

## A study on the effect of microstructural parameters on the mechanical properties of HTPB-based propellants

Ali Chanaani<sup>1</sup>, Yasin Kaykha<sup>2</sup>

Chemical Engineering Department, Imam Hossein Comprehensive University, Tehran, Iran

### Abstract

The difference in polymerization method and conditions leads to the formation of Hydroxyl-terminated polybutadiene (HTPB) with different microstructural parameters. The difference in microstructural parameters strongly effect on the curing behavior and mechanical properties of the binder system and composite propellants based on this prepolymer. It should be noted that the mechanical properties requirement of composite propellant is very stringent. Therefore, many articles have investigated the effect of HTPB microstructural parameters on the mechanical properties of binder system and composite propellants. By properly understanding how these parameters affect mechanical properties, propellants with optimal mechanical properties, high solid load and low viscosity can be prepared. In this article, a comprehensive overview of the effect of these parameters on mechanical properties has been tried to be expressed in a simple way. The results show that the most important parameter affecting the mechanical properties of HTPB is the functionality distribution and functionality type of hydroxyl. The effect of all microstructural parameters has been investigated in this article.

**Keywords:** "Microstructure", "HTPB", "Propellant", "Mechanical properties", "Aerospace".

### 1. Introduction

HTPB is one of the most widely used prepolymers for the binder system of composite propellants. This material is widely used as an binder in composite propellants due to its excellent rheological and mechanical properties and very high solids loading (approximately 90%). Due to the above properties, in recent years, much attention has been paid to HTPB as binder for aerospace propellant [1, 2]. For example, the investigation of Ammonium perchlorate-/Hydroxyl-terminated polybutadiene (AP/HTPB) as solid propellant in the micro thruster with Micro-Electro-Mechanical System (MEMS) constitutes a hot research topic attracting the attention of several research works [3-7].

The changes in factors affecting on processing such as temperature, pressure, type of catalyst, solvent, etc. during the synthesis of HTPB cause the formation of HTPB with different microstructural parameters [8].

Mechanical properties are the most important properties of solid composite propellant. The mechanical properties of the propellant strongly depend on the microstructural parameters of the binder. Binders are mainly low molecular weight prepolymers. Because their polymerization is limited to the desired molecular weight [9]. The term microstructure is commonly used to describe the molecular structure of a polymer and should include all changes in molecular structures from one polymer to another. Microstructure of HTPB mainly includes topics such as functionality distribution, functionality type distribution, molecular weight, molecular weight distribution, concentration of cis, trans and vinyl microstructures [10].

In the next parts of the article, the influence of the mentioned microstructural parameters on the mechanical properties of the binder system and propellant based on HTPB has been investigated.

### 2. Effect of molecular weight

The mechanical properties of polyurethane systems based on HTPB show a significant difference depending on the molecular weight. Tensile strength, modulus and hardness decrease with increasing molecular weight of HTPB. On the other hand, elongation increases linearly with increasing molecular weight of HTPB (Fig. 1) [11].

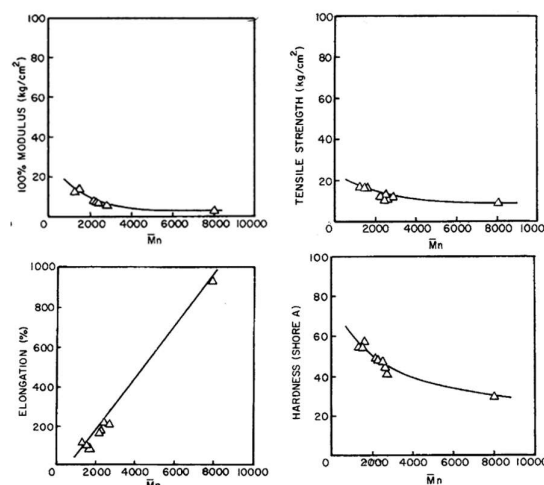


Fig. 1: Mechanical properties curves in terms of molecular weight [11].

reason for these observations is the difference in the molecular weight of HTPB chains, causes a difference

<sup>1</sup> Master's student

<sup>2</sup> Assistant Professor, Fax: 021-74189350 and Tel. number: 021-74189478, email address: kaykha@iut.ac.ir (corresponding author)

in the size of the formed networks. Small networks have lower molecular weight, which show higher tensile strength and lower elongation at break [12]. Also, in polyurethane systems, the concentration of urethane bonds increases by decrease the molecular weight of the HTPB prepolymer, which increases the position of intermolecular hydrogen bonds and formation bonds similar to Cross-links bonds in the system. These bonds increase tensile strength, modulus and hardness [11]. Also, the results of DMA analysis for HTPB cured with TDI show that as the molecular weight of the HTPB prepolymer increases, the storage modulus decreases, in other words, the stiffness of these systems decreases (Fig. 2) [12].

