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Cross-Linked Slurry Cast Composite Modified Double Base Propellants : Mechanical Properties

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ABSTRACT

Cross-linking of NC by TDI in slurry cast CMDB propellant enhanced TS by about 100 per cent. Coated AP with resorcinol, phloroglucinol, hexanetriol or silicone oil etc. along with cross-linking of NC raised TS from 18 - 30 kg/cm^2. Inclusion of phloroglucinol and silicone oil gave increased burning rates. The probable mechanism of action of cross-linking and improvement of mechanical properties by coating of AP has been discussed.

1. INTRODUCTION

Composite Modified Double Base (CMDB) propellants are capable of producing highest energy (Isp) along with wide flexibility of burning rates among the solid rocket propellants. In addition, nitramine based CMDB propellants can provide smokeless combustion products and high density. In view of these special features, CMDB propellants have been used for tactical missiles/space missions like Sea dart, Minuteman II, Scout, Poseidon, Trident IV, etc. Present day missions generally demand advanced propellants of high structural integrity along with high energy. However, to accommodate oxidizer/energetic materials, nitrocellulose (NC) content in the composition is reduced to the extent of maintaining processibility. Reduction of NC content in the composition affects mechanical properties adversely, resulting in propellants of poor structural integrity. To overcome this limitations attempts have been made to cross-link unnitrated *-OH* group of NC or to use wetting/bonding agents.[1-3] Patents have claimed 100-300 per cent increase of tensile strength (TS) for cross-linked propellants and oxidizer coated with chemicals like triethanolamine.[1,4] However, no definite studies have been conducted on the mechanical properties of cross-linked CMDB propellants. Hence, a systematic study was conducted on the

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effect of cross-linking and coating of oxidizer on mechanical properties and burning rates of CMDB propellants. In the present study unnitrated *–OH* group of NC was cross-linked with toluene di-isocyanate (TDI) and ammonium perchlorate (AP) oxidizer was coated with potential stabilizers for CMDB propellants.

2. EXPERIMENTAL

NC of 12.2 per cent nitrogen content in dense (spheroidal) form was used. NG was extracted by water percolation method from dynamite (65 parts NG and 35 parts kieselguhr) received from Ordnance Factory. Coating agents (AR grade) dissolved in ethyl alcohol were applied to AP. Propellant compositions were made by slurry casting technique.[5] Calculated quantity of TDI was added to obtain required degree of cross-linking (10-30 per cent) at the final stage of mixing. Mechanical properties were determined with the help of Instron Testing Machine. Burning rates were determined in Crawford bomb using 6 mm diameter strands, cut from the propellant slabs. Cal-Val for the propellant samples were determined in the Calorimetric bomb at a loading density of 0.016 gm/cc.

3. RESULTS AND DISCUSSIONS

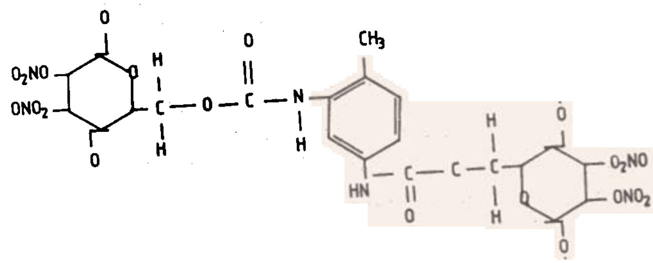
The results on the effect of varying degree of cross-linking on the mechanical properties of CMDB propellants are given in Table 1. Ten per cent cross-linking of NC increased TS from 13 to 25 kg/cm^2, without affecting elongation adversely. Increase in cross-linking from 10 to 20 per cent maintained higher TS obtained with 10 per cent cross-linking. Further increase of cross-linking to 30 per cent showed reducing trend, as TS was reduced to 23 kg/cm^2 level and percentage elongation was lowered from 14 to 7 per cent. Increase in cross-linking beyond 30 per cent resulted in the propellant slabs of very brittle nature and cracks were observed on the surface of the cured propellant. Hence, the effect of cross-linking beyond 30 per cent was not studied.

Table 1. Effect of cross-linking on mechanical properties of CMDB propellants.

