

Military Technical College
Kobry El-Kobbah,
Cairo, Egypt



7th International Conference
on
Chemical & Environmental
Engineering
27 - 29 May, 2014.

ENMB-1

Effect Of Different Parameters On Tensile Properties Of Polymeric Matrices Used In Composite Solid Rocket Propellant

By

Islam. Kamal. M^{*}, A. I. ELBIEH^{*}, Hosam.E. Mostafa^{*}

Abstract

Glycidyl azide polymer (GAP) and hydroxyl terminated polybutadiene (HTPB) have been evaluated for use as binder for solid propellants. Characterization of the used prepolymers (GAP & HTPB) by employing the possible means to examine their : Density (Densimeter) , Characteristic groups and IR spectrum by Fourier transformation infrared (FTIR), Nitrogen content (CHN 240), Viscosity (viscometer) , Humidity (using Karl-Fisher) and Milligram equivalent (OH)/ Milligram binder (By Titration) . The effects of various parameters like cross-linking conditions, concentration of crosslinker, and the ratio of isocyanate to hydroxyl functional groups (NCO/OH ratio) on the mechanical properties were studied in detail , by preparation of different cross-linked GAP network and cross-linked HTPB network binder formulations using selected materials, From survey it was observed that GAP based binders have poor mechanical characteristics compared with HTPB binders ,So GAP functionality must be raised by the addition of triol (trimethylol propane (TMP)) to generate the desired extended polymeric matrix, also using a curing catalyst dibutyltin dilaurate (DBTDL), to ensure curing completion ,the NCO/OH ratio was varied from 0.7 to 1.5, keeping the crosslinker content at 5% with respect to binder (for GAP only), The GAP based specimens were also prepared with cross-linker content varying from 3–9% by weight with respect to binder, keeping the NCO/OH ratio constant at 1, Stress-strain relation for the prepared samples were measured to evaluate the effect of crosslinker, and the ratio of isocyanate to hydroxyl functional groups (NCO/OH ratio) on the mechanical properties to perform the comparison between them from curing & mechanical behavior point of view .

KEY WORDS

Glycidyl Azide Polymer (GAP), hydroxyl terminated polybutadiene (HTPB) . mg equivalent (OH), solid propellants. TMP.

* Egyptian Armed Forces

1. Introduction

Glycidyl azide polymer (GAP) is one of the most promising high-energy propellant binders better in performance than hydroxyl terminated polybutadiene (HTPB) which is the currently used propellant binder worldwide. This polymer containing highly energetic azide group (C-N₃ group) along the polymer chain as pendent groups in combination with energetic oxidizer like ammonium dinitramide (ADN) can give improved performance in terms of specific impulse and chlorine-free exhaust [1-5]. GAP is a unique binder of high density with positive heat of formation of +117.2 kJ/mole and is compatible with advanced oxidizer like ADN. The scission of C-N₃ group is highly exothermic and is accompanied by release of 685 kJ/mol. The terminal hydroxyl group in GAP can be reacted with diisocyanate to form a three dimensional network structure as in the case of HTPB propellant. Evaluation of physical and mechanical properties of the binder is one of the criteria for assessing its suitability for use in propellants. The functionality of the binder, NCO/OH equivalent ratio, concentration of the cross linker and curing conditions significantly influence the three dimensional network formation which imparts the necessary mechanical properties to the binder matrix [6-7]. HTPB binders exhibit superior elongation capacity at low temperature and better ageing properties over CTPB. It has since become the most widely-used binder in solid propellant formulations with excellent mechanical properties and enhanced insensitive munition (IM) characteristics [8]. For case bonded rocket motor applications, the binder is to be converted into crosslinked network structure which encompasses the metallic fuel and oxidizer particles. By cross linking GAP binder with an appropriate curing agent, it develops the required mechanical strength to meet the requirements of the propellant. Selection of the curing agent, cross linker and catalyst are to be done based on the matrix properties of the binder. Other factors involved are feasibility of processing, curing conditions, and safety aspects[9]. HTPB makes self crosslinking because it is mix of 1,4 butadiene (85%) & also 1,2 or 3,4 butadiene (15%) in which the double bond in the side group could make the required cross linking. The mechanical property of GAP based propellant is quite poor due to its structural characteristics: 1-low cross linking density, 2- irregular curing network, 3-poor interface between fillers & binder. To improve mech. Property: 1-using high molecular weight GAP (2000-3000), 2-Using suitable crosslinking agent & chain extender (crosslinking agent) [10].

