

# Investigation of the Gum Stock Behavior of Polyurethane Crosslinking Matrix by Adding Triol/Diol Mixtures for the Application of Composite Solid Rocket Propellants

Islam Kamal Boshra, Tarek Mahmoud Elhedery, and Ahmed Elbeih\*

*Military Technical College, Cairo, Egypt*

*\*E-mail: elbeih.czech@gmail.com*

## ABSTRACT

The addition of some advanced additives to improve the mechanical properties of polyurethane (PU) polymeric matrix, which acts as a binder system in composite solid rocket propellants (CSRPs), is a target for the energetic materials researchers. In this investigation, 45 compositions of different crosslinked PU matrices were produced to demonstrate the effect of adding crosslinking mixture (CM) on the mechanical capabilities of polyurethane gum stock. The crosslinking mixture (CM) is composed of a triol crosslinker, trimethylolpropane (TMP), and a chain extender, 1,4-butanediol (BD). For comparison, traditional PU samples without crosslinking additives were formulated. As a prepolymer, HTPB was used with a curing agent (HMDI). The research was carried out with different ratios of TMP to BD, different curing ratios (NCO/OH=0.7, 0.9, and 1.1), and crosslinking mixture contents in the range of 0-5 wt.%. The mechanical characteristics of all the cured formulations were measured. It was demonstrated that changing the ratio of TMP to BD has a significant impact on the mechanical performance causing a wide range of elongation and strength qualities. Increasing the wt.% of triol crosslinker in the sample enhanced the tensile strength, whereas the strain has been decreased. The addition of diol chain extender increased the strain rate of the samples. The mechanical parameters were adjusted simply by employing the crosslinking ingredients to get exceptional mechanical characteristics at each NCO/OH curing ratios. Also it was concluded that PU samples of curing ratio (NCO/OH= 0.7-0.9) with TMP:BD (1:1) showed a promising results and could be used according to the requirements of the rocket system designers.

**Key words:** Polyurethane; Hydroxyl terminated polybutadiene; Crosslinker; Mechanical properties; Trimethylol propane; Butane diol

## 1. INTRODUCTION

Polyurethane (PU) matrix has several applications in the building constructions field<sup>1</sup>, industries of furniture and electronic technology and in the field of energetic materials due to its special properties such as strength, elongation, aging and resistance to solvent<sup>2-6</sup>. Currently polyols are substituted in the production of polyurethanes by small diol compounds to enhance their structural and thermal capabilities. The application of different polyols or isocyanates in the design of PU matrices resulted in a reliable products with adjustable chemical and physical properties<sup>7</sup>. PU structure exhibits a complicated dependency on the chemical formula, procedure of preparations and history of materials. There are no clearly defined guidelines to achieve optimum characteristics of polyurethane elastomer which could be suitable for the different applications. Different researches have studied the relationship between the structure and the properties of the PU polymeric matrix and proved that the desired characteristics depend on the crosslink density, hydrogen bonding, morphology and mechanical characteristics of the studied matrix<sup>8</sup>.

Investigation of the mechanical characteristics is the most common used methodology to identify the binders. In

addition, the crosslink density (CLD) represents the most important polymeric parameter that determines the mechanical properties of the binder structure and damping performance. Linear relationships between the CLD results and tensile characteristics were approved<sup>9</sup>. Polyurethanes tend to exhibit phase segregation where the soft components generate polymeric reactions while the physical cross-linking process, which takes place by the microphase, enriched within the hard segments. The phase segregation significantly increases the PU mechanical abilities. The properties of hydroxyl-terminated polybutadiene (HTPB) such as OH number, microstructure, functionality and mean molecular weight are considered the most important aspects that affect the mechanical and thermal properties of HTPB-based PU<sup>10-15</sup>.

Furthermore, some manufacturing defects, including a shortage of an acceptable grade of HTPB, allow the researchers to utilise specific additives to achieve crosslinking reactions with optimal thermal and physical capabilities. Chain extenders and crosslinkers are two of the most efficient additives used to improve the PU quality by converting its morphology from a linear to a branched net structure<sup>16-18</sup>. Polyurethane chain extenders have received a lot of investigations<sup>19</sup>. Introducing chain extenders in gum stock formulations, such as low molecular weight diols, increases the elastomeric properties of the prepared PUs because the link formed between those

diisocyanates and diols creates hard spots that perform as branching locations for the chains of PU<sup>20</sup>. HTPB-based polyurethanes with 1,4-butanediol (BD) besides curing agents such as 1,6-hexamethylene diisocyanate (HMDI) and Toluene diisocyanate (TDI) were investigated<sup>21</sup>. Adding more content of urethane group will cause increasing the interchain forces as a result of larger hydrogen bonds formed inside the chains of the polymer. As a result, the most popular aliphatic diol (BD) can be added as an extending agent for the PU chains. Hard polyurethane sections include diisocyanate residues, chain extenders, and urethane groups. The higher the symmetry of the diisocyanate backbone and chain extension, the harder segments will crystallise, whereas the soft segments will contain elastic chains that will not be crystallised (polybutadiene).

