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Optimization of Network Forming Agents for Different Types of Composite Propellant Grain

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Abstract: There has been a constant endeavour to improve the mechanical properties of hydroxyterminated polybutadiene (HTPB)-based, composite solid propellants. In order to have a better understanding of the requirements, a systematic study has been conducted on the effects of varying the network forming agents on the mechanical properties of nitramine based composite propellants. Under this scheme, a series of compositions was formulated using various chain extenders [1,6-hexanediol (HD) and 1,4-butanediol (BD)] and cross linkers [1,2,6-hexanetriol (HT) and trimethylolpropane (TMP)] in different proportions. Propellant formulation experiments were conducted wherein the network forming agent composition was systematically varied to achieve the maximum possible strain capability and moderately high tensile strength, keeping the weight % of the network forming agents and other ingredients constant. The mechanical properties (% elongation, tensile strength and elastic-modulus) of the finished propellant have been plotted *vs.* formulation number; this can be used to select a suitable network forming agent composition for a specified grain architecture and application. Network forming agents containing 1,2,6-hexanetriol provide a high elastic-modulus (120 kg/cm^2) and a high tensile strength (~12 kg/cm^2), which can be used in free standing grains. Network forming agents based on 1,6-hexanediol and 1,2,6-hexanetriol (in 1:1 proportion by weight) give high elongation (~50%) and a moderately high tensile strength (~9 kg/cm^2), useful for case bonded propellant grains.

Keywords: mechanical properties, diol-triol ratio, chain extender, cross linker

Introduction

Composite solid propellants are used in either case bonded or in free standing configurations, depending upon the mission requirement. In order to perform successfully in its mission, it is necessary for a solid rocket motor to retain its structural integrity under the wide variety of mechanical loads, which are imposed on it during manufacture, transportation, storage and operational use. The structural integrity of the motor is governed by the mechanical properties of the propellant and design considerations [1]. A propellant grain should have sufficient tensile strength and elongation to withstand these stresses and strains. A suitable combination of tensile strength, elongation and initial elastic modulus are normally specified to check the applicability in a particular mission. The mechanical properties of solid propellants depend on (a) the intrinsic or constitutional variables and (b) the extrinsic or environmental variables. The important intrinsic variables are (i) the molecular weight of the resin, (ii) the effect of cross-linking, branching and crystallinity, (iii) plasticisation, and (iv) quality and quantity of fillers.

The literature indicates that various studies have been made for modelling the mechanical behaviour of composite solid propellants [2-16]. Ozgur Hocaoglu [10] studied the changes in the mechanical properties of hydroxy-terminatied polybutadiene and ammonium perchlorate based, solid composite propellants during the curing period with respect to variations in the crosslink density, which was predominantly determined by the equivalent ratio of di-isocyanate to total hydroxyl group number (NCO/OH ratio, R value) and the equivalent ratio of diol to triol (diol/ triol ratio). R. Manjari *et al.* [11-12] reported propellant formulation tailoring of a HTPB based propellant for better mechanical properties. They also used HTPB, with varying molecular weight and hydroxyl value, in propellant formulation experiments with a view to studying the production variables and their influence on the resultant propellant properties [13]. D.V.B. Pinto [14] synthesized a new bonding agent and incorporated it in propellant compositions. The optimum mechanical properties were achieved by fine adjustment of the NCO/OH ratio. When the effects of solid loading on the mechanical properties was also studied, it was found that the mechanical properties become weaker as the solid loading is increased [15]. Modelling of the effects of moisture in solid ingredients was performed by M.M. Oqbal *et al.* [16]. They reported that a propellant's mechanical properties are improved by decreasing the moisture content in the solid raw materials, but extensive drying of solid raw materials has an adverse effect on the propellant's mechanical properties.

A propellant's mechanical properties play an important role in decisions regarding the application of a special type of grain (free standing or case bonded). In view of this we have undertaken a detailed comparative study of network forming agents in the composite solid rocket propellant formulation (HTPB/AP/Al/RDX based) in order to improve its mechanical properties. The purpose of this work was to increase knowledge on how to enhance the elongation and tensile strength of solid rocket propellants by the addition of network forming agents, and to optimize the propellant formulation for various applications.