In this paper, we report the results of our continuing study on the curing of GAP and HTPB, with a special emphasis on the curing characteristics depending on the NCO/OH ratio, ratio of crosslinker and the effect of a catalyst on the mechanical properties of the cured GAP and HTPB. Stress-strain relation and modulus of elasticity for the prepared samples were measured to perform the comparison between them from curing & mechanical behavior point of view.

2. Experimental

The following materials were used as purchased: GAP (linear GAP diol from Zibo Qilong Chemical Industry Co., Ltd, Shandong Province China; $M_n = 2880$ g/mole), HTPB (Poly bd R-45M from Zibo Qilong Chemical Industry Co., Ltd, Shandong Province China, $M_n = 2800$ g/mole), 1,1,1-trimethylol propane (TMP) 97% supplied by SIGMA-ALDRICH (23235-61-2) Germany, 1,4-butane diol 99% supplied by SIGMA-ALDRICH (110-63-4) Germany, dibutyl tin dilaurate (DBTDL) 95% supplied by SIGMA-ALDRICH (77-58-7) Germany.

2.1 Characterization of prepolymer (GAP Diol and HTPB) .

Infrared Spectroscopy

Shimadzu 8000 Fourier transformation infrared (FTIR) was used for HTPB and GAP to detect the presence of the azide group ($-N_3$), which is an indication of the azidation reaction and the appearance of GAP. In case of viscous liquids as HTPB, GAP samples, a thin layer of the polymer was placed on the surface of the KBr tablet. The used wave number range was $500-4000\text{ cm}^{-1}$, which is the appropriate range for most organic compounds¹¹. It is well known that IR spectra of the organic compounds can be divided into three main regions; functional group region $4000 - 1300\text{ cm}^{-1}$, finger print region $1300 - 910\text{ cm}^{-1}$ and aromatic region from $910 - 500\text{ cm}^{-1}$.

Elemental Analysis (GAP only)

PERKIN-ELMER 240 CHN elemental analyzer with AD-4 auto balance was used to detect the % of C, H and N in the prepared samples which facilitates the detection of nitrogen content taken as a reference to the explosophorous azide group, responsible for the excess energy of the energetic prepolymer. Obtained results make it possible to compare the theoretical and determined experimental % of C, H and N in the used samples [5].

Determination of mg Equivalent (OH)

The determination of the mg equivalent is very important because curing of solid rocket propellant formulations is fully dependant on it together with NCO groups (curing ratio) [2]. Value of mg equivalent of (OH) was determined according to following equation:

$$\text{mg. eqv. OH / g binder} = [(V_2 - V_1) * N] / W$$

- V_1 Volume in cm^3 of NaOH solution required for titration of blank.
- V_2 Volume in cm^3 of NaOH solution required for titration of sample.
- N Normality of NaOH solution.
- W Weight of sample in g.

Determination of Density

Density of the used GAP and HTPB samples were determined by selecting an ordinary densimeter in the predicted range, inserting it in the measuring cylinder filled with sample and leaving it to reset and then take the value of density.

Determination of Viscosity

The viscosity of the used GAP diol and HTPB samples were measured on a rotational-type digital Brookfield viscometer, Model DV-II, using an SPD-21 spindle at a rotational speed of 10 rpm at 25°C .

Determination of Water Content

water content is a very important property especially if we need to use GAP as an ingredient in composite propellant formulations. Karl-Fisher technique was used for determination of the water content of the used GAP diol and HTPB samples. 200 cm^3 of titrating solvent was added into the 500 cm^3 beakers with reagent until the end-point using the diluted and standardized reagent. Then, about 2.5g of the sample were added with the time of 60 seconds. Repeat the titration again with diluted standardized Karel- Fisher reagent, to the end point. The water content (% by weight) was calculated as follows:

$$\text{Water content \% by weight} = \frac{K.F_{\text{reagent}} * \text{titer} * 100}{\text{wieght}_{\text{sample}}}$$

K.F_{reagent} Karel – Fisher (cm^3)

Titer Ratio of the employed water (g) / volume of Karel – Fisher reagent, W weight (g)

