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Influence of Bicurative on Processibility of Composite Propellant

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ABSTRACT

A new series of composite propellant compositions, based on ammonium perchlorate, hydroxy-terminated polybutadiene and having metallic fuel as aluminium powder, have been developed. Pressure cast-cum-cured compositions have also been developed with toluene diisocyanate (TDI), isophorone diisocyanate (IPDI), and a mixture of both curatives, i.e., TDI and IPDI, respectively, to study their effect on processibility, mechanical and ballistic properties of the compositions. The data indicate that the compositions based on bicurative have a pot life of 7 - 8 h, viscosity build up is from 13280 poise to 14080 poise after 4 h, and the smooth processibility of the slurry is enhanced. Further, the mechanical properties are in the range 12.2 kg/cm^2, 40.2 kg/cm^2, and 40.2 per cent for tensile strength, E-modulus and elongation, respectively, and burn rate is almost the same, i.e., 16 ±0.5 mm/s.

Keywords: Composite propellants, ammonium perchlorate, bicurative, hydroxy-terminated polybutadiene, toluene diisocyanate

1. INTRODUCTION

Hydroxy-terminated polybutadiene (HTPB)- based solid rocket propellants are currently being used in space as well as in different ongoing missile programmes[1]. The low viscosity and low specific gravity along with high fuel value of HTPB makes it attractive to enable higher solid loading. The HTPB pre-polymer used for propellant slurry mixing is cured with a difunctional isocyanate curative. The urethane linkages -*NH COO*- formed by the -*NCO* with -*OH* reaction is chemically stable and is able to impart flexibility to the cured binder and makes the polymer an ideal elastomer[2]. A number of diisocyanates, like toluene diisocyanate (TDI), isophorone diisocyanate (IPDI), hexamethylene diisocyanate (HMDI), diphenylmethane diisocyanate (MDI) and 4,4-dicyclohexylmethane diisocyanate (H_{12}MDI) have been reported and used for HTPB system[3,4]. However, the most commonly used curative for the HTPB pre-polymer is TDI. The reactivity of TDI is comparatively more than other curatives except MDI and due to this, the pot life of TDI-cured propellant is only in the order of 4-5 h. IPDI is another curative which is preferred to TDI mainly on merits of its slow reactivity, resulting in much extended pot life, i.e., 15-18 h as well as low toxicity[5-7].

Also, there is increasing trend to substitute TDI with other curatives in composite propellant based on HTPB. For structural integrity of grains, IPDI may not be a suitable curator for a case-bonded motor. The thermal stresses in propellant grains are higher as the curing temperature is generally 70 °C. The curing temperature of a composition based on TDI is less as the reactivity is higher compared to IPDI. Owing to this, a new curative system has been conceived and utilised as bicurative

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system, means a mix of two curatives of high reactivity and low reactivity to overcome the disadvantage of TDI as a curative offering less pot life in a composite propellant formulation having trimodal ammonium perchlorate (AP) along with burn rate catalyst during pressure casting. The bicurative system has TDI and IPDI in 70:30 ratio and both are added individually. The pattern of addition of bicurative system followed is first adding IPDI followed by TDI. The pressure casting not only provides voids-free grains but also higher density as well as higher performance in comparison to gravity casting under vacuum. This technique is mostly employed for low-calibre grains. However, in some missile system, this technique is being used for the manufacture of pyrogen igniter.

The main objective to study this system was to develop a composition having moderately higher pot life (7-8 h) compared to TDI (4-5 h) and also to avoid IPDI system with pot life (13-15 h) having viscosity build-up almost not changing too much so that this system can be used for pressure casting where moderately higher pot life as well as 14,000-18,000 poise viscosity were the prime requirements.

In the present study, the influence of bicurative system in trimodal AP composite propellant formulations has been reported. Also, evaluation of viscosity build-up, mechanical and ballistic properties of pressure cast-cum-cured compositions.

2. EXPERIMENTAL

2.1 Materials

Ammonium perchlorate procured from ammonium perchlorate experimental plant (APEP), Alwaye (India), > 99 per cent pure, was used in trimodal distribution having particle size 300 mm, 60 mm and 6 mm, respectively. HTPB, manufactured by the free radical solution polymerisation[8] with Mn^{-} 2600 along with hydroxyl value of 43 mg *KOH*/g, was also procured from trade. Aluminium powder of ultrafine pyrotechnique grade was procured from Metal Powder Company, Madurai (India) and used as such. Dioctyl adipate (DOA), toluene diisocyanate (TDI), and isophorone diisocyanate (IPDI)[9] used as plasticiser and curatives, respectively, were procured from trade. Other ingredients such as *N*-phenyl-2-naphthylamine (NONOX-D), trimethylol propane (TMP), 1,4-butanediol (nBD), ferric oxide and copper chromite were also procured from trade and used as such.

