Influences of NCO/OH and triol/diol Ratios on the Mechanical Properties of Nitro-HTPB Based Polyurethane Elastomers

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ABSTRACT: *The present study describes the effect of NCO/OH and triol/diol ratios on the mechanical properties of Nitro functionalized Hydroxyl-terminated polybutadiene (Nitro-HTPB) elastomers. The progress of the cure reaction of Nitro-HTPB and toluene diisocyanate (TDI) is evaluated by following up the variations in the IR absorption bands of the NCO stretching and the CO Stretching. Experiments are carried out at NCO/OH ratios (R values) ranging from 0.8 to 1.2 and triol/diol ratios in the range of 0.05-0.7. Also as the R-value increases, the tensile strength increases, and elongation decreases. The rubbery character of elastomers is improved followed by increased rigidity with an increase in triol/diol value of 0.05. In general, desirable mechanical properties were achieved for the polyurethane elastomers of Nitro-HTPB as a novel energetic binder.*

KEYWORDS: *Mechanical properties; Elastomer; Nitro-HTPB; Polyurethane; TDI.*

INTRODUCTION

Hydroxyl-Terminated PolyButadiene (HTPB) as a telechelic liquid binder containing hydroxyl groups is widely used in composite solid propellants and explosives due to its low viscosity, high solids loading and excellent mechanical properties after curing. Because of the outstanding mechanical properties of polyurethane made from the HTPB, HTPB has been used in the field of explosives since 1989 as a cross-linkable prepolymer. Several commercially available explosives are qualified with the HTPB in propellant formulation [1, 2]. HTPB is, however, non-energetic and thus the performance of the composition is limited unless there is a high solids loading. Although the HTPB has been frequently utilized in the explosive composition, however, there is a necessity for the development of energetic binders [3, 4]. Preparation of energetic polymers both by polymer modification and by polymerization of an energetic monomer is described. The term energetic polymer implies that energetic functional groups such as nitro (NO_2), nitrate (NO_3) or azide (N_3) are present. In this regard, several energetic polymers are developed such as poly-3-nitratomethyl-3-methyl oxetane (polyNIMMO), polyglycidyl nitrate (polyGLYN) and Nitrated Hydroxyl Terminated PolyButadiene (NHTPB). The potential of nitration the HTPB was recognized many years ago and early studies concentrated on

a nitromercuration-demercuration route. There were problems regarding its solubility and stability, which have been solved by elimination of side reactions and control of the reaction conditions to create interesting products [5-7]. Therefore the modification of HTPB has been studied by different routes. Nitrated HTPB has been synthesized by a polymer modification route which relies upon the reaction of N_2O_5 with epoxide groups to form dinitrate esters. The synthetic route in the early stages involved epoxidation of HTPB in the manner similar to that reported by Zuchowska using in-situ peracetic acid as the epoxidation reagent. Reaction of the epoxide groups with N_2O_5 in dichloromethane gives a polymer with a percentage of double bonds converted to dinitrate ester groups dependent upon the epoxide content of the intermediate polymer. The properties of Nitrated HTPB depend on the percentage of converted double bonds and it is usually about 10%, as the best compromise between energetic and physical properties. Despite all the advantages offered by these methods, some double bonds in the molecular structure of HTPB are destroyed; consequently, the physical and chemical nature of the molecule is changed [8, 9]. Despite these attempts, none of these methods were able to replace the use of HTPB in the propellant. The aims for the future in this area are centered around the increasing awareness of the effects of energetic formulations on the environment, finding ways of disposing of unwanted ordnance and increasing the safety of in-service stores. The safety benefits of using energetic polymers have already been described and polymers with increased energy and better mechanical properties would further lower the number of fillers needed in formulations thus making them much less likely to react to external stimuli. Recently a method by means of Nitrile Iodide (NO_2I) as the active reagent [13] was considered to be useful for nitro functionalizing of HTPB, based on ease of synthesis and product purity without manipulation of the main backbone. The thermal stability of the Nitro functionalized HTPB (Nitro-HTPB) was verified by simultaneous thermogravimetric analysis and differential scanning calorimetry (TG–DSC) measurement [14]. One of the major advantages of Nitro-HTPB which makes it a candidate for use in the formulation of propellant is miscibility with the energetic plasticizers such as N-n-Butyl-N-(2-Nitroxy-Ethyl) Nitramine (Bu-NENA), while HTPB is not. This