2.2 Preparation of poly urethane binder (based on GAP and based on HTPB)

Different formulations were prepared on lab scale, For preparation of cross-linked GAP network, GAP was first mixed with cross-linking agent (mixture of 1,4 butane diol and TMP in the ratio of 1 : 2), and the mixture was dried at 100 °C for nearly 30 min After cooling the mix, weighed quantity of isocyanate (Hexamethelene Diisocyanates (HMDI)) as per required NCO/OH ratio was added and mixed thoroughly. For the purpose of the study, the NCO/OH ratio was varied from 0.7 to 1.5, keeping the crosslinker content at 5% with respect to binder. The composition of the GAP samples prepared are shown in Table (1). Cross-linker content is 5% by weight with respect to binder. Catalyst content(10% solution of dibutyl tin dilaurate (DBTDL) in toluene) is 0.018%. Measured quantity of catalyst (0.018%) was added, and the mix was stirred . The specimens were also prepared with cross-linker content varying from 3–9% by weight with respect to binder, keeping the NCO/OH ratio constant at 1,Table (2) . The resin mix was then poured into a mold Curing of the samples was done in air oven at 60 °C.For cross linked HTPB network the same preparation steps but without using crosslinking agent or curing catalyst only curing agent (Hexamethelene Diisocyanates (HMDI)) The composition of the HTPB samples prepared are shown in Table (3).

Determiration of mechanical properties

LLOYD testing machine measured stress-strain relation for the prepared samples. The tensile test was carried out for at least three times for each prepared formulation and the mean value of the obtained results was recorded. The tensile test for all the prepared samples was carried under the following conditions:

Cross head sped = 50 (mm/min). Ambient temperature.

Load cell = 5000 (N) Cross head speed accuracy = 0.5. Internal extensometer

Table (1). Poly Urethane samples based on GAP [Varying NCO/OH Ratio (5% crosslinker)]

Composition(%) I	S1	S2	S3	S4
GAP	86.95	83.82	81.86	79.08
HMDI	8.7	11.99	14.05	16.96
Cross-linker mixture	4.35	4.19	5.49	3.96
Curing catalyst	0.018	0.018	0.018	0.018
NCO/OH	0.7	1.0	1.2	1.5

Table (2) . Poly Urethane samples based on GAP [Varying Cross-Linker Content]

Composition(%)	S5	S6	S7	S8
GAP	87.44	83.82	80.5	77.42
HMDI	9.94	11.99	13.87	15.6
Crosslinker mixture	2.62	4.19	5.63	6.98
Curing catalyst	0.018	0.018	0.018	0.018
Cross-linker (%)	3	5	7	9
NCO/OH	1	1	1	1

Table (3). Poly Urethane samples based on HTPB [Varying NCO/OH Ratio]

Composition(%)	S9	S10	S11	S12	S13
HTPB %	95.3	94.6	93.4	92.1	90.37
HMDI %	4.7	5.4	6.6	7.9	9.63
NCO/OH	0.7	0.8	1.0	1.2	1.5

3. Results

3.1 Characterization of the used prepolymer

Infrared Spectroscopy

The azide as a functional group and more significantly as stretching vibration was inserted into the GAP structure as appears on figure (1) due to the existence of the absorption band at 2105 cm^{-1} which characterize the azide group. Other absorption bands that were detected can be classified according to table (4), Also IR spectral data of HTPB have been summarized in Table (5) and appears on figure (2) .

Table (4) IR characteristic absorption peaks of GAP

Group	Wavenumber (cm^{-1}) (Theoretical)[12]	Wavenumber (cm^{-1}) (Present Study)
-OH	3600-3300	3448.0
C-O-H	near 1450	1431.1
-CH ₂ -CH	near 3000	2920.0
C-H	2900-2750	2873.7
C-Cl	667-600	628.8
C-O-C	1300-1000	1122.5
CH ₂ -N ₃	near 1280	1280.6
CH ₂ -O-CH ₂	1650-1450	1627.8
CH ₂ -N ₃	near 2100	2102.3

Table (5) IR Characteristic Absorption bands of HTPB

Group	Wavenumber (cm ⁻¹) (Theoretical)[13]	Wavenumber (cm ⁻¹) (Present Study)
OH with intramolecular hydrogen bonding	3140-3520	3405.78
Vibrational stretching of olefinic CH	3040-3120	3073.85
OH with intermolecular hydrogen bonding	2980-3040	3005.27
Vibrational stretching of OH of -CH ₂	2800-2880	2844.63
Vibrational stretching of vinyl, cis and trans C=C	1600-1680	1639.03
Vibrational bending of CH group of alcoholic group	1380-1480	1437.2
Vibrational bending of C-O from 1° alcohol that is attach to C=C	940-1080	966.26
Vibrational bending of (C=C) vinyl	880-940	911.22
vibrational bending of (C-H) out of plane	600-800	723.7