The particle size of solid ingredients was determined by Malvern Particle Size Analyser model 2600C in non-aqueous medium. The viscosity build-up was determined by Brookfield Viscometer model HBT dial type. The density of cured grains was determined by Archimedes principle. The mechanical properties like tensile strength[10] elongation and E-modulus of cured propellant samples were evaluated on uniaxial tensile mode. Dumbbells were tested on tensile testing machine, Instron 1185 conforming to ASTM D638 at a cross-head speed of 50mm/min at ambient temperature. Solid strand burn-rate (SSBR) was determined using acoustic emission technique at 70 kg/cm^2 pressure in nitrogen atmosphere. The results reported here are the average value of five tested samples.

Further, all the compositions were analysed for their homogeneity, solid loading percentage of AP, and aluminium by following the standard method.

2.2 Procedure

The experimental mixing of different composite propellant formulations was carried out at 60 kg batch level in planetary vertical mixer. The general outline of preparation of 83/17 compositions is described herein.

(a) The liquid ingredients, (HTPB, DOA & Adduct) antioxidant and burn-rate modifiers were charged into mixer and the whole mass was mixed well for half an hour followed by vacuum mixing for another half an hour to drive out entrapped air.

(b) Then, ultrafine aluminium powder was added in two equal instalments. Ammonium perchlorate in trimodal particle size distribution was added in such a way that homogeneous mixing temperature was maintained at 45 ± 1 ^{o}C.

(c) After addition of complete solid portion, the mixing of composition was put under vacuum for half an hour.

(d) In the meantime, the temperature of mixer was brought down to 37 ± 0.5 °C to avoid exothermic reaction on addition of bicurative.

(e) At this stage, the bicurative consisting of TDI and IPDI, in the ratio of 70:30 was weighed separately. The portion of IPDI was added first followed by 10 min mixing.

(f) Then TDI was added and the whole system was further mixed for another 40 min.

(g) The composition was pressure cast into specially designed 200 mm (ID) mould and cured at 50 °C for 5 days. The cured composition was used for the determination of solid strand burn rate (SSBR) as well as evaluation of its different properties.

The other compositions using TDI and IPDI separately were also prepared and pressure cast by following the procedure described above. In all the experiments, the equivalent molar ratio of *OH*/*NCO* was 1: 0.84 and was kept constant by taking into consideration equivalent weights of TDI and IPDI. The total percentage composition was adjusted using coarse AP. The ratio of *R* value, i.e., *OH*/*NCO* has been kept as 1:0.84 for all the experiments and excess of *OH* value will remain unreacted and give better elongation to the grain.

3. RESULTS AND DISCUSSION

The three different composite propellant compositions were prepared using AP as oxidiser (trimodal form), aluminium powder as a metal fuel, and HTPB as binder-cum-fuel cured with TDI, bicurative (TDI and IPDI) and IPDI, respectively, along with process aids like dioctyl adipate (DOA), burn-rate modifiers (Fe_2O_3 and $CuO.Cr_2O_3$) and antioxidant (NONOX-D). The different compositions prepared in this way are presented in Table 1. These compositions were analysed for solid loading content and viscosity build-up. Under identical conditions, all the samples were cast in test controls. Mechanical and ballistic properties of different compositions were also evaluated and results reported are based on the average value of 5 trials each.

During this study, initially the viscosity build-up of gum stock was studied using HTPB and DOA with TDI, IPDI, and a mixture of both at 50 °C and the data obtained are presented in Table 2. It is clear from the Table 2 that the viscosity build-up rate is much faster in the case of HTPB-TDI as compared to HTPB- IPDI system, while a remarkable build-up rate was observed in the case of bicurative system.

