INFLUENCE OF ISOMER RATIO OF TOLUENE DI ISOCYANATE ON SOLID PROPELLANT BEHAVIOR

CH Devi Vara Prasad[1], Srinivas Babu N [2], Lakshmana Rao V[3], Ranganathan V[4]
[1]Scientist, Solid Propellant Plant, Satish Dhawan Space Center, Sriharikota, India
[2]Manager, Solid Propellant Plant, Satish Dhawan Space Center, Sriharikota, India
[3]Former Manager, Solid Propellant Plant, Satish Dhawan Space Center, Sriharikota, India
[4]Deputy Director, Solid Propellant Plant, Satish Dhawan Space Center, Sriharikota, India

***Abstract:** Composite solid propellants based on hydroxyl terminated poly butadiene (HTPB) have become the workhorse propellants in the present-day solid rocket motors world-wide. Sufficiently long pot life for the propellant paste is a favorable condition to enhance the ease of processability and thereby to manufacture defect-free propellant grains. A study on the effect of isomer ratio of toluene di isocyanate (TDI)on a mixture of polymer and curative in the processing of rocket propellants was reported. Viscosity build-up of a HTPB–TDI propellant slurry was measured using a Brookfield viscometer. Viscosity build-up of propellant slurry at a constant temperature affected remarkably by the isomer ratio of TDI. The pot-life of the propellant slurry using Type-B TDI was found as 5 hrs. in comparison to 4 hrs. on using the Type-A TDI as curative. The viscosity build-up data of the HTPB–TDI system showed a power function (allometric function) with time. The mechanical behavior of the propellant was not affected by the isomer ratio of TDI.*

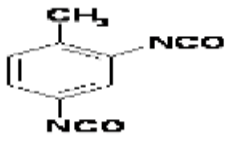
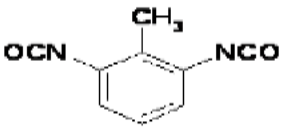
1. Introduction:

Processability characteristics of solid propellant mixing are greatly dependent on the kinetics of binder network formation. Thus, understanding the kinetics of the urethane network formation can help to arrive at optimum conditions with regard to acceptable pot lives for propellant slurries [1]. Because of the high solid loading, the rheological behavior of such propellants is quite complex. A knowledge of the rate of cure and the kinetic parameters is of utmost importance as it gives an understanding of the processability and pot life of the propellant slurry [2-3].

Conventionally, toluene diisocyanate (TDI) is used as a curative for HTPB based propellant system. TDI is an aromatic di-isocyanate. TDI is a mixture of 2, 4 TDI and 2, 6 TDI with an isomer ratioof4:1 respectively named as Type-ATDI which is presently used in all solid propellant segments of ISRO. In the present work, for a comparative study Type-B TDI (with an isomer ratio of ~2:1) was used to explore the possibility of enhancement in pot life of the propellant slurry.

The major problem associated with HTPB is the high reactivity of primary hydroxyl groups with TDI results in higher viscosity of the propellant slurry and faster build-up and hence suffers from lower pot life [4-6].The cure reaction of HTPB with various curatives has been investigated by several workers using various techniques, with relatively more literature available on solution kinetics of the urethane formation [8-9].Coutinho and co-workers reported the uncatalyzed reaction rates of HTPB with different diisocyanates [7-9].The urethane linkages (-NH-CO-O-) formed by the [–NCO] with [–OH] reaction is chemically stable and is able to impart flexibility to the cured binder which makes the polymer an ideal elastomer.The kinetic parameters for the overall cure reaction of HTPB with the different isocyanates were computed using the coats-redfern equation [10]. Table.1 shows the physical and chemical properties of isomers of TDI. It was observed that there was no change in physical and chemical properties of two different isomers except melting/freezing point.