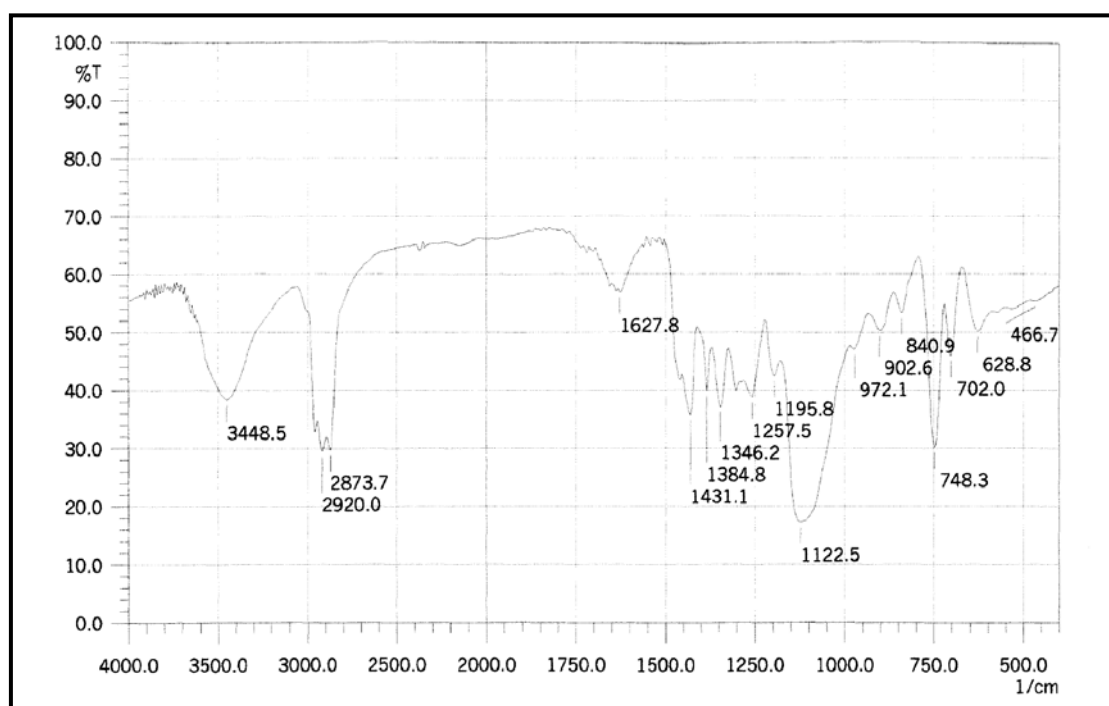


Fig (1) IR Spectrum of GAP Diol

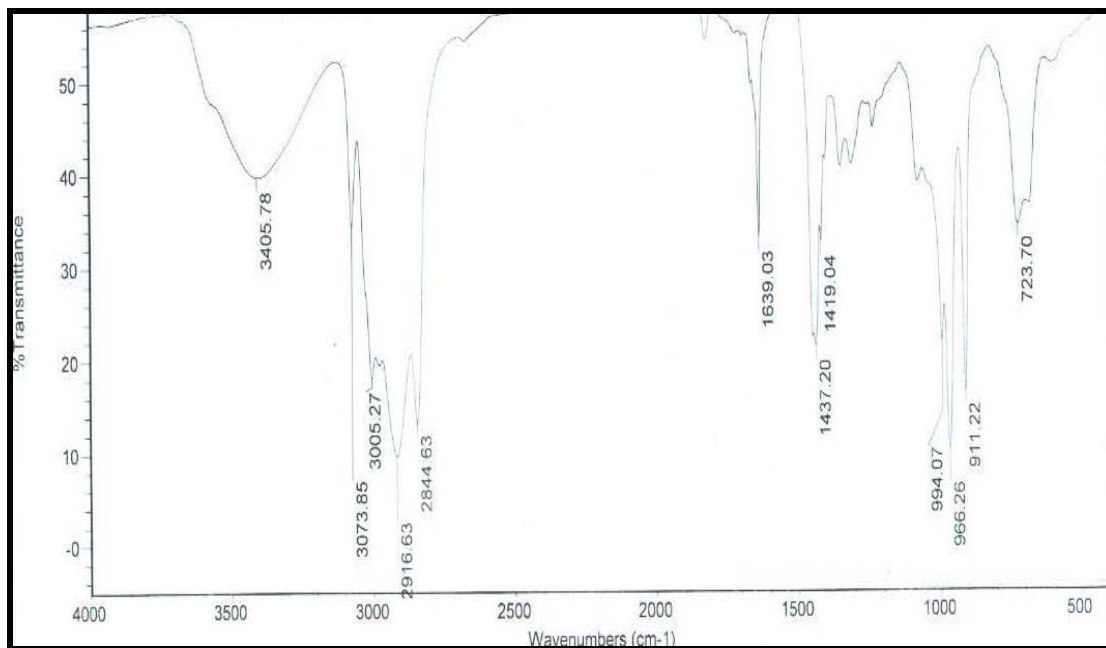


Fig (2) IR Spectrum of HTPB

3.1.2 Elemental Analysis

Elemental analysis shows a good agreement between theoretical composition and the results of experimental elemental analysis, table (6).