Experimental

Material

Ammonium chlorate(VII), procured from Pandian Chemicals (purity >99%), was used as a bimodal distribution having particle sizes 300 and 60 µm. Aluminum powder (particle size 15 ±3 µm) was procured from Metal Powder Company, Madurai (India). RDX (1,3,5-trinitro-1,3,5-triazacyclohexane) was procured from Ordnance Factory Bhandara and used after drying (moisture 0.1%). Iron(III) oxide [Fe_2O_3] and copper chromite [$CuCr_2O_4$] were procured from trade and used as burn rate modifiers. The binder consisted of hydroxyterminated polybutadiene (HTPB, purity 99%, OH value 40-50, moisture 0.15%, purchased from ANABOND) and cured with toluene di-isocyanate (TDI, purity 9%, RI at 30 °C 1.565-1.567, purchased from Bayers Chemicals). Di-octyl adipate (DOA, ester content 99%, saponification value 303 ±3, moisture 0.5%, purchased from Subhas Chemicals) was used as a cross linker. 1,4-Butanediol (BD), 1,6-hexanediol (HD), trimethylolpropane (TMP) and 1,2,6-hexanetriol (HT) were used for the preparation of network forming agents and were also procured from trade.

Propellant formulation experiments

The basic resin matrix was a four component system with HTPB, diol (1,4-butanediol or 1,6-hexanediol), triol (trimethylolpropane or 1,2,6-hexanetriol), and toluene di-isocyanate as the constituents. The propellant trials were conducted with the baseline formulation given in Table 1. The investigation involved propellant formulation experiments with eight batches of the network forming agents at various combinations of diol/triol ratios and R-values (Table 2).

Table 1. Baseline formulation of propellant composition

Ingredients	wt%
HTPB+DOA+TDI+ Pyrogallol	13.88
Bonding agent	0.12
Ammonium perchlorate	63
Aluminium powder	16.6
RDX	5
Burn rate modifiers	1.4
Total	100.00

Table 2. Compositions of network forming agents

No.	Formulation
I	1,4-Butanediol (BD) at R-value 0.7356
II	Trimethylolpropane (TMP) at R-value 0.7237
III	BD:TMP in 1:1 ratio by weight at R-value 0.7296
IV	BD:TMP in 2:1 ratio by weight at R-value 0.7316
V	1,6-Hexanediol (HD) at R-value 0.778
VI	1,2,6-Hexanetriol (HT) at R-value 0.7344
VII	HD:HT in 1:1 ratio by weight at R-value 0.7557
VIII	HD:HT in 2:1 ratio by weight at R-value 0.7630

The bonding agents were prepared by continuous mixing of the chain extender (1,4-butanediol or 1,6-hexanediol) and the cross linker (trimethylolpropane or 1,2,6-hexanetriol) in a rotary evaporator under vacuum at 50-60 °C for 2 hours. The propellant was mixed in a planetary blade mixer in 600 g batches at 50 ±5 °C. All of the binder ingredients except the curing agent were blended thoroughly in a vertical mixer. The burn rate modifier, Al, RDX, AP(f), AP(c) were added sequentially and each blended for 10 min. The mixing was then continued, without vacuum for 1 h and under vacuum for 1 h. After the addition of the curing agent to the slurry, the mixing was continued for 20 min. Freshly prepared propellant slurries were cast into Teflon coated moulds, under vacuum. The moulds were cured for 5 days at 60 °C.

Characterization method

The particle size of ammonium chlorate(VII) was determined by the sieve analysis method. Tensile tests of the propellants were carried out by using a conventional uniaxial testing system according to the ASTM D638 procedure with a uniaxial testing machine (Model No. INSTRON 1185). The cured samples were tested for their mechanical properties (E-modulus, tensile strength, elongation at maximum stress) at room temperature and with a crosshead speed of 50 mm/min. The solid strand burn rate (SSBR) was determined using the acoustic emission technique at 70 kg/cm^2 pressure under a nitrogen atmosphere.