Table 1: The physical and chemical properties of the isomers of TDI

Property	2,4 TDI	2,6 TDI
Physical state	liquid	liquid
Molecular weight (g/mol)	174	174
Sp. gravity (water=1)	1.22	1.22
Melting point (^{0}C)	8.8	13.5
Boiling point (^{0}C)	250	250
Molecular structure		

The fact that 2-position isocyanate, the 4-position isocyanate and the 6-position isocyanate groups in TDI have significantly different reactivity with the hydroxyl group. The para isocyanate group was four times more reactive than the ortho isocyanate group in the absence of the catalyst and under identical conditions of solvent and temperatures. The temperature enhances the reactivity of ortho isocyanate group rather than the para group. Hence it was found that the catalysts also favour the less reactive group than the more reactive one [4].The activation energy for the reaction of the 2-position - NCO group is higher compared to 6-position [–NCO]. This isdue to the inductive and steric effects provided by neighboring methyl substituent in the 1 position. Extending the pot life, by fine tuning the present HTPB-TDI formulation is our approach.

Hence, an attempt was made to study the effect of the isomer ratio of TDI on pot life of the propellant slurry. Type-B TDI has lesser amount of higher reactive isocyanate group and enriched with less reactive isocyanate group compared to Type-A TDI. Because of the higher amount of slower reacting isocyanate content in Type-B TDI, the overall rate of cure reaction is reduced, leading to longer pot life [11].

Table 2 & 3 shows the reactivity of 2-methoxy ethanol [–OH], water and amine with two different isomers of TDI namely 2,4 TDI and 2,6 TDI and it was evident that the reactivity of 2,4 TDI was faster than 2,6 TDI.

Table 2. Reactivities of isocyanates with $CH_3OCH_2CH_2OH$ [2]

Isomer	velocity constant	velocity constant
	k_1	k_2
2,4- TDI	42.5	1.6
2,6- TDI	5	2

Table.3 Overall reaction rate constants of 2,4-TDI and 2,6-TDI [3]

Isomer	10^4k (reaction velocity constant, l/mol. sec x 10^{-4})			E (activation energy, kcal/mol)		
	-OH	water	amine	-OH	water	amine
2,4- TDI	21	5.8	36	7.9	10	9.5
2,6- TDI	7.6	4.2	6.9	10	24	9.0

2. Materials& Equipments:

TDI of two different isomer ratios namely Type-A TDI & Type-B TDI were procured from M/s. Bayer and used as such without further purification. Ammonium perchlorate (AP) was procured from ISRO's Ammonium Perchlorate Experimental Plant, Alwaye. HTPB pre-polymer was received from VSSC, ISRO and from ASL, Tanuku. Ambilink, chain modifier prepared at SHAR, ISRO.

The evaluation of mechanical properties of cured samples (gum stocks and propellant dumbbells) were done using Universal Testing Machine(UTM).

3. Experimentation:

To study the influence of the isomer ratio of TDI on propellant, gum stock studies were carried out initially and later the experiments were carried out with propellant system for evaluating the viscosity build-up of propellant and mechanical properties to make a comparative assessment. The pre-polymer HTPB was stirred thoroughly with the ambilink and was finally added with curative two types of TDIs for preparing gum stocks. The pre-polymer and the di-isocyanates were mixed at various [-NCO]/ [-OH] equivalent ratios (*r*- value) to investigate the effect of isomer ratio of TDI on mechanical properties of gum stocks. The gum stock samples were cured at different cure cycles of 60^0Cfor 3,5 & 7 days for Type-ATDI & Type-B TDI gum stocks. This study was carried out for the optimization of cure cycle for the gum stocks using both types of TDI as curatives seperately.

3.1 Gum stocks preparation:

Manjari et al [14] studied the properties of gum stocks prepared from HTPB prepolymers and toluene diisocyanate. They have calculated network properties like sol content, crosslink density and effective chain length of polyurethanes using the models of Miller [13]. These relationships were used to predict the mechanical properties of several propellant formulations, with very good agreement between observed and predicted properties. It was found that HTPB resins with a wide range of hydroxyl values could be effectively utilized in propellant formulations [13-16].

