Effect of process parameters and cure catalysis on the HTPB-IPDI based solid propellant behavior

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Abstract: Conventionally Toluene diisocyanate (TDI) and Isophorone di isocyanate (IPDI) are used as curatives for HTPB to form crosslinked urethane networks. Urethane formation is a fairly rapid reaction with TDI. Since this limits the useful pot life of the propellant, lesser reactive IPDI is more suitable in propellant formulations where a high pot life of the propellant paste is needed for processing big size grains. The aliphatic nature of IPDI makes it slow reactive, thus yielding a longer pot-life and penetrometric pot life which are the favorable factors for processing large boosters[1-3].IPDI is also less toxic and hence used by many manufacturers. One disadvantage is that its longer cure time.In this paper, a detailed study was made on the HTPB-IPDI propellant behaviour and also a comparative study was made with HTPB-TDI propellant system to understand the viscous and mechanical behaviour of the propellant system by its process parameters and cure catalysis system for HTPB-IPDI system.

1. Introduction:

Extension of pot life for HTPB based propellant binder systems was attempted through employing a bi-curative system comprising of TDI and IPDI at various compositions [4]. Various parameters such as HTPB-IPDI stoichiometry, process temperature, pot-life, zero flow time, cure cycle, failure boundary and ageing characteristics were studied [5-8]. The activation energy for the cure reaction is found to be 27.1 kcal/mole for HTPB-IPDI system in comparison to 12.4 kcal/mole for HTPB-TDI system[9].The ballistics are comparable for both HTPB-TDI and HTPB-IPDI propellants, however the pressure index is found to be lower for HTPB-IPDI propellant. The mechanical properties and failure envelope showing the margin of safety and the ageing characteristics of HTPB-IPDI propellant show an edge over HTPB-TDI system [10-11]. In the present investigation, the viscosity build-up after mixing, propellant slurry viscosity vs. final mix timewas studied.Since sufficient pot life is available for IPDI based propellant slurry, it is possible to extend the mixing time to get the lower viscosity.Therefore the studies were carried out on the final mix time.Prolonged mixing of IPDI propellant slurry shows a thixotropic phenomenon since the viscosity decreases with final with time.

2. Materials & Equipments:

HTPB resin used in the present study was produced at PFC, VSSC. Hydroxyl content of HTPB was determined through acetylation method (34.8 mg KOH/g). TDI and IPDI were procured from M/s. A.G.Bayers. Estimation of [NCO] content in the isocyanate compound was undertaken by reacting the isocyanate with a known excess of n-butyl amine and back titrating the un-reacted amine. Assay of TDI and IPDI were found to be more than 99.0%.For all compositions, [NCO]/[OH] equivalent ratio (r value) was maintained at 0.95. The slurry was degassed under vacuum, poured into aluminum moulds and cured at 60°C for pre-specified period. The comparison of physical and chemical properties of IPDI and TDI used in the propellant system were tabulated in table1.
Stress-strain data and the mechanical properties for the propellant slabs were evaluated with an Instron Universal Testing Machine (Model 4469) using dumbbell shaped specimens as per the ASTM-D412 test method.

Table.1 Physical and chemical properties of IPDI & TDI

	IPDI	TDI
Purity (%)	99.5	99.5
NCO Content %	37.5	48
Boiling Point,^{0}C	150	120
Viscosity, cps, 30^{0}C	10	3
Molecular weight, g/gmol	222	174
Refractive index ,30^{0}C	1.567	1.483
Specific gravity, 30^{0}C	1.218	1.059

3. Experimental Results and discussion

3.1 Viscosity build-up profile for TDI &IPDI propellant slurry:

The hydroxyl functional groups of HTPB undergo stoichiometric urethane reaction with a variety of isocyanates to form the polyurethane network which imparts good mechanical properties to the propellant. HTPB-IPDI propellant system has got greater process ability and flexibility to meet any contingency especially during casting of large sized segments of propellant. IPDI has low volatility and hence low toxicity in comparison to TDI. Its boiling point is 150^0C against 120°C for TDI, both at 10 mm of Hg. pressure. This ensures higher human safety and less plant operational hazards during manufacture of the propellant. One disadvantage of HTPB-IPDI propellant system is that its longer cure time. The process temperature for TDI based propellant and IPDI based propellant was maintained at 40^0C and 60^0C respectively. IPDI is a slow reacting curative, hence it can be processed at higher temperatures, however the usual process temperature is restricted to 60^0C because of hazards involved. The batch size was 4 kg and the final mix time was 40 minutes. All the propellant experimentations were done using standard HTPB formulation containing 86 % solid loading with 18% metallic fuel**.** Ammonium perchlorate prepared in house with a bimodal distribution was used as oxidizer.The results of an experiment are shown in the table 2.