Table (6) Theoretical and experimental percentage of C, H, N

Element	C	H	N
Theoretical %	36.8	5.5	39.6
Practical %	36.5	5.1	40.3

3.1.3 Hydroxyl number (OH)

The mg. equivalent OH / g GAP was found to be .825 , also mg. equivalent OH / g HTPB was found to be .84 and it is well known that the value of mg. equivalent OH / g polymer is very important for calculation of curing ratio (NCO/OH) which effects on mechanical properties of cured polymer .

3.1.4 Density

The density of the sample was determined using a suitable densimeter. Density of GAP was found to be about 1.28 g/cm³ and it was a promising value compared to the measured value of HTPB which was .9 g/cm³ , so we can say that GAP enables producing high density propellant making high loading masses in rocket motors .

3.1.5 Water Content

The optimum water content for GAP & HTPB to be promising in CSRFP formulations is about 0.05%. For the used GAP samples the water content was found to be 0.0089% and for HTPB samples was found to be .04 % and for both prepolymers they are promising results in CSRFP field as a binder .

3.1.6 Viscosity

The measured viscosity of the used GAP was 5000 cp and for HTPB was 5800 cp , so the low viscosity for GAP binder ensures favorable processability characteristics for propellant slurry .

3.2 Characterization of Mechanical properties of the cured networks prepared

GAP samples with the composition of crosslinker ratio 5% and different values of NCO/OH illustrated in table (1) . The results of the mechanical properties was illustrated in the following table (7), Also GAP samples with the composition of NCO/OH = 1 and different values of crosslinker ratio illustrated in table (2) The results of the mechanical properties was illustrated in the following table (8) , HTPB samples with the composition of different values of NCO/OH illustrated in table (3) The results of the mechanical properties was illustrated in the following table (9)

Table (7) Mechanical properties of GAP based Poly urethane samples (5% cross-linker)

Samples	NCO/OH	Strength (Kg _f /cm ²)	Strain (%)
S1	0.7	4.2	460
S2	1.0	11.4	330
S3	1.2	35.1	250
S4	1.5	52.4	220

Table (8) Mechanical properties of GAP based Poly urethane samples
(NCO/OH = 1)

Samples	Cross-linker (%)	Strength (Kg _f /cm ²)	Strain (%)
S5	3	7.8	490
S6	5	11.4	330
S7	7	16.1	190
S8	9	24.2	160

Table (9) Mechanical properties of HTPB based Poly urethane samples

Samples	NCO/OH	Strength (Kg _f /cm ²)	Strain (%)
S9	0.7	4.8	420
S10	0.8	9.6	380
S11	1.0	40.2	270
S12	1.2	58	180
S13	1.5	64.6	140

The influence of the NCO/OH ratio on the gum-stock properties of GAP matrix was investigated experimentally by varying the NCO/OH ratio in the range of 0.7 to 1.5 for a constant cross-linker content of 5% and also for HTPB matrix but without using of cross-linker, Figure 3, 4 show the variation of tensile strength and elongation with NCO/OH ratio of the cross-linked network with HMDI. The increase in tensile strength and reduction in elongation with increase in NCO/OH ratio could be related to the increase in crosslink density of the network. The results show that increasing the NCO content improves the tensile

strength. Elongation is found to be sharply decrease up to a NCO/OH ratio of 1 beyond which major change was not observed. This may be due to the fast depletion of hydroxyls leading to more side reactions by excess NCO, the same way occurs for HTPB cured samples but with little higher values which means that the presence of crosslinking agent improves the mechanical behaviour and gum stock properties of GAP samples to give such close results to HTPB samples.

The cross-linking agent content in the GAP mix was varied from 3–9% for an NCO/OH ratio of unity. When the cross-linking agent content was reduced below 3%, the cohesive strength of the slab was affected severely that the sample could not be tested, The test results show that increase in cross-linker content improves the tensile strength and reduces the strain capability due to increased crosslink density as expected. Figure 5,6 show the graphical representation of the variation in tensile strength and elongation with cross-linker percentage. The cross-linker content was evaluated up to 9%, as the effect seems to diminish at this concentration level.