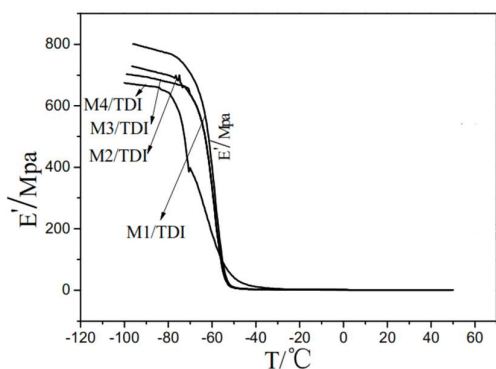


Fig. 2: Storage modulus curve in terms of temperature, molecular weight:  $M_4 > M_3 > M_2 > M_1$  [12].

It is worth noting that higher molecular weight prepolymers are used in case-banded grains, because increasing the molecular weight increases elasticity and elongation even at high NCO/OH proportional [13].

### 3. Effect of high molecular weight fraction

The HTPB prepolymer Prepared by free radical polymerization has two peaks in the molecular weight distribution curve. in other words, it consists of high and low molecular weight fractions. The high molecular weight fraction is shown by  $F_h$ . The Ratio of high molecular weight fraction to low molecular weight fraction in HTPB significantly affects the mechanical properties of the binder [14]. Increasing the high molecular weight fraction decreases the elongation of the polyurethane system (Fig. 3) [15].

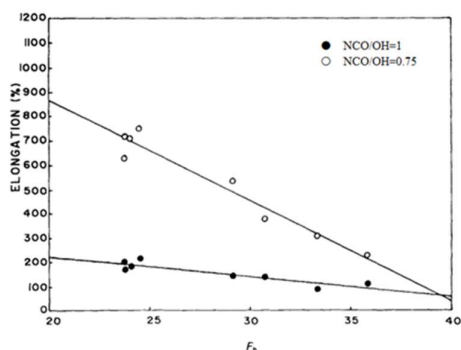


Fig. 3: Elongation diagram in terms of high molecular weight fraction [15].

The reason for this observation is that increasing the prepolymer functionality increases the molecular weight. On the other hand, the number of functionality in the prepolymer chains is different [16]. By extending the above items, it can be concluded that the high molecular weight fraction has a higher functionality and high functionality causes an increase in elongation [17].

### 4. Effect of cis and trans content

Mechanical properties of composite propellants strongly depend on the on the content of isomers in the prepolymer [18]. HTPB monomers have three type isomers, cis, trans, and vinyl (Fig. 4).

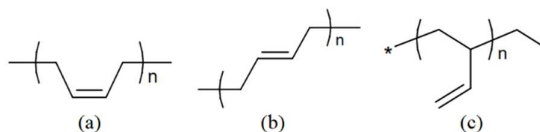


Fig. 4: (a) 1,4-Cis (b) 1,4-Trans, (c) 1,2-Vinyl [19].

Also, the vinyl isomer itself has three types of stereoisomers: isotactic, syndiotactic, atactic (Fig. 5). when all monomers have the same configuration, isotactic, when the configuration is alternating, syndiotactic and it is atactic when the configurations are randomly distributed along the prepolymer chain [20].

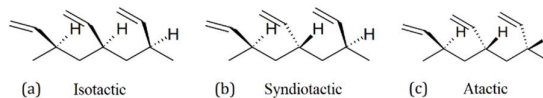


Fig. 5: Types of stereoisomers of vinyl [19].

The content of each isomer depends on the polymerization by which it is prepared. In the HTPB chain if all monomers are cis, due to the bending all parts of the carbon backbone, HTPB shows good elongation. But if all monomers are trans, the prepolymer structure becomes smooth and stiff like a rod, which shows good tensile strength and less elongation (Fig. 6). However, complete cis or trans polymerization is very difficult and usually a mixture of these configurations is randomly distributed along the chain [9, 19].