The ability of macromolecular slip decreases due to increasing the forces of inter-chain, crystallinity and stiffness of hard segments; it causes a rise in the tear, stress and modulus of elasticity which has an enormous influence on the mechanical characteristics<sup>22-23</sup>. It was noted that linear polyurethanes show insufficient mechanical characteristics such as dumping, low elasticity, etc.<sup>24</sup>. To improve the mechanical capabilities of the PU, the matrix has to be converted from a linear to a branching network structure<sup>25-26</sup>. The crosslinking process of polyurethane polymeric matrix can be obtained by different methods<sup>27-28</sup>. Trimethylolpropane (TMP) and triethanolamine (TEA) are low molecular weight triols that have been utilized as crosslinkers in several sorts of researches<sup>29-35</sup>. Triols such as trimethylolpropane (TMP) create spots to allow the crosslinking process to take place<sup>36-37</sup>. Polymer chains are not planar but have different groups and atoms projecting in different angles<sup>38</sup>. PU structure design gives a three-dimensional stability grain of composite solid propellant which allows it to withstand the heat cycle during the combustion<sup>39</sup>. A long pot life is required during the mixing and casting process of the propellant<sup>40</sup>. Due to the fact that aliphatic diisocyanates have a longer pot life than aromatic diisocyanates, aliphatic isocyanates are preferred<sup>41-42</sup>. The functionality of the binder, curing ratio, selection of crosslinker, concentration and curing circumstances have an impact on the gum stock architecture that supplies the binder system with the required mechanical qualities<sup>43-44</sup>. The mechanical capabilities of HTPB-based propellants are superior to those of other propellants which based on energetic prepolymers such as glycidyl azide polymer (GAP) due to its inert performance and the stability of HTPB prepolymer structure<sup>45-47</sup>.

In our investigation, 45 crosslinked PU compositions were produced and tested to demonstrate the effect of CM on the mechanical properties of PU gum stock in comparison with traditional samples. As a prepolymer, HTPB was used with a curing agent (HMDI). Five various crosslinking mixtures based on different ratios of TMP to BD were investigated. The research was carried out with different curing ratios (NCO/OH=0.7,0.9, and 1.1) and different crosslinking mixture contents. After curing, the mechanical characteristics of all the cured formulations were measured.

## 2. EXPERIMENTAL WORK

### 2.1 Materials

HTPB R-45M hydroxyl-terminated polybutadiene

received from Zibo Qilong Chemical Industry, Shandong, China (viscosity at 25 °C: 5800 cps; OH number: 0.84 meq/g; density: 0.9 g/mL; (Mn): 2800 g/mol), Both 1,4-butane diol 99 per cent and 1,1,1-trimethylol propane (TMP) 97 per cent were purchased from Aladdin reagents, China, both hexamethylene diisocyanate (HMDI) and dibutyl tin dilaurate (DBTDL) 95 per cent supplied by Sigma-aldrich Germany.

### 2.2 Preparation of Polyurethane Gum Stock

To improve the mechanical performance of polyurethane formulations, a crosslinking mixture (CM) including triol crosslinker (TMP) and chain extender (BD) was added. This investigation employed five various crosslinking mixtures as a result of adjusting the ratio of TMP to BD (1:1,1:0, 0:1, 1:2 and 2:1 respectively) to explore the influence of the crosslinking compositions on the mechanical characteristics of PU samples.

The preparation process of the crosslinking mixture was performed separately in a spinning vacuum mixer under a temperature of 50-60 °C for 2 hours to mix the proportional amount of the cross-linker (TMP) and the chain extender (BD). Polyurethane was produced by adding the corresponding crosslinking mixture to the HTPB at 25 °C and stirred with 250 rpm for 1 hour. Following the mixing process, the slurry was reacted with the calculated amount of HMDI and catalyst DBTDL and stirred at the same temperature under vacuum for 10 minutes. Finally, the mixture was casted in the moulds (Jannaf) and put into oven for curing within three days at a temperature of 60 °C.

### 2.3 Mechanical Characterization of the Prepared PU Samples

After removing of the JANNAF shaped specimens from the mould, an experimental evaluation of the tensile strength-strain relationship was carried out using testing machine LRX-5K – LLOYD. The tensile test was tested 3 times for each composition, and the mean value of the data obtained was reported. The test was performed at normal temperature +25 °C with 5000 N load cell and cross head speed 50 mm/min (accuracy 0.5 of set speed). The machine contains remote control software (DAPMAT) which could acquire recording, analysing, storing and printing test data. 45 samples were prepared as reported in Table 1, 2 and 3 and were used to analyze the influence of the applying CM on the mechanical properties of PU gum stock based on the following parameters:

#### 2.3.1 Influence of Different Curing Ratios on the Mechanical Behavior

Three different curing ratios, NCO/OH ratio (0.7, 0.9, and 1.1), were prepared for all the samples with various content of crosslinking mixture; 1, 3, and 5 wt.% of the prepolymer HTPB in comparison with samples with 0% content of CM as indicated in Table 4. The results were plotted in Fig. 1-5.

#### 2.3.2 Influence of the CM wt.% on the Mechanical Behavior

The influence of the CM wt% on the PU gum stock behavior were studied at different curing ratios for

all the prepared samples based on the different TMP:BD ratios. The results were determined and plotted in Fig. 6-8.

### 2.3.3 Influence of TMP-BD Ratio on the Mechanical Behavior

The influences of TMP-BD ratio on the mechanical behavior at different NCO/OH ratios were studied for all the prepared samples with different CM wt%. The results were determined and plotted in Fig. 9-11.

## 3. RESULTS AND DISCUSSION

To investigate the influence of the crosslinking mixtures on the mechanical behaviour of the PU matrix, 5 different mixtures of CM based on changing the ratio of TMP to BD were studied. The different mixtures of CM were studied at 3 various curing ratios NCO/OH starting from 0.7 to 1.1 and at different wt.% of the samples to obtain eventually 45 samples of PU gum stock. Samples of PU without any crosslinking additives were also tested for comparison. All the PU formulations were characterised mechanically by tension test to indicate their tensile strength and elongation as reported in tables 1-4.

The influence of different curing ratio on the mechanical behavior of crosslinked PU gum stock with various crosslinking mixtures is presented in Fig. 1 to Fig. 5 respectively including different weight percentages (0, 1, 3 and 5 %). It was observed from the results of all samples that the default gum stock behaviour for all crosslinking mixtures (CM) occurred such that the increase of curing ratio with varied weight percentages of CM resulted in increasing the tensile strength and decreasing the strain. The influence of the different CMs addition with varied percentages on the tensile strength and strain is based on the mechanical characteristics of the PU samples without the crosslinking additives.

