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Effect of NCO/OH ratio and binder content with micro-AP on HTPB/AP/Al-based propellants mechanical properties

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Abstract. This study evaluates the ratio of Toluene di-isocyanate (TDI) functional group isocyanate (NCO) to the binder functional hydroxyl group (OH) in HTPB/AP/Al-based propellants on their mechanical properties, flow rate, and viscosity to determine the limitations of NCO/OH in the composition of solid propellants. The propellants consisted of hydroxyl-terminated polybutadiene (HTPB) polyurethane (PU), aluminum (Al) and tri-modal ammonium perchlorate (AP). The tri-modal AP consisted of 30% of coarse AP, 30% of medium AP, and 8% of fine AP. The ratio of NCO/OH varies from 0.73 to 0.85, with two binder percentages of 10.5% and 12%. An increase in NCO/OH ratio with 10.5% binder provided 20%, 95%, and 8 to 9% increments in UTS, modulus, and hardness, respectively. However, the propellant elongation, density, and flow rate decreased by 170%, 0.2%, and 11-12%, respectively. Viscosity increased 20% based on initial hour reading. The 12% binder provides 27%, 47%, and 5~6% an increment of UTS, modulus and hardness respectively. However, the propellant elongation, density, and flow rate decreased by 47%, 0.17% and 27%, respectively. The viscosity increased 30% based on initial hour reading. This study suggests the NCO/OH value of 0.77 and 10.5~11% binder content in propellant based on the mechanical properties, flow rate, and viscosity for better processing and pot life.

Keywords: flow rate; HTPB/AP/Al Propellant; mechanical properties; NCO/OH ratio; toluene di-isocyanate; viscosity

1. Introduction

Composite solid propellants are widely used in aerospace applications, particularly in solid rocket motors (SRMs), owing to their high energy density, good processing, and mechanical properties (Zhang *et al.* 2023). Much research has been carried out on liquid bi-propellants, hybrid rocket motors, and solid rocket motors (Nagata *et al.* 2014, Saito *et al.* 2017). The main components of solid composite propellants are fuel and oxidizers. Aluminum powder (Al) and ammonium perchlorate (AP) are examples of fuels and oxidizers, respectively, which are mostly used to provide high-energy combustion. The fuel and oxidizer were mixed in a matrix form using a binder. Instead of impacting the mechanical and chemical properties, propellant processing, and aging of the propellant, the binder also acts as a fuel that oxidizes during combustion. The binder itself serves as

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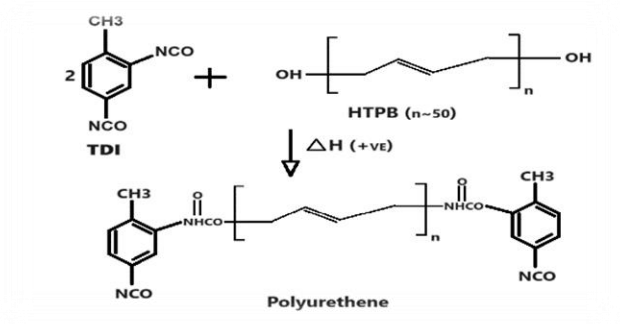


Fig. 1 Chemical reaction of the TDI and HTPB functional group (Quagliano Amado *et al.* 2022)

a propellant that contributes to the structural integrity and overall performance and improves the mechanical properties of the propellant (Chaturvedi and Dave 2019, Yaacob *et al.* 2023).

HTPB is commonly used as a binder for composite propellants. The HTPB binder system has been proven to be superior to other systems, as it allows high solids loading up to 86% weight without sacrificing the-process of preparing the solid propellant (Chen *et al.* 2017, 2023). HTPB is a polybutadiene-based pre-polymer used in solid propellants as a precursor for the polyurethane binder. Solid energetic charges and other additives are incorporated into the binder formed by the reaction between polybutadiene-based pre-polymers, normally hydroxyl-terminated polybutadiene (HTPB), and di- or poly functional isocyanates during the preparation of a solid composite propellant (Guo *et al.* 2018, Chaturvedi and Dave 2019, Lv *et al.* 2023). The solidification of the binder requires a small portion of curing agent or crosslinker. Although the amount of curing agent in solid propellant manufacturing is small, the effect of the curing agent on improving the physical properties, manufacturability, and aging of the propellant is tremendous. Isophorone diisocyanate (IDPI), 1,6-hexamethylene diisocyanate (HMDI), and toluene diisocyanate (TDI) have been used as curing agents for solid propellants (Sekkar and Raunija 2015). The literature has shown that TDI is the most reliable curing agent in comparison to IDPI and HMDI (Quagliano Amado *et al.* 2022). Studies have shown that the ultimate tensile strength (UTS) and modulus value of TDI are better than those of IDPI and HMDI (Sekkar and Raunija 2015). However, TDI is highly toxic and volatile under atmospheric pressure, and is harmful to humans (Kim *et al.* 2022). Therefore, special care is needed while handling TDI. In addition, the combustion of solid propellants containing TDI may produce poisonous gases. Although TDI can produce better performance than IDPI and HMDI, the composition of TDI as a curing agent in solid propellants needs to be investigated so that the propellant can produce less poisonous combustion gases while maintaining the performance.