significant feature increases the total energy of propellant. Energetic plasticizers are described as the fluid materials having a positive heat of combustion [13, 15]. Owing to the multiphase systems, the physical properties of these materials can be modified over a wide range. In so far as mechanical properties are concerned, increase in the cross-link density increases the strength and modulus. The degree of cross-linking can be controlled either by using polyfunctional groups such as triols or by controlling the NCO/OH ratio [16]. In this work, Nitro-HTPB elastomers are synthesized by the reaction of the Nitro-HTPB with TDI. The effect of the NCO/OH and the triol/diol ratios on the mechanical properties of Nitro-HTPB based polyurethane elastomers was investigated.

EXPERIMENTAL SECTION
Materials
Nitro-HTPB was synthesized (Fig. 1) as proposed by Ref. [13], Bu-NENA was synthesized following the method of *Rao et al.* [17]. HTPB (R45-M, the number-average molecular weight of 2600, Zibo Qilong Chemical Co., China), Toluene diisocyanate (TDI, Bayer Material Science, Germany) and Trimethylolpropane (TMP, Perstorp AB, Sweden) were used as purchased.
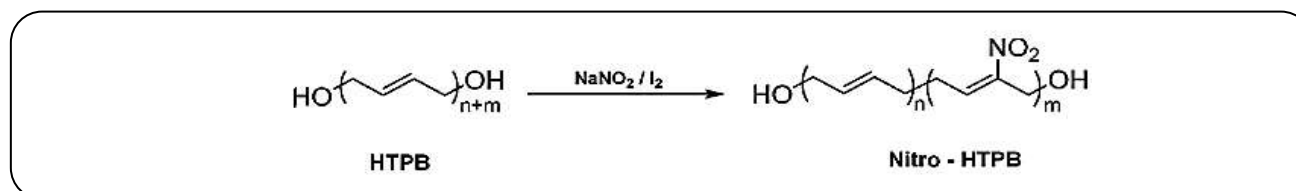
Nitro-HTPB based polyurethane preparation
To prepare the polyurethane-based elastomers, all the components with the exception of the curing agent (Nitro-HTPB+Bu-NENA+TMP) were mixed completely in a horizontal blender for 5 hours under vacuum environment at 65 °C. After adding curing agent to the mixture, the slurry was mixed for 45 minutes vacuum environment. The nitrogen atmosphere was kept across the blending. The freshly prepared composition was poured into Teflon molds and placed in the vacuum oven for five days at 65 °C. The dumbbell-shaped elastomers were used in the tests. The physical properties of synthesized Nitro-HTPB prepolymer were expressed in Table 1.

Methods of testing
The mechanical properties of the polyurethane elastomers were determined in the form of dumbbells under planned conditions based on ASTM D638 standard test [18]. The dumbbell-shaped elastomers were tested for their mechanical properties (tensile strength, elongation at break) at 20 °C with a cross-head speed of 50 mm/s,

Table 1: Physical properties of the Nitro-HTPB prepolymer.

Sample	Number average molecular weight (g mol^{-1})	Viscosity at 30℃ (Pa s^{-1})	Glass transition temperature(℃)	Hydroxyl value (mg KOH per g)	Functionality (Eq mol^{-1})
Nitro-HTPB	3130	23.06	-64	33.1	1.84

Fig. 1: Nitro-HTPB preparation [10].