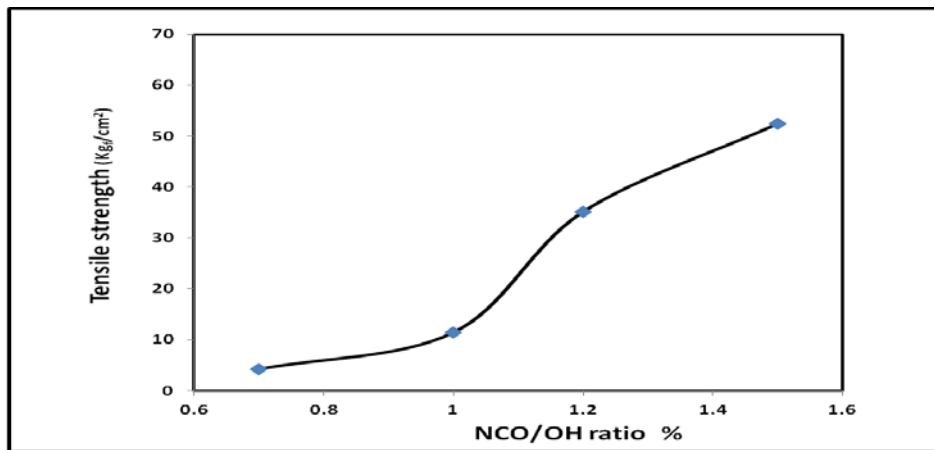


Fig (3) Variation of tensile strength with NCO/OH ratio, 5% crosslinker (GAP network).

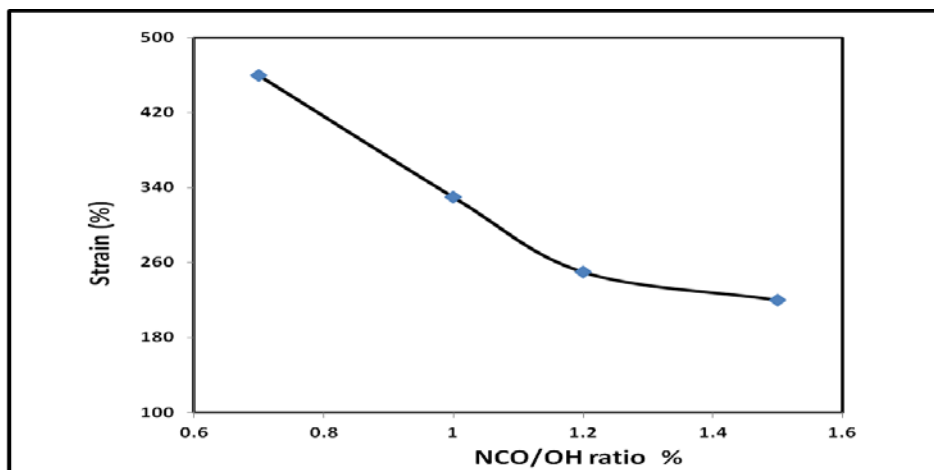


Fig (4) Variation of % strain with NCO/OH ratio , 5% cross-linker (GAP network)

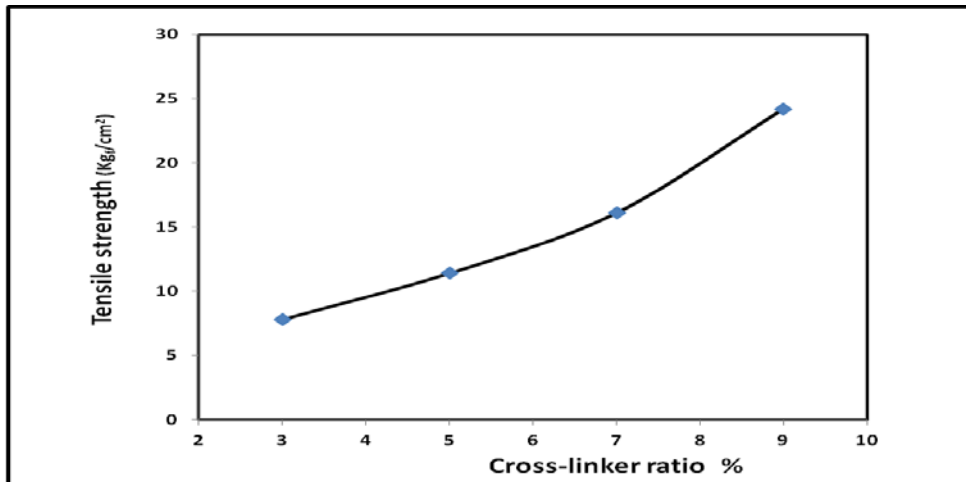


Fig (5) Variation of tensile strength with cross-linker ratio ,NCO/OH=1 (GAP network)