TDI is an organic compound with the formula, $CH_3C_6H_3(NCO)_2$. The chemical reaction of the TDI functional group (NCO) with the binder functional group (OH) is shown in Fig. 1. The reaction between the two functional groups forms polyurethane.

The isocyanate functional groups in TDI react with the hydroxyl groups to form carbamate (urethane) compounds. TDI contains two isocyanate groups that react at different rates. 2,6-TDI is a symmetrical molecule and, therefore, has two isocyanate groups with similar reactivity. As both isocyanate groups are attached to the same aromatic ring, the reaction of one isocyanate group leads to a change in the reactivity of the second isocyanate group. The chemical reactions between the functional groups affect the structural reliability, mechanical properties, and performance (Gligorijević *et al.* 2016, Wang and Qiang 2022). Adequate mechanical properties are necessary to

avoid fracture and crack formation (Chaturvedi and Dave 2019, Pimont 2019). The cracks form and propagate in propellant grains when the maximum stress or deformation capacity is exceeded (Nevière and Tixier 2009, Chen *et al.* 2023). Therefore, it is essential to study the mechanical properties of solid propellants. Tensile strength testing and hardness determination are commonly used methods to characterize mechanical properties such as elastic modulus, maximum and ultimate stresses, strains, and hardness. Therefore, this study focuses on evaluating the mechanical and physical properties of the TDI functional group NCO/OH (as curing agent) with 13 μ Aluminum (Al) and tri-modal AP containing coarse, medium, and fine particle. The size of coarse particle AP is 300 μ, 65 μ for the medium size and 20 μ is for the fine particle size.

2. Experimental methodology

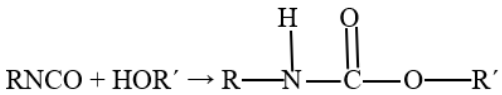
2.1 Chemistry of TDI/HTPB

The chemical kinetics of TDI and HTPB can be defined by an n-order reaction as per the curing kinetics of the polymer binder (Ou and Jiao 2018). The curing kinetics can be defined as follows

$$\frac{d\alpha}{dt} = k(1-\alpha)^n \tag{1}$$

$$k = Aexp(-E_a/RT) \tag{2}$$

where k is the rate of the reaction constant, α is the degree of curing, t is the reaction time, and A is the Arrhenius pre-exponential factor. E_a (kJ/mol) of curing reactions can be obtained from 0~100% curing degrees. Reaction 3 describes the chemical reactions of TDI and HTPB, which are responsible for the hardening of the propellant during curing (Chen and Brill 1991).



(3)

Literature shows that the Thermogravimetric analysis (TGA), differential scanning calorimetry (DSC) and derivative thermogravimetry (DTG) were used to analyze HTPB and TDI, revealing a two-step weight loss process. The first step involved the decomposition of HTPB, while the second step encompassed the depolymerization and crosslinking of HTPB. The reactions were confirmed using infrared spectroscopy (IR). This confirms the bonding phenomena between HTPB and TDI. In order To complete the reaction about 200 h is required at 55-60℃ (Christiansen *et al.* 1981). In this study, the behavior of TDI on the viscosity and flow rates of the propellant slurry and the mechanical properties of the cured HTPB-based propellant were investigated by changing the ratio of NCO to OH.