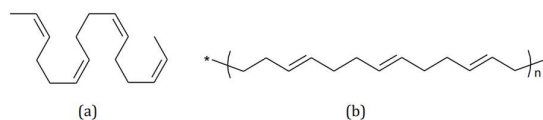


Fig. 6: (a) Cis-HTPB (b) Trans-HTPB [9].

An ideal HTPB should have trans: cis: vinyl in the ratio 55:25:20. As a rule of thumb, increasing the trans content, enhances the tensile strength of the cured polymer, increasing the cis content normally enhances the elongation [9].

Recently, a new type of HTPB with a very high cis content of about 96% and a very low glass transition temperature was prepared via the oxidolysis of butadiene rubber. The advantage of this method is that the hydroxyl functionality of HTPB is almost 2, which ensures that each end of the HTPB chain ends with one

hydroxyl group. This increase in cis content greatly increases the tensile strength and elongation of HTPB prepared by the oxidolysis method (Fig. 7). Also, HTPB-based polyurethanes with very high cis content have outstanding elasticity (Fig. 8) [21].

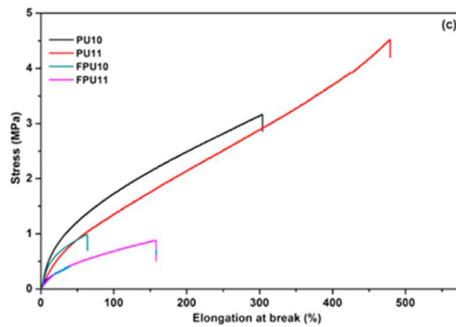


Fig. 7: HTPB stress-strain curves: FPU with low cis content, PU with high cis content [21].

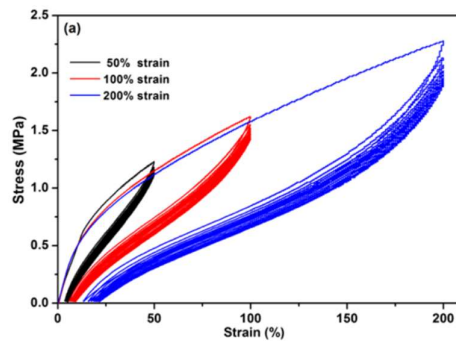


Fig. 8: Cyclic tensile response curves, HTPB-based polyurethanes with high cis content [21].

### 5. Effect of hydroxyl value

As the hydroxyl value increases, the cross-links density increases [22, 23]. Therefore, it can be concluded that the hydroxyl value strongly affects the mechanical properties of the binder system as well as the composite propellant. Increasing the hydroxyl value increases tensile strength and initial modulus and decreases elongation (Fig. 9) [13].

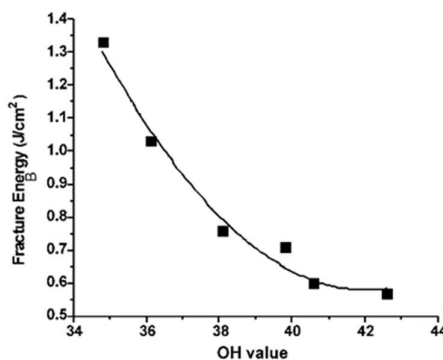


Fig. 10: Variation of fracture energy with hydroxyl values of HTPB [22].

