EFFECTS OF TOLUENE DIISOCYANATE`S CHEMICAL STRUCTURE ON POLYURETHANE`S VISCOSITY AND MECHANICAL PROPERTIES FOR PROPELLANT

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Toluene diisocyanate (TDI) is a curing agent that is used by LAPAN in developing composite solid propellant. TDI`s characteristics, such as %NCO, %2,4-TDI and %2,6-TDI can change during storage and depend on the availability of TDI`s specifications that are produced by its manufacturer. This changes can lead to differences in the characteristics of polyurethane that composes rocket propellant. Research about the effects of TDI`s characteristics changes on polyurethane`s characteristics are needed as a direction to invent a new and better HTPB / TDI mass ratio composition for propellant`s formula. In this research, viscosity, rate of increasing of viscosity, % elasticity and tensile strength of ***"polyurethane A"*** (Hydroxy Terminated Polybutadiene (HTPB) 2013 + TDI 2011 contains 2,4-TDI/2,6-TDI 58.4 : 41.6) and ***"polyurethane B"*** (HTPB 2013 + TDI 2013 contains 2,4-TDI/2,6-TDI 42.2 : 57.8) that its HTPB / TDI mass ratio were 11:1, 12:1, 13:1, 14:1, 15:1 and 16:1, were measured. The correlation`s types and levels on the graphs of NCO / OH ratio versus viscosity, rate of increasing of viscosity, % elasticity and tensile strength were determined by using Microsoft Excel. TDI isomer content`s influences to those polyurethane`s properties were analysed. It is discovered that higher 2,4-TDI content increases the level of positive correlation between NCO / OH ratio and polyurethane`s viscosity and rate of increasing of viscosity, because of its isocyanate group`s reactivity. While, higher 2,6-TDI content increases the level of positive correlation between NCO / OH ratio and polyurethane`s tensile strength because of its symmetry chemical structure. But, the differences in TDI 2011 and 2013`s isomer contents only causes a few difference in the level of negative correlation between NCO / OH ratio and polyurethane`s % elasticity.

Key Words: Toluene diisocyanate, viscosity, tensile strength, elasticity, propellant

Nomenclature

EW	:Equivalent Weight
W	:Mass (gram)
η	:Viscosity (Poise)
t	:Time (Second)
$d\eta/dt$	:Rate of Increasing Viscosity (P/s)
R^2	:Determination coefficient
r	:Correlation coefficient

Subscripts

1	:after 10 minutes mixing
2	:after 20 minutes mixing

1. INTRODUCTION

Space technology is one of the leading technology for advanced countries, especially rocket technology. This technology has to be developed by Indonesia which is an archipelago and a large maritime country. One of the rocket`s parts that is important to be developed is propellant. Solid propellant is a kind of propellants that is developed by LAPAN.

Solid propellant is a solid rocket propulsion that can be burned without the absence of oxygen in nature. Composite propellant is a type of solid propellant which contains fuel and oxidizer that are not linked by chemical bonds and require a binder [1]. HTPB (Hydroxy Terminated Polybutadiene) is a binder that mostly used because of its ability to produce high energy when its burned, as well as its low viscosity and specific gravity that are useful in the process of mixing and loading of solids [2].

Composite solid propellant that is developed by LAPAN is HTPB / AP / Al type propellant. Propellant`s characteristics are determined by the result of the polymerization reaction and curing process of Hydroxy Terminated Polybutadiene (HTPB) with a curing agent [3].Curing agent that is often used is a diisocyanate compound. It is because of its polyurethane polymer that has high suitability for filler and extender, and flexible to formulation[4]. Propellant grain that contains polyurethane should has sufficient tensile strength and elongation to withstand various types of stresses experienced during handling and transportation, thermal cycling, sudden pressurization on ignition, and acceleration during flight of the rocket motor. A tensile strength of approximately 7-8 kgf/cm^2, an elongation of 40-50 % and initial modulus of 40-50 kgf/cm^2 are reasonable for a typical case bonded rocket motor[4].These mechanical properties are influenced by the characteristics of polyurethane`s structures, such as molecular weight, intermolecular forces, stiffness of chain, crystallization and cross-linking [5].