using a conventional uniaxial testing system (Hewlett & Packard-Inspect 50). Every test was carried out on the three elastomer samples. The infrared spectral range of 400-4000 cm^{-1} for thin polymeric layers was measured using a JASCO-5300 Fourier spectrometer (FT-IR) with the resolution of 4 cm^{-1}. The curing trend was followed by observation the IR spectra of a composition of raw materials prepared at room temperature and situated in potassium bromide pellets in an inert condition. The number average molecular weights (M_n) of HTPB and Nitro-HTPB were determined by Gel Permeation chromatography (GPC). The apparatus was a Hewlett-Packard GPC, model 1100, using Styragel columns. Viscosity measurements were carried out using an Ubbelohde-type capillary viscometer, they were performed at 30 °C. The viscometer was immersed in a constant temperature bath that was controlled to within ± 0.1 °C, the efflux times were reproducible to ± 0.2 %, and the flow times were measured with an accuracy of ± 0.06 s. The glass transition temperatures (Tg) were obtained on a Perkin-Elmer DSC-7 differential scanning calorimeter. Scans were conducted under nitrogen at a heating rate of 10 °C /min. Second heat Tg values are reported as the midpoint of the change in the slope of the baseline. In order to measure of hydroxyl value, the Nitro-HTPB sample is acetylated with a solution of acetic anhydride (Caution: see Note 2) in pyridine in a pressure bottle at 98°C. The excess reagent is hydrolyzed with water and the acetic acid is titrated with standard potassium hydroxide solution. The hydroxyl content is calculated from the difference in the titration of the blank and sample solutions. The functionality of a Nitro-HTPB

resin is the number of isocyanate-reactive sites on a molecule and calculated by "total moles of OH / total moles of polyol". The density of elastomer was measured by ASTM D792-08 standard method [19]. The ISO 10364:2015 standard method was applied for determining the pot-life of polymer in order to be able to determine whether the pot-life conforms to the minimum specified working life [20]. The hardness (shore A) of Nitro-HTPB elastomers was determined by digital shore hardness tester HT-6600C. A common matrix structure and its features were presented in Table 2.

RESULTS AND DISCUSSION
Effect of NCO/OH ratio on mechanical properties

To investigate the effect of the NCO/OH molar ratios (R-value) on the mechanical properties of the polyurethane elastomers, experimental tests were done at NCO/OH molar ratios ranging from 0.8 to 1.2 by keeping the triol/diol ratio (0.05), and the concentrations of all the other components constant (Nitro-HTPB: 89%, Bu-NENA: 4%). Processing was carried out in a sigma blender at the 200g level. The obtained values are the mean of three measurements for every elastomer sample. Mechanical properties of the elastomeric samples with different R values are presented in Table 3. The elongations and tensile strengths are given as a function of the NCO/OH molar ratios in Figs. 2 and 3, respectively.
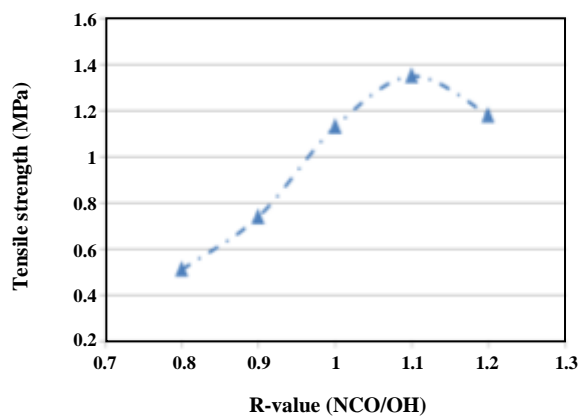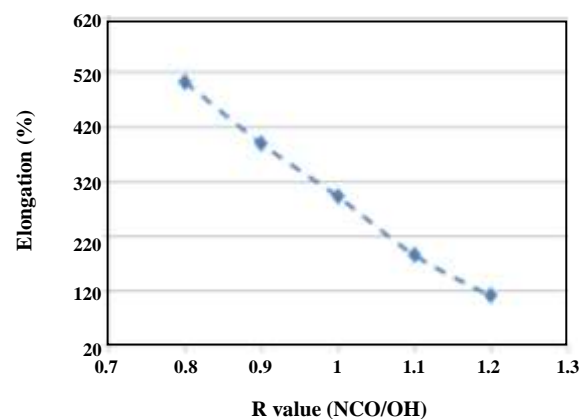
It was found that tensile strength increases and elongation decrease, as the *R*-value increases. It seems that the elastomer samples with an *R*-value of 0.80 express the elongation of about 500% before failure. On the other hand, this sample shows the very low tensile

Table 2: Composition and material properties of unfilled polyurethane elastomers.

