Synthesis of polytetrahydrofuran-polyethylene glycol copolymer by depolymerization method for use in Launch Vehicle

Hossein Karimi Shahmarvandi[1], Abbas Kebriychi[2], Yahya Ebrahimabadi[3], Milad Qane[4]
1-Chemical Engineering Department, Imam Hossein Comprehensive University, Tehran, Iran

Abstract
Rockets are used to carry satellites and other items into space. One of the main components of satellite launchers is its engine .The solid fuel rocket engine usually uses a composite propellant to achieve high thrust and impulse. Considering the stresses and pressures applied to the solid propellant during construction, maintenance, transportation and use, the solid propellant must have excellent mechanical properties. The solid propellant consists of polymer binder and solid load. which is responsible for maintaining and improving the mechanical properties of the binder. Propellant based on polyether is widely used in space and military industries. In this paper, the synthesis of one of the new polyethers used in the upper stages of satellite launchers (third stage of Minotaur) was investigated. Due to the progress in the field of polyether binder, copolymerized from polytetrahydrofuran (PolyTHF) and polyethylene glycol (PEG) was introduced as a binder with excellent mechanical properties and more impulse than conventional propellants. Synthesis of PolyTHF and PEG copolymer is done by depolymerization method.
In this method, in two simultaneous steps, PolyTHF is depolymerized using sulfuric acid as a catalyst, and in the next step, the depolymerized material reacts with the hydroxyl at the end of the PEG, and then two polymers are paired and a copolymer is formed The synthesized copolymer was characterized using various tests, which revealed that there is an almost equal amount of both polymers in the copolymer, as well as the molecular weight (M_n) of 4490 g/mol, which is useful for use in composite propellant.
Keywords: *"composite propellant" "binder" "TPEG" "synthesis"* .

1. Introduction
Rocket engines that use solid propellants are widely used in the commercial space flight trade for powering orbital-class launch vehicles and little analysis rockets. Thrust and also the specific impulse developed by a missile engine are essential properties of a rocket propulsion system, and it specifies the performance of a rocket. These properties heavily influenced by the burn-rate properties of the solid propellants[1].
Composite solid propellants have found a large vary of applications, each military and civil in nature. Out and away their most typical use is in rocket engines, like within the case of sounding rockets used for observation and launch vehicles used for putting satellites in orbit [2].
A typical composite solid propellant is a mixture of many chemical constituents which can embody polymeric fuel, organic plasticizer and polymeric binder, crystalline inorganic oxidant and additives. The ultimate processed style of a solid propellant that's cast within a solid rocket motor (SRM) is named propellant grain [3].
within international community, the chemical names of binders normally represent solid propellants. Polymeric binder is that the connection to promote high-energy materials, oxidizers, metallic fuel, and alternative parts as integration thus it's one among the necessary segments in solid propellan [4, 5].
the performance of the propellant depends chiefly on the binder matrix; then, improvement for the binder might cause the development or innovation of the solid propellant [6].[5]
Hydroxyl-terminated polybutadiene (HTPB) has been a common polymeric binder/fuel within the Ammonium perchlorate (AP) based solid rocket propellants [7].The hydroxyl-terminated polyether solid propellants, that use a block copolymer of polytetrahydrofuran (polyTHF) and polyethylene glycol (PEG) as a binder to interchage the normally used (HTPB) for up the insensitive munition characteristics of composite solid propellant [8]
In tactical and strategic missile systems and higher stage space launch vehicles, it's expected that percent (%) elongation values ought to be over than %40 at -30 °C, and it's glorious that mechanical properties of HTPE based propellants are superior than HTPB based ones at coldness conditions [9].
hydroxyl-terminated polyether solid propellants are widely well known as promising alternatives for HTPB solid propellants because of their compliance with insensitive munition characteristics of composite solid

