

Studies on the effect of plasticiser and addition of toluene diisocyanate at different temperatures in composite propellant formulations

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ABSTRACT

Different composite propellant mixtures have been prepared using ammonium perchlorate, aluminium powder and hydroxyl terminated polybutadiene by varying the percentage of plasticiser and addition of toluene diisocyanate at different temperatures, and studied their different properties such as viscosity build-up, mechanical and ballistic properties and sensitivity. The data on different plasticiser level indicate that on decreasing the plasticiser content, there is a significant enhancement in end of mix viscosity, tensile strength and modulus while elongation decreases drastically. The data on sensitivity of the studied mixtures reveal that on decreasing the percentage of plasticiser, the sensitivity increases, accordingly. Further, the data on the effect of addition of TDI at different temperatures (35–60 °C) infer that on increasing the addition temperature of TDI there is a decrease in end of mix viscosity i.e. 800 Pa s at 35 °C to 448 Pa s at 60 °C. Moreover, there is no effect on mechanical and ballistic properties on higher temperature addition of TDI was observed.

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1. Introduction

Hydroxyl terminated polybutadiene (HTPB) based propellants are the most important class of solid rocket composite propellants being used in various missile programmes [1]. The basic ingredients of composite propellant are an oxidizer such as ammonium perchlorate (AP), a metallic fuel like aluminium powder and a liquid binder such as HTPB. The composite propellant also contains certain additives such as plasticiser, burning rate catalysts, bonding agents and curatives. The unbonded liquid additives such as plasticisers are bound to migrate towards the propellant interfaces, is considered as an important ageing behaviour [2,3], which may affect ballistic properties of grain due to change in composition and structural integrity as well as mechanical properties [4].

Plasticisers, which are added to the mixture to increase their plasticity and flow behaviour, are basically moderate molecular weight species. These are also responsible for lowering the glass transition temperature (T_g) of the binder/mixture. As plasticiser

species are unbonded in nature they migrate in the propellant adjacent to the insulation, thus, responsible for deterioration of mechanical properties of mixture on ageing [5,6]. The migration of plasticisers [7–10] continues to attract attention in understanding the thermodynamic, structural, mechanical and ballistic implications in composite propellants [11–13]. Therefore, internally or self-plasticised binders are highly desirable to overcome such potential problems.

In continuation to this work further, composite propellant mixtures based on HTPB is generally cured with bi-functional isocyanates [14] to achieve required mechanical properties. Moreover, based on the casting parameters and pot life of mixtures different curatives such as toluene diisocyanate (TDI), isophorone diisocyanate (IPDI), hexamethylene diisocyanate (HMDI) and methylene diphenyl diisocyanate (MDI) are being used, however, most commonly used curative is TDI [15,16].

Further to this, there is always a demand for high burn rate mixtures having solid loading up to 90% for specific mission. In such conditions, casting of propellant slurry with high solid loading is practically difficult due to high viscosity of the mixtures. Moreover, composite propellant mixtures are heterogeneous in nature and binders used in such systems are bi-functional and always cured with bi-functional curatives (TDI). Because of the chemical reaction between –OH and –NCO groups of HTPB and TDI, respectively, the nature of mixtures becomes non-Newtonian [17,18]. Thus, the viscosity of slurry/mixture increases on increasing time indicates time dependent mixture. This study further reveals that rheology of composite propellant slurry is also influenced by the particle

Abbreviations: EOM, end of mix; HTPB, hydroxyl terminated polybutadiene; DOA, dioctyl adipate; TDI, toluene diisocyanate; IPDI, isophorone diisocyanate; HMDI, hexamethylene diisocyanate; MDI, methylene diphenyl diisocyanate; AP, ammonium perchlorate; Nonox-D, *N*-phenyl-2-naphthylamine; SSBR, solid strand burn rate.