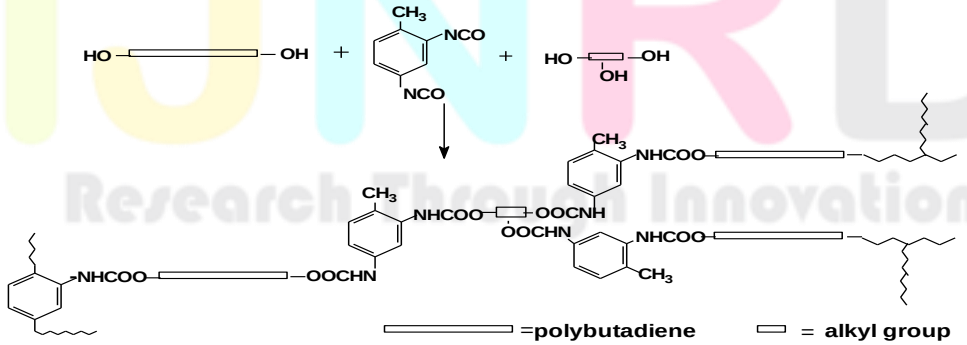


Fig.1The chemical reaction between the HTPB, crosslinking agent and the curative

The chemical reaction between the pre-polymer, chain modifying agent and the curative is shown in fig. They have also conducted a systematic study on propellant formulation experiments [12-16] wherein the ratio of chain extender to cross-linker was systematically varied, with a view to achieve the maximum possible strain capability and moderately high tensile strength, keeping all other parameters constant [17-24].

120 g of HTPB of was taken for all experiments along with ambilink was added and the concentration of curative is varied as per the specific "r" value and mixed thoroughly to form uniform phase. Then it is kept under vacuum for removing bubbles. After degassing it was poured into

teflon coated aluminum mould and cured in oven at 60°C for 3, 5 & 7 days. To study the effect of isomer ratio of TDI on gum stocks, two different hydroxyl value HTPBs were chosen.

Table 4: Effect of isomer ratio of TDI on mechanical properties of gum stocks with different hydroxyl value of HTPB for 5 days of curing at 60^0C. (r = 1.0)

[-OH] Value of HTPB	TDI type	Tensile strength, (kg/cm^2)	Elongation (%)	Modulus, (kg/cm^2)
34.8	Type-A	4.9	304	3.1
	Type-B	5.4	208	3.0
41.0	Type-A	7.2	144	7.0
	Type-B	7.9	130	9.0

The experimentation was carried out at an "r" value of 1.0 and the ingredients were HTPB with different hydroxyl content and TDI with isomer ratios of TDI. Table. 4 shows the results of the mechanical properties of gum stocks made only with HTPB and TDI. Since, the low hydroxyl value HTPB was having a lower functionality, the tensile strength and modulus were found lower in comparison to higher hydroxyl value HTPB gum-stock. The tensile strength and modulus were found higher for the Type-BTDI gum stock in comparison to the gum stock made with Type-A TDI. This is because of the reactive sites of 2, 6 TDI are prone to bonding quicker with hydroxyl groups and reduces the flexibility. From the figures: 2 & 3 the increase in tensile strength, modulus, and a decrease in elongation (%) with the r-value is in expected trend because an increase in the NCO/OH ratio leads to an increase in the crosslink density of the matrix. Four different r-values (1.0, 0.95, 0.9 & 0.85) were chosen for experimentation. The results are shown in table.5 and the mechanical properties against "r" values are depicted in figures. From fig.2, the mechanical properties using Type-B TDI as curative: both tensile strength and modulus increases and followed a logarithmic function with "r" value, whereas the elongation (%) decreases with "r" value, the decrease followed an exponential function.