[1] Master of Propulsion Chemistry, Imam Hossein University
[2] PhD, Polymer Engineering Assistant Professor Chemical Engineering Department (Polymer Branch)Imam Hossein Universit A.Kebritchi@ippi.ac.ir
[3] PhD, organic chemistry
[4] Master of Propulsion Chemistry, Imam Hossein University

propellant. The event of solid propellants with insensitive munition (IM) characteristics is that the scientists' persistent pursuit in ammunition analysis field, as vulnerable propellant charges might ignite and cause catastrophic incidents once suffer from sudden external thermal stimulation throughout operation, storage, and transportation [8].
Although hydroxyl-terminated polyether has been delineated as a replacement kind of new type of binder. polyether binders are utilized in formulations since the middle Fifties.They were hydroxyl-terminated random copolyethers (HTPE) and were utilized within the nitrate ester plasticized polyether (NEPE) propellant. HTPE binders utilized in rocket propellant compositions as delineated by Comfort and coworkers were created by Alliant Techsystems (ATK) below a DuPont patent and selected as a hydroxyl-terminated block copolyether (TPEG). The chemical structures of the 2 sorts of hydroxyl-terminated polyether prepolymers are unit similar, nevertheless their performance properties dissent considerably [10, 11].
In this paper we have a tendency to report a preliminary study on the characterization and synthesized of TPEG binedr, Analyses of the copolymers were allotted to see relatve molecular mass, molecular Structure. These properties were determined employing a vary of techniques including Gel Permeation Chromatography (GPC), Nuclear Magnetic Resonance (NMR) spectroscopy and Fourier Transform Infrared (FTIR) spectroscopy.

1.1. hydroxyl-terminated polyether Binder

the polymeric binder have important effects in forming these components into an overall structure. Hydroxy-terminated Polyether is has low viscosity, high solid loading and good chemical properties of isocyanate curing[12]. hydroxyl-terminated polyether binder is in non-crystalline form and has a polar structure. For this reason, it is compatible with energetic plasticizers and Electrical conductivity of hydroxyl-terminated polyether propellants is high. in hydroxyl-terminated polyether propellant the same thrust levels and improve ispacefice impulse can be obtained with less amount of solid fillers in proportion to Hydroxyl-terminated polybutadiene (HTPB) and the probability of accidents that can result from electrostatic discharges is lower [13].
Two kinds of Hydroxy Terminated PolyEther binders were alternative; HTPE and TPEG has been synthesized. TPEG is a block copolymer synthesized by the reaction between poly-1,4-butanediol (poly THF; or Terathane) and polyethylene glycol (PEG) that was synthesized by depolymerization. The synthesis process was reported to be performed with 25% of sulphuric acid (as a catalyst) at a reaction temperature of approximately 130 ℃ [14]. HTPE is a random copolymer of ethylene oxide (EO) and tetrahydrofuran (THF) was carried out through cationic bulk polymerization under subzero temperature conditions using ethylene glycol (EG) as a proton reservoir and tetrafluoroboric acid diethyl ether complex as a catalyst Polyether is used in many missile systems. And it is used as a propellant in propulsion systems and rocket engines such as the Minotaur and Trident2 [15].

2. Experimental

2.1. Materials

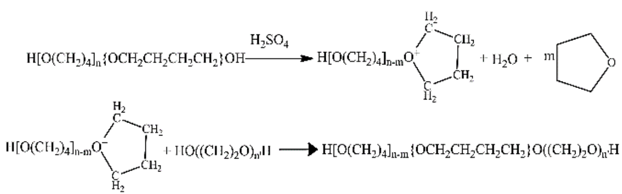
Polytetrahydrofuran (PolyTHF) with molecular weight (*Mn*) 250-2000 g/mol, Polyethylene glycol with M_n 200-1000 g/mol, Sulfuric Acid 98% (H_2SO_4) and Calcium hydroxide $Ca(OH)_2$ was procured from Merck Germany and water.