Results and Discussion

In order to investigate the dependence of the mechanical properties on the network forming agents, eight different sets were prepared by using selected combinations of the chain extenders (BD, HD) and the cross linkers (TMP, HT) whilst keeping the total bonding agent content constant at 0.12% by weight. Experimental batches of propellant were prepared using each of these eight formulations of network forming agents. The propellant processing was carried out using the standard procedure for composite propellant processing and cast under vacuum by the slurry cast technique. The cured propellants were analysed for their mechanical and ballistic properties. In order to understand the influence of the network forming agents on the mechanical properties, the modulus, elongation and tensile strength were evaluated as a function of diol to triol ratio and R-value as shown in Figure 1. All of the values listed in Table 3 were obtained as an average of five specimens.

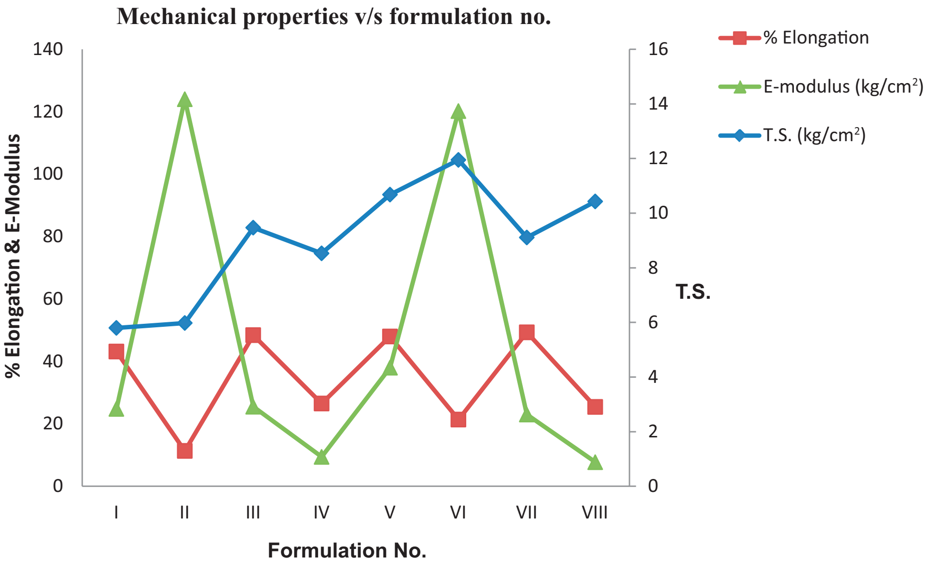

Figure 1. Variation in mechanical properties of the propellants *vs*. composition of network forming agents (P.No.5).

Table 3. Mechanical and ballistic properties of the propellant compositions

Propellant composition with network forming agent	R-value	Tensile strength (kg/cm^2) [S.D.]	Elongation % (at max) [S.D.]	Elongation % (at break) [S.D]	E-modulus (kg/cm^2) [S.D]	SSBR at 70 ksc (mm/s)
I(BD)	0.7356	5.8[0.15]	37.8[0.43]	43.18[0.72]]	24.8[0.08]	12.2
II(TMP)	0.7237	5.98[0.06]	8.43[0.05]	11.35[0.37]	124[3.40]	12.1
III(BD:TMP=1:1)	0.7296	9.47[0.23]	46.62[0.92]	48.43[1.18]	25.5[0.12]	12.3
IV(BD:TMP=2:1)	0.7316	8.53[0.14]	23.15[0.63]	26.53[0.23]	9.43[0.05]	11.9
V(HD)	0.778	10.68[0.12]	47.13[1.13]	48.57[1.48]	38.0[0.15]	12.4
VI(HT)	0.7344	11.95[0.32]	19.72[0.99]	21.39[0.84]	120.0[2.14]	12.1
VII(HD:HT=1:1)	0.7557	9.11[0.11]	47.05[1.55]	49.33[1.76]	23.0[0.13]	11.8
VIII(HD:HT=2:1)	0.7630	10.43[0.16]	23.55[0.96]	25.44[1.32]	7.73[.05]	12.3