Composition of a typical elastomer	
Nitro-HTPB (Prepolymer) (%)	82-95
Bu-NENA (Energetic Plasticizer) (%)	3-8
TDI (Curing agent) (%)	2-10
TMP (Crosslinking agent) (%)	0.3-1.4
Physical properties of elastomer	
Density at 25°C (g/cm^3)	0.95-1.15
Pot-life at 20°C (min)	15-20
Glass transition temperature (ºC)	-27
Mechanical properties of elastomer (Tensile Loading Rate 50 mm/min at 20 °C)	
Tensile strength (MPa)	0.5-1.2
Elongation at Break (%)	110-500
Elastic modulus (MPa)	0.1-1

Table 3: Mechanical properties of the elastomer samples with various NCO/OH ratios.

Sample	R-value (NCO/OH)	Tensile Strength (MPa)	Elongation at Break (%)	Elastic Modulus (MPa)	Hardness (Shore A)
1	0.8	0.51	502	0.101	7
2	0.9	0.79	397	0.199	9
3	1	1.13	292	0.387	19
4	1.1	1.35	185	0.675	24
5	1.2	1.18	110	1.07	26

Fig. 2: Influence of R-value (NCO/OH) on the maximum tensile strength of elastomers.

Fig. 3: Influence of R-value (NCO/OH) on elongation at break of elastomers.
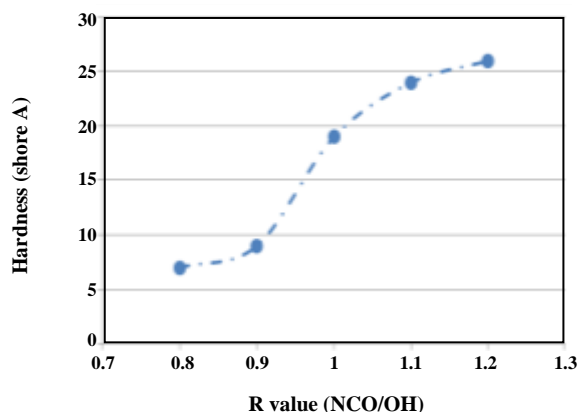
Fig. 4: Influence of R-value (NCO/OH) on the hardness of elastomers.

Fig. 5: Influence of R-value (NCO/OH) on Elastic Modulus of elastomers.

the strength of 0.51 Mpa, as expected, and acceptable mechanical strength could not be given due to low *R*-value. The tensile strength of the elastomer samples increases, as NCO/OH molar ratio increases up to $R = 1.1$ and then begins to decrease. Extra quantities of diisocyanate cause a rapid diminishing of OH groups which could be disadvantageous to the tensile properties at $R = 1.2$. For such complicated system that used in this investigation, it is difficult to make a relationship between the tensile strength and the *R* values. However, the favorable conditions for giving high molecular weights or numerous crosslinks depend on the presence of tiols, molecular weight distribution, and functionality of Nitro-HTPB. The maximum tensile strength observes at *R* values larger than 1.00 might be attributed to the consumption of extra diisocyanate by hydroxyl groups. Figs. 4 and 5, respectively, show that hardness and modulus of the elastomeric samples increase, as *R*-value increases. In fact, polyurethane formation determines the hardness of elastomers. The polyurethane polymer-forming reaction is nearly terminated as long as the composition becomes rigid, and the hardness gets stable level as a result of no additional curing reaction and crosslink formation. The polyurethane-forming reaction is limited by the restricted number of OH groups of Nitro-HTPB at the *R* values higher than 1.0. It was found that crosslink formation at a higher NCO/OH ratio proceeds through the allophanate formation and isocyanurates linkages. However, it was shown that allophanate formation can be occurred higher than 170°C in a significantly prolonged time [21]. Thus, in this study, the formation of allophanate was ignored
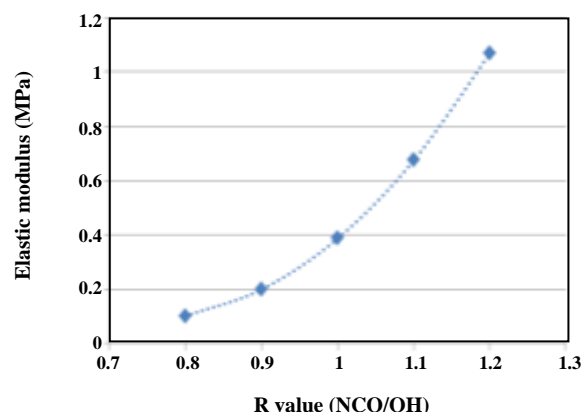
for the given conditions. The only possibility for formation of isocyanurates can happen at high temperatures via a strong organic base; hence, the chemical bond formation between NCO and OH groups is the major reaction.