2.2. Instrumental

^{1}H NMR spectra were recorded with a BRUKER 400MHz instrument, using $CDCl_3$ as solvent. Chemical shifts were reported as parts per million downfield from tetramethylsilane (TMS). Fourier transform infrared (FTIR) spectra were measured with a BRUKER TENSOR 27 infrared spectrometer in the range 400–4000 cm^{-1} using KBr plates. GPC measurements were performed with a Waters GPC instrument equipped with four Ultrastyragel columns (10, 50, 100 and 1000 nm), a refractive index detector and a Datamodule 730. Tetrahydrofuran THF was used as the mobile phase at a flow rate of 1 $mL\cdot min^{-1}$ through the columns at 25 °C.

3. TPEG Preparation

TPEG is a block copolymer synthesized by the reaction between poly-1,4-butanediol (polyTHF) and polyethylene glycol (PEG). Polytetrahydrofuran is depolymerized in the presence of an acid catalys (H_2SO_4 98%) at a temperature of 120-150 ℃ and at a pressure of 50 -500 mbar. Depolymerization produces oxonium ions from polytetrahydrofuran.for the synthesis of TPEG binder, produced oxonium ions react with PEG hydroxyl. When the reaction is complete the reaction is quenched by adding water. In the next step, the product is neutralized by using calcium hydroxide, separated by decantation. Then the solvent is removed and the copolymer is purified. A transparent yellow copolymer is obtained.



Scheme 1: Schematic of the synthesis of hydroxyl terminated polyether

4. Characterization

4.1. FTIR Spectroscopy Results and Discussion

The FTIR spectra of synthesized sample were found to be just like to TPEG and in sensible agreement with the results of HTPE. In every case 3 main absorption bands were ascertained at regarding 1094, 2884, and 3414 cm^{-1} with smaller bands at regarding 800, 1354, and 1354 cm^{-1} (see Fig. 1 and tabel 1).

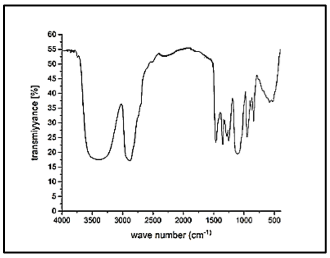


Fig. 1: FTIR spectrum of the synthesized sample

Table 1: Main infrared absorption bands in FTIR spectrum of the synthesized sample [16]

Assignment	Group	Wavenumber (cm^{-1})
O-H sterch in hydrogen bonded primary alcolol and water	$-CH_2OH$	3414
C-H2 symmetric stretch in methylene group	$-CH_2-$	2884
C-H2 deformation in ether group	$-CH_2-O-CH_2-$	1461
O-H in plane deformation in primary alcohol	$-CH_2OH$	1354
C-O-C asymmetric stretch in ether group	$-CH_2-O-CH_2-$	1094
O-H out of plane deformation in primary alcohol	$-CH_2OH$	800

4.2. ^{1}H NMR Results and Discussion

Copolymers contain the subsequent continuation units: $-OCH_2CH_2CH_2CH_2-$ (THF unit) and $-OCH_2CH_2-$ (EO unit). In ^{1}H NMR spectra, protons of groups $-OCH_2-$ in each EO and THF units provides a complex pattern of signals at 3.5–3.8 ppm σ region. So the overall composition of the polymer was determined from the combination of each groups of signals.

the peak at 3.76-3.80 ppm (A in Fig. 2) corresponds to the protons of the CH_2 groups within the alpha positions relative to HO- terminal groups in an EO segment (**H**O-CH_2CH_2-O-). The peak selscted B (at 3.71-3.75 ppm) corresponds to the protons of the CH_2 groups in the alpha positions in an EO-EO segment ($-OCH_2C\mathbf{H}_2-OC\mathbf{H}_2CH_2O-$). The peak designated C (at 3.71-3.66 ppm) corresponds to the protons of the CH_2 groups within the alpha positions in an EO-THF segmen (-OCH2C**H**$_2$-O-$CH_2CH_2CH_2CH_2$). Peak at 3.65-3.62 ppm (D in fig.2) corresponds to the protons of the CH_2 groups in the alpha positions during a THF-EO segment ($CH_2CH_2CH_2C\mathbf{H}_2$–$OCH_2CH_2$-O), and peak E (at 3.62-3.56 ppm) corresponds to the protons of the CH_2 groups in the alpha positions during a THF-THF ($CH_2CH_2CH_2C\mathbf{H}_2$- O-$C\mathbf{H}_2CH_2CH_2CH_2$) [16, 17].