A careful inspection of the results given in Table 3 indicates that the mechanical properties show a dependence on both the diol/triol ratio and the R-value. When the sample of composite propellant was subjected to uniaxial tensile stress, the deformation was accommodated in the binder matrix. The tensile properties of a composite propellant depend on the characteristics of the polymeric binder matrix, due to the changes in the crosslink density. The mechanical properties were predominantly determined by the crosslink density in the binder matrix, which decreases with an increase in the diol/triol ratio, as revealed by an increase in the strain capability and a decrease in the tensile strength and modulus. But the R-value also plays an important role in creating the crosslink and network chains of the binder matrix, which in turn determine the mechanical properties of the propellant. Since the mechanical properties of a composite propellant mainly depend on the binder-cure characteristics, which in turn determines the strain capability of the propellants, this is an important property of HTPB-TDI based propellant grains. Since most of the bonding agents are small, highly polar, organic diols or triols, which accumulate on the surface of the oxidizer particles and enable the propellant surface to have a dense layer of hydroxy groups at the point of TDI addition. Upon addition of TDI, the rapidly reacting hydroxyl groups of the network forming agents, immediately propagate the polymerization to establish a two and three dimensional network as the reaction proceeds, and the propellant attains flow characteristics and viscoelasticity.

The following points have emerged from this investigation.

1. Irrespective of the R-value and the nature of the diols and triols, propellants having a diol/triol ratio of 1:1 (composition III, VII) give very high strain capability (~50%) with moderately high T.S. (~9 kg/cm^2).

2. Composition V (HD) has a higher strain capability than composition I (BD), though it has a higher R-value. The reason for this may be the formation of longer carbon chains. In this case the influence of the R-value is less significant, but its effect can be seen in terms of a higher tensile strength.
3. In composition VIII, there is a smaller elongation, though the diol/triol ratio is higher than in composition VII, but at the same time the R-value has also been increased to 0.7630. The combined influence of a higher diol/triol ratio and R-value causes a decrease in the elongation and an increase in T.S. A similar trend was also observed for compositions III and V.
4. Another observation made from Figure 1 is that the propellant with bonding agent composition VI, although having a high R-value has a higher T.S., but at the same time the enhancement in elongation can be attributed to the longer carbon chain in HT, which here acts as both chain extender and cross linker.

Hence to achieve the desired mechanical properties for a propellant, without compromising the physical and ballistic properties, three major parameters can be optimized:

1. Selection of cross linker and chain extender;
2. Adjustment of the NCO/OH ratio (R-value);
3. Variation of the ratio of diol to triol (chain extender/cross linker).

Conclusions

Careful formulation of the network forming agents is a good way of improving the mechanical properties of a composite propellant. In essence, good mechanical properties require the optimum combination of chain extender and crosslinker. This leads to the conclusion that under the influence of the R-value and the diol/triol ratio, the modulus, elongation and tensile strength vary with the composition of the network building agents. From all of the data listed in Table 3, it can be seen that the composition of the network forming agents can be optimised to achieve the desired mechanical properties for a specified application. The propellant compositions with network forming agent formulations II (TMP) and VI (1,2,6-HT) have very high modulus, of the order 120-124 kg/cm^2. By using 1,2,6-hexanetriol we obtained a very high modulus of 120 kg/cm^2, together with a high T.S. of 12 kg/cm^2. Hence this is an effective network forming agent for a free standing grain (cartridge loaded). Whilst formulations III (BD:TMP = 1:1), V (HD) and VII (HD:HT = 1:1) impart high elongation to the propellant, of the order of 48-50%, with a T.S. of 9-11 kg/cm^2 and a modulus of

23-38 kg/cm^2, 1,6-hexanediol imparts very good elongation with a sufficiently high T.S. and modulus of the propellant. Hence this can be used for a case bonded composite propellant.

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