Studies on Structure Property Correlation of Cross-Linked Glycidyl Azide Polymer

S. K. Manu,[1] T. L. Varghese,[2] S. Mathew,[3] K. N. Ninan[4]

[1]*Propellant Fuel Complex, Vikram Sarabhai Space Centre, Indian Space Research Organisation, Thiruvananthapuram, Kerala 695 022, India*
[2]*Formerly of Propellants and Special Chemicals Group, Vikram Sarabhai Space Centre, Indian Space Research Organisation, Thiruvananthapuram, Kerala 695 022, India*
[3]*School of Chemical Sciences, Mahatma Gandhi University, Kottayam, Kerala 686 560, India*
[4]*Formerly of Propellants Chemical and Materials Entity, Vikram Sarabhai Space Centre, Indian Space Research Organisation, Thiruvananthapuram, Kerala 695 022, India*

Received 4 February 2008; accepted 26 May 2009
DOI 10.1002/app.30845
Published online 7 August 2009 in Wiley InterScience (www.interscience.wiley.com).

ABSTRACT: Glycidyl azide polymer (GAP) has been evaluated for use as binder for solid propellants. 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. It was observed that the type of curing agent and the NCO/OH ratio have a strong influence on the gum-stock properties. Similar impact was seen for cross-linker concentration also. The swelling characteristics of the cross-linked binder prepared with different NCO/OH ratios were evaluated with toluene and tetrahydrofuran (THF). The polarity and the solubility parameter of the solvents were found to influence the swelling of GAP. The NCO/OH ratio and cross-linker concentration of the polymer were also found to affect the swelling characteristics. The sol fraction determined for the polymer was found to follow a similar pattern. The cross-link density and average molecular weight between crosslinks (Mc) were determined from the swelling studies and also from the stress–strain relationship. The Mc values were found to be influenced by the NCO/OH ratio. Finally, the Mc values determined from the swelling data were correlated to the gum-stock properties, and the model parameters were estimated. © 2009 Wiley Periodicals, Inc. J Appl Polym Sci 114: 3360–3368, 2009

Key words: GAP; gum stock properties; swelling; cross-link density; molecular weight between crosslinks

INTRODUCTION

GAP is a unique binder of high density with positive heat of formation of +117.2 kJ/mol and is compatible with advanced oxidizer like ammonium dinitramide (ADN). The scission of $C—N_3$ group is highly exothermic and is accompanied by release of 685 kJ/mol. The synthesis and characterization of GAP have been presented by a number of authors.[1–8] 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 crosslinker, and curing conditions significantly influence the three-dimensional network formation, which imparts the necessary mechanical properties to the binder matrix.[9,10] For case-bonded rocket motor applications, the binder is to be converted into cross-linked 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. Concentration of the curing agent and crosslinker affect the matrix properties of the binder. Polymer network build up during the cross-linking reaction determines the structural integrity of the binder. Chain propagation due to urethane linkage formation and chain branching may not be complete in any such reaction. The cross-link density or molecular weight between crosslink is characteristic parameters, which are related to the integrity of the network. Different methods can be employed to estimate the molecular weight between crosslinks.[11–13] Detailed study results have been presented in literature on the structure property relations of polyurethane systems. Oikawa and Murakami[14] presented a detailed analysis of relation between molecular weight between crosslinks and swelling behavior of vulcanized natural rubber and end-linked polydimethyl siloxane with Flory-Rehner equation and a method based on theory of semidilute polymer solutions advanced by deGennes. Seneker et al.[15] reported the effect of trans–trans content of 4,4′-diisocyanato

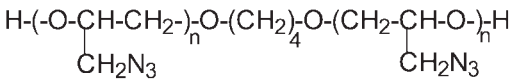
Correspondence to: S. K. Manu (skmpillai@rediffmail.com).