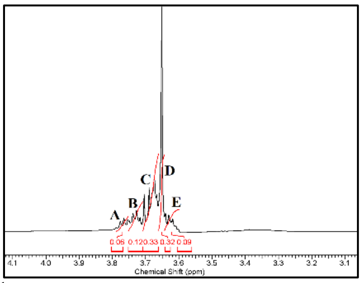


Fig. 2: ^{1}H NMR spectrum of the synthesized sample

The ratio n (THF/EO) between THF and EO groups presents in the TPEG copolymer chain obtained from ^{1}H NMR results are presented in Table 2. n was obtained from the ratio of the peak areas corresponding to the protons of the –O**CH₂-** groups present in both THF and EO.

4.3. GPC Results and Discussion

The molecular weight of the polymer is one of the main parameters to determine the binder properties and propellant properties. According to the previous studies of researchers, the ideal molecular weight for polyether binder is from 4000 to 5000. Also, the narrowness of the Polydispersity Index (PDI) makes it possible to achieve reproducible properties in the composite propellant. In this copolymer, the increase in molecular weight is related to melting temperature and viscosity. As the molecular weight of the copolymer increases, the melting temperature and viscosity increase. GPC test with THF solvent was used to determine the molecular weight. The results of the GPC test are shown in fig.3 and Table 2.

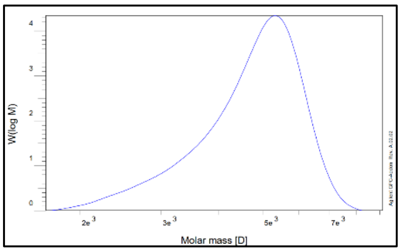


Fig. 3: GPC spectrum of the synthesized sample

Table 2. Molecular weight and n ratio of the synthesized sample

Properties	Mn	MW	DPI	THF	EO	THF/EO (n)
unit	g/mol	g/mol	g/mol	%	%	-
TPEG	4490	4784	1.065	48	52	0.93

4.4. Glass-transition temperature (T_g)

in some cases copolymers having similar M_n have a different Glass-transition temperature (T_g). The differen copolymer chain structure can be the reason for this difference. As the THF/EO ratio increases T_g decreases. These results are consistent with what is observed for PolyTHF and PEG. PolyTHF has a T_g of -82.5 °C for a M_w of 2000 while for PEG the T_g is -58.3 °C for a M_w of 1000. The T_g of the synthesized sample was equal to -76 ℃, which can be increased by increasing the percentage of THF.

Also, higher n (higher number of THF groups in the copolymer chain) leads to a higher melting temperature. but, for a similar THF/EO ratio, the higher the molecular weight the higher the melting temperature.

The melting point of the synthesized sample is 9 °C and Changes in melting temperature (T_m) are in the opposite sense with respect to the THF/EO ratio in comparison with T_g [18].

5. Conclusion

Composite propellants are an important component in rocket engines, which are considered as part of the space industry .One of the best ways to improve current engines to achieve better performance is to modify and replace the new engine binder with a conventional engine. The currently used polyether binders have different synthesis methods. In the selected method, polytetrahydrofuran is depolymerized with sulfuric acid and copolymerized by reacting with polyethylene glycol. Copolymerization increases mechanical and thermal properties and also increases molecular weight.
Characterization was done using various tests and it was determined that the synthesized copolymer has a molecular weight (M_n) of 4500 g/mol and also THF/EO is almost equal to 1, and its T_g and melting point are -75 ℃ and 9 ℃ respectively.

References

[1] R. K. A Adharsh Unni, Chanchal Singh, Vishal Singh, Vasireddi Mouli Priya Varshini and Gopinath Shanmugaraj, "Effects of adding powdered metals with the solid propellants – A review," *J. Phys.: Conf. Ser. 1,* vol. 1473, 2020.