2.2 Propellant composition/formulation

The formulation of the solid propellant in this study was experimentally conducted, as shown in Table 1. The propellant formulation consisted of approximately 84% solids loading. Each propellant consists of 15% Al, 68% of tri-modal AP consisting 30% of coarse AP, 30% of medium AP and 8% of fine AP, and 2% of additive. The samples of P1 to P4 contained 10.5% of binder, while P5 to P8

Table 1 Chemicals of compositions

S/N	Composition	R	Binder Mix	Al (13 μ)	Medium size AP (65 μ)	Coarse size AP (300 μ)	Other Additives	Fine Size AP (20 μ)
01	P1	0.73	10.5	15	30	30	2.0	8
02	P2	0.77	10.5	15	30	30	2.0	8
03	P3	0.81	10.5	15	30	30	2.0	8
04	P4	0.85	10.5	15	30	30	2.0	8
05	P5	0.73	12	15	30	30	2.0	8
06	P6	0.77	12	15	30	30	2.0	8
07	P7	0.81	12	15	30	30	2.0	8
08	P8	0.85	12	15	30	30	2.0	8

contained 12% of binder with some other additives. The change in R value remains the same i.e., 0.73 to 0.85, for both 10.5% and 12% binders. Previous studies carried out by Noureldin *et al.* (2020) shows that, the R values lower than 0.9 will shows low ultimate stress and maximum strain capability along with good % elongation (Hocaoglu *et al.* 2001) carried aging studies which revealed that sharp changes occur in the mechanical properties with an R value of 0.85 or greater, while R in Table 1 is the ratio of NCO/OH. Therefore, this study focused on the lower value of R from 0.73 to 0.85.

The HTPB resin with bonding agent Methyl Aziridinyl Phosphine Oxide (MAPO) was used as binder. The resin was manufactured by Yantai Shunda Polyurethane Co. Ltd. The resin has an average molecular weight of 4000 (hydroxyl value=48.5 mg KOH/g), batch number:192724 and TDI 2,6 batch 11/0022 with NCO content of 48. Three different APs, supplied by Pyro Chem Source, with three different average particle sizes (65 μ, 300 μ, 20 μ), classified as medium, coarse, and fine, respectively, were used. Al with an average particle size of 13 μ was purchased from Alco Products (Pakistan). The other additive was the 1% ferric oxide (Fe_2O_3), and bonding agent MAPO was used. The plasticizer used was dioctyl adipate (DOA) at 4±0.1% for P1 to P4 and 2.4±0.1% for P5 to P8 to the total weight. Parameter R is defined as the mass ratio of TDI to HTPB, based on the functional groups NCO and OH contained in the formulation. The number of moles of each component in the formulation was calculated based on the mass ratio. In the present study, the value R was assumed to vary between 0.73 and 0.85, with an increment of 0.4, as shown in Table 1. The slurry was processed in eight batches of 3 kg each, keeping all parameters constant. The total weight of each component (slurry) was 3 kg.

2.3 Experimental parameters and procedure

This section describes the method used to produce composite propellants. A 5 kg two-blade vertical mixer was used to prepare the slurry. Initially, DOA, additives, and HTPB were mixed at 20 rpm for 30 min under normal pressure. Subsequently, the slurry was mixed at 25 rpm for another 30 min under vacuum to remove air. The temperature of the mixture was maintained at 50±2°C during the addition of 13 μ Al and AP powders. The blade speed was maintained at 15 rpm, and each component was mixed for approximately 10 min. The mixture was again mixed at a pressure of 1 atm for approximately 80 min. Mixing was continued under vacuum for approximately 20 min to remove the air trap. The temperature was then lowered to 42±2°C and TDI was added to the mixture and mixed for approximately 25 min under vacuum. A Fifty grams of each composite sample were

Table 2 Mechanical properties and hardness

S/N	Propellant	Density (g/cc)	UTS (MPa)	% Elongation	Modulus (MPa)	Hardness (Shore-A)
01	P1	1.761	0.52	38.41	3.1	56
02	P2	1.759	0.58	30.66	3.8	58
03	P3	1.756	0.61	18.22	4.9	59
04	P4	1.755	0.63	14.23	6.1	61
05	P5	1.753	0.61	34.88	6.5	61
06	P6	1.752	0.67	26.63	7.8	63
07	P7	1.751	0.72	16.82	8.9	64
08	P8	1.750	0.78	12.26	9.6	64

taken from the mixture for viscosity and 200 g for flow rate characterization, and the rest of the slurry was cast at 50±2°C under vacuum into cubical mold and cured at 55°C for approximately 200 h (Christiansen *et al* 1981). The cured propellant was then cut into the samples required for mechanical and hardness testing. The same method was repeated for all the eight slurries.