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Nomenclature

E	modulus
\emptyset	constant
x	DOA in the composition
X	solid loading (%)
γ	burn rate at 68.6×10^5 Pa (mm/s)

Greek letters

μ_T	1/2 h viscosity at 400 °C
ρ	density (g/cc)

size, shape and distribution of solid particles, solid loading levels, packing fraction and over all the level of plasticisation [19].

In order to achieve high solid loading and better processibility of non-Newtonian composite propellant mixtures, a successful attempt has been carried out to develop such compositions/mixtures, which have less percentage of plasticiser to reduce migration at the propellant interfaces. Further, on reduction of plasticiser from the mixture, the viscosity of the slurry increases drastically. To avoid the enhancement of the viscosity of the mixture, addition of TDI at higher temperatures [20] in mixture has also been studied to have comparatively low viscosity and processable pot life.

In the following section, we report the effect of plasticiser and addition of TDI at different temperatures on the viscosity build-up, mechanical and ballistic properties of composite propellant formulations.

2. Experimental

2.1. Materials

AP, procured from Ammonium Perchlorate Experimental Plant (APEP), Always (India), was used in trimodal distribution having average particle size of 300 μm , 60 μm and 6 μm , respectively. HTPB, manufactured by free radical solution polymerization [21] having number average molecular weight (Mn) 2300–2900, was procured from trade. Aluminium powder, having average particle size $15 \pm 3 \mu\text{m}$, was procured from 'The Metal Powder Company Limited', Madurai (India) and used as such. Bis-(2-ethyl hexyl) adipate or dioctyl adipate (DOA) and TDI used as plasticiser and curative, respectively, were procured from trade. Other ingredients such as *N*-phenyl-2-naphthylamine (Nonox-D), 1,1,1-trimethylol propane, 1,4-butanediol, ferric oxide and copper chromite used as antioxidants, cross linking agents and burn rate modifiers, respectively, 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 the cured propellant mixture was determined by Archimedes principle using a density attachment with 0.1 mg precision balance of Mettler Toledo make. The mechanical properties like tensile strength, % elongation and *E*-modulus of cured propellant mixtures were evaluated using dumb-bells on tensile testing machine, Instron 1185 conforming to ASTM D638 at a cross head speed of 50 mm/min at ambient temperature. Solid strand burn rate (SSBR) was determined using acoustic emission technique in nitrogen atmosphere at 70 kg/cm² pressure. The calorimetric value (cal-val) of the mixture was evaluated by Parr Bomb Calorimeter using 1 g of sample.

Deflagration temperatures [22] were determined by heating 0.02 g of mixture in a glass tube in a Wood's metal bath at a heating rate of 5 °C/min and the temperature at which sample

got ignited/decomposed was recorded as deflagration temperature. The impact sensitivity was determined by "Fall Hammer" method using 2 kg drop weight and friction sensitivity was determined on Julius Peter's apparatus following standard methods [23].

All the mixtures were analysed for their homogeneity, solid loading percentage of ammonium perchlorate and aluminium as per standard methods [24].

2.2. Procedure

2.2.1. Preparation of composite propellant mixture

All the experimental mixing of composite propellants were carried out at 15 kg batch level in a vertical planetary mixer. A general procedure for the preparation of composition is described in detail.

HTPB and other liquid ingredients (except curative) were charged into vertical planetary mixer. It was mixed well for half an hour followed by vacuum mixing for another half an hour to drive out entrapped air. After this, aluminium powder ($15 \pm 3 \mu\text{m}$) was added in two steps. Ammonium perchlorate (powder) was added in such a way that homogenous mixing could take place. The overall mixing temperature was maintained at $55 \pm 1 \text{ }^\circ\text{C}$. After addition of complete solid ingredients, the mixing of mixture was carried out under vacuum for half an hour. In the meantime, the temperature of the mixer was brought down to $37 \pm 1 \text{ }^\circ\text{C}$. At this stage, TDI was added and it was further mixed for another 35 min. The mixture was cast into 200 mm (ID) mould and cured at 50 °C for 5 days and used for evaluation of its different properties.