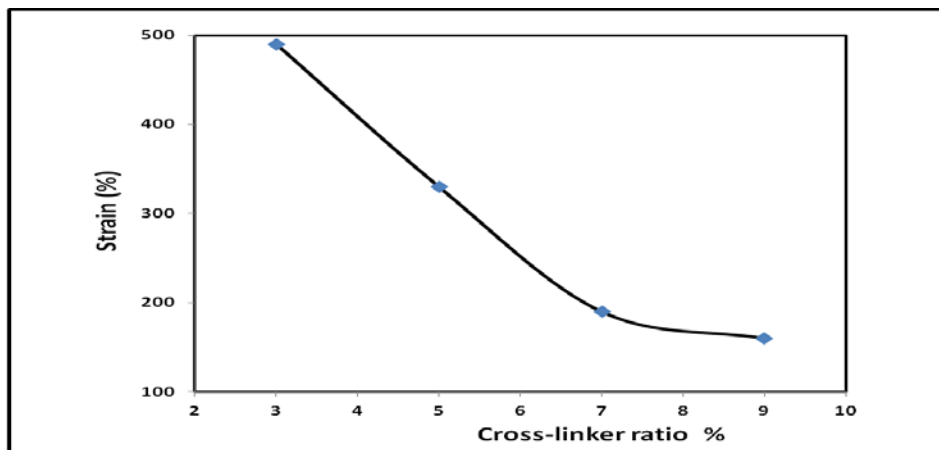


Fig (6) Variation of % strain with cross-linker ratio , NCO/OH=1 (GAP network)

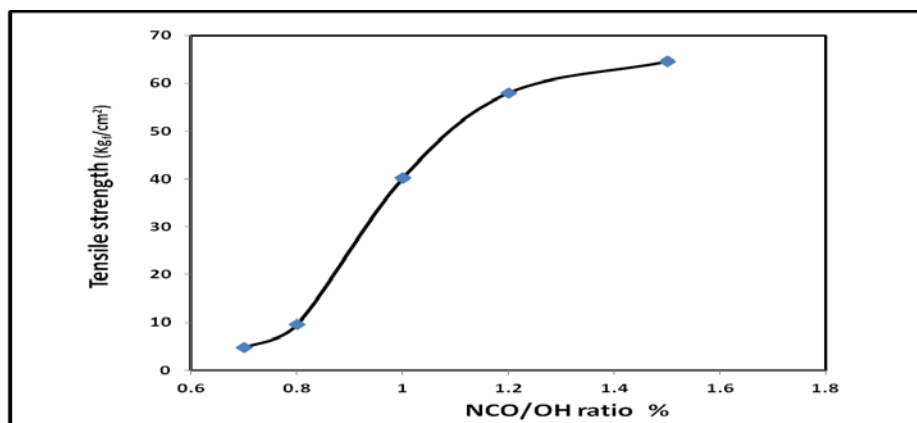


Fig (7) Variation of tensile strength with NCO/OH ratio (HTPB network)

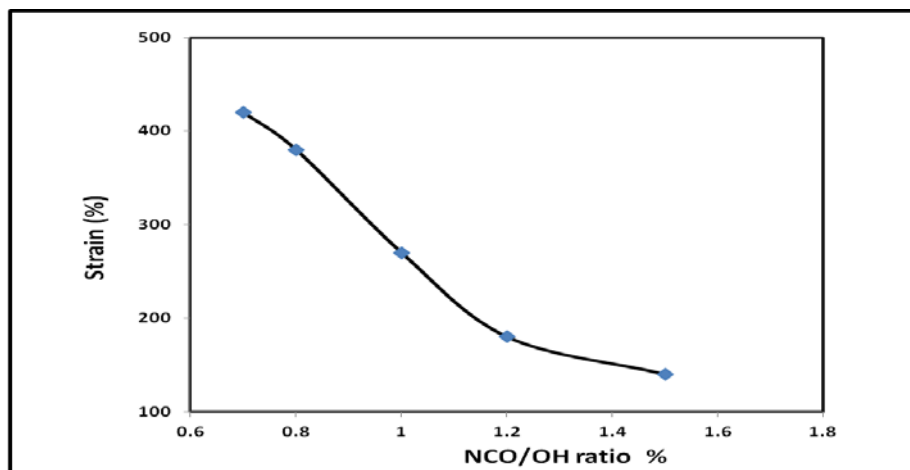


Fig (8) Variation of % strain with NCO/OH ratio (HTPB network)

4. Conclusions

Infrared Spectroscopy of the used GAP and HTPB was all in theoretical ranges which characterize the used polymers and ensure kind of polymers and its source, GAP prepolymer has density higher than HTPB which is required in propellant design, water content for both samples was in range for using in propellant production specially for GAP which causes gassing problems with isocyanates due to presence of water, Low viscosity for GAP binder ensures favorable processability characteristics for propellant slurry.