**Table 1. Tensile strength – strain characteristics of gum stock samples at NCO/OH = 0.7**

CM (TMP:BD)	Crosslinking mixture (wt%)	Strain (%)	Tensile Strength (kg <sub>f</sub> /cm <sup>2</sup> )
1 : 0	1	345	6.7
	3	311	7.5
	5	282	8.1
0 : 1	1	621	2.8
	3	592	3.2
	5	568	3.5
1 : 1	1	478	4.9
	3	460	5.1
	5	439	5.5
2 : 1	1	410	6.2
	3	393	6.7
	5	378	7.1
1 : 2	1	583	3.3
	3	557	3.6
	5	528	4.1

**Table 2. Tensile strength – strain characteristics of gum stock samples at NCO/OH = 0.9**

CM (TMP:BD)	Crosslinking mixture (wt%)	Strain (%)	Tensile Strength (kg <sub>f</sub> /cm <sup>2</sup> )
1 : 0	1	274	47.2
	3	233	54.1
	5	204	59.8
0 : 1	1	451	16.1
	3	418	19.8
	5	396	25.1
1 : 1	1	346	32.8
	3	330	35.1
	5	312	38.2
2 : 1	1	301	39.7
	3	284	47.2
	5	265	51.3
1 : 2	1	427	19.8
	3	398	23.2
	5	361	27.5

**Table 3. Tensile strength-strain characteristics of gum stock samples at NCO/OH = 1.1**

CM (TMP:BD)	Crosslinking mixture (wt%)	Strain (%)	Tensile Strength (kg <sub>f</sub> /cm <sup>2</sup> )
1 : 0	1	186	79.1
	3	159	93.5
	5	138	105.1
0 : 1	1	305	27.9
	3	279	33.5
	5	259	40.9
1 : 1	1	231	56.1
	3	218	63.8
	5	207	71.1
2 : 1	1	209	64.2
	3	181	79.1
	5	170	91.5
1 : 2	1	291	31.9
	3	269	39.1
	5	240	45.1

**Table 4. Tensile strength-strain characteristics of PU gum stock without CM**

NCO/OH	HTPB (wt %)	HMDI (wt %)	Strain (%)	Tensile Strength (kg <sub>f</sub> /cm <sup>2</sup> )
0.7	95.27	4.73	420	4.8
0.9	94.0	6.0	320	27.8
1.1	92.76	7.24	215	48.2

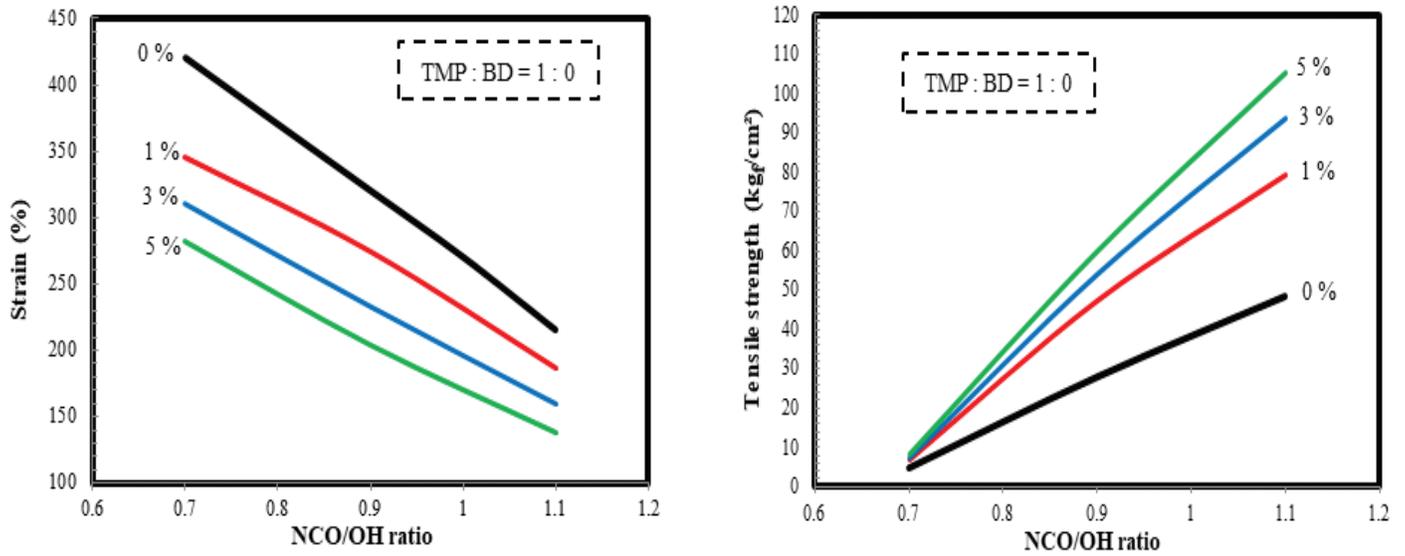


Figure 1. The influence of different curing ratio on the mechanical behavior CM (1:0).