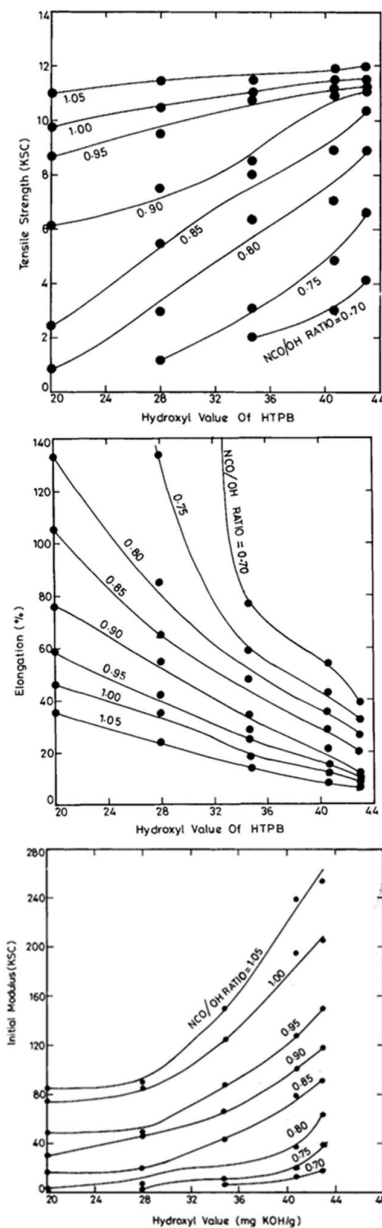


Fig. 9: Mechanical properties curves in terms of hydroxyl value [13].

The increase in tensile strength and initial modulus, as well as the decrease in elongation at break, is due to the increase in the concentration of urethane polar bonds, or in other words, the increase in the cross-links density. Investigation of HTPB prepolymers with low hydroxyl value show that the propellant based on these prepolymers can withstand more pressure. The area under the stress-strain curve gives the fracture energy. The fracture energy shows a significant decrease with increasing hydroxyl value. In fact, prepolymers with low hydroxyl value have high fracture energy (Fig. 10). These prepolymers can be better binder for solid composite propellants [22].

### 6. Effect of functionality distribution

The most important parameter affecting the mechanical properties of the binder system and composite propellants is the functionality distribution [17]. Functionality distribution is defined as the average number of reactive groups in each polymer. HTPB prepared by anionic polymerization is telechelic, but HTPB prepared by free radical polymerization mainly is not telechelic due to transfer reactions occurring during polymerization, and has a wide functionality distribution [24]. Therefore, the functionality distribution strongly depends on the polymerization method. The functionality increases with increasing molecular weight for HTPB prepared by free radical polymerization, while in the case of HTPB prepared by anionic method, the functionality is constant in the range of two and then decreases sharply from a certain molecular weight until it reaches zero (Fig. 11) [25].

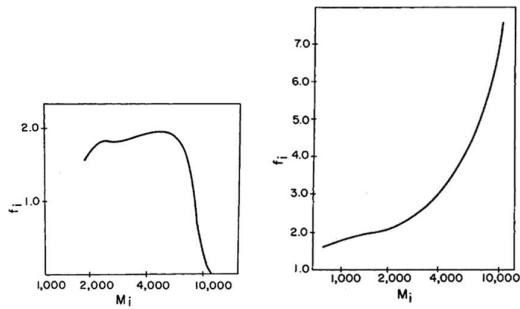


Fig. 11: functionality curves in terms of molecular weight [26].

Since the functionality distribution curve is a continuum, It is necessary to propose a reasonable method in order to investigate the effect of functionality distribution on the mechanical properties of binder system and composite propellants. According to the method proposed by Ninan et al. in the polymer chain build-up using a difunctional curing agent such as toluene diisocyanate (TDI), moieties with functionality less than 1 do not contribute to polymer networking and are classified as non-participating (NP) species. Likewise the moieties with functionality 3 and above contribute to crosslinking of the network and therefore they can be classified as crosslinker (CR). The species falling between these two values having functionality assignment  $> 1$  to  $< 3$  contribute to chain extension in the cure reaction and are classified as chain extender (CE). Since the ratio of CE/CR chains in the prepolymer changes even without considering the polymerization method. Therefore, we can relate the ratio of CE/CR chains to the mechanical properties. The ratio of CE/CR chains is related to the mechanical properties of the binder system as follows:

- Elongation increases with the increase of CE/CR ratio.
- Tensile strength decreases with increasing CE/CR ratio.
- The initial modulus depends on the stress-strain values. However, it shows a significant relationship.

Investigating the effect of the CE/CR ratio on the mechanical properties of the binder system shows that the functionality distribution has a significant effect on these properties (Fig. 12) [25].