Based on the evaluation of gum-stock properties of GAP, it was noted that the functionality of the polymer and NCO/OH equivalent ratio significantly influence the mechanical properties of the crosslinked GAP networks, addition of crosslinking agent improves the mechanical properties of GAP cured polymeric matrix leads to mechanical behaviour close to cured HTPB polymeric matrix which possesses excellent mechanical properties, from this study for using GAP as a binder for composite propellant it was found that using of crosslinking agent is very important to maintain good mechanical properties compared to HTPB based propellant also using of crosslinking agent with range of (5-7)% and curing ratio (.9-1.2) according to the application and design of the propellant produced.

References

- [1] M.B. Frankel, L.R. Grant and J.E. Flanagan "Historical Development of Glycidyl Azide Polymer", Journal of Propulsion and Power, Vol.8, No.3, Page 560-563. May-June 1992.
- [2] A.N. Nazare, S.N. Asthana, and Haridwar Singh, "Glycidyl Azide Polymer- an Energetic Compound of Advanced Solid Propellants", Journal of Energetic Materials Vol. 10, pages 43-63, 1992.
- [3] Yuxiang Ou, Boren Chen, Hong Yan, Huiping Jia, Jianjuin Li, and Shuan Dong, "Development of Energetic Additives for Propellants in China", J. Propulsion and Power Vol.11, No.4 Pages 838- 847, July-August 1995.

- [4] Andrew Sanderson, "The Characterisation and Development of New Energetic Materials", Energetic Materials-Technology manufacturing and Processing, 27th International Annual , Conference of ICT, 1996, Karlsruhe, Federal Republic of Germany.
- [5] J. A. Mul, P. A. O. G. Korting, and H.F.R. Schoyer, "A Search for New Storable High Energy Propellants", ESA Journal, Vol.14, Pages 253-270. 1990.
- [6] R.Manjari, U.I. Somasundaram, V.C. Joseph, T. Sriram, "Structure Property Relationship of HTPB Based Propellants. II. Formulation tailoring for Better Mechanical Properties", Journal of Applied Polymer Science, Vol.48, 1993. Pages 279-289.
- [7] Ozgur Hocaoglu, Tulay Ozbelge, Fikret Pekel, and Saim Ozkar, "Fine Tuning the Mechanical Properties of Hydroxyl Terminated Polybutadiene/ Ammonium Perchlorate Based Composite Solid Propellants by varying the NCO/OH and Triol/Diol ratios", Journal of Applied Polymer Science, Vol. 84, pages 2072-2079. March 2002.
- [8] Energetic Polymers: Binders and Plasticizers for Enhancing Performance(Historical Perspective, First Edition. How Ghee Ang and Sreekumar Pisharath. 2012 WILEY-VCH
- [9] PHYSICAL, MECHANICAL AND MORPHOLOGICAL CHARACTERISTICS OF CHAIN MODIFIED GAP AND GAP-HTPB BINDER MATRICES. SK. Manu*, TL.Varghese*, MA Joseph*, K Shanmugam*, and Suresh Mathew, Scientists, Vikram Sarabhai Space Centre
- [10] Investigation on the Mechanical Properties of GAP-based Low Signature Propellants ,Zheng Jian Pang Aimin Wu Jinhan Hubei Institute of Aerospace Chemotechnology (HIACT). P, R, China, ICT 2005.
- [11] I. M. Kamal*, M. A. Radwan*, H.E. Mostafa * and M. A. Borham 2nd ICEE Conference,MTC November, 2004 "Preperation And Characterization Of Glycidyle Azide Polymer (GAP) As A Plasticizer In Composite Solid Rocket Propellant"
- [12] Simmons R.L., "NENAs - New Energetic Plasticizers", NIMIC-S-275 94,NATO,Brussels,Belgium,1994.
- [13] "Determination of Average Degree of Polymerization and Average Number of Molecular Weight for Hydroxy Terminated Polybutadiene Polymer using ¹H NMR ".,FARIDEH GOURANLOU , Malek-Ashtar University of Technology Lavizan, Tehran, Iran, Asian Journal of Chemistry Vol. 19, No. 3 (2007), 1757-1760.