In fact, the comparison of the FT-IR spectra taken before and after curing (Fig. 7) gives convincing proof for the reaction between NCO and OH groups to yield polyurethane linkages.

Mechanism of Curing Reaction for the Polyurethane Formation

The reaction between Nitro-HTPB prepolymer and diisocyanate was monitored by following the variations of IR absorption bands of NCO stretch of 2255 cm^{-1} and CO stretch of 1730 cm^{-1} (Fig. 7). The intensity of IR absorption band for NCO stretch of 2255 cm^{-1} decreased and intensity of the band for the CO stretching at 1730 cm^{-1} increased, while there was almost no variation within the intensity of C=C stretching peak at 1640 cm^{-1} during the curing reaction. IR absorptions of OH stretch of 3400-3600 cm^{-1} were identified to be quite broad and weak. It was observed that there is no considerable variation in this spectrum rage. Reduction of specific absorption for NCO stretch of 2255 cm^{-1} and also the growth of the band for the CO stretch of 1730 cm^{-1} are assigned to polyurethane formation (-NHCOO-) [22]. The IR band at 1515 cm^{-1} is indicative of N-H bending. The mechanism of curing reaction of Nitro-HTPB prepolymer for the polyurethane formation is presented in Fig. 6.
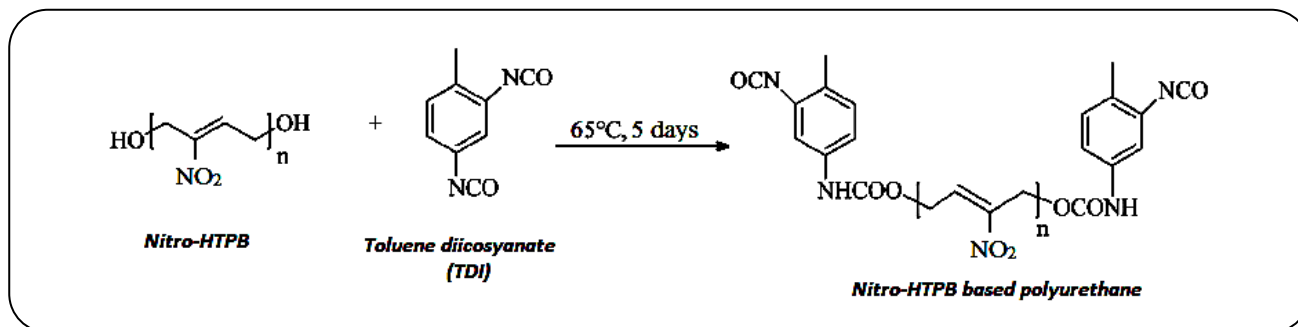
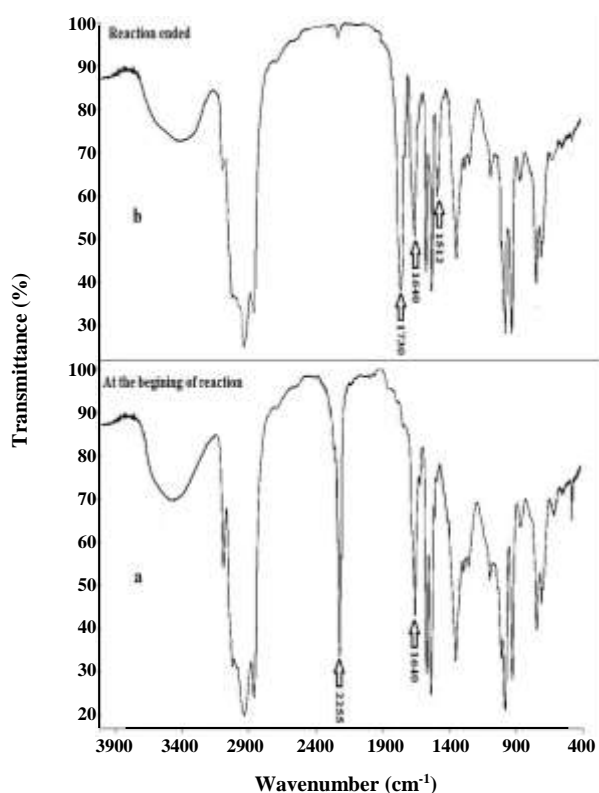*Fig. 6: Reaction scheme for the synthesis of Nitro-HTPB base polyurethane.*