2.4 Characterization of propellant

2.4.1 Mechanical properties, density and hardness of the propellant

Mechanical test samples were prepared from cured blocks of each propellant composition. The universal testing machine JVJ model 2015 was used to evaluate the mechanical properties of China with a maximum load capacity of 2 kg. The specimens were tested at a speed of 5 mm/min and room temperature (25°C). The propellant specimens were prepared in the form of dumbbells, according to ASTM D638 type IV. According to the standard, the specimen thickness and width were maintained at 4 and 6 mm, respectively. The clamp spacing was set to 60 mm during tensile testing, and the crosshead displacement was considered as the displacement. A gauge length of 45 mm was used to calculate the elongation. Five specimens from each batch were tested to obtain the average value of UTS, and the percentages of elongation and modulus were analyzed statistically. All propellant samples were conditioned in a dry environment at room temperature (25°C) before testing. Table 2 shows the average value of five samples for each composition.

The American Society for Testing and Materials (ASTM) D2240 standard using the Instron A Durometer model 2017 was used to measure the final hardness of the cured propellant. Five measurements for each composition were made at room temperature (25°C). The specimen size was maintained at 25 mm×25 mm×25 mm, and a uniform force was applied to each sample. All propellant samples were conditioned in a dry environment at room temperature (25°C) before testing, and the average hardness of each propellant was determined, as shown in Table 2.

The density of the cured sample was measured as per ASTM-D792-20 using Xiangli density testing machine, model 200-3M) at room temperature (25°C). The test specimens were conditioned at 25°C, specimen size was maintained at 15mm×15mm×15mm. Five samples were tested for each composition to obtain average values, as shown in Table 2.

2.4.2 Viscosity and flow rate of propellant

A Brookfield viscometer (model RVDV II +) was used to measure the viscosity of the cured

Table 3 Viscosity and flow rate of Propellant

S/N	Propellant	Viscosity 10^2×Pa.s (0 hr)	Viscosity 10^2×Pa.s (01 hr)	Viscosity 10^2×Pa.s (02 hr)	Viscosity 10^2×Pa.s (03 hr)	Viscosity 10^2×Pa.s (04 hr)	Viscosity 10^2×Pa.s (05 hr)	Flow rate (cm/5 min)
01	P1	5.82	5.88	6.62	7.11	8.02	9.25	7.56
02	P2	6.02	6.11	7.11	8.11	9.12	10.11	7.10
03	P3	6.78	6.89	7.68	8.97	9.99	11.10	6.81
04	P4	6.89	7.02	8.21	9.88	11.55	14.26	6.67
05	P5	6.01	6.45	6.95	7.43	8.87	10.10	7.11
06	P6	6.52	6.78	8.10	9.15	10.36	12.10	6.20
07	P7	6.93	7.92	8.81	10.20	11.12	13.48	5.80
08	P8	7.21	8.40	9.23	10.90	13.12	16.95	5.12

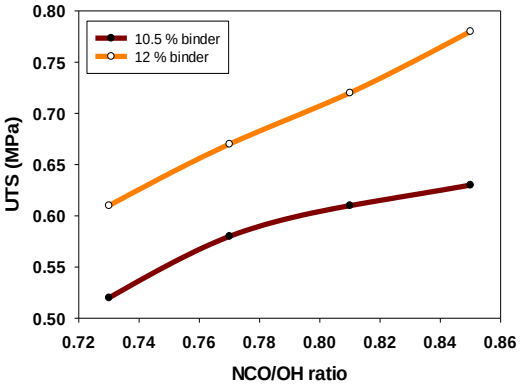
polymer mixture during the curing reaction. The slurry was degassed under vacuum before loading into the sample cell. The sample cell used was a small adapter with a capacity of 7 mL. Viscosity measurements were performed under isothermal conditions at 40°C for 5 h, as shown in Table 3.

Meanwhile, the flow rate was measured immediately after the slurry preparation and tested at 40°C in a graduated glass tube flow meter with a 100 mL capacity. Displacement in centimeters per 5 min was noted for each composition. For accuracy, three composition samples were tested, and the average values are listed in Table 3.