[2] K. Lysien, A. Stolarczyk, and T. Jarosz, "Solid Propellant Formulations: A Review of Recent Progress and Utilized Components," (in eng), *Materials (Basel),* vol. 14, no. 21, Nov 4 2021.

[3] N. Yadav, P. K. Srivastava, and M. Varma, "Recent advances in catalytic combustion of AP-based composite solid propellants," *Defence Technology,* vol. 17, no. 3, pp. 1013-1031, 2021/06/01/ 2021.

[4] T. Zhang *et al.*, "Synthesis and characterization of a novel fluorine-containing copolymer P(FPO/NIMMO) as a potential energetic binder," *Journal of Fluorine Chemistry,* vol. 249, p. 109861, 2021/09/01/ 2021.

[5] X. Wu, J. Li, H. Ren, and Q. Jiao, "Comparative Study on Thermal Response Mechanism of Two Binders during Slow Cook-Off," (in eng), *Polymers (Basel),* vol. 14, no. 17, Sep 5 2022.

[6] S. Ma *et al.*, "Investigation of a Low-Toxicity Energetic Binder for a Solid Propellant: Curing, Microstructures, and Performance," *ACS Omega,* vol. 5, no. 47, pp. 30538-30548, 2020/12/01 2020.

[7] K.-H. Kim, C.-K. Kim, J.-C. Yoo, and J. J. Yoh, "Test-Based Thermal Decomposition Simulation of AP/HTPB and AP/HTPE Propellants," *Journal of Propulsion and Power,* vol. 27, no. 4, pp. 822-827, 2011.

[8] X. Wang *et al.*, "Experimental and simulative thermal stability study of HTPE solid propellants in different scales," *Case Studies in Thermal Engineering,* vol. 28, p. 101566, 2021/12/01/ 2021.

[9] H. Eşiyok, "A study on hydroxyl terminated polyether based composite propellants," PHD, Middle East Technical University, 2016.

[10] K. Mao, M. Xia, and L. Yunjun, "Thermal and mechanical properties of two kinds of hydroxyl-terminated polyether prepolymers and the corresponding polyurethane elastomers," *Journal of Elastomers and Plastics,* vol. 48, 11/13 2015.

[11] S. H. S. Hanne Mørkeseth, "Synthesis of TPEG, and curing and characterization of polymer matrices based on TPEG," Norwegian20/01688, 2020.

[12] T. Zhang *et al.*, "Synthesis and characterization of a novel fluorine-containing copolymer P(FPO/NIMMO) as a potential energetic binder," *Journal of Fluorine Chemistry,* vol. 249, p. 109861, 2021.

[13] R. Caro, I, " Hydroxy-Terminated Polyether Binders for Composite Rocket Propellants," PhD, Cranfield University Defence College of Management and Technology Academic (2006).

[14] F. G. comfort t . "Progress in HTPE Propellants," in *NDIA 39 th Annual Gun & Ammunition/ Missiles & Rocket Conference* Baltimore, 2004.

[15] Q. Zhang *et al.*, "PolyNIMMO-HTPE-polyNIMMO triblock copolymer as a potential energetic binder: Synthesis and characterization," *European Polymer Journal,* vol. 119, pp. 514-522, 2019.

[16] R. Caro and J. Bellerby, "Characterization and comparison of two hydroxyl-terminated polyether prepolymers," *International Journal of Energetic Materials and Chemical Propulsion,* vol. 9, pp. 351-364, 01/01 2010.

[17] M. Bednarek and P. Kubisa, "Cationic copolymerization of tetrahydrofuran with ethylene oxide in the presence of diols: Composition, microstructure, and properties of copolymers," *Journal of Polymer Science Part A: Polymer Chemistry,* vol. 37, no. 17, pp. 3455-3463, 1999.

[18] R. Caro, J. Bellerby, and E. Kronfli, "Synthesis and characterization of a Hydroxy Terminated Polyether (HTPE) copolymer for use as a binder in composite rocket propellants," *International Journal of Energetic Materials and Chemical Propulsion,* vol. 6, pp. 289-306, 01/01 2007.