Table 1. Details of different composition formulation

Ingredient (%)	TDI-based composition I	IPDI-based composition II	Bicurator-based composition (TDI + IPDI) (70 : 30) III
HTPB	11.90	11.90	11.90
DOA + others	4.17	4.17	4.17
AP	80.25	80.02	80.18
Al (ultrafine)	2.38	2.38	2.38
Curator	0.85	1.08	0.92
Copper chromite and ferric oxide	0.45	0.45	0.45

Table 2. Viscosity build-up based on different curatives (gum stock) at 50 °C

Time (min)	TDI (Poise)	IPDI (Poise)	Bicurator (TDI + IPDI) percentage (Poise)		
			70 : 30	50 : 50	30 : 70
0	8.00	5.60	6.81	6.26	6.03
60	12.60	6.45	9.06	7.28	6.96
120	20.46	7.23	12.72	10.40	8.16
180	25.43	8.16	16.45	12.80	9.48
240	36.10	9.68	20.46	15.60	11.00
300	40.79	11.00	25.43	21.80	13.65

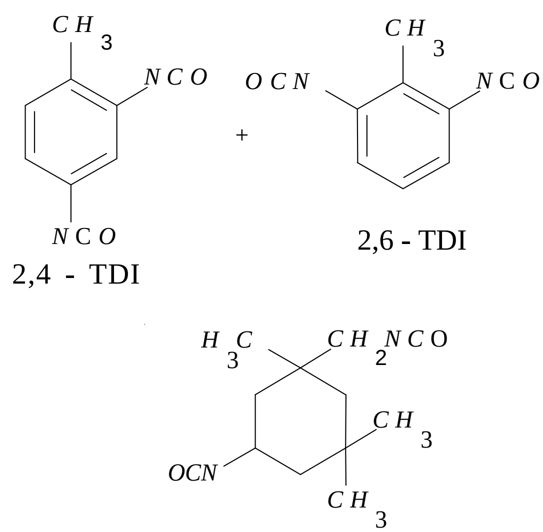
The effect of bicurative was further studied on the same system using different proportions of IPDI and the data are presented in Table 2. It is clear from Table 2 that bicurative containing 70 per cent TDI and 30 per cent IPDI showed remarkable enhancement in viscosity build-up which is a very good characteristic property of the resin system for the application of pressure casting technique[10]. Furthermore, a viscosity build-up in the range of 14000-18000 poise is considered good pressure cast slurry. In view of this, the presence of IPDI acts as plasticiser for the pressure casting system as it requires higher temperature for curing. On addition of less quantity of TDI (30 %), the reaction is further slowed down and thus lowered the overall viscosity in the case of gum stock studies.

Based on these experimental results, the bicurative containing 70 per cent TDI and 30 per cent IPDI, was chosen for further experimentation.

3.1 Effect of Curatives on Viscosity Build-up

The effect of TDI, IPDI, and bicurator on viscosity build-up is presented in Table 3. It is clear from Table 3 that viscosity of slurry is more in the case of TDI and lowest in IPDI while a moderate value in the case of bicurative. The value of end of mix (EOM) viscosity was found to be 18240 poise at slurry unloading temperature based on TDI curative while it was only 6560 poise with IPDI in the same condition. Further in the case of bicurative, EOM viscosity was found to be 13280 poise, giving a clear cut signal that viscosity build-up is slowest with IPDI system while faster with TDI system. Furthermore, the viscosity build-up was also studied at a constant temperature, i.e., 40 °C for 4 h. The data reveal that there is no change in viscosity using IPDI system while a drastic increase in viscosity was observed with TDI system and after 4 h, the viscosity reaches to 22400 poise at 40 °C. The viscosity build-up with bicurative was almost negligible, i.e., 13920 poise after 4 h.

The chemical structure of curative is responsible for the reaction rate with HTPB. Since TDI is available in 2,4 and 2,6 isomers form in the ratio of 80:20, the reactivity of isomers is different. In the same way, IPDI contains primary and secondary -*NCO* groups which also differ in their reactivity. The chemical structure of TDI and IPDI is presented to justify the findings.



IPDI

Chemical structure of TDI and IPDI

The reaction of TDI and HTPB is as follows:

$$HO\text{-}(CH_2\text{-}CH{=}CH\text{-}CH_2)_n\text{-}OH + R\text{-}NCO \rightarrow HO\text{-}(CH_2\text{-}CH{=}CH\text{-}CH_2)_n\text{-}OCONH\text{-}R$$

Urethane linkage

Table 3. Viscosity build-up with different curatives

Viscosity (Poise)	TDI-based composition I	IPDI-based composition II	Bicurative-based composition III
EOM viscosity at 37 ^{0}C	18240	6560	13280
Viscosity at 40 ^{0}C after 1 h	18880	6880	13600
Viscosity at 40 ^{0}C after 2 h	19840	6880	13920
Viscosity at 40 ^{0}C after 3 h	20320	7200	13920
Viscosity at 40 ^{0}C after 4 h	22400	7380	14080