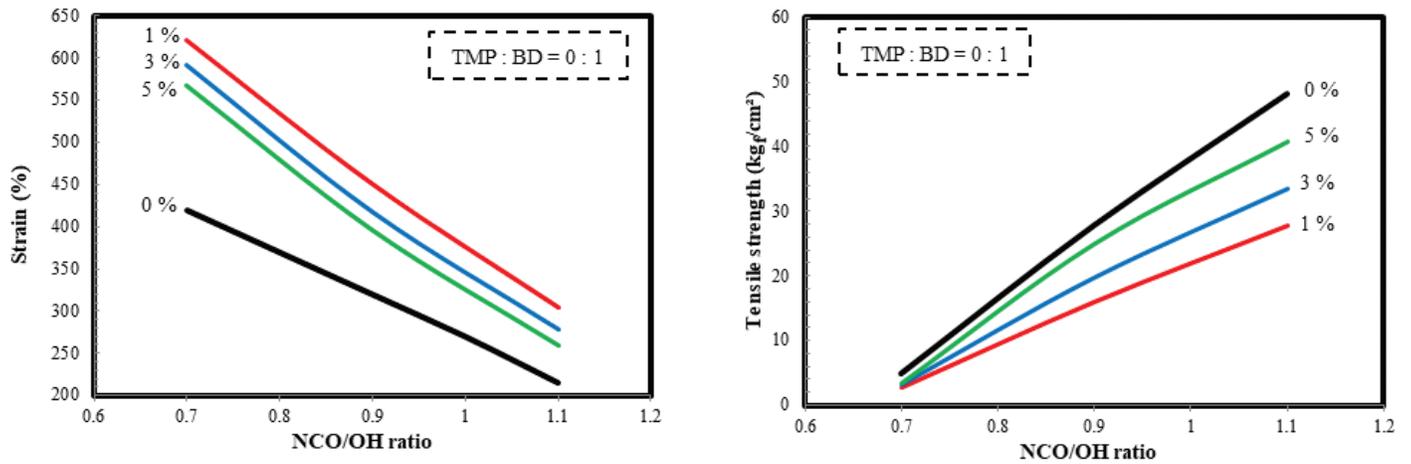


Figure 2. The influence of different curing ratio on the mechanical behavior CM (0:1).

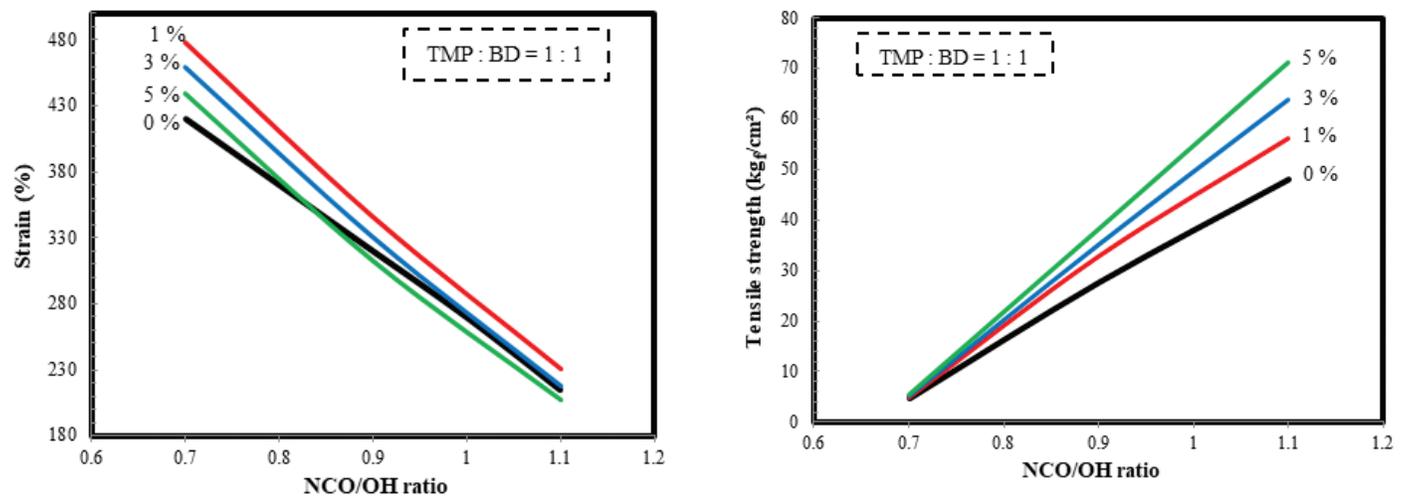


Figure 3. The influence of different curing ratio on the mechanical behavior CM (1:1).

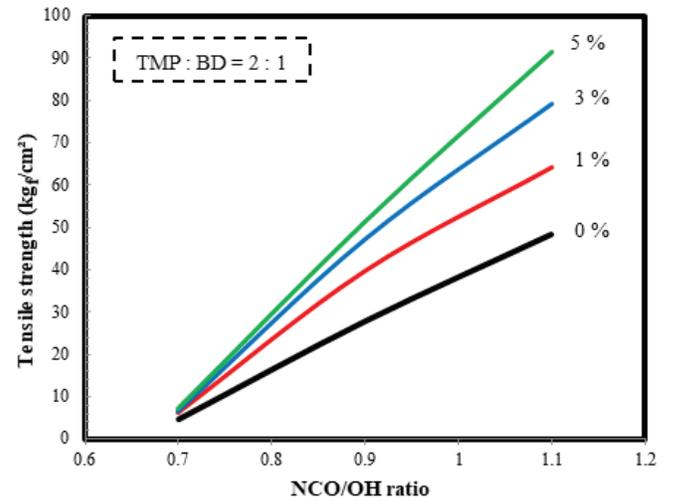
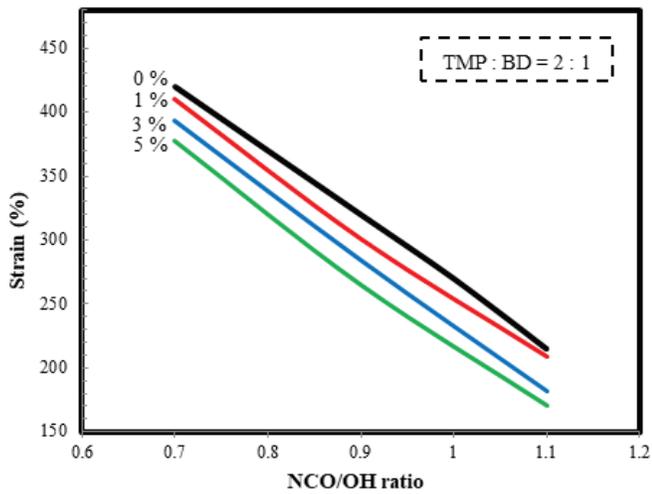


Figure 4. The influence of different curing ratio on the mechanical behavior CM (2:1).