Table 5: Effect of isomer ratio of TDI on mechanical properties of gum stocks with different r-values, curing at 60^0C.

r- value	[-OH] Value of HTPB	TDI type	Tensile strength, (kg/cm^2)	Elongation (%)	Modulus, (kg/cm^2)
1.0	41.0	Type-B	7.1	116	8.0
0.95			7.0	208	6.5
0.9			6.3	287	3.5
0.85			4.9	376	1.5
1.0		Type-A	7.2	144	7.0
0.95			7.0	223	6.5
0.9			6.8	335	3.0
0.85			5.0	372	2.0

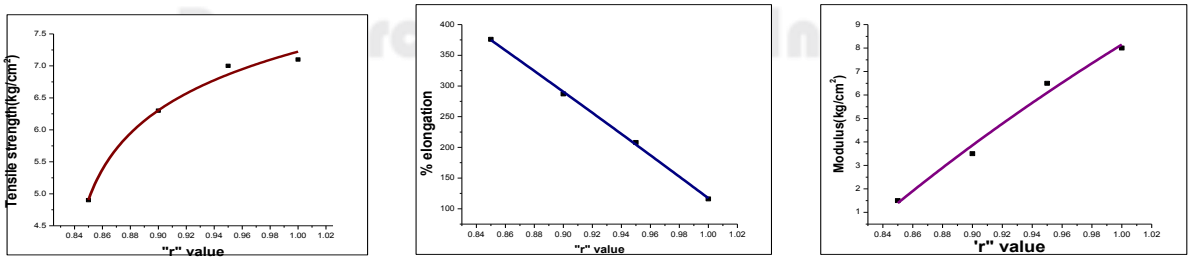


Figure:2 The effect of equivalence ratio on the mechanical properties of gum stocks using Type-B TDI as curative (a) Tensile strength (b) % elongation and (c) Modulus.

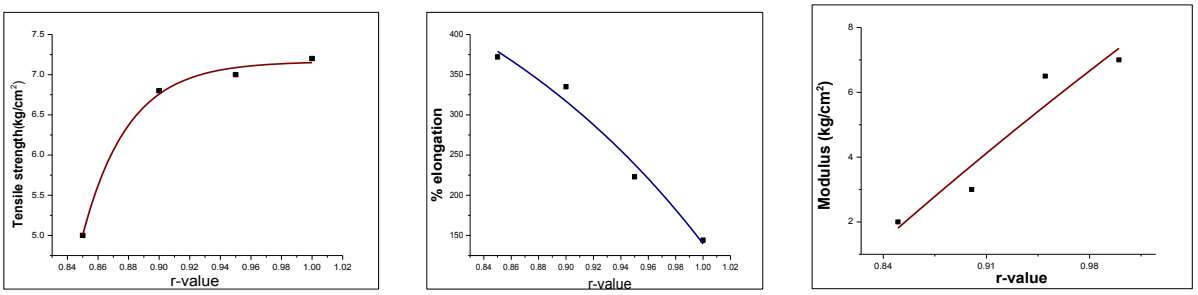


Figure: 3 The effect of equivalence ratio on the mechanical properties of gum stock using Type-A TDI as curative r-value vs. (a) Tensile strength (b) elongation (%) and (c) Modulus profile.

The optimum value was chosen inferred from gum stock studies for propellant formulation trials. Similarly from fig.3, The mechanical properties using Type-A TDI as curative: tensile strength increases with r- value and followed an exponential function with r- value and modulus increases with r-value and followed a logarithmic function with r- value, whereas the elongation (%) decreases with r-value, the decrease followed an exponential function. The optimum r-value can be chosen from the plots to achieve the desired mechanical properties.

3.2 Cure time optimization:

Latter the experimentation was carried out for 3-7 days for the cure time optimization studies and table. 6-8 shows the results of the mechanical properties of the gum stocks cured at 3, 5 & 7 days at 60^0C (maintained by hot air circulation with controllers). The experimentation was carried out at an optimized r-value of 0.85. The samer-value was chosen for the preparation of gum stocks for cure time optimization. It was evident from the results that even after 5 days, there is no change in mechanical properties, thereby the cure time was fixed as 5 days at a temperature of 60^0C for both the isomer ratios of TDI for gum stock studies and propellant studies as well.