Polyurethane`s chemical structure is influenced by diisocyanate`s chemical structure [2]. Diisocyanate compound is a compound that contains two isocyanate groups. Important characteristics of diisocyanate compound are the main chain structure, % NCO content and viscosity [6]. In addition to mechanical properties, diisocyanate`s chemical structure also affects viscosity that is an important aspect in casting process of the propellant and forming a homogeneous propellant that does not have any porous [7]. The ideal viscosity of propellant`s slurry for pressure casting is between 14000-18000 poise[2)]. Whereas, vacuum casting requires viscosity below 16000 poise [8].

Diisocyanate compound that is used by LAPAN is Toluene diisocyanate (TDI), which contains two isomers, namely 2,4- TDI and 2,6 - TDI. The percentage content of the two isomers as well as the % NCO of the TDI can change during storage and depend on the availability of TDI`s specifications that are produced by its manufacturer. This changes can lead to differences in the characteristics of the polyurethane that compose rocket propellant. So that the research about the effects of TDI`s characteristics (%NCO, %2,4-TDI, %2,6-TDI) changes on polyurethane`s characteristics is needed as a direction to invent a new and better HTPB / TDI mass ratio composition for propellant.

This research aims to invent the correlation`s types and levels between NCO / OH ratio, as a ratio between isocyanate and hydroxyl group that react in the formation of polyurethanes, and polyurethane`s viscosities, rate of increasing of viscosities, % elasticities and tensile strengths for propellant, as well as the effects of the changes in TDI isomers contents to the level of those effects. The benefit of this research is the discovery of directions to determine the new and better composition of HTPB / TDI ratio in propellant`s formula.

2. EXPERIMENTAL

2.1. Materials

Polyurethanes were made of HTPB and TDI manufactured by Dalian Chlorate co. Ltd., with mass ratio of HTPB / TDI were 11:1 , 12:1 , 13:1 , 14:1 , 15:1 and 16:1. HTPB that was used was HTPB 2013 with an OH number of 144.7873 and a molecular weight of 2470 g / mol . While TDI that was used was TDI 2011 and TDI 2013, with the characteristics presented in Table 2-1.

Table 2-1 TDI`s Characteristics

Type	% NCO	% 2,4-TDI	% 2,6-TDI
2011	40,4183	58,39	41,61
2013	41,52255	42,20	57,80

2.2. Methods

Equivalent weights of HTPB and TDI were calculated by using Eq. (1) and Eq. (2). The ratios of NCO / OH were calculated by using Eq. (3) and the results were shown in Table 2-2.

EW HTPB = 56100 : OH Number (1.)
EW TDI = 4200 : %NCO (2.)
NCO / OH Ratio = (W TDI : EW TDI) : (W HTPB : EW HTPB) (3.) [9]

Table 2-2 The Results NCO / OH Ratio Calculation

No.	HTPB : TDI mass ratio (gram / gram)	NCO / OH Ratio of Polyurethane A (HTPB 2013 + TDI 2011)	NCO / OH Ratio of Polyurethane B (HTPB 2013 + TDI 2013)
1	11 : 1	0.34	0.35
2	12 : 1	0.31	0.32
3	13 : 1	0.29	0.29
4	14 : 1	0.27	0.27
5	15 : 1	0.25	0.26
6	16 : 1	0.23	0.24

Polyurethanes were made by stirring HTPB and TDI at 42 ^{0}C. HTPB and TDI were stirred for 20 minutes. Its viscosities after the first 10 minutes and the second 10 minutes stirring were measured by using VT - 04F Rion Viscometer with spindle 01. The rate of polyurethane`s increasing viscosities were calculated by using Eq. (4), which t was 600 seconds. Viscosity after the first 10 minutes stirring is referred as η_1. While, viscosity after the second 10 minutes stirring is referred as η_2. Polyurethane curing process was carried out at 60 ^{0}C for 5 days. The percentage of elasticities and tensile strengths of those polyurethanes were measured.

