An experimental study on mechanical and ballistic characteristics of different HTPB composite propellant formulations

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Abstract. The main goal of this paper is to investigate the changing in the tensile behavior and the burning rate characteristics of hydroxyl-terminated polybutadiene (HTPB) propellant under the variations of the crosslinking density, which was predominantly determined by the equivalent ratio of diisocyanate to total hydroxyl (NCO/OH ratio), which known as the curing ratio. Four various batches with different curing ratios (NCO/OH) percentage were produced in which the production processes were fixed. Uniaxial tensile tests were conducted at different temperatures (-40, 20 and 55°C), and different strain rates (0.000656 1/s, 0.0328 1/s) using a Zwick universal test machine. In order to measure the burning rate, cured solid propellant strands were tested using the acoustic wave emission method under different pressure ranging from 4 to 10 MPa. The experimental results indicate that the tensile behavior of HTPB propellant is remarkably influenced by curing ratio, strain rate, and temperature. It was observed that a great change on stress-strain curves affected various curing ratios and temperatures on the mechanical behavior of propellant composition. The results showed that high curing ratio leads to increase the ultimate stress and decrease the strain at maximum stress, but higher temperatures lead to decrease the ultimate stress and the strain at maximum stress. The curing ratios (NCO/OH) have an intense impact on mechanical characteristics, but slightly impact on ballistic characteristics for propellant. Furthermore, careful measurements of these parameters are important to control the production quality and to provide a reliable comparison between different propellant batches.

1. Introduction
Composite solid propellants have wide applications in strategic, tactical missiles, as it is responsible for delivering the required thrust to the missiles [1]. Additionally, it is characterized with its simplicity of design, simplicity of operation, safety, dependability, high specific impulse, stretched off life time and low cost [2,3]. Composite solid propellant is a heterogeneous mixture of solid particles including oxidizer and metallic fuel which are scattered in a polymeric matrix [4]. Hydroxyl terminated polybutadiene (HTPB) constructed composite solid propellants are the most common classification of composite propellants due to their developed performance and conventional processing technology. Polymeric binder is answerable for stock the solid components into the matrix and providing the composite propellant with its viscoelastic nature [5].

Composite propellants are unprotected to thermal and mechanical loads during manufacturing, transportation, storage and operation, as a result composite formulation must endure throughout these numerous times [6]. Mechanical disappointment means a decrease in life time or it is a complete
The mechanical properties and life time of the composite propellant are mostly evaluated by applying uniaxial tensile [8,9]. Crafting design of composite propellant with perfect performance parameters, ballistic characteristics and mechanical properties are critical features for propellant formulation selection [10,11]. The composite solid rocket propellant (CSRP) burning rate has been reported to be an essential ballistic parameter that must be predicted and controlled throughout the combustion process [12-14]. The result show that, a small change in operating pressure would result in a dramatic increase in the burning rate, which could lead to a catastrophic ignition process resulting in an explosion of the missile motor. The ballistic characteristics could be evaluated using small scale test motor, strand burners include (i.e. Crawford burner, Acoustic wave emission technique, etc.) [14-16]. However, small scale test motor provides actual ballistic parameters, strand burners are characterized with its easiness, low price, high reliability although sample with minor amount of propellant are existing [16].

On the other hand, the mechanical behavior of solid propellants is mainly influenced by the polymeric nature of binder, curing agent and interaction between binder and solid elements [17]. The curing ratio (NCO/OH) plays a critical role because it has a significant impact on the crosslinking kinetics and on the mechanical properties of the solid propellant composition [18]. In this study, the impact of the curing ratio (NCO/OH) on the mechanical and ballistic characteristic of composite propellants was successfully estimated using uniaxial tensile test and acoustic wave emission technique respectively [19]. The tensile tests were performed at different operating temperatures (-40, 20 and 55°C) and different strain rates (0.000656 1/s, 0.0328 1/s) using Zwick universal test machine. For burning rate measurement, the acoustic emission system was used at different pressures (40, 50, 68, and 90 bar) as a superior tool for measuring statistical effects in small preparation changes for quality control work and it is used as a regular technique of propellant strands in full-scale motors. Such technique was mentioned previously by some researchers [20, 21 and 22].