(Composition : NC 35.0, NG 28.0, DEP 6.3, AP 18.0, *Al* 12.0, 2NDPA 0.7)

Degree of cross-linking (% of *OH* remaining unnitrated in NC)	Mechanical properties	
	T.S. (kg/cm^2)	% Elongation
Control	13	14
10% cross-linking	25	13
20% cross-linking	25	9
30% cross-linking	23	7

As regards the mechanism of action of cross-linking agent in the improvement of mechanical properties, the unnitrated hydroxyl groups in NC react with TDI to form urethane linkage $(\sim NH\text{-}\underset{\underset{O}{\|}}{C}\text{-}O\text{-})$ and the three dimensional network thus formed is responsible for enhancement of TS, as a result of enhancement of cross-link density. With cross-linking relative movement of NC molecule is restricted, which produces increase in TS of the matrix at lower degree of cross-linking. However, with increased cross-linking the plasticizing effect of NG is adversely affected as intermolecular gap to accommodate plasticizer molecule is reduced, thereby decreasing the percentage elongation of the matrix.



For further improvement of mechanical properties of CMDB propellants, experiments were carried out with coated AP. AP was coated with 5 per cent or of resorcinol, or phloroglucinol or trimethylol propane (TMP), or hexanetriol or silicone oil for casting of propellant grains. The results on the effect of coated oxidizer with 10 per cent cross-linking of NC on mechanical properties are tabulated in Table 2. TS increased from 18 - 30 kg/cm^2 level for CMDB propellant containing AP coated

Table 2. Effect of coating on mechanical properties of 10% cross-linked CMDB propellants.

(Composition : NC 32.0, NG 27.4, DEP 6.2, AP 19.0, *Al* 12.7, Fe_2O_3 2.0, 2NDPA 0.7)

Coating agent for oxidizer (5 % coating)	T.S. (kg/cm^2)	% Elongation
Control	18	13
Resorcinol	30	12
TMP	31	11
Phloroglucinol	31	9
Hexanetriol	26	12
Silicone oil	25	15

with resorcinol/phloroglucinol/TMP. Coating with hexanetriol or silicone oil raised TS to 25 kg/cm^2 level. Percentage elongation was marginally reduced in all the cases, except with silicone oil. Silicone oil improved elongation by 2 per cent, which may be due to its plasticizing property of silicone oil.

In case of wetting agents/bonding agents, improvement in TS is expected, if a strong chemical bond is formed between binder and filler through the bonding agent. Compounds used as bonding agents either react chemically with the oxidizer or get adsorbed physically on the oxidizer surface and react with the binder to form a chemical bond. Processing aids function by making solids and polymeric fuels more compatible, resulting in a better wetting of solids by liquids. In the present study, resorcinol, phloroglucinol and TMP showed an increase of 60-70 per cent of TS, whereas hexanetriol and silicone oil showed an increase of 40 per cent. Coating agents namely, resorcinol, phloroglucinol and TMP are adsorbed on the polar surface of AP oxidizer. During cross-linking TDI reacts both with NC and coating agents having free hydroxyl group simultaneously and forms chemical bond. The enhancement of TS is the net result of two competing reactions namely, reaction of TDI with unnitrated *–OH* groups of NC and *–OH* groups of coating agents.

The results on the effect of cross-linking on burning rates of CMDB propellants[6] have been reported earlier. With 10 per cent cross-linking lowering of the burning rates was observed at all pressures between 50-105 kg/cm^2. The burning rates were lowered by 1.4 - 2.2 mm/sec at various pressures. Burning rate results with the coated AP and 10 per cent cross-linked NC are tabulated in Table 3 and shown in Fig. 1. Results obtained reveal that phloroglucinol, hexanetriol and silicone oil increased the burning rates at all pressures studied, whereas TMP decreased the burning rates throughout and resorcinol showed more or less same burning rates as those with control.

Table 3. Effect of coating on burning rates of cross-linked CMDB propellants.

(Composition : NC 32.0, NG 27.4, DEP 6.2, AP 19.0, *Al* 12.7, Fe_2O_3 2.0, 2NDPA 0.7)

Coating material (5 % coating of AP)	Burning rate (mm/sec) @ pressures (kg/cm^2)				
	35	50	70	90	105
Control	6.7	8.3	9.9	11.8	13.5
Resorcinol	6.3	7.9	9.8	11.8	13.7
Phloroglucinol	7.0	8.5	10.6	12.9	14.0
TMP	5.8	7.2	8.7	11.0	12.8
Hexanetriol	5.8	8.7	10.6	13.9	16.0
Silicone oil	7.1	9.0	12.0	13.3	14.4