$$d\eta/dt = (\eta_2 - \eta_1) / t \quad (4.)$$

The influences of NCO / OH ratio to polyurethane`s viscosities after 20 minutes of stirring, rate of polyurethane`s increasing viscosities, % elasticities and tensile strengths were graphed by using Microsoft Excel. Its line equation (y = mx + c) and determination coefficient were determined by using Microsoft Excel. The percentages of the effects were obtained by using Eq. (5). While, correlation coefficients were obtained from Eq. (6). The level of correlations were determined based on Table 2-3. The chemical structures were typed by using ChemDraw Ultra 8.0 software.

$$\% R^2 = R^2 \times 100\% \quad (5.)$$
$$r = (R^2)^{½} \quad (6.)$$

Table 2-3 The Levels of The Correlations

r value	Level
0.00 – 0.199	Very low
0.20 – 0.399	Low
0.40 – 0.599	Medium
0.60 – 0.799	Strong
0.80 – 1.000	Very Strong(10)

3. RESULTS AND DISCUSSION

TDI is used as a curing agent in producing propellant. Figure 3-1 shows the chemical structure of TDI . TDI will reacts with HTPB to produce polyurethane bond. Figure 3-2 shows the polymerization reaction of HTPB and TDI, which R is hydrocarbons chain of HTPB.

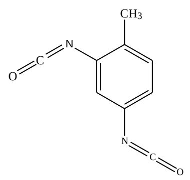

Figure 3-1 Toluene diisocyanate [11].

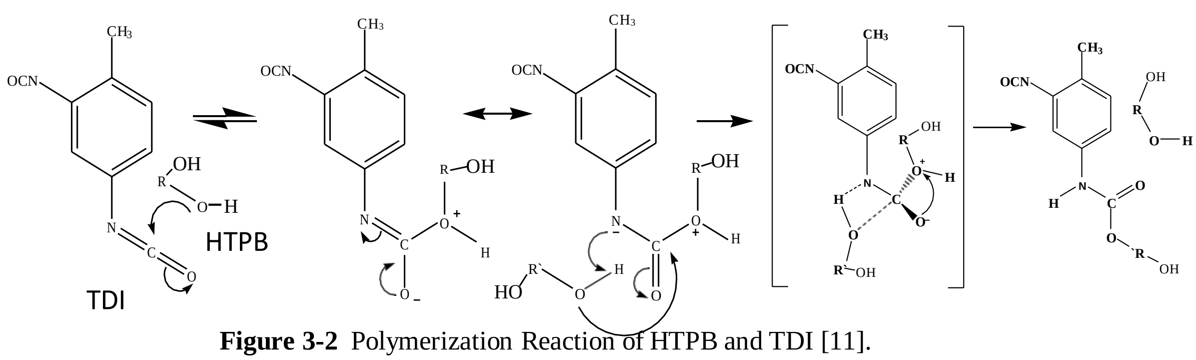

Figure 3-2 Polymerization Reaction of HTPB and TDI [11].

TDI`s characteristics, such as %NCO, %2,4-TDI, 2,6-TDI can change during storage and depend on the availability of TDI`s specifications that are produced by its manufacturer. Two polyurethanes that composed by the same formula of HTPB / TDI mass ratio can have different NCO / OH ratio because those two polyurethanes have different %NCO in its TDI and that difference will lead to polyurethane and propellant`s characteristics changes. Those effects will be more complicated when its TDI`s isomers contents are also different. In order to understanding the effects of NCO / OH`s changes on polyurethane`s properties, the types of the correlation graphs between NCO / OH ratios versus polyurethane`s viscosity, rate of increasing of viscosity, elasticity and tensile strength were analysed. The effects of TDI`s isomer contents changes on polyurethane`s properties were done by analysing the changes in the level of those correlations.