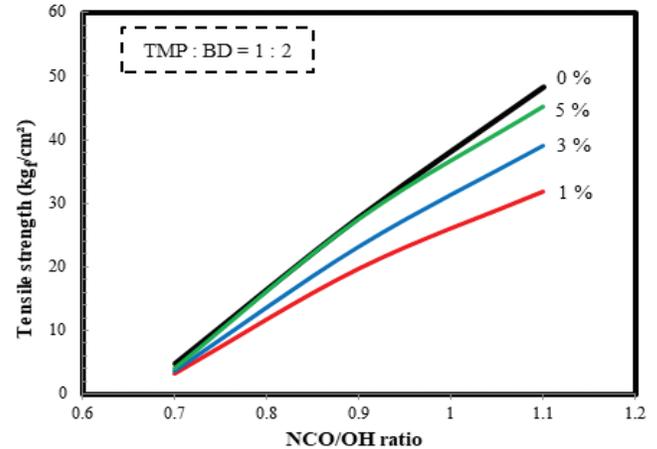
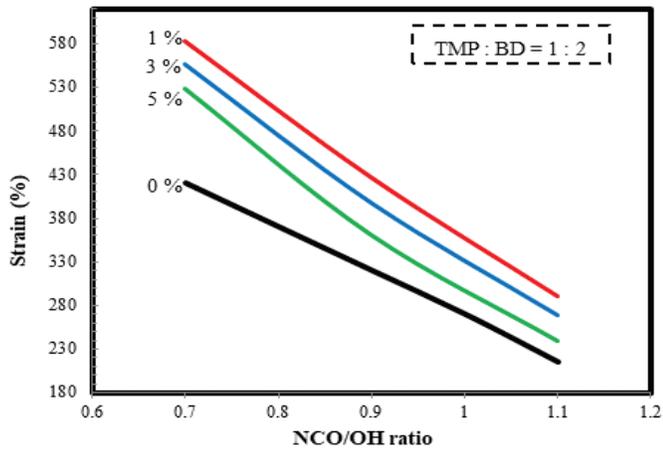


Figure 5. The influence of different curing ratio on the mechanical behavior CM (1:2).

Since CM (1:0) and (2:1) have a higher TMP ratio than BD, the tensile strength increases with increasing the wt.% of CM due to the high cross-linking density of TMP. As a result, the greatest stress results were observed for samples without BD, CM (1:0). On the other hand, increasing the wt.% of CM in the samples resulted in increasing the interchain cross-linking content with poor extension capacity causing a significant drop in the strain values. In case of PU formulations containing CM (0:1) and (1:2) of higher BD extender ratio than TMP crosslinker, it was evident that BD showed a significant influence on reducing the tensile strength due to the longer chains produced by the act of chain extender BD as showed in CM 1%. However, as a consequence of the high reactivity of BD hydroxyl group (OH), it forms a hydrogen bond that has a significant influence on the crosslinking and interchain forces. The hydrogen bond produces forces that restrict the molecular flow and decrease the elongation capacity of the gum stock elastomer. As a result, samples without TMP, CM (0:1), have the lowest tensile strength of all the other samples. On the other hand, adding CMs (0:1) and (1:2) raise the strain of the samples due to the presence of the diol which is required to maintain the elongation feasibility.

Figures 6, 7 and 8 present the influence of the CM composition on the mechanical behaviour of PU gums stock at various curing ratios = 0.7, 0.9 and 1.1 respectively. For PU containing CM (1:1), the strain and tensile strength values exist between the values of all the prior findings that contain varied ratios of TMP to BD. Samples with higher wt.% of TMP than BD have higher tensile strength and lower strain than samples containing CM (1:1) while samples with higher wt.% of BD than TMP have higher strain and lower strength. Also the tensile strength of PU samples containing CM (1:1) increase as the NCO/OH ratio increase.

The utilised crosslinking combination of diol (BD) and triol (TMP) has an obvious effect on the mechanical characteristics of the produced PU gum stock polymeric matrix due to the change of the triol to diol ratio. Figures 9, 10 and 11 present the variation of the mechanical behavior of the samples with the change of the weight ratio of TMP to BD at the three curing ratios 0.7, 0.9 and 1.1 respectively. It is clear that the tensile strength of the samples increase and the elongation decrease by increasing the triol/diol ratio.