The other mixtures, based on plasticiser or without plasticiser as well as addition of TDI at different temperatures, were also prepared and cast by following the same procedure.

3. Results and discussion

Different composite propellant mixtures were prepared using ammonium perchlorate as an oxidizer (in trimodal form), aluminium powder as a metal fuel ($15 \pm 3 \mu\text{m}$) and HTPB as a binder-cum-fuel along with process aids like DOA, burn rate modifiers (Fe₂O₃ and copper chromite) and an antioxidant (Nonox-D). Initially, the percentage of DOA was kept 4.05% in the mixture and subsequently decreased to 2.2%, 1.6% and 0% with proportional increase in ammonium perchlorate. Further, to study the effect of addition of TDI at different temperatures, initially it was added at 35 °C followed by incremental increase of temperature by 5 °C from 35 °C to 60 °C. The different mixtures prepared in this fashion are presented in Tables 1 and 2, respectively. The prepared mixtures were used for analysis of solid loading content and viscosity build-up. The mechanical, ballistic properties and sensitivity of mixtures were also evaluated, and results reported are an average values of five trials each.

3.1. Effect of plasticiser content and temperature on viscosity build-up

The effect of plasticiser on viscosity build-up is presented in Fig. 1. It is clear from the figure that viscosity of slurry increases

Table 1
Formulation details of mixtures based on different plasticiser level

S. no.	Ingredient (%)	Composition I	Composition II	Composition III	Composition IV
1	HTPB + TDI + others	11.4	11.4	11.4	11.4
2	DOA	4.05	2.0	1.5	0.0
3	AP	67.55	69.6	70.1	71.6
4	Al	17	17	17	17

Table 2

Formulation details of higher temperature addition of toluene diisocyanate (TDI)

S. no.	Ingredients	Addition of TDI @ 35 °C	Addition of TDI @ 40 °C	Addition of TDI @ 45 °C	Addition of TDI @ 50 °C	Addition of TDI @ 55 °C	Addition of TDI @ 60 °C
1	HTPB	10.085	10.085	10.085	10.085	10.085	10.085
2	DOA + others	3.22	3.22	3.22	3.22	3.22	3.22
3	AP	68	68	68	68	68	68
4	Al	18	18	18	18	18	18
5	Curative	0.695	0.695	0.695	0.695	0.695	0.695

as percentage of DOA decreases. It is also clear from this study that plasticiser plays an important role in end of mix (EOM) viscosity and build-up. The pattern of viscosity build-up is necessary for finalization of the optimum level of plasticiser for vacuum/gravity casting of slurry. For high viscosity slurry, which contains low level of plasticiser or high percentage of solid loading, pressure casting may be applied to achieve void free grain having higher density as well as higher burn rate. Further, the effect of solid loading on viscosity build-up was also studied and data obtained are shown in Fig. 1. It is clear from the figure that higher the solid loading (in place of plasticiser) higher the EOM viscosity as well as build-up.

The effect of plasticiser on viscosity build-up of different mixtures is also given in Fig. 1. It is clear from the figure that on increasing the temperature of mixture up to 40 °C, there is a marginal decrease in viscosity was observed while viscosity decreases drastically at 60 °C for the same mixture after half an hour. This pattern is also observed with HTPB resin having viscosities 4.0–6.5 Pa s at 40 °C and 0.9–1.6 Pa s at 60 °C reveals that at higher temperature the entangled segments of HTPB resin get separated, thus decreasing the cohesive forces between HTPB resin segments, which is responsible for decrease in viscosity of HTPB. The same finding is also observed in this study as there is a competing effect on slurry rheology at elevated temperatures. Thus, at 60 °C with higher percentage of plasticiser (4.05%), the viscosity build-up was not effective even after 4 h. However, on reducing the percentage of plasticiser, viscosity build-up of the mixture was very effective. Further, there is a drastic rise in viscosity build-up was observed for the mixture having 0% of plasticiser, indicating enhanced reaction rate between OH and NCO groups of HTPB and TDI. Also, the increase in viscosity of the mixtures at lower plasticiser level is due to the absence of blanketing effect of plasticiser. The reduction in viscosity at elevated temperatures is mainly due to the mobility of segmental chains of HTPB, thus causes reduction in cohesiveness of HTPB segments and reduces the reaction rate between OH and NCO groups.