3.1. The Influence of NCO / OH Ratio on Polyurethane`s Viscosity

The polymerization reaction will increases the viscosity of the slurry propellant. The ideal viscosity of the slurry propellant is needed to the easiness of its casting process. Viscosity of slurry propellant must be lower than 16000 P for vacuum casting[8] and between 14,000 to 18,000 P for pressure casting[2]. A good casting process will produces a homogeneous solid propellant that is not porous. Importance of the propellant slurry`s viscosity makes viscosity measurements of polyurethanes are necessary to be done before polyurethane`s formula applied to the propellant`s formula. Knowledge about the effect of TDI`s chemical structure on polyurethane`s viscosity will facilitate the discovery of HTPB / TDI mass ratio that produces ideal viscosity for slurry propellant. Table 3-1 shows the viscosity datas after the first and second 10 minutes stirring and the rates of increasing of viscosity of polyurethane A and B. The effects of NCO / OH ratios on viscosities of the polyurethanes A and B after 20 minutes of stirring is presented in Figure 3-3 and 3-4.

Table 3-1 Viscosity of Polyurethanes A and B

No	HTPB/ TDI Ratio	Poliuretan A				Poliuretan B			
		NCO/OH Ratio	η_1	η_2	$d\eta/dt$	NCO/OH Ratio	η_1	η_2	$d\eta/dt$
1	16 : 1	0.23	23	34	0,018333	0.24	23	31	0,0133
2	15 : 1	0.25	24	31	0,011667	0.26	17	22	0,0083
3	14 : 1	0.27	25	36	0,018333	0.27	23	33	0,0167
4	13 : 1	0.29	28	35	0,011667	0.29	19	27	0,0133
5	12 : 1	0.31	21	42	0,035	0.32	23	36	0,0217
6	11 : 1	0.34	17	39	0,036667	0.35	18	24	0,0100

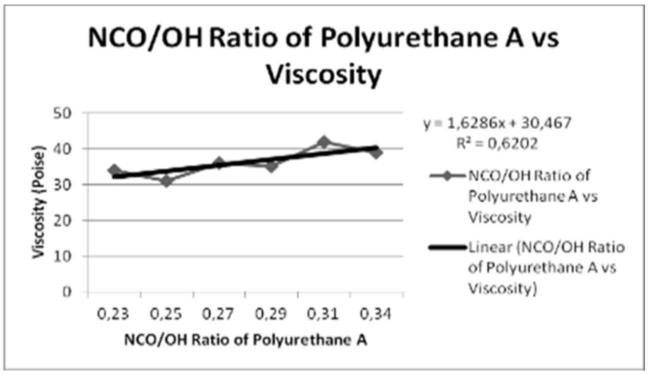

Figure 3-3 The Influence of NCO / OH Ratio on Viscosity of Polyurethane A

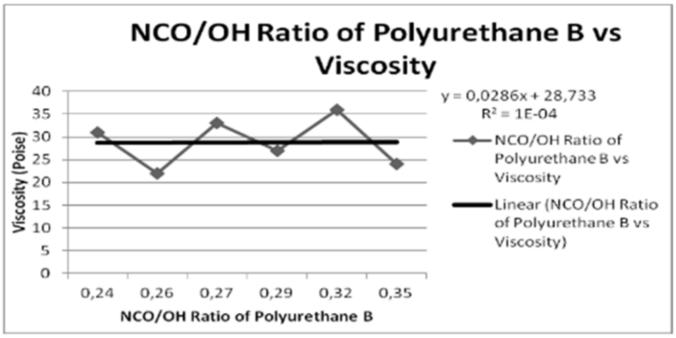

Figure 3-4 The Influence of NCO / OH Ratio on Viscosity of Polyurethane B

Positive coefficients of x on the linear equations shown in Figure 5 and 6 show that the increase in the NCO / OH ratio correlated to the viscosity of the polyurethane A and B positively. It means, the greater the NCO / OH ratio, the higher the viscosity of the polyurethane. It can due to the reactivity of the carbon atom in the TDI`s isocyanate group, -N = C = O. The partial positive charge on the carbon atom makes isocyanate group more reactive to nucleophilic attack. The benzene ring in TDI`s chemical structure adds the positive charge of carbon atom by distributing negative charge of nitrogen, so that it prevents the electrons relocated back to carbon atom rapidly during its resonance[7]. Resonance structure of TDI that involves isocyanate group and the benzene ring can be seen in Figure 3-5.