2. Experimental Work

2.1. Mechanical Characteristics Evaluation

2.1.1 Propellant Formulations and Specimens Preparation. In this work, four different propellant formulations containing 87% solids and 13% HTPB based binder with different curing ratio (NCO/OH) as listed in Table 1 were produced. The main solid additives include ammonium perchlorate (AP) as an oxidizer, aluminum powder (Al) as metal fuel. The employed binder composed of hydroxy-terminated polybutadiene (HTPB) as pre-polymer, dioctylsebacate DOS as plasticizer, NG321 as a bonding agent based on aziridine groups, and hexamethylenediphenylisocyanate (HMDI) as a curing agent. These gradients are mixed under vacuum at specified temperatures and times, so the newly prepared fresh viscous slurry is a vacuum discharge brick to produce bulk molds. Then the molds are placed in a large curing oven with temperature controlled at 55°C, for a total curing time of 168 hours. After curing the molds are cut into sheets with a uniform thickness. Then the test samples are produced using special pneumatic cut press according to Joint Army- Navy-NASA-Air Force Propulsion Committee (JANNAF) standard, and the dimensions of the test specimens are illustrated in figure 1 [14].

To ensure the results of the mechanical tests, the produced samples were checked by a non-destructive method for voids like air bubbles or micro cracks by X-Ray as a quality control step. After that, the accepted specimens were stored in desiccators at ambient temperature and relative humidity RH ≤ 30%.
Table 1. Composite Solid Propellant Formulations

|      | Binder HTPB (%) | Oxidizer AP (%) | Fuel AL (%) | NCO/OH |
|------|-----------------|-----------------|-------------|--------|
| BM 10| 13              | 70              | 17          | 1.0    |
| BM 11| 13              | 70              | 17          | 0.975  |
| BM 12| 13              | 70              | 17          | 0.94   |
| BM 13| 13              | 70              | 17          | 0.9    |

Figure 1. Main dimensions of JANNAF specimen.

2.1.2 Tensile Tests. All the tensile tests were conducted using a computer controlled universal test machine (Zwick /Roell) Z050. The machine was provided by a thermal chamber to set and keep the temperature constant at the desired temperature during the test. Before the test, the thickness and width of each specimen were measured in its gauge length region accurately. The effective gauge length (L_G) is 70 mm, and the crosshead speed of the machine was maintained constant during the test at the desired value according to the producer instruction. Every experimental test was carried out on five specimens and the average value of the measurements was used for the analysis. Also, for every test the specimens were pre-conditioned for two hours in an external conditioning chamber. The specimens were tested at three different temperatures (20, 55, and -40 °C), and at two different crosshead speed (2, 100 mm/min).

The load-displacement data was used to generate stress-strain curves at different loading conditions, from which the ultimate stress, strain at maximum stress, were obtained for all solid propellant batches used in this investigation.

2.2. Ballistic Characteristics Evaluation

2.2.1 Strands Preparation. Ballistic characteristic of the applied formulations was evaluated applying acoustic wave emission technique where the specimens were cut into the specified position and direction of the block by using pneumatic grain cutter. Specimens must be in accordance with standard dimensions as (5 x 5 x 100) mm as shown in figure2. The strands were visually inspected and rejected if shape irregularities, cracks, or pores were observed.
2.2.2 Test Methodology. The propellant strand is mounted on a panel board with the help of Ni-chrome ignition wire and kept inside the bomb partially filled with water. The bomb is pressurized with nitrogen gas at the required pressure (4, 5, 6.8 and 10 MPa). The strand is ignited electrically by the firing unit. The acoustic emission (AE) wave generated due to the propellant burning in water is sensed by the acoustic emission transducer. The electrical signal is sequentially passed through the preamplifier and the post amplifier to the oscilloscope and the burning rate is calculated from the recorded graph.

This method has several advantages including low cost, a more accurate pressure value, and more reliable and accurate results. It avoids complex wiring, inhibition of the strands and sample preparation, and thus helps to improve the precision and accuracy of the measurement. An acoustic emission may be defined as a transient wave generated by the rapid release of energy within a material as sensed by a piezoelectric transducer. The signal passes through amplifier and recorded on an oscilloscope. A schematic diagram of an acoustic emission system is presented in figure 3.

2.2.3 Burning Rate Calculation. The burning rate of propellants plays a vital role among the parameters controlling the operation of solid rocket motors; therefore, it is essential to surely measure the burning rate in the successful design of a solid missile motor. The burning rate of a solid propellant as a function of pressure is widely measured by an acoustic strand burner. The burning speed is calculated as per the following formula by equation (1), as mentioned in references[23,24].

\[
r = \frac{L}{\Delta t}
\]
where:  \( L \) is the sample exact length (mm) and  \( \Delta t \) is the burning time (s). Additionally, the pressure exponents as the main ballistic parameter could be calculated using the empirical vielle equation represented by equation (2),

\[
r = aP^n
\]

(2)

where: \( r \) is the burning rate (mm/s), \( a \) is the burning rate constant, \( P \) is the operating pressure (bar) and \( n \) is the pressure exponent. Figure 4 demonstrate how to obtain the burning rate from equation (2), then the calculated coefficient with the burning rate values were listed in table 2.