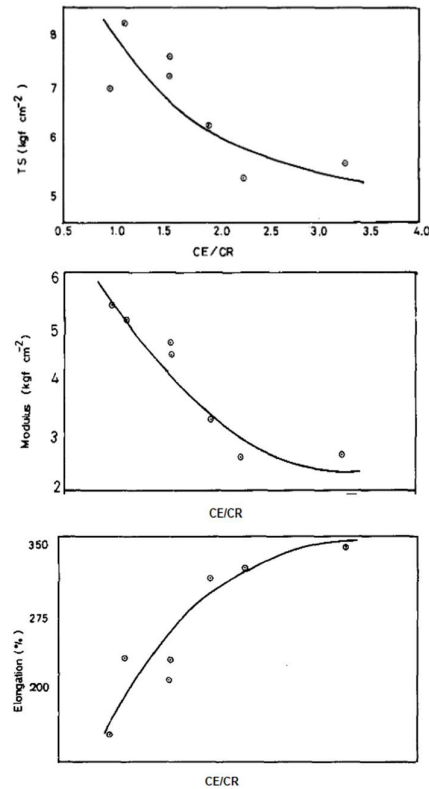


Fig. 12: Mechanical properties curves in terms of CE/CR ratio [25].

Investigating the behavior of several HTPB samples with different functionality shows that increasing the functionality distribution increases the tensile strength and decreases the elongation at break (Fig. 13) [16, 27]. Also, HTPB with low functionality distribution causes a decrease in cross-linking density and a corresponding decrease in tensile strength, but increasing functionality distribution does not necessarily increase cross-linking density and tensile strength [28].

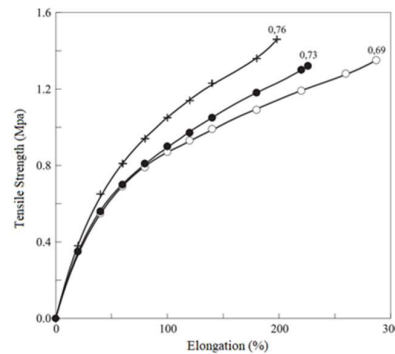


Fig. 13: Stress-strain curves for the different functionality distribution [27].

### 7. Effect of functionality type distribution

The functionality type distribution such as functionality distribution has a significant effect on the mechanical properties of binder system and composite propellants. Pham et al. studied HTPB by <sup>1</sup>H-NMR and <sup>13</sup>C-NMR techniques. They identified three types of hydroxyl functionality (Fig. 14) [15].

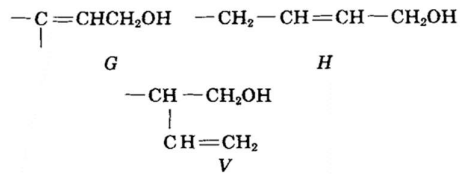


Fig. 14: Types of hydroxyl functionality in HTPB [29].

Between these three types of hydroxyl functionality, G is branched, while H and V are terminal. Also, G helps to form crosslinks during curing, while H and V only act as chain extenders. The higher the proportion of G content in the polymer, cause the higher the tensile strength and the lower the elongation of the cured polyurethane network. The V content form the urethane single bonds on the  $\alpha$ -carbon atom, so V type functionality is expected to cause more elongation increase. Increasing the ratio V/G increases the elongation and decreases the tensile strength in the solid propellant (Fig. 15).

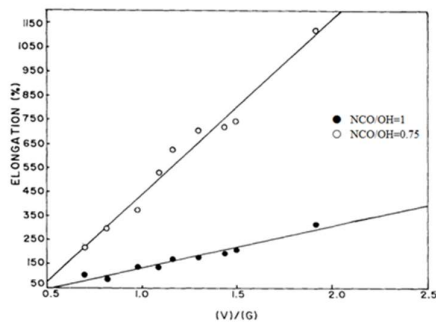


Fig. 15: Elongation diagram in terms of V/G ratio [15].

Also, increasing the ratio of H/V increases the high molecular weight fraction, which leads to a decrease in the elongation of the prepolymer (Fig. 16). Polymers with high molecular weight fraction are formed from the initiation of curing with H functionality [15].

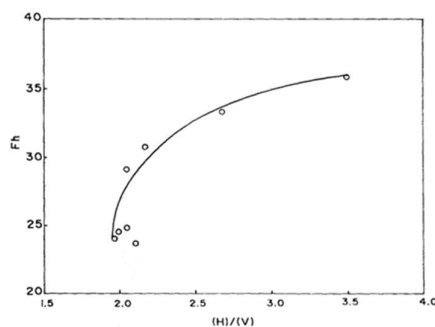


Fig. 16: High molecular weight fraction curve in terms of H/V ratio [15].