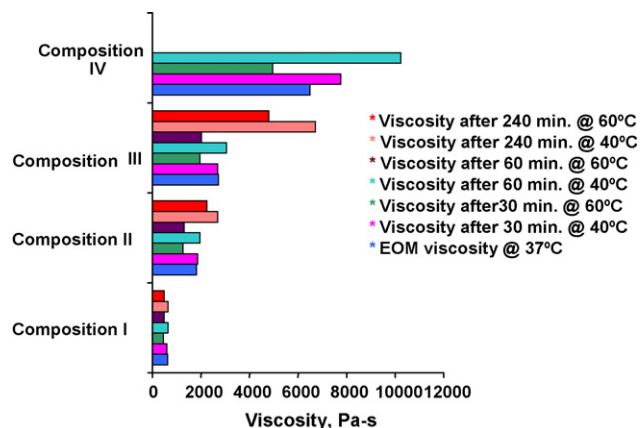
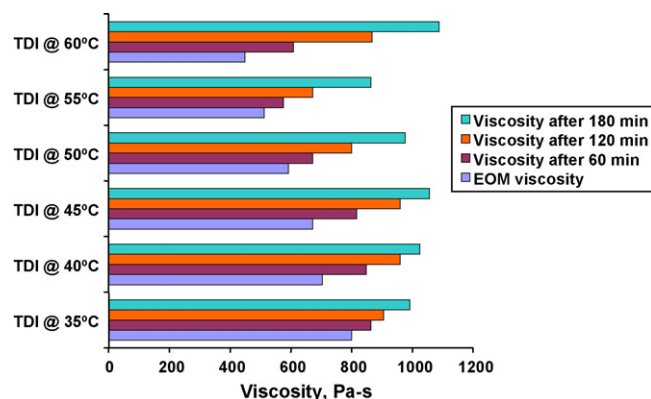
Furthermore, the data on effect of addition of TDI at higher temperature on viscosity build-up is presented in Fig. 2. It is clear

from the figure that viscosity of mixture decreases as temperature of TDI addition increases. Thus, the value of EOM viscosity was found to 800 Pa s when TDI was added at 35 °C. It subsequently decreases when temperature of addition of TDI increases i.e. the EOM viscosities were found 672 Pa s and 448 Pa s when addition of TDI was carried out at 45 °C and 60 °C, respectively. The decrease in viscosity is due to decrease in cohesive forces between polymeric chains which is responsible for the segmental mobility of HTPB and less availability of OH group to NCO group for the reaction to form urethane linkage on increasing the addition temperature of TDI. Further, DOA which was used as a plasticiser, also responsible for decreasing the viscosity, as it penetrates in between the polymeric chains. The penetration of DOA thus reduces cohesive forces between the polymeric chains leading in reduction of viscosity and enhancement of segmental mobility.

3.2. Homogeneity and density aspects

All the premix mixtures were analysed before addition of TDI for the homogenous mixing of the mixture as well as for solid loading content, and data obtained are presented in Fig. 3. Ammonium perchlorate content was analysed by dissolving binder part in toluene followed by addition of formaldehyde, which was further titrated with standard NaOH solution [24]. The data indicate that content of ammonium perchlorate was in good agreement with theoretical values. The percentage of Al was obtained by subtracting binder and AP content from the whole mixture. It is clear from the data that the dispersion of AP is homogeneous and solid content as per specified limit.