dicyclohexyl methane on the ultimate tensile strength of polyurethane network. Erogulu and Guven[16] have shown that sol fraction of GAP cross-linked with different isocyantes follow a linear relationship with average chain length between junctions. Dependency of concentrations of triol and diol on the properties and structure property correlations of copolyurethanes based on hydroxyl-terminated polybutadiene (HTPB) and castor oil was reported by Jain et al.[17] A systematic study reported by Manjari et al.[9] shows the impact of hard and soft segments domain structures on mechanical behavior of HTPB-based polyurethane systems. Ramarao et al.[18] reported the impact of microstructure and molecular weight distribution of the binder on mechanical properties. Correlations between network parameters and mechanical properties for polyurethanes based on hydroxyl-terminated polybutadiene and poly(12-hydroxy stearic acid-co-TMP) ester polyol was reported by Sekkar et al.[19] Impact of diol/ NCO ratio and diol/triol ratio on the mechanical properties of HTPB-based propellants have been reported by Hocaoglu et al.[10] A comparison of cross-link density determined by various methods and a correlation between network parameters and mechanical properties were presented by Sekkar et al.[20,21] The structure property relationship of binder network may render correlation between mechanical properties and structural parameters of the polymer feasible. In this study, the results of the swelling experiments and the tensile property evaluations done for cross-linked GAP are correlated by a best fit method. The correlations derived show a simple two parameter equation between molecular weight between crosslinks and tensile properties. The correlations may allow prediction of properties of propellant and save time and material.

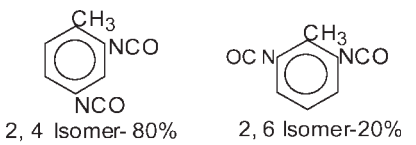
EXPERIMENTAL

Materials

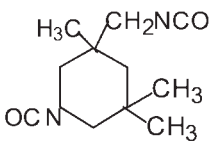
GAP resin with molecular weight of 2000 (by VPO) and hydroxyl value of 45 mg KOH/g was prepared by cationic ring opening polymerization of epichlorohydrin followed by azidation reaction[1,2,4] with sodium azide in polar approtic medium and was used for the study. The crosslinker used was a mixture of 1,4-butane diol and 1,1,1-trimethylol propane (TMP) in the ratio of 1 : 2. In this, butane diol acts as difunctional chain extender, and TMP acts as trifunctional crosslinker. The cross-linker composition was prepared by completely dissolving TMP in butane diol. Toluene diisocyanate (TDI), supplied by M/s. Bayer, Germany and isophorone diisocyanate (IPDI), supplied by M/s Merck, Germany (both with purity >99%) were used as curatives. The catalyst used was a 10% solution of dibutyl tin dilaurate (DBTDL) in toluene. The solvents, toluene and THF were obtained from commercial sources and distilled before use. The chemical structure of GAP and other ingredients are shown below.



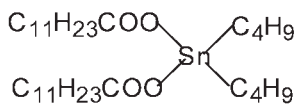
GAP



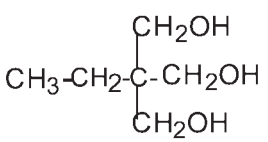
Toluene diisocyanate (TDI)



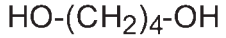
Isophorone diisocyanate (IPDI)



Dibutyl tin dilaurate (DBTDL)



1,1,1-Ttrimcthylol propanc (TMP)



1,4-Butancdiol

Sample preparation

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. The quantity of curing agent was estimated as per following expression.

$$\text{Quantity of curing agent} = \left[\frac{\text{Quantity of binder}}{\text{Equivalent weight of binder}} + \frac{\text{Quantity of crosslinker}}{\text{Equivalent weight of crosslinker}}\right] \times \text{Equivalent weight of curing agent} \quad (1)$$

After cooling the mix, weighed quantity of isocyanate as per required NCO/OH ratio was added and mixed thoroughly. For the purpose of the study, the NCO/OH ratio was varied from 0.8 to 1.75, keeping the cross-linker content at 5% with respect to binder. The composition of the samples prepared are shown in Table I.

Cross-linker content is 5% by weight with respect to binder. Catalyst content is 0.018%.

Measured quantity of catalyst (0.018%) was added, and the mix was stirred and evacuated to remove the entrapped air and moisture. 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. The composition of the samples prepared with varying cross-linker content is shown in Table II.

The resin mix was then poured into a mold, evacuated, and allowed to cure under N_2 atmosphere for 24 h. Curing of the samples was done in desiccator for room temperature curing and in air oven at 60°C for 48 h for elevated temperature curing. By this procedure, cured specimens without blow holes could be realized.

The reaction between hydroxyl-terminated GAP and isocyanate curative can be represented by the following scheme. The path of such a reaction can be easily

$$\text{R–OH} + \text{R}'\text{NCO} \longrightarrow \text{R–O–}\overset{\overset{\text{O}}{\|}}{\underset{\underset{\text{H}}{|}}{\text{C}}}\text{–N–R}'$$

followed by recording FTIR spectra of the curing mixture at various time intervals. For instance, the spectra of GAP-TDI mixture immediately after mixing and after completion of cure cycle are shown in Figure 1. It can be observed that there is a sharp reduction in the absorbance of NCO peak (2273 cm^{-1}) after curing.