Fig. 7: FT-IR spectra of a mixture of Nitro-HTPB and TDI with a NCO/OH ratio of 1.00 (a) before and (b) after curing.
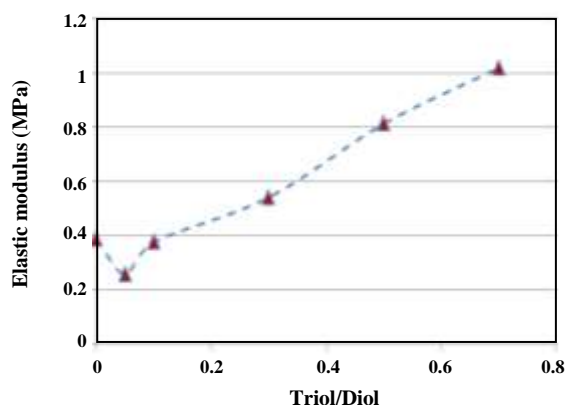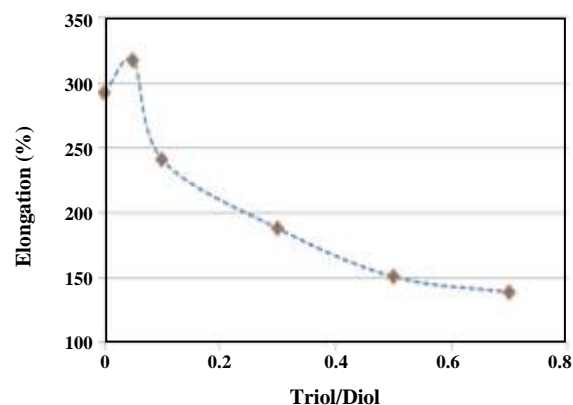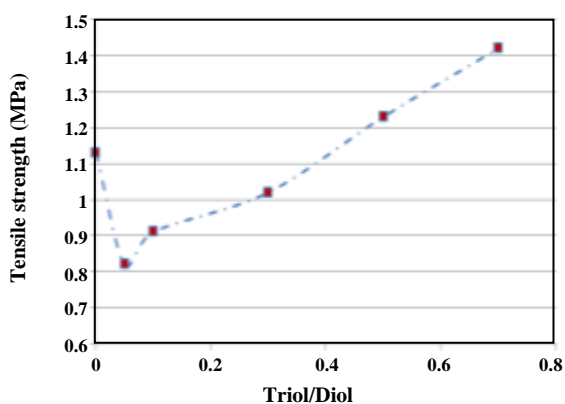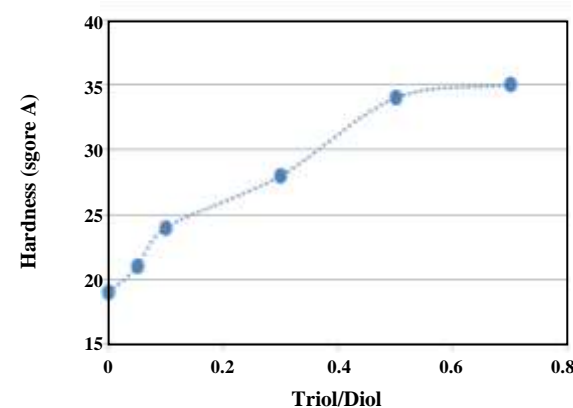
Influence of triol/diol Molar Ratio on Mechanical Properties