The stress progression was observed for samples with a high percentage of butane diol due to the significant influence

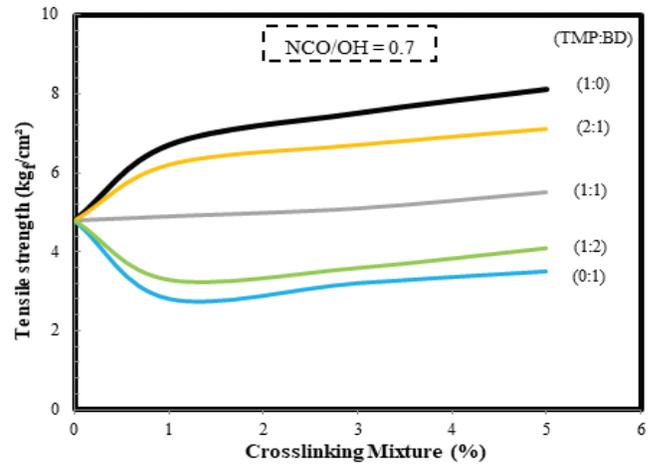
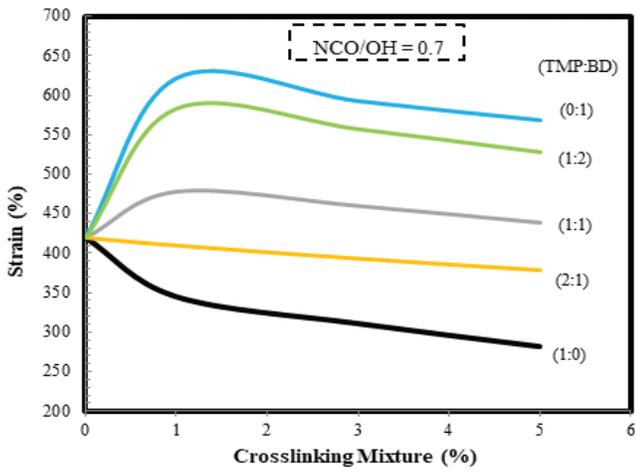


Figure 6. The effect of CM content on the mechanical behaviour at NCO/OH = 0.7

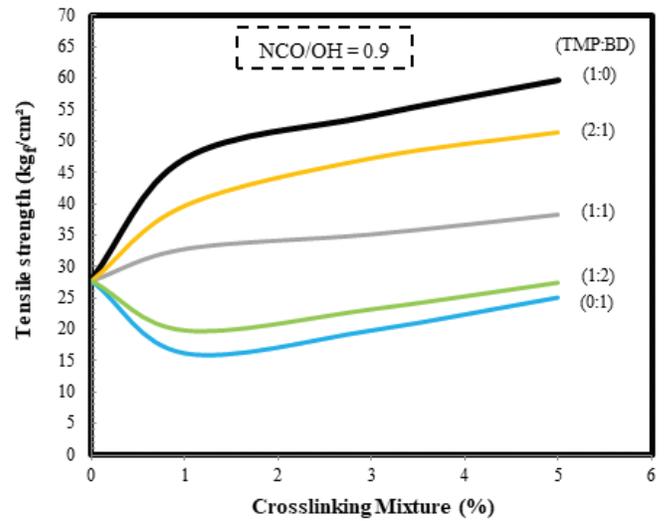
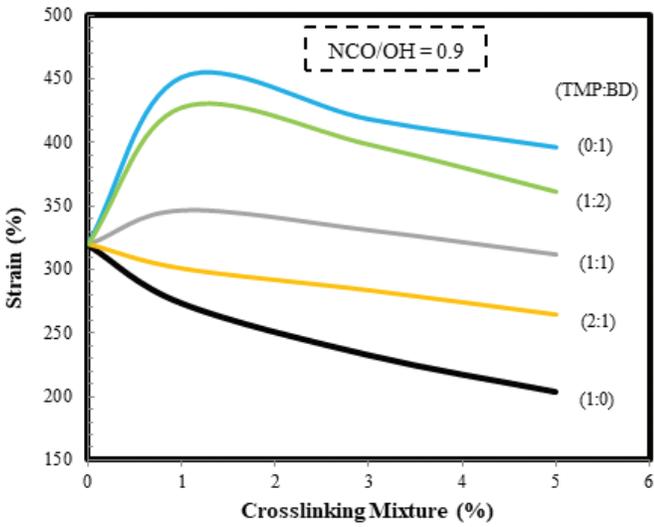


Figure 7. The effect of CM content on the mechanical behaviour at NCO/OH = 0.9

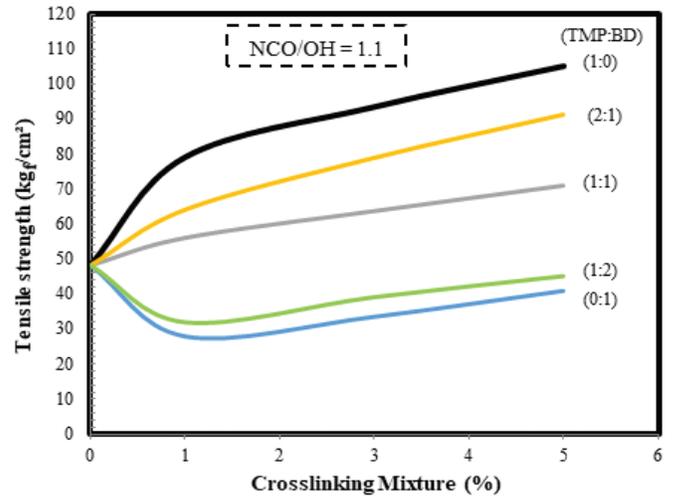
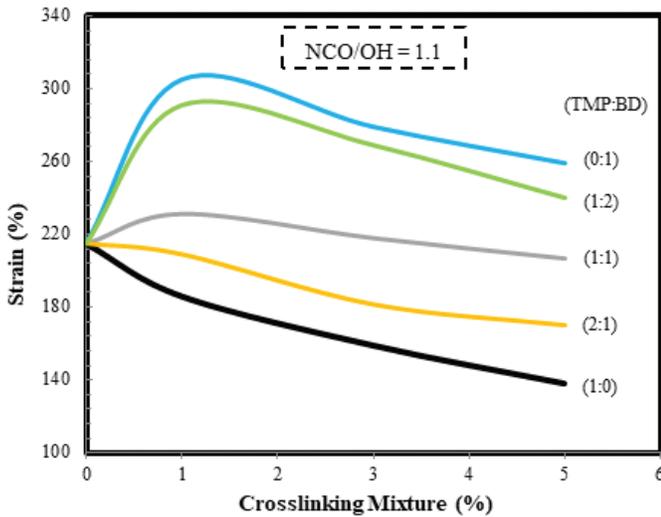


