 (955)	20
10	10	0.3975	0.4730	67 (60)	75 (52)	380 (955)	20
15	15	0.2970	0.4557	55 (45)	70 (48)	880 (880)	20

(Values in brackets are those measured after six months)

A considerable improvement in castability was observed when pedosperse-1 was replaced by pedosperse-2 at the same isocyanate index in the mixed curator combination viz. 80 : 10 : 10. However, elongation of the system was only 15 per cent and the propellant was characterised by a very high modulus. Since pedosperse-2 is trifunctional, lowering R or increasing α_f is expected to improve the elongation of the system. It was observed to be so and the trend shown in Table 5 indicates the need for higher levels of (ρ_T and α_f) to observe better elongation viz. ($\rho_T = 0.3771$ and $\alpha_f = 0.7236$) as against (0.3471 and 0.5124) required with pedosperse-1.

Table 5. Effect of R in mixed curator system : (pedosperse-2 + triethanolamine castor oil) improving elongation with prepolymer-A.

R	ρ_T	α_f	T. S. (psi)	Elongation at break (%)	Modulus (psi)	Hardness (Shore-A)
1.333	0.3375	0.4571	103	20	1175	90
1.111	0.3752	0.6813	108	25	1175	85
1.000	0.3960	0.8658	99.5	45	660	70
0.909	0.3771	0.7236	51.5	76	515	60
0.833	0.3797	0.6407	Soft cured system			

Thus, prepolymer-A based propellants could be modified to give systems possessing about 75 per cent elongation at break. The experiments performed have also enabled to nomographically relate the tensile strength and elongation with R as shown in Fig. 2.

4.2 Studies with Prepolymer-B

As regards polymer network formation, prepolymer-B differs from prepolymer-A in containing a higher level of mono functional polymeric isocyanate. Thus it is made up of Difunctional, polymeric 'NCO'—69.70 per cent Difunctional, monomeric

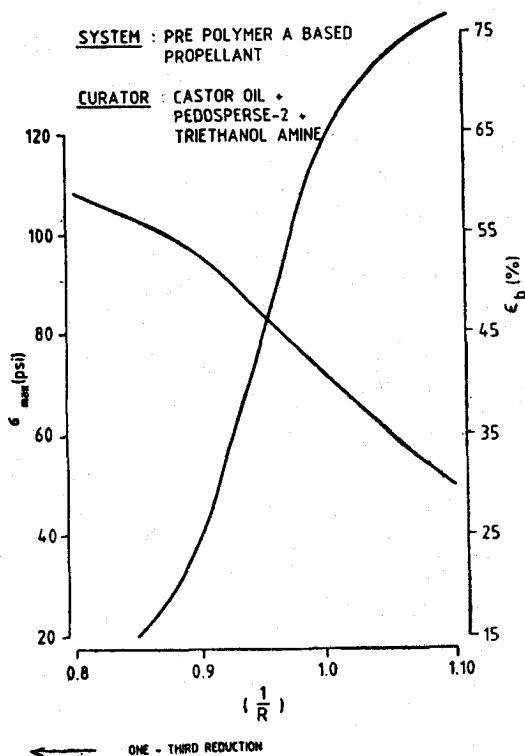


Figure 2. Relation between R , σ_{max} and ϵ_b .

'NCO'—9.47 per cent and Monofunctional, polymeric 'NCO'—20.83 per cent. However, prepolymer-B is also having a higher number average \bar{DP} viz. 2.85 which is more than twice that of prepolymer-A. Since most of the physical properties of the binder polymer like tensile strength, elongation, modulus and creep resistance bear a direct relation¹⁰ to the \bar{DP} , prepolymer-B can be expected to tolerate the presence of higher levels of monofunctional impurities and still give rise to extensible networks.

The high viscosity of prepolymer-B necessitates use of warmer conditions for propellant processing. Thus, all experiments with this prepolymer were performed at a mixing and casting temperature of 50°C. Using a 80 : 10 : 10 mixture of castor oil : pedospers-2 : triethanolamine, a premix was obtained at 50°C having the same flow characteristics as the one from prepolymer-A at 30°C. This could be achieved using DOA at 35 per cent weight of the binder. Under these conditions, the system was studied for its sensitivity to good/poor cure boundaries in terms of R . The results, as summarised in Table 6 indicate a wider useful range of α_f and R compared to prepolymer-A and much higher levels of elongation achievable.