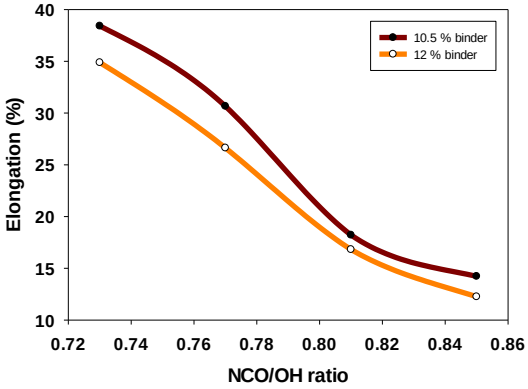
3. Results and discussion

3.1 Mechanical properties

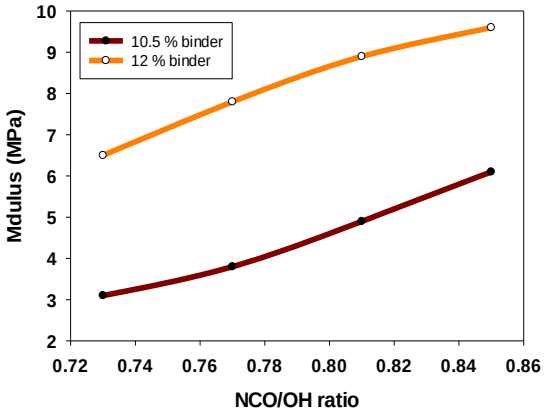
The mechanical properties such as tensile strength, elongation, and modulus of the cured propellant samples (P1, P2, P3, and P4) for 10% binder and (P5, P6, P7, and P8) for 12% binder with the same propellant composition and R-values of (0.73, 0.77, 0.81, 0.85) are compared and shown in Figs. 2 (a)-(c), respectively. All propellant samples were conditioned in a dry environment at room temperature (25°C) before testing. It is observed that for the 10.5% binder the ultimate tensile strength (UTS) increases 20% with the increase of R value from 0.52 (MPa) to 0.63 (MPa). On the other hand, the elongation decreased 170% from 38.41 to 14.23. A 96% increment in modulus of the propellant as R increases from 3.1 (MPa) to 6.1 (MPa). While for the 12% binder the ultimate tensile strength (UTS) increases 27% with the increase of R value from 0.61 (MPa) to 0.78 (MPa). On the other hand, the elongation decreased 47% from 34.88 to 12.26. The 47% increment in modulus of the propellant from 6.5 (MPa) to 9.6 (MPa) as R increases. In comparison of 10.5% binder with 12% binder, the UTS and modulus on average increased by approximately 50% and 200%, respectively while, the elongation decreased by 68% to the P1 as a base value. It can be seen in Fig. 2(b) that there is a sharp decline in elongation for the 12% binder as compared to the 10% binder, which may be the effect of plasticizer as the concentration of plasticizer is greater in 10.5% binder as compare in the 12% binder. In addition, increasing the binder concentration in the mix will increase the holding capacity of the solids, and thus the tensile strength and modulus will increase, but the plasticity will decrease.



(a) Change of UTS with R

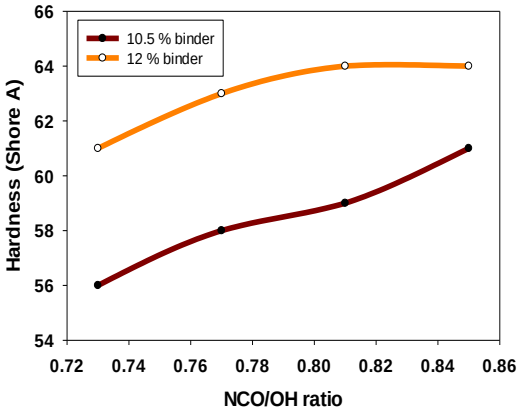


(b) Change of elongation with R

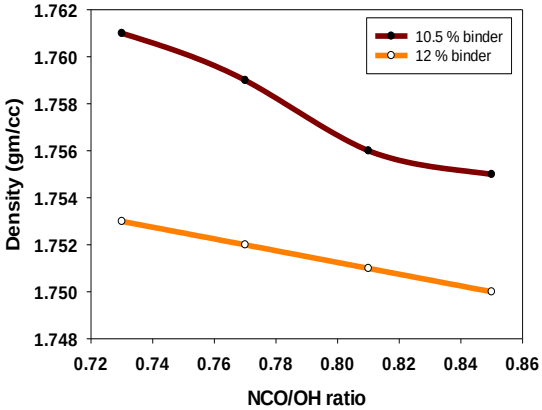


(c) Change of modulus with R

Fig. 2 UTS, elongation and modulus comparison of 10.5% and 12% binder with variation of R



(a) Change of hardness with R



(b) Change of density with R

Fig. 3 Hardness and density comparison of 10.5% and 12% binder with variation of R

It is worth to mention that in this present study, the particle size and percentage of all three types (65 μ, 300 μ, 20 μ) of AP were kept the same in all compositions, as mentioned in Table 1. This is to ensure that the effect of changes in binder composition and percentage of NCO/OH can be determined based on the tri-modal AP composition.