Table 6 Mechanical properties of HTPB-TDI gum stocks made with Type-A & B TDIs along with chain modifying agents cured for 3 days at 60°C with (a) Low hydroxyl value HTPB (b) High hydroxyl content HTPB

HTPB hydroxyl content, , mg KOH/g	Mechanical Properties						Hardness (Shore A)	
	Tensile Strength (kg/cm²)		Elongation (%)		Modulus (kg/cm²)			
	Type-A TDI	Type-B TDI	Type-A TDI	Type-B TDI	Type-A TDI	Type-B TDI	Type-A TDI	Type-B TDI
34.8	6.5	5.7	435	389	2.8	2.6	23-25	19-21
	5.5	5.8	339	386	2.8	2.7		
	5.3	3.9	323	219	2.8	2.6		
	4.5	4.6	257	309	2.8	2.5		
Mean (x)	5.5	5.0	339	326	2.8	2.6		
S.D (σ)	0.82	0.91	73	80	0	0.08		

HTPB hydroxyl content, , mg KOH/g	Mechanical Properties						Hardness (Shore A)	
	Tensile Strength (kg/cm²)		Elongation(%)		Modulus (kg/cm²)			
	Type-A TDI	Type-B TDI	Type-A TDI	Type-B TDI	Type-A TDI	Type-B TDI	Type-A TDI	Type-B TDI
41	5.9	6.2	191	168	3.5	3.6	27-29	24-28
	5.6	5.3	151	200	3.6	3.7		
	6.0	6.0	223	197	3.9	3.6		
	5.6	5.7	211	196	3.6	3.6		
Mean (x)	5.8	5.8	194	190	3.7	3.6		
S.D (σ)	0.21	0.39	32	15	0.17	0.05		

Table 7 Mechanical properties of HTPB-TDI gum stocks made with Type A & B TDIs cured for 5 days at 60°C with (a) Low hydroxyl value HTPB (b) High hydroxyl content HTPB

HTPB hydroxyl content, , mg KOH/g	Mechanical Properties						Hardness (Shore A)	
	Tensile Strength (kg/cm²)		Elongation(%)		Modulus (kg/cm²)			
	Type-A TDI	Type-B TDI	Type-A TDI	Type-B TDI	Type-A TDI	Type-B TDI	Type-A TDI	Type-B TDI
34.8	5.1	5.1	319	212	3.0	3.1	25-27	24-27
	5.1	5.6	298	291	3.1	3.1		
	4.4	5.2	313	316	3.1	2.9		

	5.1	5.1	287	312	3.1	3.0		
Mean (x)	4.9	5.3	304	283	3.1	3.0		
S.D (σ)	0.35	0.24	15	48	0.05	0.10		

HTPB hydroxyl content, , mg KOH/g	Mechanical Properties						Hardness (Shore A)	
	Tensile Strength (kg/cm^2)		Elongation (%)		Modulus (kg/cm^2)			
	Type-A TDI	Type-B TDI	Type-A TDI	Type-B TDI	Type-A TDI	Type-B TDI	Type-A TDI	Type-B TDI
41.0	5.9	6.2	191	168	3.5	3.6	27-29	24-28
	5.6	5.3	151	200	3.6	3.7		
	6.0	6.0	223	197	3.9	3.6		
	5.6	5.7	211	196	3.6	3.6		
Mean (x)	5.8	5.8	194	190	3.7	3.6		
S.D (σ)	0.21	0.39	32	15	0.17	0.05		

Table 8 Mechanical properties of HTPB-TDI gum stocks made with Type A & B TDIs cured for 7 days at 60°C with (a) Low hydroxyl value HTPB (b) High hydroxyl content HTPB.

HTPB hydroxyl content, , mg KOH/g	Mechanical Properties						Hardness (Shore A)	
	Tensile Strength ((kg/cm^2)		Elongation (%)		Modulus (kg/cm^2)			
	Type-A TDI	Type-B TDI	Type-A TDI	Type-B TDI	Type-A TDI	Type-B TDI	Type-A TDI	Type-B TDI
34.8	5.0	4.9	240	235	3.1	3.1	24-27	25-28
	6.0	4.7	318	220	3.2	3.2		
	5.3	5.4	264	275	3.2	3.2		
Mean (x)	5.4	5.1	274	246	3.2	3.2		
S.D (σ)	0.51	0.31	40	24	0.06	0.05		