Table. 2 Effect of curative on the viscosity build-up of propellant slurry

Time (hours)	Viscosity build-up (poise)	
	TDI (measured at 40^0C)	IPDI (measured at 60^0C)
0	8960	5120
1	9280	5760
2	10560	6080
3	12320	6620
4	14220	7120
5	16000	8400
6	-----	8900
7	----	9300
8	-----	10200

The rate of viscosity build-up was found to be lower for IPDI propellant slurry, despite a higher process temperature. IPDI cured HTPB based composite propellant system has considerably longer pot life because of relatively slower cure kinetics. The viscosity of the propellant slurry was measured at the respective process temperature.

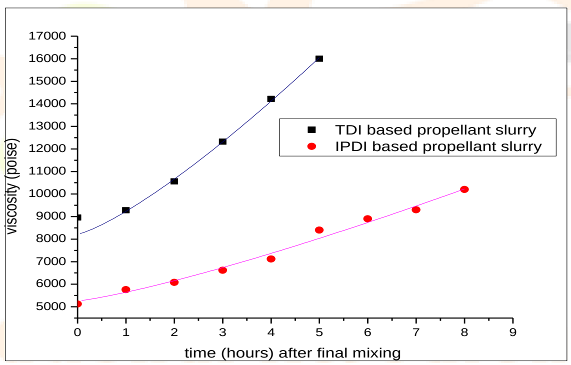

Fig.1 The viscosity build-up profile for propellant slurries using IPDI and TDI as curatives

The increase in viscosity for both the slurries, followed a power function with time, and in the form

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$$\eta = m + n*t^{o} \qquad (1)$$

where "m"," n" and "o" are the empirical constants which depends upon the type of curative and 't' is the pot life in hours. From the equation, the pot life of the propellant slurry can be computed. The time to reach a viscosity of 15000 poise i.e. pot life, has been computed. From the eq., pot life of TDI propellant is 4.4 hours, whereas for IPDI propellant it is 13.8 hours.

4.2 Influence of process parameters on mechanical properties of IPDI propellant:

(a) Effect of mixing time on the mechanical properties of the propellant

Since TDI propellant slurry has a lower pot life, sufficient pot life is available for IPDI based propellant slurry, it is possible to extend the mixing time to get the lower viscosity. Therefore the studies were carried out on the final mix time.A 4 kg capacity horizontal sigma blade mixer was used for the experiments. Prolonged mixing shows thixotropic behavior. EOM viscosity is found to reduce with mixing time.Hence the final mix time varied from 20 to 120 minutes to study the viscous behaviour and mechanical properties.Brookfield viscometer was used to measure the viscosity of the propellant slurry during the cure reaction.

From fig.1, EOM viscosity is found to reduce with mixing time. The viscosity, time data are fitted into a logarithmic function in the form

$$\eta = h_1 - h_2 * \ln (h_3 + t) \qquad (2)$$

where h_1, h_2, h_3 are empirical constants and "t" is the final mix time in minutes (fig.2). From the curve, the values of empirical constants are: h_1=21797; h_2=3856.6; h_3= -8.062.The optimum mechanical properties such as tensile strength, elongation and modulus are achieved by tuning the [NCO]/[OH] equivalent ratios and the optimum level of [NCO]/[OH] ratio for HTPB-IPDI propellant was found to be in the range of 0.95 to 0.98 for the HTPB hydroxyl content of 34.8 mg KOH/g. It is observed that the cure reaction was found to be slower for IPDI.IPDI propellant slurry shows a thixotropic phenomenon since the viscosity decreases with final with time and reaches a plateau at its optimum mixing time.Tensile tests were performed at a cross-head speed of 50 mm/min. Initial modulus (Young's Modulus) was calculated from the slope of the initial linear portion of the stress-strain curves. At a final mix time of 20-40 minutes, higher viscosity rendered the propellant porous. The optimized time for IPDI propellant processing is around 80-100 minutes. From table 3, there is no systematic trend in mechanical properties with reference to mix time. The final mixing time is mostly decided by the viscosity and plant convenience.

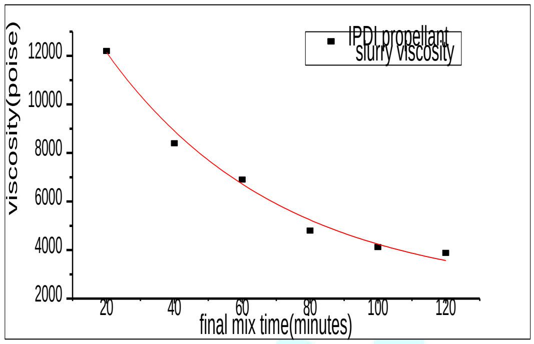

Fig.2Influence of final mix time on the viscosity of the HTPB- IPDI based propellant slurry.