It is clear from the chemical structure that the reactivity of TDI with *OH* group is very fast (probably due to resonance-stabilised benzene ring) while IPDI shows a very slow reaction (due to presence of primary and secondary isocyanates groups as well as alicylic ring)[11,12]. The reactivity of IPDI is also affected by steric hindrance produced by methyl groups present in the molecule. This property of IPDI provides more pot life to the slurry composition, which is helpful during casting. Also, the IPDI acts as plasticiser for propellant slurry during propellant processing because IPDI/*OH* reaction rate becomes significant only at an elevated temperature during curing.

All the premix compositions were analysed for solid loading content to check the homogeneous mixing and their distribution. The obtained data of AP are in good agreement with the actual quantity used. Further, the percentage of aluminium calculated by subtracting binder and AP content from the whole also agrees with the quantity used. The density of cured sample of different compositions was determined by Archimedes principle. The data indicate that there is no change in density of compositions whether the composition is based on TDI or IPDI or bicurative systems.

3.2 Mechanical and Ballistic Properties

The mechanical properties of the cured compositions were evaluated on dumbbell (as per IS-3400) using tensile testing machine–Instron and data obtained are presented in Table 4. It is clear from the table that tensile strength of the TDI system is on higher side in comparison to IPDI system whereas a marginal improvement is obtained in the case of a bicurative system in comparison to IPDI system. Thus, tensile strength of TDI system is in the range of 15-20 kg/cm^2 while it is 12-14 kg/cm^2 in the case of bicurative. The IPDI system shows 10-12 kg/cm^2 of tensile strength. In the same way, higher E-modulus values were obtained for TDI system whereas for IPDI and bicurative systems, it is found to be 45.1 kg/cm^2 and 40.2 kg/cm^2, respectively. The values for E-modulus for TDI system is in the range of 55-60 kg/cm^2 and 50-55 kg/cm^2 in the case of bicurative while for IPDI system it is almost 45-50 kg/cm^2. The higher E-modulus in the case of TDI system may be due to aromatic ring, which resists the applied force to some extent. The values of percentage of elongation are obtained reverse to the tensile strength and E-modulus. The percentage of elongation is less in the case of TDI system and high in the case of IPDI system while a slight enhancement in the value of elongation against TDI system is found in the case of bicurative system (i.e., 30-35 % for TDI system, 45-50 % for IPDI system, and 35-40 % for bicurative system). The above data clearly support the effect of aromatic and alicyclic nature of curatives which are responsible for high or low percentage of elongation of the compositions.

The SSBR, the main ballistic property of the propellant composition, was determined at 70 kg/cm^2 pressure in inert atmosphere for the propellant strands using acoustic emission technique and the data obtained are presented in Table 4. It is clear from the table that burn rates of all the compositions are almost the same, i.e., 16±0.5 mm/s. This reveals a very good homogeneity of the compositions.

The newly developed bicurative having 70 per cent TDI and 30 per cent IPDI fulfills the need to cast a void-free grain with reproducible mechanical as well as ballistic properties. In further trials, it was observed that spectrum of mechanical properties can be achieved by tailoring TDI/IPDI ratio.

Table 4. Mechanical and ballistic properties of the compositions

Composition	Homogeneity (%)	Tensile strength (kg/cm^2)	E-modulus (kg/cm^2)	Elongation (%)	SSBR at 70 kg/cm^2 (mm/s)
TDI-based composition I	80.15	17.2	57.6	34.5	16.0
IPDI-based composition II	79.90	10.9	45.1	47.1	15.9
Bicurator-based composition III	80.15	12.2	40.2	40.2	16.1

4. CONCLUSION

A new bicurative system containing TDI and IPDI (70:30 ratio) has been developed and its properties have been compared with TDI and IPDI based systems. The data indicate that this system has 7-8 h pot life as compared to pot life of TDI system (4-5 h) whereas viscosity build-up values for 4 h are 13280 poise to 14080 poise at 40 °C, revealing an edge over conventional TDI-based systems for smooth processing of the slurry. Furthermore, the developed bicurator system has been utilised successfully in pressure casting technique where higher pot life (7-8 h) and low viscosity build-up (14000-18000 poise) are of prime interest.

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