The Influence of the triol/diol molar ratio on the mechanical properties of polyurethane elastomers was investigated by varying the amount of trimethylolpropane (TMP) as triol for crosslinks formulation with $R = 1$ to reach desirable mechanical attributes. Polyurethane samples were determined in regards to studying of tensile strength, elongation, and hardness. These related results are presented in Table 4. The tests were performed by changing the triol/diol molar ratio in the limited range of 0.05-0.7. The main background of applying the cross-linking agents is the modification of total properties of polymers. Crosslinking agents can be penetrated to a polyurethane matrix via triols and small polyols as chain extender with functionality larger than 2. With increasing the crosslink density of the polyurethane matrix, some fundamental changes occur in the mechanical properties. As an example, modulus of the polyurethane matrix decreases at first and begins to increase as given in Fig. 8. An initial reduction in the modulus indicates the attainment of a rubbery attribute with the inclusion of crosslinks into the matrix along with a decrement of average molecular weight, as three molecules of Nitro-HTPB are substituted by two small molecules of TMP. As the quantity of crosslinks improves above a crucial level, which may be correlated to the formation of unlimited networks, the matrix becomes more rigid. The tensile stress values also increase coincide with increasing the triol concentration of polymeric matrix (Fig. 9). In the lack of triol molecules, the polyurethane elastomer reveals a great tensile strength (1.13 Mpa), owing to the high average molecular weight. Since a few triol molecules are entered into the matrix, the average molecular weight is reduced. Therefore, there is not a balance between the crosslink density and the average molecular weight. This is supposed to be accountable for reduction of tensile strength. An observation which reflects the change in the modulus (Fig. 8), is the variation of maximum elongation with triol/diol molar ratio (Fig. 10). The elongation at break increases first with the increasing concentration of triol, and after reaching a maximum at the triol/diol ratio of 0.05, it starts to decrease. This observation indicates that the attainment of a rubbery feature followed by increased hardness

Table 4: Mechanical properties of the elastomer samples with various triol/diol ratios.

Sample	triol/diol	Tensile Strength (MPa)	Elongation at Break (%)	Elastic Modulus (MPa)	Hardness (Shore A)
3	0	1.13	292	0.387	19
5	0.05	0.82	317	0.258	21
6	0.1	0.91	241	0.377	24
7	0.3	1.02	188	0.542	28
8	0.5	1.23	151	0.814	34
9	0.7	1.42	139	1.02	35

Fig. 8: Influence of triol/diol on the elastic modulus of elastomers.

Fig. 10: Influence of triol/diol on elongation at break of elastomers.

Fig. 9: Influence of triol/diol on the maximum tensile strength of elastomers.

Fig. 11: Influence of triol/diol on the hardness of elastomers.

with an increment in triol/diol molar ratio. In general, Hardness varies with the concentration of the matrix components and the crosslink density. In these experimental tests, the amount of linkages of polyurethane is fixed at *R*-value of 1. The amount of hard segments per matrix unit increases with the increment of triol/diol molar ratio. Accordingly, the increment

of hardness (Fig. 11) is directly attributed to the increment of the matrix crosslink density and the number of hard segments.

CONCLUSIONS

The effects of the *R*-value and triol/diol molar ratio on mechanical properties of the Nitro-HTPB based unfilled

polyurethane elastomers were investigated. The conclusions deduced from this investigation show some considerable trends. As a result, the elastomeric polyurethane sample indicated the highest value of tensile strength at $R = 1.1$, and the value of 185% for elongation. It was observed a decrement of modulus and tensile strength with a resultant increment of elongation for the elastomeric samples with a triol/diol molar ratio under 0.05. With a triol/diol ratio higher than 0.05, the tensile strength reached approximately the identical value for the elastomeric polyurethane in absence of triol molecule. It was recognized a stable increment of hardness and elongation for the triol/diol molar ratios under 0.5. For the elastomer samples possessing a triol/diol molar ratio higher than 0.3, the modulus is about 40% higher than for the elastomer samples in lack of triol. The expected mechanical properties have been exhibited by Nitro-HTPB based polyurethane elastomers. Therefore, the future study will focus on Nitro-HTPB as the potential energetic binder for solid composite propellants.

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