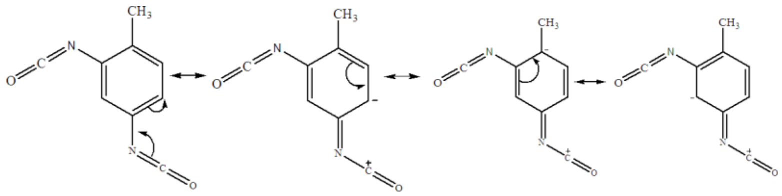

Figure 3-5 Resonance Structures of TDI [11].

3.2. The Influence of NCO / OH Ratio Against The Rate of Increasing Polyurethane`s Viscosity

Besides the magnitude of the viscosity, the rate of slurry propellant`s increasing viscosity is also an important factor in the ease of the casting process. It is because the range of the slurry propellant`s ideal viscosity is needed for the casting process. Casting process takes about 1 - 2 hours for experiments and 3 - 4 hours for large-scale manufacturing [12]. In the curing process, the rate of slurry propellant`s increasing viscosity is also important because the lower the rate, the longer the curing time, the more expensive the cost of curing. Knowledge about the effect of NCO / OH ratio to the rate of polyurethane`s increasing viscosity is needed to facilitate the discovery HTPB / TDI mass ratio that has a good rate of increase in viscosity for a slurry propellant. The influences of NCO / OH ratios to the rates of polyurethanes A and B`s increasing viscosities are shown in Figure 3-6 and 3-7.

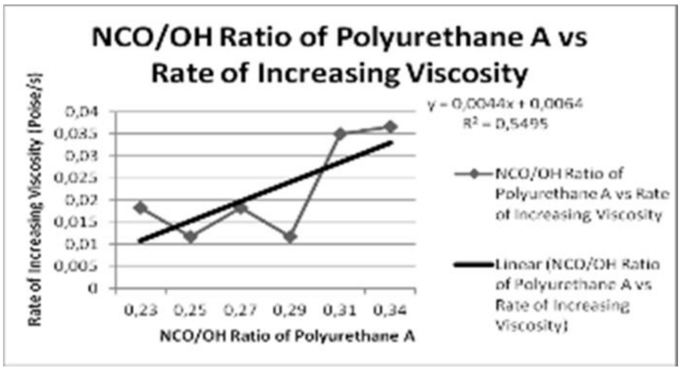

Figure 3-6 The Effect of NCO / OH Ratio on The Rate of Increasing Viscosity of Polyurethane

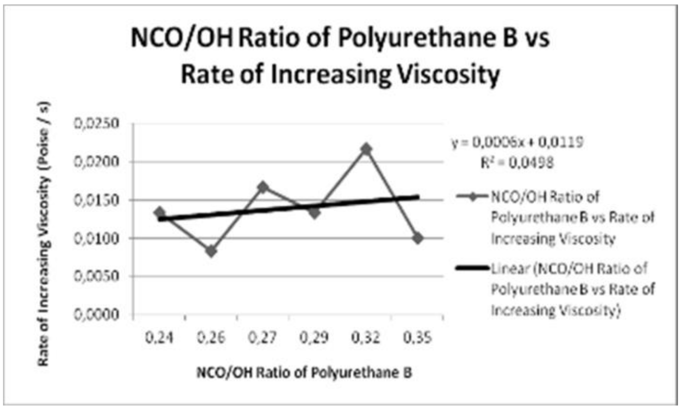

Figure 3-7 The Effect of NCO / OH Ratio on The Rate of Increasing Viscosity of Polyurethane B

Positive coefficients of x on the linear equations shown in Figure 3-6 and 3-7 show that the NCO / OH ratio correlated to the rate of increasing of polyurethane`s viscosity positively. The greater the NCO / OH ratio, the faster the increasing of viscosity of the polyurethane. It is also caused by the reactivity of the carbon atom in the isocyanate group of TDI.