HTPB hydroxyl content, , mg KOH/g	Mechanical Properties						Hardness (Shore A)	
	Tensile Strength (kg/cm^2)		Elongation (%)		Modulus (kg/cm^2)			
	Type-A TDI	Type-B TDI	Type-A TDI	Type-B TDI	Type-A TDI	Type-B TDI	Type-A TDI	Type-B TDI
41.0	6.1	6.7	221	275	3.8	3.6	28-30	29-32
	5.1	6.3	167	252	3.8	3.6		
	6.6	6.0	248	239	3.8	3.5		
	5.3	5.3	174	197	3.8	3.6		
Mean (x)	5.8	6.1	203	241	3.8	3.6		
S.D (σ)	0.70	0.59	39	33	0.00	0.05		

The optimum cure time for gum stocks is around 4 days; however 5 days at 60^0C is recommended to give a positive margin of one day. By optimizing the NCO/OH ratio (r-value) and diol/triol equivalent ratios in the propellant formulation, cross link density can be varied and the desired mechanical properties, viz., tensile strength (TS), elongation(%) at break and initial modulus could be achieved.

3.3 Propellant studies:

The optimized "r" value of 0.85 was chosen for the experimentation. Accordingly, the formulation was fixed. The propellant formulation selected for this study was with 86 **%** solid loading consisting of 18% metallic fuel and the balance was a bimodal distribution of coarse and fineammonium perchlorate. The liquid portion (14% wt. /wt.) consists of binder, plasticizer, chain modifying agents, anti-oxidant and the curative. The mixture was degassed under vacuum before casting. The propellant formulation used was the same except a change in isomer ratios of TDI Type-A & B.

4 kg capacity horizontal sigma blade mixer was used for experiments with a batch size of 3.5 kg. A constant temperature of 40 ± 2^0C was maintained by circulating hot water in the mixer jacket. The influence of the isomer ratio of TDI with same propellant formulation on the mechanical properties were studied. Readings of the viscosity were made at regular time intervals.

Table 9 Viscosity build-up data using different isomer ratios of TDI as curatives for the propellant system

Time (hrs)	Propellant slurry viscosity build-up with Type-A TDI as curative, poise	Propellant slurry viscosity build-up with Type-B TDI as curative, poise
0.5	7680	7680
1.0	8000	8000
1.5	8640	8640

2.0	10080	9600
2.5	11680	10880
3.0	12960	11680
3.5	14560	12640
4.0	15520	13760
4.5	17280	15040
5.0	18880	16480
5.5	20480	17920
6.0	22080	19520

The viscosity build-up of the propellant slurry followed a power function (allometric function) with time. It was observed that the Type-B TDI propellant slurry has a better pot-life compared to the Type-A TDI propellant slurry. Table. 9 shows the viscosity build-up data of propellant slurry for 6 hrs using two different isomer ratios of TDI as curatives.
The derived equation from the plots is

$$\text{Viscosity build-up (poise)} = k_1 + k_2\, t^{\,c} \qquad (1)$$

where k_1 (poise) and k_2(g/cm) and c are the empirical constants derived from the plots.