3.2 Hardness and density of propellant

The hardness of the propellant increased with Increasing the R value for both 10.5% and 12% binder, as shown in Fig. 3(a). For the 10.5% binder, hardness on the scale of shore-A increased from 56 to 61 is observed which is approximately 8 to 9%. However, for the 12% binder, hardness on the scale of shore-A increases from 56 to 61 is observed which is approximately 8 to 9%.

The hardness of the propellant is also dependent on the chemistry of the binder and the curator. Increasing the value of R, increases the cross-linking density (CLD), and more bonds are formed because of the availability of a curing agent functional group (NCO) to react with the binder functional group (OH) (Chen and Brill 1991). The more functional groups available, the greater the CLD and vice versa, which will have a direct effect on the toughness of the propellant. In comparison of 10.5% binder with 12% binder, the hardness is increased by approximately 14% to the P1 as a base value.

Fig. 3(b) shows a comparison of the densities for 10.5% and 12% binder with variation of R from 0.73 to 0.85. The densities of P1 to P4 and for P4 to P8 decrease about 0.2% and 0.17%, respectively.

In comparison to the base value of 10.5% binder P1, the density declined by approximately 0.62%. This decrease may be due to the increase in CLD and thus the increase in the volume of the propellant, which will reduce the density to some extent, and increase the fraction of binder will contribute to the decrease in density as HTPB has a density of 0.902 g/cc.

3.3 Flow rate of the propellant

Fig. 4 shows a comparison of the flow rates for 10.5% and 12% binder with variation of R from 0.73 to 0.85. The flow rate of the propellant slurry decreased with increasing R. The flow rates for the 12% binder drop very rapidly, which may be due to concentration of binder, as curing speed will increase in the presence of more binder functional groups. A higher R value increases the crosslinking of the propellant and interlaminar shear forces, thus reducing the flow rate. flow rates for the P1 to P4 at 10.5% binder and for P4 to P8 at 12% binder decreased about 11-12% and 27%, respectively. In comparison to the base value of 10% binder P1 to the 12% binder P8, flow rate decreased about 32%.

3.4 Viscosity of the propellant

Although the viscosity and flow rate of a solid propellant are related to the shape, size, and content of the solid (Ke *et al.* 1986), they are also related to the intermolecular and interlayer shear forces, which are linked to the CLD. Cross linking starts rapidly, when the curator TDI is added to the binder system, the reaction causes the increase in viscosity with passage of time (Mahanta *et al.* 2010), which results in increase of interlayer shear forces and so the viscosity. A solid propellant is a non-Newtonian fluid that is affected by the process parameters and the amount of curator added (Abdillah *et al.* 2020). As soon as the propellant starts curing over time, the flow rate decreases because of the increase in CLD and intermolecular forces (Asghar *et al.* 2019). Fig. 5 shows