![Figure 4. Chart of determination the ballistic characteristics.](image)

**Table 2.** Main ballistic parameters of prepared formulations.

|          | 0.9 | 0.94 | 0.975 | 1.0  |
|----------|-----|------|-------|------|
| a        | 1.366 | 1.136 | 1.127 | 1.583 |
| n        | 0.392 | 0.440 | 0.444 | 0.365 |
| \( r \) at (40 bar) | 5.8 | 5.75 | 5.797 | 7.41 |
| \( r \) at (50 bar) | 6.33 | 6.35 | 6.4 | 6.6 |
| \( r \) at (68.65 bar) | 7.168 | 7.30 | 7.37 | 7.41 |
| \( r \) at (90 bar) | 7.97 | 8.227 | 8.31 | 8.18 |

3. Results and Discussion

During the tensile test, the physical nature of the propellant increases the sample size, due to the presence of vacuum holes around some crystalline fillings due to the breakage of glue bonds between the binder and oxidizer, resulting in the formation of voids. Two characteristic mechanical properties have to be determined in each single test, the ultimate stress (\( \sigma_m \)), and the strain at maximum stress (\( \varepsilon_m \)). The values of these parameters are changing with each propellant type, and also with the temperature, and strain rate. As seen in figures 5, 6, and 7 at all test temperatures and strain rates, after a rather straight initial part, the shape of stress-strain curves shows a sharp bend and then the stress continues to increase gradually over a prolonged strain range before rupture finally occurs.
Figure 5. Stress-strain curves for different propellant batches at temperature (20°C).

Figure 6. Stress-strain curves for different propellant batches at temperature (55°C).

Figure 7. Stress-strain curves for different propellant batches at temperature (-40°C).

Figure 8. The ultimate stress at different test temperatures.

Figure 9. The strain at maximum stress at different test temperatures.

In figures 8 and 9 we can show clearly the effect of the temperature on the stress and strain respectively; the stress increased when the temperature decreased, but the strain increased when the temperature decreased from (20°C to -40°C), and also when the temperature increased from (20°C to 55°C) due to the nature of the bonding agent. For more details description, when the temperature
decreased from (55°C to 20°C), and curing ratio (NCO/OH) is 0.9, the stress increased by about 58.89% and also the elongation decreased by about 11.28%. Also, when the temperature decreased from (20°C to -40°C), the stress increased by about (95.8 %) and also the elongation increased by about 16.67%. When the temperature decreased from (55°C to 20°C), curing ratio (NCO/OH) is 0.94 , the stress increased by about 106.4 % and also the elongation decreased by about 17.8 %. Also, when the temperature decreased from (20°C to -40°C), the stress increased by about 39.13 % and also the elongation increased by about 16.67%. When the temperature decreased from (55°C to 20°C), curing ratio (NCO/OH) is 0.975 , the stress increased by about 108.2 % and also the elongation decreased by about 13.27 %. Also, when the temperature decreased from (20°C to -40°C), the stress increased by about 58.4 % and also the elongation increased by about 9.84 %. When the temperature decreased from (55°C to 20°C), and curing ratio (NCO/OH) is 1, the stress increased by about 70.21 % and also the elongation decreased by about 17.21 %. Also, when the temperature decreased from (20°C to -40°C), the stress increased by about 60.42%, and also the elongation increased by about 10.91 %.

Whereas curing ratio (NCO/OH) increased from (0.9 to 1) at a temperature (20°C) the ultimate stress increases by (50.34 %), and maximum strain decreases by (33.71 %). Figures 10 and 11 demonstrate the effect of curing ratio (NCO/OH) on the mechanical properties of the propellant. The curing ratio is defined as the ratio between isocyanate (NCO) group and hydroxyl (OH) group to form the polyurethane (—O—CO—NH—), which is practically formatted within the curing period. By increasing the curing ratio the number of (NCO) groups increased and by default the density of crosslinking inside the polyurethane matrix increased, also the stress increased as seen in figure 10, maximum strain decreased at the ultimate stress as seen in figure 11, and finally the burning rate increased as seen in figure 12, due to the opportunity to form a large number of hard segments.