The density of cured mixtures was determined by Archimedes principle and data obtained are presented in Fig. 4. The data indicate that as solid loading increases the density of mixture also increases. Thus, the density of 85/15 mixture was found to 1.74 g/cc while densities of 87/13, 87.5/12.5 and 89/11 mixtures are 1.78 g/cc, 1.80 g/cc and 1.85 g/cc, respectively, indicating a very good compactness of the mixtures. The increase in density with increase in solid loading

**Fig. 1.** Effect of plasticiser level on viscosity build-up @ 40 °C and 60 °C temperatures.**Fig. 2.** Effect of curative on viscosity build-up of mixtures at different temperature.

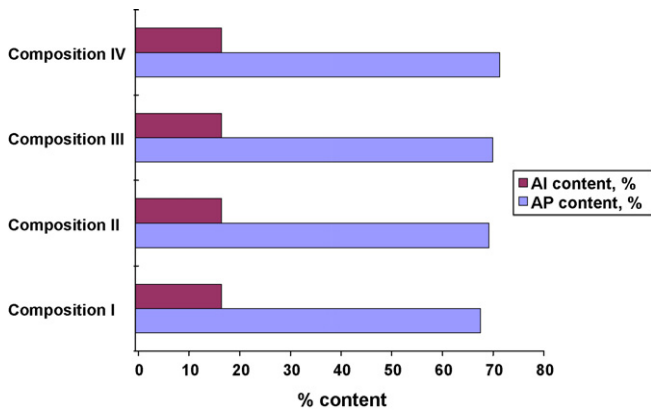


Fig. 3. Data on homogeneity of mixtures at different plasticiser level.

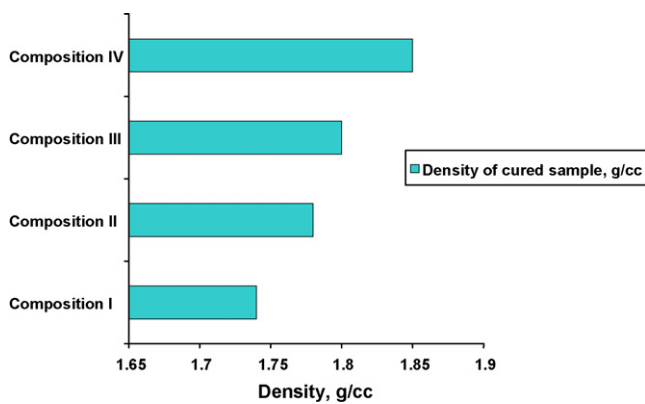


Fig. 4. Data on density of cured sample at different plasticiser level.

can also be expressed in the form of following correlation

$$\rho = 0.271X - 0.5654$$

where ρ is the density (g/cc) and X is the % of solid loading.

3.3. Mechanical and ballistic properties aspects

The mechanical properties of the cured mixtures were evaluated on dumb-bell (as per IS-3400) using tensile testing machine, Instron and data obtained are presented in Fig. 5. It is clear from the figure that tensile strength of the mixture increases from 85% to 89% solid loading which is in the order of $7.86\text{--}18.18 \times 10^5$ Pa while reverse trend is observed in the case of elongation where the % elon-

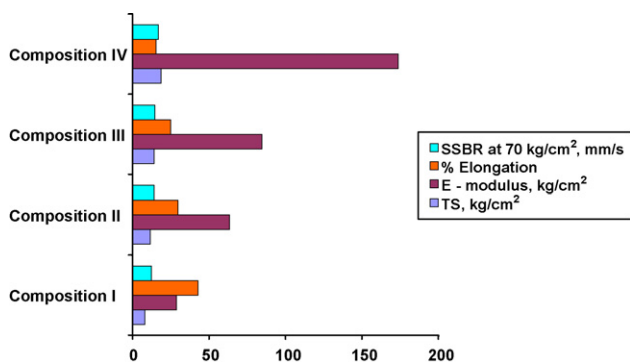


Fig. 5. Data on mechanical and ballistic properties of the mixtures at different plasticiser level.