Table 3: Influence of final mix time on propellant mechanical properties

Propellant Property	Final mix time (minutes)					
	20	40	60	80	100	120
TS (kg/cm^2)	10.7	9.4	10.3	10.2	10	9.3
% E	37	38	34	39	43	40
Mod (kg/cm^2)	71	63	75	67	64	67
EOM viscosity(ps) x 1000	12.2	8.4	6.9	4.8	4.12	3.8
Toughness(kgf-cm/cm^3)	2.94	2.94	2.728	3.140	3.305	2.92

(b) Influence of cure time on HTPB-IPDI propellant:

It is observed that the cure reaction was found to be slower for IPDI in comparison to TDI. The activation energy for cure reaction is found to be higher for HTPB-IPDI propellant and hence enhanced cure cycle is required for getting optimum mechanical properties. The cured propellant properties were leveledoff only after 12 days whereas for HTPB-TDI propellant system it was only 4-5 days at 60^0C.The tensile properties of the polyurethane elastomer are determined in the form of dog-bone test specimens under predetermined conditions.The cured samples are tested for their mechanical properties (tensile strength, elongation on break) at room temperature and with a cross-head speed of 50 mm/min using a conventional uniaxial testing system. The results are shown in table 4. Hence the cure cycle was optimized to 12 days @ 60^0C.

Table 4: Influence of cure time on mechanical properties of IPDI propellant.

Cure time, days	Tensile strength (kg/cm^2)	% elongation	Modulus (kg/cm^2)
8	5.1	70	14
12	8.1	55	32
16	7.9	52	35

(c) Effect of sequence of addition on mechanical properties of IPDI and TDI based propellant:

Since coarse & fine ammonium perchlorate and metallic fuel are the major ingredients in propellant composition, studies were done to investigate the effect of the sequence of addition of these major ingredients on the rheological and mechanical behavior of the propellant. For all the addition sequences, first the weighed mass of HTPB and other minor ingredients were added into the mixer and mixed thoroughly for 10 minutes and thereafter the major solid ingredients were added in various following sequences of addition namely: (a) If the solids were added in the sequence of coarse AP in two lots followed by fine AP in two lots and then metallic fuel with an interval of 10 minutes after each addition is represented as 2C+2F+A. (b) If the solids were added in the sequence that half of the coarse AP followed by fine AP and then the remaining coarse AP and fine AP followed by metallic fuel in two lots with an interval of 10 minutes after each addition is represented as C+F+C+F+2A . From the table, the sequence 2C+2F+A has given higher fracture energy compared to other sequence of addition. Hence, the better sequence ofaddition could be opted from the fracture energy data. The results are tabulated in table 5. The Sequence 2C+2F+A is better than the sequence C+F+C+F+2A, in terms of mechanical properties. Hence the sequence 2C+2F+A was employed for other experiments. The strain capability, toughness of IPDI propellant is marginally higher compared to TDI propellant.

Table 5: Effect of sequence of addition on mechanical properties for TDI and IPDI propellants.

Property	2C+2F+A for TDI propellant	2C+2F+A for IPDI propellant		C+F+C+F+2A for TDI propellant	C+F+C+F+2A for IPDI propellant
TS (kg/cm^2)	8.1(8.1)	7.9 (7.8-7.9)		8.3(8.0-8.5)	7.3 (7.2-7.3)
% elongation	51(51-52)	52(51-53)		46(44-48)	56(55-57)
Modulus (kg/cm^2)	37(36-37)	35 (34-36)		43(41-45)	26(25-26)
Toughness kgf-cm/cm^3	2.931	3.058		2.778	2.928

4.3 Influence of cure catalyst on mechanical properties of HTPB-IPDI propellant:

IPDI cured HTPB based composite propellant system has considerably longer pot life because of relatively slower cure kinetics and also it takes longer time for curing. But when extra-large size grains are the requirement for modern launch vehicle systems, an extended pot life becomes imperative with regards to achieving defect free propellant grains. The reaction between IPDI and HTPB, in the absence of a catalyst is extremely sluggish even at elevated temperatures. Hence, an attempt was made to add a cure catalyst which can enhance the cure kinetics. In the non-catalyzed IPDI system, propellant curing was done at 60°C for 12 to 15 days. Fe-01 (iron based) was added as a cure catalyst for IPDI based propellant system to reduce the cure time. The rate constant of an un-catalyzed reaction is smaller than those obtained when a catalyst is employed. The propellant mixing was carried out in a 4 kg level mixer and the final mix time was 80 minutes. The propellant was cured at 60^0C. The mechanical properties were studied with cure time. It was evident from the Fig.3that the required properties were achieved in shorter duration in comparison to the non-catalyzed system. The results are shown in table 6. The toughness observed was lower for the catalyzed system (1.58 J/cm^2) when compared to the non-catalyzed system (1.72 J/cm^2).