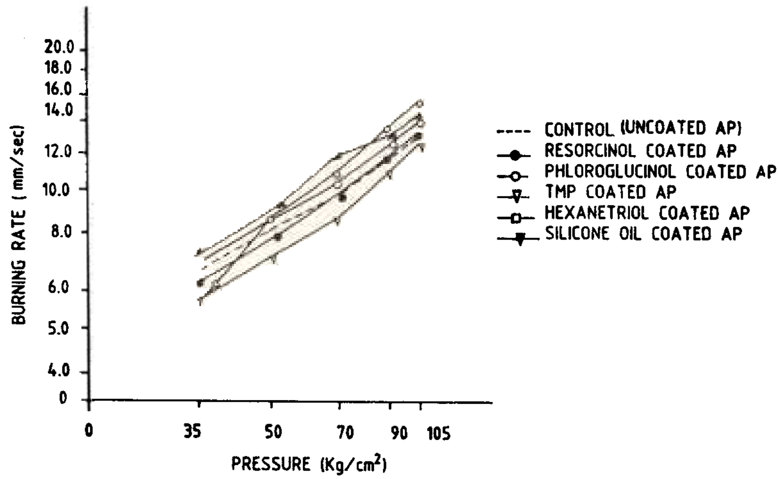


Figure 1. Effect of coating and cross linking on burning rates of CMDB propellants.

Burning rate of any propellant is dependent upon a series of complex processes taking place during combustion. The condensed phase decomposition of oxidizer and binder, the gas phase reactions near and away from the burning surface and the heat feedback from these gaseous reaction zones are some of the important factors controlling the burning rates. Cross-linking of NC is expected to decrease the total heat output, as energy is absorbed in the breaking of the chains. Further, cross-linking results in lowering of energy content of the propellant, which is confirmed from the results of Cal-Val of cross-linked compositions (1295-1385 cal/gm as against 1439 cal/gm for control).

Polyhydroxy phenols (resorcinol, pyrogallol) are reported to increase the burning rates in presence of lead salts in double base propellants.[7] Pyrogallol decomposes exothermally in the temperature range 370-430°C. In the present study, trihydroxy phenols were also found to increase the burning rates, indicating thereby that a similar mechanism involving formation of carbon/carbonaceous matter may be operative.[8] Kumar[9] has reported that in the case of HTPB based composite propellants, silicone oil increases burning rates by about 10 per cent. However, no mechanism has been proposed for this observation. Hori et al.[10] have suggested that in case of HTPB and AP based composite propellants hydrogen bonding is responsible for adhesion of bonding agents to AP and role of bonding agents consists in the concentration increase of polar groups. At an early stage of curing, electronegative atoms are oriented to hydrogen atoms of AP and electropositive atoms to oxygen atoms due to high mobility of polar groups. Thus, hydrogen bonds, strengthen the bond between AP and binder.

4. CONCLUSION

Maximum increase of TS is obtained with CMDB propellant compositions having 10 per cent cross-linking of NC and oxidizer (A.P.) coating with phloroglucinol or TMP. While cross-linking reduces the burning rates, coating of oxidizer with silicone oil and phloroglucinol enhances the burning rates of CMDB propellants. Inclusion of phloroglucinol produced highest TS along with increased burning rates at various pressures.

REFERENCES

1 Pierce, E.M., U.S.P., No. 3,726,729 (1973), p. 3; *Chem. Abstr.*, **78** (1973), 160650a.

2. Allen, H.C., U.S.P., No. 3,745,074 (1973), p. 3; *Chem. Abstr.*, **79** (1973), 94196z.

3. Elrick, D.E., U.S.P., No. 3,894,894 (1975), p. 8; *Chem. Abstr.*, **83** (1975), 181621k.

4. Henry, D.C., U.S.P., No. 4,038,115 (1969), p. 5; *Chem. Abstr.*, **87** (1977), 154308q.

Camp, A.T., Propellants manufacture, hazards and testing, Advances in Chemistry Series 88, (American Chemical Society Publication, Washington), 1969, pp. 29-35.

6. Raman, K.V., Singh H. & Rao, K.R.K., Ballistic modification of CMDB propellants containing AP, Propellant, Explosive and Pyrotechnics, **12** (1987), 13-16.

7. Singh, H., Raman, K.V. & Rao, K.R.K., *Combustion Science & Techn.*, **23** (1980), 1-2.

8. Singh, H. & Rao, K.R.K., Mechanism of combustion of catalysed double base propellants, (33rd Aeronautical Congress, Paris, France), 1982, pp. 82-359.

9 Kumar, R., *Combustion & Flame*, **39** (1980), 53-62.

10 Hori, K., Iwana, A. & Fukuda, T., *Propellants, Explosives, Pyrotechnics*, **10** (1985), 176-180.