gation for 85% solid loading is 42.8 which subsequently decreases to 15.45 for the mixture containing 89% solid loading. The value of E -modulus, which is the initial slope of load versus extension curve, is drastically increased from 28.13×10^5 Pa to 170.13×10^5 Pa for the composition containing 85% and 89% solid loading, respectively. It is also clear from the figure that as the viscosity increases the modulus rises exponentially [25]. This relationship can be expressed in the form of the following equation.

$$E = \frac{\mu_T^{0.75}}{\emptyset}$$

where E is modulus, μ_T 1/2 h viscosity at 40°C and \emptyset is a constant.

Thus, it is clear from this study that plasticiser content affects the mechanical properties significantly. Since, OH/NCO ratio is same in all the mixtures, the increase in modulus may be attributed due to decrease in plasticiser content. Moreover, the behaviour of the mixtures having less or zero percentage of plasticiser indicates that plasticiser not only improves the processibility of mixture but also affects the mechanical properties as well as viscosity build-up. Furthermore, plasticiser also reduces cohesiveness forces between cross-linked chains and thus improves elongation capability.

Burn rate, the main ballistic property of the studied mixtures, was determined using acoustic emission technique at 68.6×10^5 Pa pressure in inert atmosphere and the data obtained are presented in Fig. 5. It is clear from the figure that burn rate increases on increasing the solid content. Thus, burn rate of the mixture containing solid loading up to 85% is 12.46 mm/s (plasticiser content is 4.05%) where as burn rate for other mixtures having solid loading 87%, 87.5% and 89.0% are found to 14.15 mm/s, 14.65 mm/s and 16.8 mm/s, respectively, at the same pressure. It is clear from the above findings that higher the percentage of DOA lowers the burn rate or vice versa. This finding can be represented by the following correlation.

$$\Upsilon = 16.8 - 1.07x$$

where Υ is burn rate, at 68.6×10^5 Pa (mm/s) and x is DOA in the mixture.

In continuation to this work further, the data obtained on addition of TDI at different temperatures on mechanical and ballistic properties are presented in Fig. 6. It is clear from the figure that no major change in mechanical and ballistic properties of the cured mixtures was observed on addition of TDI at different temperatures from 35°C to 60°C . This finding helps in optimization of addition of TDI at higher temperature without compromising mechanical and ballistic properties. Further to this, it also realises reduced viscosity providing a wide scope to process a rocket motor by conventional casting technique smoothly taking full account of pot life.

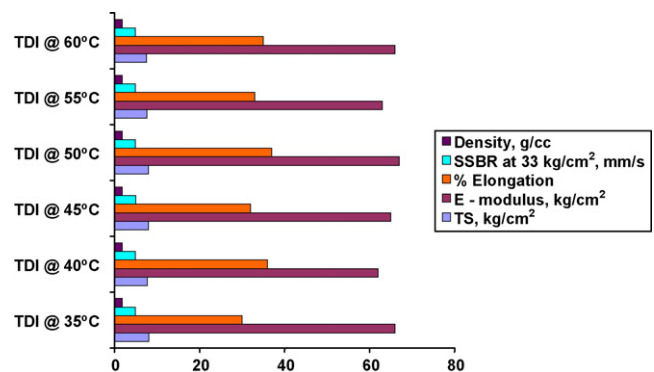


Fig. 6. Data on mechanical and ballistic properties of the mixtures at addition of different temperature of curative.