### 8. Conclusion

The study of the effect of microstructural parameters of HTPB on mechanical properties showed:

- The Functionality is the most important parameter affecting mechanical properties.
- increasing the functionality distribution, decreases elongation and increase tensile strength and modulus.
- Also, increasing the hydroxyl value decreases elongation and increases tensile strength and modulus.
- Increasing the V/G proportional increases elongation and decreases tensile strength and modulus.
- In general, with the increase of the cis content, the Elongation increases and also with the increase of the trans content, the tensile strength increases.
- Increasing the molecular weight increase elongation and decreases tensile strength and modulus.
- Considering that the microstructural parameters are strongly influenced by the polymerization method and conditions, by controlling microstructural parameters, composite propellants with high solids loading and low viscosity can be easily achieved.

### 9. Reference

- [1] T. Zhang, G.-x. Li, J. Chen, Y.-S. Yu, and X.-h. Liu, "Effect of wall heat transfer characteristic on the micro solid thruster based on the AP/HTPB aerospace propellant," *Vacuum*, vol. 134, pp. 9-19, 2016.
- [2] J. C. Thomas and E. L. Petersen, "HTPB Heat of Formation: Literature Survey, Group Additive Estimations, and Theoretical Effects," *AIAA Journal*, vol. 60, no. 3, pp. 1269-1282, 2022.
- [3] H. Hideto Mashidoria, A. Kakamib, T. Muranakaa, and T. Tachibanaa, "A Coaxial Pulsed Plasma Thruster Using Chemical Propellants," *Kyushu Institute of Technology*, 2006.
- [4] J. Esper, S. Neeck, J. A. Slavin, W. Wiscombe, and F. H. Bauer, "Nano/micro satellite constellations for earth and space science," *Acta Astronautica*, vol. 52, no. 9-12, pp. 785-792, 2003.
- [5] R. Hamann, C. J. Verhoeven, and A. Bonnema, "Nano-satellites, a fast way to pre-qualify new micro-technology," in *2005 International Conference on MEMS, NANO and Smart Systems*, 2005: IEEE, pp. 263-264.
- [6] B. Hou, X. Wang, T. Li, and T. Zhang, "Steady-state behavior of liquid fuel hydrazine decomposition in packed bed," *AIChE Journal*, vol. 61, no. 3, pp. 1064-1080, 2015.
- [7] S. Wu, W. Chen, Y. Zhang, W. Baan, and T. An, "SULFRO: a swarm of nano-/micro-satellite at SE L2 for space ultra-low frequency radio observatory," 2014.
- [8] J. C. Quagliano Amado, P. G. Ross, L. Mattos Silva Murakami, and J. C. Narciso Dutra, "Properties of Hydroxyl-Terminal Polybutadiene (HTPB) and Its Use as a Liner and Binder for Composite Propellants: A Review of Recent Advances," *Propellants, Explosives, Pyrotechnics*, vol. 47, no. 5, p. e202100283, 2022.
- [9] A. Dey, A. K. Sikder, and J. Athar, "Micro-structural effect on hydroxy terminated poly butadiene (HTPB) prepolymer and HTPB based composite propellant,"