Figure 8. The effect of CM content on the mechanical behaviour at NCO/OH = 1.1

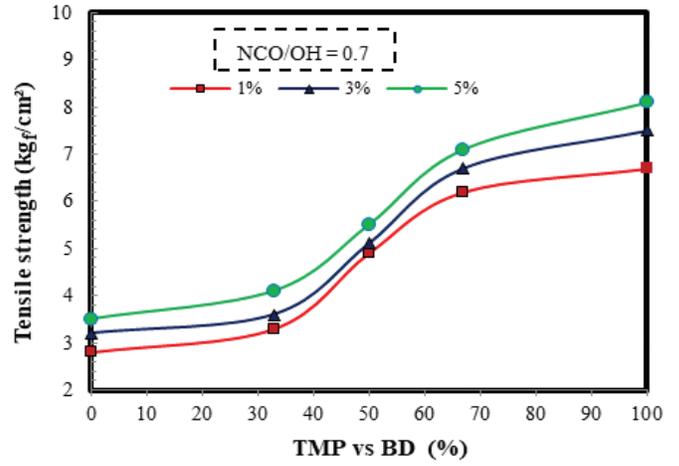
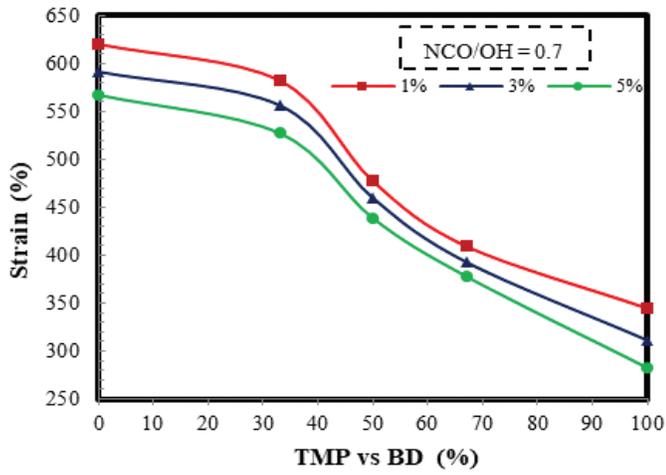


Figure 9. The influence of TMP-BD ratio on the mechanical behaviour at NCO/OH = 0.7

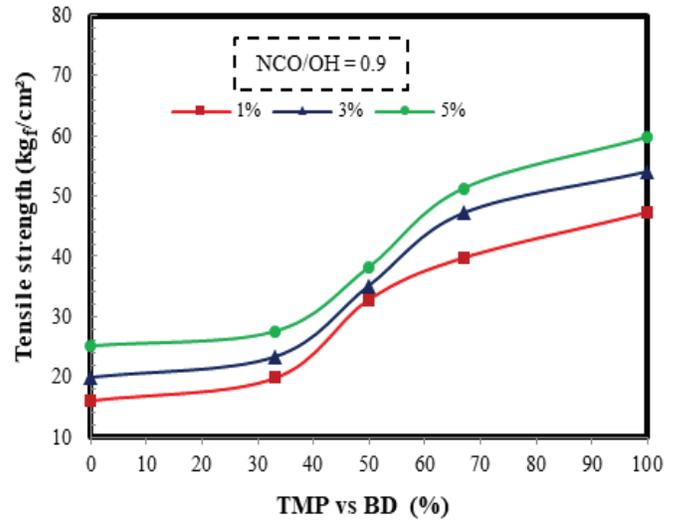
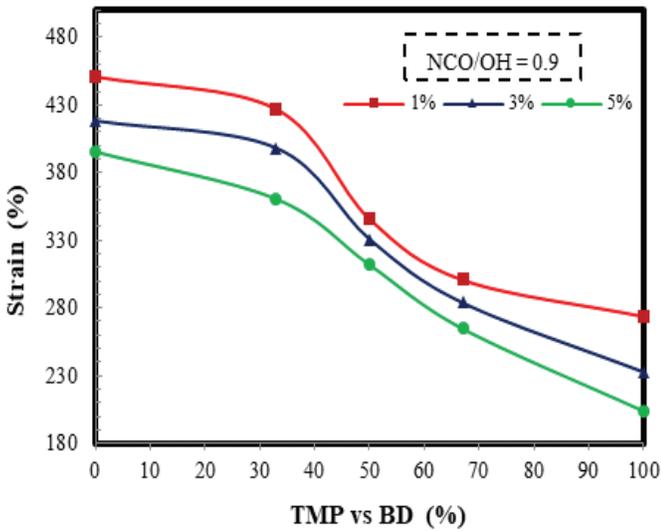


Figure 10. The influence of TMP-BD ratio on the mechanical behaviour at NCO/OH = 0.9