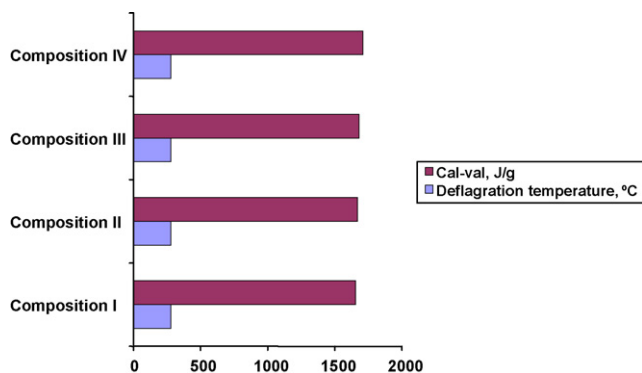


Fig. 7. Data on thermal properties of the mixtures at different plasticiser level.

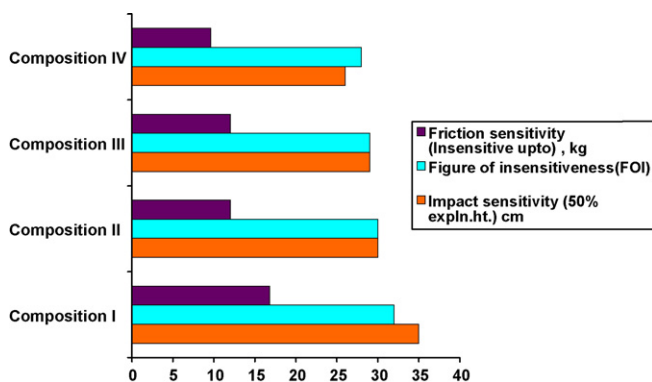


Fig. 8. Data on sensitivity of the mixtures at different plasticiser level.

3.4. Thermal and sensitivity properties

The thermal (deflagration temperature and calorimetric value) and sensitivity (impact and friction) properties of the studied mixtures are presented in Figs. 7 and 8, respectively. It is clear from Fig. 7 that deflagration temperature of all the studied mixtures are in the same range i.e. 278–279 °C further confirms good thermal stability of the mixtures. The calorimetric value of mixture containing 85% solid loading produces 1654 Cal/g whereas the mixture containing 87% solid loading produces 1668 Cal/g. Similarly, the cal-val of the mixtures containing 87.5% and 89% solid loading is found to 1688 Cal/g and 1710 Cal/g, respectively. The higher value of cal-val is mainly due to higher content of oxidizer in the mixture. The data on sensitivity (Fig. 8) indicate that mixture containing zero percent of plasticiser is more sensitive towards impact and friction (50% explosion height ~26 cm and insensitive to friction up to 9.6 kg) while the mixture containing 4.05% plasticiser is less sensitive (50% explosion height ~40 cm and insensitive to friction up to 16.8 kg) as it reduces the force of friction between ammonium perchlorate particles and aluminum powder (fuel).

4. Conclusion

Composite propellant mixtures having solid loading 85–89% with and without plasticiser and higher temperature addition of TDI have been successfully prepared and studied for viscosity build-up, mechanical and ballistic properties as well as for sensitivity aspects. The data on mixtures having different plasticiser level indicate that on decreasing the percentage of plasticiser in the mixture, there is an increase in EOM viscosity and burn rate. The mechanical and sensitivity properties of the mixtures were also influenced by

plasticiser level. Further, data on addition of TDI at different temperatures also reveal that on increasing the addition temperature of TDI from 35 °C to 60 °C, there is decrease in EOM viscosity. The decrease in EOM viscosity is found more effective in the range of 50–60 °C having processable pot life (3–4 h). However, there is no change in mechanical and ballistic properties of the mixture, was observed.

The prime interest of this study was to explore the utility of plasticiser free composition with higher solid loading (up to 89%) to get moderately high burn rate with processable pot life and acceptable mechanical properties. Moreover, casting of highly viscous slurry can be carried out either at higher temperature addition of TDI or by resorting to improvised technique like bottom casting of complicated web geometry where viscosity is the main concern.

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