**Figure 10.** The ultimate stress at different curing ratio.

**Figure 11.** The strain at maximum stress at different curing ratio.
The tensile characteristics of a composite propellant depend on the properties of the polymeric binder matrix due to the differences in density of the crosslink, which is intensely affected by the curing ratio NCO/OH. The differences in the mechanical characteristics of propellants with the curing ratio NCO/OH at the end of the curing time were shown in figures 10 and 11 for different temperatures values for the mechanical characteristics of five samples. A careful check up of the results given in Table 3 specifies that the stress and strain at maximum stress, first diminution with the curing ratio NCO/OH, reaching a minimum at an curing ratio NCO/OH of 0.9, and then start to rise for the propellants with increase curing ratio NCO/OH.

Whereas for propellant at 55 °C with increase curing ratio NCO/OH from 0.9 to 0.94 the stress increase by 23.8% and strain at maximum stress decrease by 8.7%, whereas increase curing ratio NCO/OH from 0.94 to 0.975 the stress increase by 18.13% and strain at maximum stress decrease by 11.71% whereas increase curing ratio NCO/OH from 0.975 to 1 the stress increase by 28.6% and strain at maximum stress decrease by 11.92%.

Whereas for propellant at 20 °C with increase curing ratio NCO/OH from 0.9 to 0.94 the stress increase by 45.5% and strain at maximum stress decrease by 15.4%, whereas increase curing ratio NCO/OH from 0.94 to 0.975 the stress increase by 19.13% and strain at maximum stress decrease by 6.8% whereas increase curing ratio NCO/OH from 0.975 to 1 the stress increase by 5.11% and strain at maximum stress decrease by 15.9%.

Whereas for propellant at -40 °C with increase curing ratio NCO/OH from 0.9 to 0.94 the stress increase by 14.3% and strain at maximum stress decrease by 6.7%, whereas increase curing ratio NCO/OH from 0.94 to 0.975 the stress increase by 35.6% and strain at maximum stress decrease by 11.4% whereas increase curing ratio NCO/OH from 0.975 to 1 the stress increase by 6.5% and strain at maximum stress decrease by 13.4%.

In figure 12, shows that, at the reference pressure, the burning rate increases slightly with increasing the curing ratio (NCO/OH), such slight increase was recorded to be around 3%. For different batches, the values of the ultimate stresses and strains at maximum stress were listed in Table 3 for all temperature tests.

**Table 3. Mechanical properties for propellants at different temperature and curing ratio.**

| NCO/OH Ratio | 55 °C | 20 °C | -40 °C |
|--------------|-------|-------|--------|
| σm (MPa)     | o (%) | σm (MPa) | o (%) | σm (MPa) | o (%) |
| 0.90         | 0.45  | 79.91  | 0.715  | 70.9 | 1.40  | 75    |
| 0.94         | 0.557 | 73     | 1.15   | 60   | 1.60  | 70    |
| 0.975        | 0.658 | 64.45  | 1.37   | 55.9 | 2.17  | 62    |
| 1.0          | 0.846 | 56.77  | 1.44   | 47   | 2.31  | 53.7  |
4. Conclusions

In this investigation, the mechanical and ballistic characteristics of different chemical compositions for HTPB solid propellant, depending on the curing ratio percentage, were studied at different temperatures, strain rates, and pressures. The results presented in this work provided the following conclusions:

1- The change of curing ratios by small percentage has a great effect and an intense impact on mechanical characteristics of the HTPB propellant but slightly impact on ballistic characteristics for propellant.

2- The stress-strain curves of HTPB propellant are remarkably influenced by temperature. The ultimate stress, improves significantly with reduction of temperature. However, the strain shows different trend, when the temperature decreased from 20 °C to -40 °C the strain increased, but when the temperature increased from 20 °C to 55 °C the strain also increased.

3- The propellants with an NCO/OH ratio of 0.9 have minimum ultimate stress, with maximum strain capability, whereas the propellants with an NCO/OH ratio of 1 show just the opposite behavior.

4- The HTPB propellant is capable for large deformation even at low temperatures and high strain rates, also displays nonlinear material behavior, which is usually associated with the occurrence of the damage in the propellant during the tensile deformation.

5- All the curing ratios percentage used in this work give us a satisfactory mechanical properties with a good ballistic performance, and they can be applied in real solid rocket motors, but the optimum one will depend on the application of the rocket motor, grain geometry, and grain structure analysis under a wide range of mechanical loads, which are imposed on it during storage and operational periods.

6- The knowledge of the curing ratio percentage effect on the propellant formulation is a useful tool for adjusting the crosslinking density and then for controlling the physical and mechanical properties of HTPB based propellants.

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