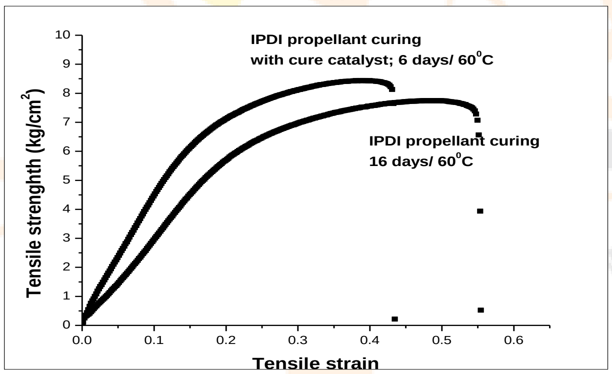

Fig.3 The stress-strain behaviour of non-catalyzed and catalysed HTPB-IPDI propellant

However, to reduce the time duration of propellant curing, the cure catalyst concentration is the deciding factor for slow-reacting curatives used for propellant processing. Initially a higher catalyst concentration was used. Then the paste was gelled during mixing. Then the concentration of catalyst was reduced to 10 times w.r.t binder.

Table 6: Effect of cure time on the mechanical properties of Fe-01 catalysed IPDI propellant.

Cure time (days)	**TS (kg/cm^2)**	**% elong**	**Modulus (kg/cm^2)**	**Shore A hardness**
3.5	6.8(6.8-6.9)	52(49-54)	37(36-38)	59-61
4.5	7.2(7.2-7.3)	49(46-49)	41(40-43)	61-63
5.5	7.6(7.5-7.7)	47(47)	44(43-44)	64-70
6.5	8.0(7.9-8.2)	50(49-51)	43(42-43)	60-64
7.5	8.1(8.0-8.3)	49(48-50)	44(43-44)	65-68
9	8.2(8.1-8.3)	48(47-49)	44(43-44)	66-68
10	8.4(8.3-8.4)	47(46-48)	46(46-47)	66-67
12	8.3(8.2-8.4)	45(44-46)	51(50-51)	64-66
14	8.5(8.5)	45(48)	55(55)	63-67

The concentration of catalyst could be optimized from the fracture toughness data and also by the pot life of the propellant slurry. From table 6, tensile strength increases with cure time and stabilizes at 8.5 kg/cm^2. Modulus also increases with cure time and stabilizes at 55 kg/cm^2. The elongation showed naturally a reverse trend, decreasing with cure time and stabilizes at 45 %. The properties of the catalyzed propellant were stabilized around 5-6 days of curing at 60^0C as against 12-16 days needed for the un-catalyzed propellant. Here the pot life of the slurry was only three hours when the lower catalyst concentration was used; therefore, it needs still lower concentrations of cure catalyst for the process able pot life for the casting of propellant slurry. Since the cure time is very slow, a cure catalyst can be used which can enhance the rate of curing. The reaction between IPDI and HTPB, in the absence of a catalyst is extremely sluggish even at elevated temperatures.

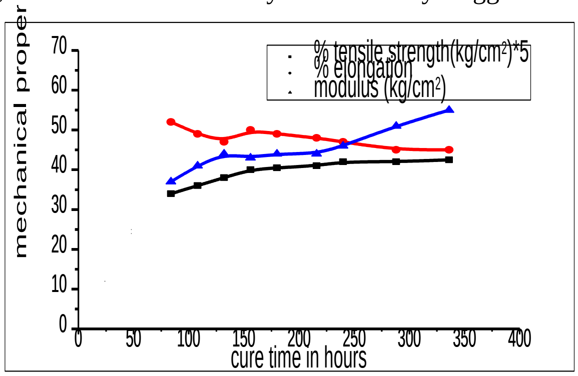

Fig.4 Effect of cure time on the mechanical properties of the propellant

4. Conclusion:

The alicyclic nature with combinations of primary-secondary isocyanate groups make IPDI slow reactive yielding longer pot-life and amenability for large scale processing.Introduction of IPDI slowed down the cure process, but at the same time, has not adversely affected the mechanical characteristics. In the absence of a catalyst, such as Fe-01, the reaction between HTPB and IPDI is extremely sluggish resulting in tardy viscosity buildup during the propellant curing. The most immediate solution that can be the use of less reactive curatives, such as isophorone-di-isocyanate (IPDI) with cure catalyst like Fe-01.

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