3.3. The Influence of % TDI Isomers Against The Viscosity and The rate of Increasing Viscosity of Polyurethanes

The NCO / OH ratio has a positive correlation to viscosity and rate of increasing of polyurethane`s viscosity which is caused by the reactivity of the carbon atom in TDI`s isocyanate groups. But there are differences in the level of correlation and the percentage of the influence on polyurethane A and B as shown in Table 3-2.

Table 3-2 The Differences of The Effects of NCO / OH Ratio to Polyurethane A and B

No	Comparisons	Polyurethane A	Polyurethane B
1	Correlation between NCO / OH ratio and viscosity		
	a. Correlation`s Level	r = 0.79, Strong correlation	r = 0,01, Very low correlation
	b. % Correlation	62.02 %	0.01 %
2	Correlation between NCO / OH ratio and rate of increasing viscosity		
	a. Correlation`s Level	r = 0.74, Strong correlation	r = 0.22, Low correlation
	b. % Correlation	54.95 %	4.98 %

Table 3-2 shows that the level and correlation`s magnitudes of NCO / OH ratio to viscosity and the rate of increasing of viscosity of the polyurethane A is greater than B. It can due to the higher content of 2,4-TDI in the TDI 2011 on polyurethane A than in the TDI 2013 on polyurethane B. 2,4-TDI isomer is more reactive than the 2,6-TDI.

In 2.4-TDI, ortho isocyanate group is less reactive than the para isocyanate group due to steric hindrance of TDI`s methyl branch. Reactivity of ortho isocyanate is only 12% of para isocyanate`s reactivity in 2.4 - TDI. While, in 2,6-TDI, the reactivities of the two isocyanate groups are same if it does not react, which is 56% of para isocyanate`s reactivity in 2.4 – TDI. But, when it reacts, reactivity of the second isocyanate is only 17% of para isocyanate`s reactivity in 2.4 – TDI [13]. In 2.4 - TDI, after para isocyanate group reacts, the reactivity of ortho isocyanate group is eight times less reactive [14]. The chemical structures of TDI isomers and relative scales to the reactivity of the para isocyanate group in 2,4-TDI are shown in Figure 3-8.

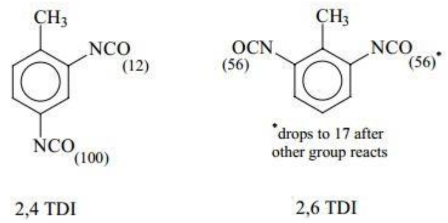

Figure 3-8 Chemical Structure of TDI`s Isomers [13].

Analysis of the above datas indicates that the use of TDI containing higher 2,4- TDI increases the level of positive correlation between NCO / OH ratio to the viscosity and the rate of increasing of viscosity. Propellant slurry with lower viscosity can be generated by lowering the ratio of NCO / OH in the HTPB / TDI`s mass composition in propellant`s formula.

3.4 . The Influence of NCO / OH Ratio Against % Elasticity

According to Mahanta et al, propellant grain for case bonded rocket motors that contains polyurethane should has % elasticity 40-50 % [4]. The discovery of HTPB / TDI ratio that can produce propellant`s ideal % elasticity requires the knowledge about the influence of NCO / OH ratio on polyurethane`s % elasticity. In this study, polyurethane`s % elasticity measurements were conducted on polyurethane A and B which have been cured for five days. The influence of NCO / OH ratio on % elasticity of polyurethane A and B are shown in Figure 9 and 10.