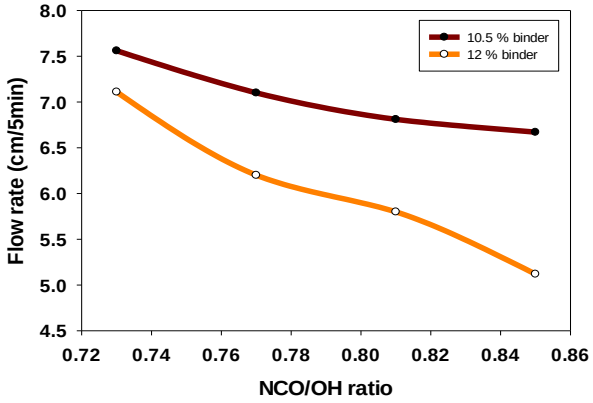
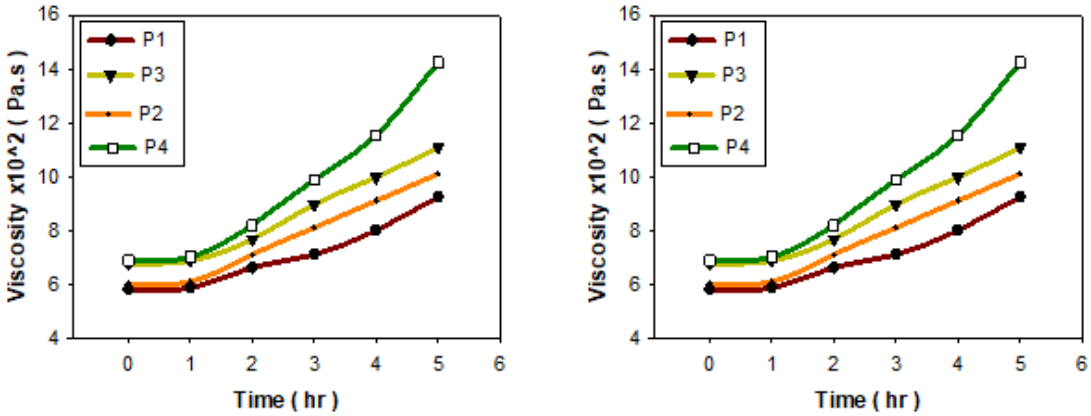


Fig. 4 Flow rate comparison of 10.5% and 12% binder with variation of R



(a) Change in viscosity of P1, P2, P3 and P4 (b) Change in viscosity of P5, P6, P7 and P8

Fig. 5 Comparison of viscosity of P1, P2, P3 and P4 with respect to time at 10.5% binder and viscosity of P5, P6, P7 and P8 with respect to time at 12% binder

viscosities of the propellant slurry samples from P1 to P4 for 10.5% and P5 to P8 for 12% binder respectively, with variation R. viscosity of the propellant was measured at constant temperature of 40. Fig. 5 shows the increase in viscosity as R and time increased. The propellant starts curing and develops crosslinking as the time increases. A higher value of R increases the number of NCO molecules and the binder bond ratio, which results in a higher viscosity of the slurry. In comparison to initial value, viscosity of propellant P1 increases 58~59% rise in viscosity from its initial value, Propellant P2 composition shows 67~68% rise in viscosity from its initial value, Propellant P3 composition shows 63~64% rise in viscosity from its initial value and Propellant P4 composition shows 100% rise in viscosity from its initial value. While viscosity of propellant P5 increased 68% rise in viscosity from its initial value, Propellant P6 composition shows 85% rise in viscosity from its initial value, Propellant P7 composition showed 94% rise in viscosity from its initial value, and Propellant P8 composition showed 135% rise in viscosity from its initial value. In comparison to the initial value of 10.5% binder P1 to the initial value of the 12% binder P5 viscosity increased about

3.26%, and P4 to P8 for its initial value increased about 4.6%.

4. Conclusions

The present study discusses the influence of the ratio of NCO/OH (R value) on the mechanical properties, hardness, flow rate, and viscosity of the propellant. Propellant compositions for both 10.5% and 12% binder were kept constant with only variation of R value, as discussed in Table 1. The samples were then tested under ambient conditions. The study observed a proportional relationship between R value and viscosity, which showed 18% rise in viscosity from R value 0.73 to 0.85, but inversely proportional to flow rate as it decreases about 11~12% for the 10.5% binder. However, with 12% binder, a 30% increase in viscosity and 27% decrease in flow rate has been observed. The increase in viscosity and decrease in flow rate were more evident in these processes. In addition, UTS increased about 20% and the modulus increased 95% with increasing R value, while the percent elongation decreased up-to 170% with increasing R value for 10.5% binder, while for 12% binder UTS and modulus increased about 27% and 47%, respectively. Increasing the percentage of binder can improve the UTS and modulus, but it also increases the stiffness and decreases the elongation of the propellant, which can affect its life. viscosity increase can be observed by increasing the binder concentration in the propellant, while the flow rate and density decrease. The hardness of the cured propellant samples also increased with increasing R value by approximately 8-9% for 10.5% binder and 5% for 12% binder mix. However, the values may change slightly, depending on the processing parameters and testing conditions. Keeping the above values, the R value can be selected based on the mechanical properties, viscosity, and flow rate. Based on the mechanical properties, flow rate, and viscosity built up with time, this study suggests the NCO/OH value of 0.77 and 10.5~11% binder content in the propellant.

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