- Journal of Molecular Nanotechnology and Nanomedicine*, vol. 1, no. 1, p. 104, 2017.
- [10] J. Randall, "Microstructure," *Encyclopedia of Polymer Science and Technology*, 2002.
- [11] K. Ono, H. Shimada, T. Nishimura, S. Yamashita, H. Okamoto, and Y. Minoura, "Effects of number-average molecular weight of liquid hydroxyl-terminated polybutadiene on physical properties of the elastomer," *Journal of Applied Polymer Science*, vol. 21, no. 12, pp. 3223-3235, 1977.
- [12] C. Y. Chen, L. L. Gao, and X. F. Wang, "Effects of HTPB with different molecular weight on mechanical properties of HTPB/TDI system," in *Advanced Materials Research*, 2013, vol. 811: Trans Tech Publ, pp. 19-22.
- [13] R. Manjari, V. Joseph, L. Pandureng, and T. Sriram, "Structure-property relationship of HTPB-based propellants. I. Effect of hydroxyl value of HTPB resin," *Journal of applied polymer science*, vol. 48, no. 2, pp. 271-278, 1993.
- [14] V. Sekkar, A. S. Alex, V. Kumar, and G. Bandyopadhyay, "Pot life extension of hydroxyl terminated polybutadiene based solid propellant binder system by tailoring the binder polymer microstructure," *Journal of Macromolecular Science, Part A*, vol. 54, no. 3, pp. 171-175, 2017.
- [15] M. Ramarao, K. Scarish, P. Ravindran, G. Chandrasekharan, S. Alwan, and K. Sastri, "Correlation of binder mechanical properties with functionality type and molecular weight distribution for hydroxy-terminated polybutadienes: <sup>13</sup>C-NMR and SEC studies," *Journal of applied polymer science*, vol. 49, no. 3, pp. 435-444, 1993.
- [16] F. S. Toosi, M. Shahidzadeh, and B. Ramezanzadeh, "An investigation of the effects of pre-polymer functionality on the curing behavior and mechanical properties of HTPB-based polyurethane," *Journal of Industrial and Engineering Chemistry*, vol. 24, pp. 166-173, 2015.
- [17] K. Ninan, V. Balagangadharan, K. Ambikadevi, and K. Catherine, "Functionality distribution and crosslink density of hydroxyl-terminated polybutadiene," *Polymer international*, vol. 31, no. 3, pp. 255-260, 1993.
- [18] N. Ahmad, S. Amir, R. Naheed, Z. I. Baig, and M.-u.-H. Rizvi, "Microstructure study of propellant binder," in *Advanced Materials Research*, 2012, vol. 570: Trans Tech Publ, pp. 37-42.
- [19] A. Dey, M. A. S. Khan, J. Athar, A. K. Sikder, and S. Chattopadhyay, "Effect of microstructure on HTPB based polyurethane (HTPB-PU)," *J. Mater. Sci. Eng. B*, vol. 5, no. 3-4, pp. 145-151, 2015.
- [20] J. Devaux and S. Demoustier-Champagne, "Chapter 2 Polymer Chemistry and Microstructure," in *Comprehensive Analytical Chemistry*, vol. 53, J. M. Chalmers and R. J. Meier Eds.: Elsevier, 2008, pp. 13-755.
- [21] Z. Cao, Q. Zhou, S. Jie, and B.-G. Li, "High cis-1, 4 hydroxyl-terminated polybutadiene-based polyurethanes with extremely low glass transition temperature and excellent mechanical properties," *Industrial & Engineering Chemistry Research*, vol. 55, no. 6, pp. 1582-1589, 2016.
- [22] C. R. Nair, J. U. Bhaskar, and K. Ninan, "Polyurethanes from Hydroxyl Terminated Polybutadiene: Effect of Hydroxyl Value on Crosslinking and Mechanical Properties," *Journal of Polymer Materials*, vol. 30, no. 4, p. 363, 2013.
- [23] G. Odian, *Principles of polymerization*. John Wiley & Sons, 2004.
- [24] W. Vilar and L. Akcelrud, "Effect of HTPB structure on prepolymer characteristics and on mechanical properties of polybutadiene-based polyurethanes," *Polymer Bulletin*, vol. 35, no. 5, pp. 635-639, 1995.
- [25] K. Ninan, V. Balagangadharan, and K. B. Catherine, "Studies on the functionality distribution of hydroxyl-terminated polybutadiene and correlation with mechanical properties," *Polymer*, vol. 32, no. 4, pp. 628-635, 1991.
- [26] S. Baczek, J. Anderson, and H. Adams, "Functionality distribution of hydroxyl-terminated polybutadienes using gel permeation chromatography. II. Measurements for commercial polymers," *Journal of Applied Polymer Science*, vol. 19, no. 8, pp. 2269-2277, 1975.
- [27] V. L. Lourenço *et al.*, "Determination of functionality distribution of HTPB and evaluation of its influence in the mechanical behaviour of polyurethane used in rocket cases," *Polimeros*, vol. 16, pp. 66-70, 2006.
- [28] E. Dossi, J. Earnshaw, L. Ellison, G. R. dos Santos, H. Cavaye, and D. J. Cleaver, "Understanding and controlling the glass transition of HTPB oligomers," *Polymer Chemistry*, vol. 12, no. 17, pp. 2606-2617, 2021.
- [29] V. Sekkar and T. S. K. Raunija, "Hydroxyl-terminated polybutadiene-based polyurethane networks as solid propellant binder-state of the art," *Journal of Propulsion and Power*, vol. 31, no. 1, pp. 16-35, 2015.