Since the plasticizer uptake of this prepolymer was good, the system was studied for higher levels of DOA incorporation in the propellant. The results are summarized in Table 7. It is notable here that up to 35 per cent incorporation, DOA exhibited

Table 6. Effect of R on the propellant-mechanical properties with prepolymer- B .

R	ρ_T	α_f	$T. S.$ (psi)	Elongation at break (%)	Modulus (psi)	Hardness (Shore-A)
1.250	0.3519	0.4904	90	25	900	85
1.111	0.3752	0.6297	97.5	50	600	75
1.000	0.3960	0.7919	102	77	405	70
0.909	0.4150	0.6754	82.5	85	195	65
0.833	0.4556	0.6073	54.0	130	165	50
0.80	0.4699	0.5620	55.0	140	75	40

Table 7. Plasticizer uptake efficiency of prepolymer- B based propellant.

DOA (% of binder)	$T. S.$ (psi)	Elongation at break (%)	Modulus (psi)	Hardness (Shore-A)
25	60	85	225	55
30	55	130	150	50
35	65	130	165	50
40	42	150	90	35
47.5	15	Soft	—	20

(At $R = 0.8333$, $\rho_T = 0.4556$, $\alpha_f = 0.6073$)

Table 8. Effect of pedosperse-2 concentration on improving the mechanical properties of prepolymer- B based propellant.

Pedo- sperse-2 (% of curator)	ρ_T	α_f	$T. S.$ (psi)	Elonga- tion at break (%)	Modulus (psi)	Hardness (Shore-A)
5	0.4107	0.5821	53	85	225	55
10	0.4178	0.5864	57	108	150	50
20	0.4321	0.5945	48.5	110	150	45
25	0.4392	0.5985	39.7	115	120	40

remarkable compatibility and never migrated out up to six months of storage under ambient conditions.

As with prepolymer- A , the individual contribution of pedosperse-2 in enhancing the elongation was also studied with this system at a constant R value. The study revealed that use of a mixture of pedosperse-2 and triethanolamine was better than using the individual components, alone, in improving castability and elongation. The results are summarised in Table 8.

5. Conclusion

The above studies reveal that use of a urethane prepolymer of higher \bar{DP} with a higher level of mono-functional impurities is capable of better performance than one

with a lower \bar{DP} and lower monofunctionals. In terms of formulation variables, such a prepolymer is capable of conceding same elongation levels with a much higher α_f value at a given ρ_T and offering scope for higher ρ_T values to observe better elongation levels. The usefulness of Castor-oil, instead of Trimeihylol propane, as an efficient and major Cross-linking agent is indicated. Although more modern versions of advanced Polyurethane propellants are based on HTPB, (instead of PPG-2000) for achieving higher solids-loading and better low temperature performance, results of the type presented in this paper will still be helpful, as a model, in tailoring the formulation parameters.

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References

1. Marsh Jr, H. E. & Udlock, J. E., *J. Space Craft*, **9** (1972), 625-626.
2. Udlock, D. E., *J. Spacecraft*, **14** (1977), 197.
3. Klager K., *et al.* 'Recent advances in solid propellant binder chemistry'-4th symp. Naval. Str. Mech. Lafayette, Indiana, (1965).
4. Smith, T. L., *Ind. Eng. Chem.*, **52** (1960), 776.
5. Flory P. J., *J. Am. chem. Soc.*, **63** (1941), 3083.
6. Marsh Jr., H. E., *Ind. Eng. Chem.*, **52** (1960), 768.
7. Stutchbury, J. E., Hryhorciw, S., Tech. Note CPD 103 Australian Defence Sci. Serv.
8. French, D. M., *et al*, *J. Appl. Polymer Sci.*, **16** (1972), 1615-1627.
9. Macosko, C. W., Miller, D. R., *Macromolecules*, **9** (1976), 206-211.
10. Mark, H. F., *Ind. Eng. Chem.*, **34**, (1942), 1343.