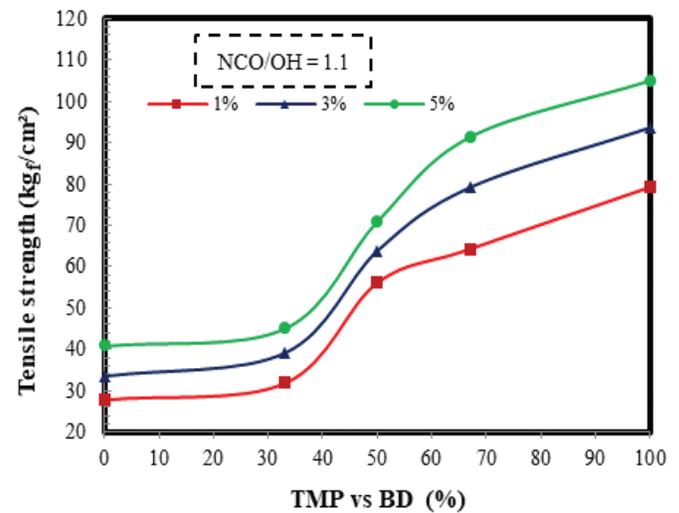
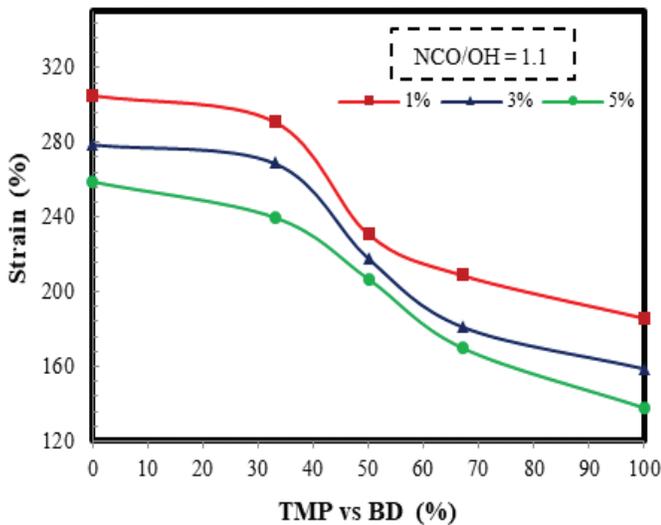


Figure 11. The influence of TMP-BD ratio on the mechanical behaviour at NCO/OH = 1.1

of the high level of chain extension. When TMP ratio starts to increase versus BD in the mixture, a decrease in the strain was observed. The strength progression occurred due to increasing the percentage of TMP in the samples which caused a building up of the crosslinking density and leading to 3-D chain crosslinking structure. A sharp slope was observed within TMP ratio (40-60%) for the strength and strain curves. Afterwards, an increase of the strength refers to the optimum reached crosslinking density at which the gum stock rubbery nature was converted to rigid structure. It was also observed that the slopes of both strength and strain are nearly the same over the various CM contents except for the interval of (40-60%). Also increasing the wt% of CMs in the samples leads to reducing the elongation and increasing the tensile strength due to increasing the quantity of crosslinking agents in the polymeric matrix. Meanwhile, the highest strength value was observed at NCO/OH = 1.1 due to the presence of higher content of curing agent and diisocyanates curative groups at higher curing ratios.

#### 4. CONCLUSIONS

The mechanical characteristics of all the prepared PU formulations having crosslinking additives (CMs) demonstrated the impact of increasing NCO/OH which caused increasing the tensile strength and decreasing the strain. Regarding to the gum stock behavior of PU formulations, samples which include crosslinking additives of higher TMP ratio than BD yielded to higher strength and lower strain. However, the sample with only TMP has the maximum strength and lowest strain of all the studied samples. The PU samples with a higher ratio of BD than TMP have low strength and high strain proportionally up to CM content of 1% while raising the CM content to 5 wt% resulted in the opposite effect. Compositions containing CM (1:1) performed increasing the tensile strength with increasing the CM content to 5 %. The composition of the crosslinking mixture is an essential parameter that influences the mechanical characteristics of the produced PU. The high percentage of TMP in the crosslinking mixture resulted in high strength and low strain while the increase of the BD percentage in the mixture led to high strain characteristics. The use of crosslinking compounds into the PU framework resulted in improving the mechanical performance. In this investigation, various combinations of the CM compositions and their contents were applied at three distinct curing ratios. As a result, a wide range of mechanical properties was obtained, which could help the designers of the rockets systems to select the suitable solid rocket propellant composition.

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**CONTRIBUTORS**

**Dr Eng. Islam Kamal Boshra** obtained his BSc and MSc (Chemical Engineering) from Military Technical College, Cairo, Egypt in 2008 and 2014 respectively. He obtained his PhD degree from School of Chemistry and Environment, Beihang University, Beijing, China. He is currently working as a researcher in the Explosives department, Military Technical College. His main areas of research include synthesis and characterization of high energy materials, development of polymer technology, Investigation of modern gun and rocket propellants. His contribution in the current study includes the preparation of the samples and participates in the experimental measurements; study of the polymeric matrices used in the manuscript and participates in the discussion.

**Dr Eng. Tarek Mahmoud Elhedery** obtained his BSc (Chemical Engineering) from Military Technical College, Cairo, Egypt in 2008 and his MSc (Chemical Engineering) from faculty of engineering (Cairo university) in 2011. He obtained his PhD degree from School of Astronautics, Beihang University, Beijing, China in 2015. He is currently working as a researcher in the Explosives department, Military Technical College. His main areas of research include synthesis and characterization of high energy materials, development of insensitive ammunition and high-performance plastic explosives and composite solid rocket propellant. His contribution in the current study includes participation in the experimental measurements, study of the polymeric matrices used in the manuscript.

**Prof Dr Ahmed Elbeih** obtained his PhD degree from the Institute of Energetic Materials, Pardubice University, Czech Republic. He was Head of Explosives department, Military Technical College and currently he is working as a Head of Explosives Research center, Military Technical College, Cairo. His main areas of research include synthesis and characterization of high energy materials, development of insensitive ammunition and high performance plastic explosives, Investigation of modern gun and rocket propellants, ageing and life extension of propellants. He obtained the Egyptian State Encouragement Award for Engineering Science in 2015. His contribution in the current study includes the analysis of the results and participates in the discussion.