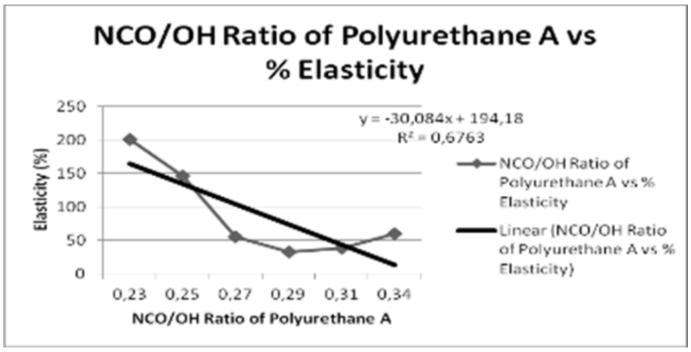

Figure 3-9 The influence of NCO / OH Ratio to % Elasticity of Polyurethane A

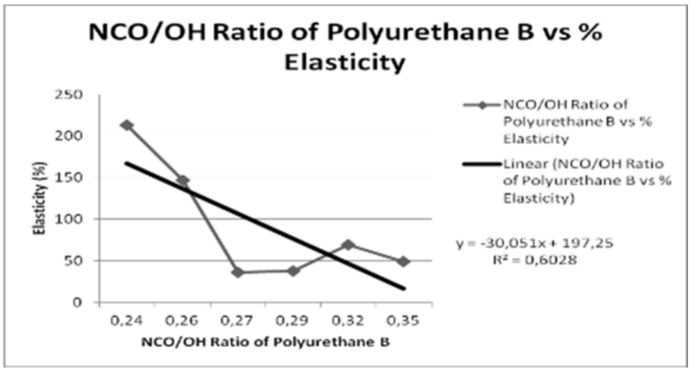

Figure 3-10 The influence of NCO / OH Ratio to % Elasticity of Polyurethane B

Negative coefficient of x in the linear equation in Figure 9 and 10 show a negative correlation between the ratio of NCO / OH with polyurethane`s % elasticity. The greater the ratio of NCO / OH, the lower % elasticity. It is caused of more isocyanate groups that react. The more isocyanate groups that react, the more urethane bonds which contain benzene ring are formed. Benzene ring`s structure is large, flat and rigid. That structure restricts the rotation of the molecule in the main chain of polyurethane, resulting a lower elasticity [5]. This effect is greater when the benzene ring resonating as shown in Figure 3-11.

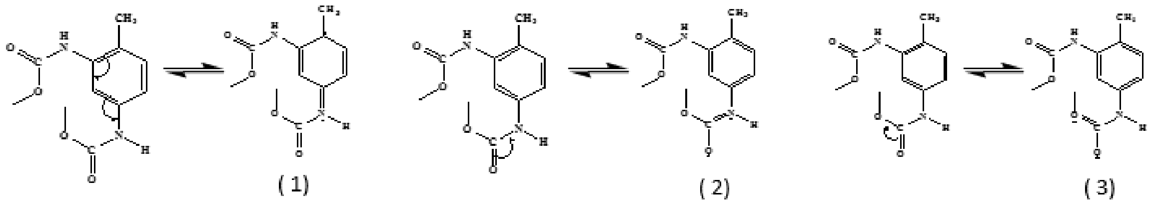

Figure 3-11 Resonance Structure of TDI in Polyurethane [5][15].

3.5. The Influence of NCO / OH Ratio Against Polyurethane`s Tensile Strength

According to Mahanta et al, propellant grain for case bonded rocket motors that contains polyurethane should has tensile strength of 7-8 kgf / cm^2 [14]. The discovery of HTPB / TDI ratio that can produce propellant`s desired tensile strength requires knowledge about the influence of the NCO / OH ratio to the tensile strength of polyurethane. In this study, the tensile strength measurements were conducted on polyurethane A and B which have been cured for five days. The influence of NCO / OH ratio to the tensile strength of polyurethane A and B are shown in Figure 3-12 and 3-13 .