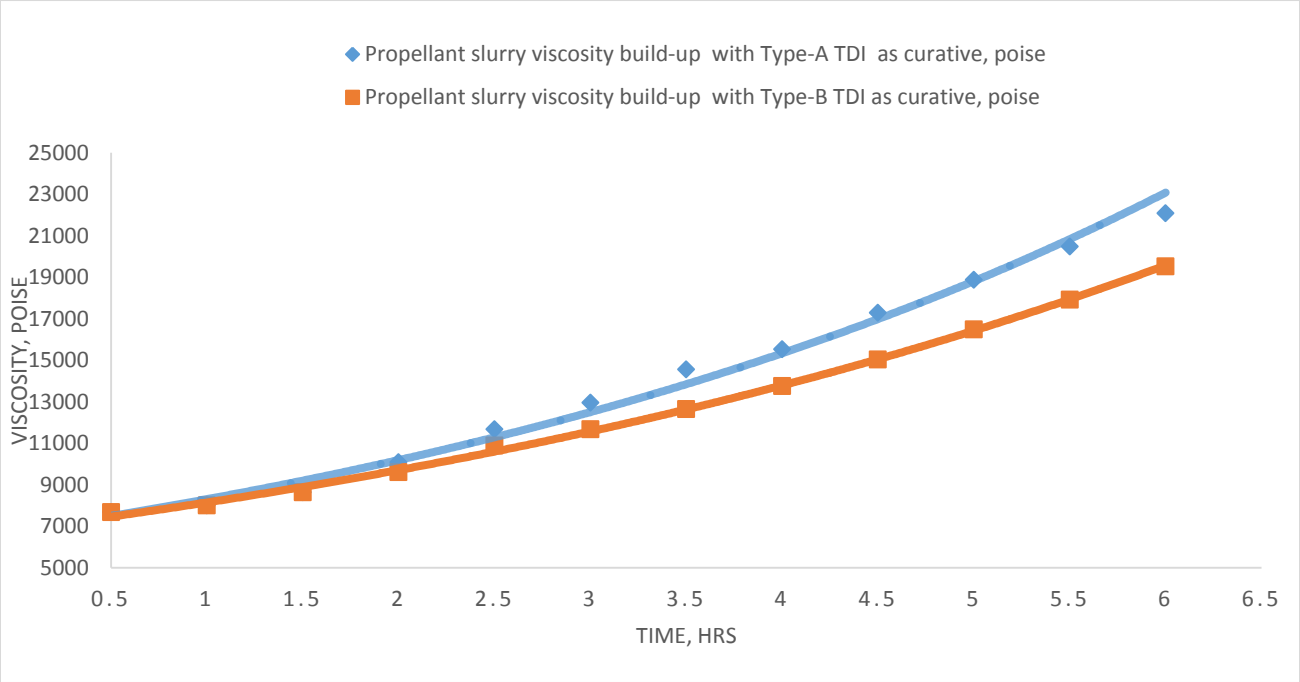


Fig.4 Viscosity build-up profile using different isomer ratios of TDI as curatives for the solid propellant system

Propellant formulations with Type-A TDI as curative gave a pot life of 4 hours and the propellant slurry using Type-ATDI was evaluated and was 5 hrs (the time taken to reach the viscosity of 16000 Ps). The latter is well suited for processing large booster motors. The penetrometric pot-life of propellant slurry was found 24 hrs for Type-A TDI propellant and 30 hrs for Type-B TDI based propellant.
Table.10 shows the mechanical properties of the propellant made using different isomer ratios of TDI as curatives. The hydroxyl value of HTPB used was 41.0 mg KOH/g. The results were comparable and it was evident that the mechanical properties are not susceptible to the isomer ratio of TDI.

Table: 10 The Mechanical property data using different isomer ratios of TDI as curatives

[-OH] Value of HTPB, mg KOH/g	TDI type	Tensile strength, (kg/cm^2)	Elongation (%).	Modulus, (kg/cm^2)
41.0	Type-B	7.83	42	36.8
	Type-A	7.85	46	36

The slab thickness was maintained around 5 mm and the mechanical properties were evaluated. The results of the mechanical properties of the propellant made with Type-B TDI &Type-A TDI presented here are comparable with the literature data for the required and realized mechanical properties of the propellant for the 2.8 m diameter solid boosters of PSLV made with HTPB of OH value of 40-50 mg KOH/g[18].

4. Conclusion:

The slurry must be sufficiently fluid to allow the escape of trapped bubbles, and to assume the shape of the container. Propellant formulations with Type-A TDI as curative gave a pot life of 4 hours which is experimentally proven and the pot life of the propellant slurry using Type-B TDI gave 5 hrs and is evaluated in this paper. The latter is well suited for processing large booster motors. This problem has been solved by using a novel curative Type-B TDI, which has the added advantage of slow reactivity and in comparison to Type-A TDI, presently employed in solid propellant system and no significant changes in mechanical properties despite an increase in pot life and penetrometric pot life.

5. Acknowledgement

The authors would like to thank Director, SDSC/SHAR for his kind support to publish this article.

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