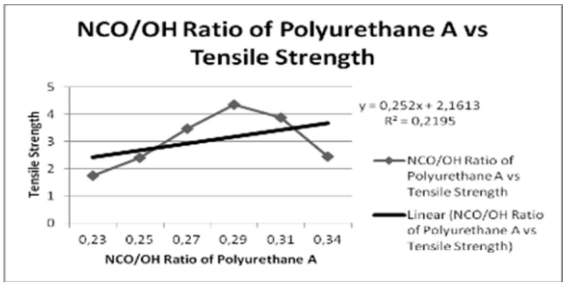

Figure 3-12 The Influence of NCO / OH Ratio to Tensile Strength of Polyurethanes A

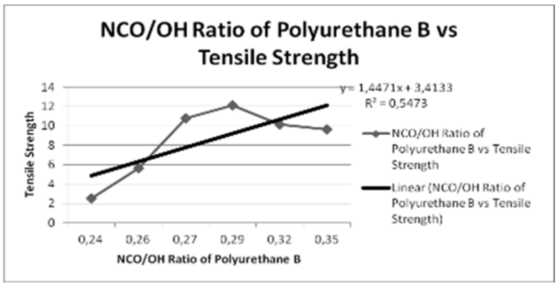

Figure 3-13 The Influence of NCO / OH Ratio to Tensile Strength of Polyurethanes B

Positive coefficient of x on linear equation in Figure 3-12 and 3-13 show that the ratio of NCO / OH positively correlated to the tensile strength of polyurethane. The greater the ratio of NCO / OH, the greater the tensile strength of polyurethane. It is also caused by the rigidity of the benzene ring in the TDI [6].

3.6. TDI Isomer Content`s Influences to Polyurethane`s % Elasticity and Tensile Strength

The ratio of NCO / OH has the same correlation` type to polyurethane A and B`s % elasticity and tensile strength. However, the levels and the percentages of those correlations on polyurethane A and B need to be compared as shown in Table 6.

Table 3-3 The Influences of NCO / OH Ratio to % Elasticity and Tensile Strength of Polyurethane A and B

No	Comparison	Polyurethane A	Polyurethane B
1	Correlation between NCO / OH ratio and % elasticity		
	a. Correlation`s level	R = 0.82, Very strong correlation	R= 0,78, Strong correlation
	b. % Correlation	67.6 %	60.2 %
2	Correlation between NCO / OH ratio and tensile strength		
	a. Correlation`s level	R = 0.47, Medium correlation	R= 0.74, Strong correlation
	b. % Correlation	21.9 %	54.7 %

Table 3-3 shows that the %correlation of NCO / OH ratio to % elasticity of polyurethane A and B is not too different. It means the difference of TDI`s isomers percentages between in TDI 2011 and 2013 only causes a few influence to negative correlation of NCO / OH ratio on polyurethane`s % elasticity. It can be caused by same HTPB`s characteristics that compose polyurethane A and B, that is HTPB 2013. Cis structure in HTPB`s structure is known to be responsible for the elasticity of polyurethanes [16]. While for tensile strength, the levels and percentages of those correlations are different on polyurethane A and B. It can be caused by different percentages of 2,6-TDI content in TDI 2011 and TDI 2013.

TDI 2013 contained in polyurethane B contains more 2,6-TDI than TDI 2011 that is contained in polyurethane A. 2,6-TDI isomer has a symmetrical structure as shown in Figure 8. Its symmetrical structure yields a linear structure thereby increases the crystallinity of the polyurethane polymer. Increased crystallinity causes an increase in tensile strength(5). In addition, higher symmetric 2,6-TDI content in polyurethane increases the forming of hydrogen bonding in polyurethane [13].

4. CONCLUSION

The higher content of 2,4-TDI in TDI increases the level of positive influences of NCO / OH ratio on polyurethane`s viscosity and rate of increasing of viscosity because of the resonance of benzene. Meanwhile, the higher content of 2,6-TDI increases the level of positive correlation between NCO / OH ratio and polyurethane`s tensile strength because of its stiffness and symmetry structure. However, the difference of TDI`s isomers percentages between in TDI 2011 and 2013 only causes a few difference to the magnitude of negative correlation between NCO / OH ratio and polyurethane`s % elasticity.

ACKNOWLEDGMENTS

The authors wish to thank Drs. Sutrisno, M.Si as The Head of Rocket Technology Centre (Pustekroket) and Dr. Heru Supriyatno as The Head of Propellant Technology Centre who have guided, helped and facilitated the research activities. We also would like to thank all the technicians who have helped the research activities.

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