Reduction in the intensity of the peak at 2273 cm^{-1} corresponds to the consumption of NCO groups, whereas increase in the intensity of the peak at 1726 cm^{-1} indicates the formation of urethane groups due to reaction between hydroxyl and isocyanate groups. The absorption bands at 2100 cm^{-1} due to stretching of azide group and CH stretching at 2930 cm^{-1} remain almost unaffected throughout the course of reaction.

Testing

The dumb-bell specimens were punched out from the cured slabs as per Afnor-H2 standards. All the test samples were conditioned and tested using Instron testing machine at 25°C and 60% RH at a cross-head speed of 250mm/min. The software version used was series IX automated materials testing system 7.43.00. Five specimens were tested for each composition and the average of the test values is presented graphically. An outlier analysis carried out showed no outlier in the data.

The swelling experiments were carried out in THF and toluene at 30°C. Cross-linked GAP samples of weight in the range of 0.3 to 0.35 g were kept in excess quantity of THF and toluene for more than 10 h, and samples were taken out at 1 h interval and wiped with blotting paper to remove solvent on surface of the sample and weighed. From the initial weight, final weight, and densities of solvent and polymer, the swelling ratio of the sample was determined. Swelling experiments were also carried out for determination of sol–gel content of the polymer. The sol–gel content was determined by solvent extraction. Samples weighing 0.9 to 1.0 g prepared with different NCO/OH ratios and cross-linker content were used for the experiment. The samples were kept in excess quantity of THF and toluene for 48 h. The samples were deswollen in chloroform and dried under vacuum at 60°C. After drying, the final weight of the sample was taken.

Determination of molecular weight between crosslinks from stress–strain relationship

Stress–strain relationship of cross-linked urethane network can be utilized for determination of molecular

TABLE I
Compositions Prepared with Varying NCO/OH Ratio with TDI and IPDI

NCO/OH ratio	Compositions with TDI (weight %)			Compositions with IPDI (weight %)		
	GAP	Crosslinker	TDI	GAP	Crosslinker	IPDI
1.0	83.33	4.17	12.49	80.54	4.03	15.42
0.9	82.19	4.11	13.68	79.18	3.96	16.85
1.1	81.08	4.05	14.85	77.87	3.89	18.22
1.2	80.00	4.00	15.98	76.60	3.83	19.56
1.5	76.93	3.85	19.21	73.03	3.65	23.31
1.75	74.54	3.73	21.72	70.30	3.51	26.27

weight between crosslinks. The Initial modulus(Young's modulus) was calculated from the initial slope of the stress–strain curve. Although the stress–strain curve is nonlinear due to visco-elastic behavior of the cross-linked network, the slope of the initial linear portion of the curve could be taken as Young's modulus.[22] The initial modulus was directly calculated from the stress–strain data using automated material testing system mentioned under subsection testing. The Mc values of the cross-linked network were determined from initial modulus determined from stress–strain data. The shear modulus is related to the Mc by the following relationships.[23–25]

$$\sigma = G\left(\lambda - \lambda^{-2}\right) = \frac{\rho\, RT}{\mathrm{Mc}}\left(\lambda - \lambda^{-2}\right) \tag{2}$$

$$G = \frac{\rho\, RT}{\mathrm{Mc}} \tag{3}$$

where σ is the tensile stress, G is the shear modulus, λ is the extension ratio in the elastic range, ρ is the density of the polymer, R is the universal gas constant, and T is the absolute temperature. The shear modulus and initial modulus (modulus of elasticity or Young's modulus) are related by the equation.

$$G = \frac{E}{3} \tag{4}$$

where E is the initial modulus. By measuring the initial modulus from the stress–strain curve, the Mc values of the polymer can be determined.

Determination of molecular weight between crosslinks from swelling data

Cross-linked GAP samples of known weight were kept in excess quantity of the solvents for specified time and weighed. From the initial weight, final weight, and densities of solvent and polymer, the swelling ratio of the sample was determined using eq. (5).

$$Q_V = 1 + \left(\frac{W_2}{W_1} - 1\right)\frac{\rho_2}{\rho_1} \tag{5}$$

where W_1 is initial weight of specimen, W_2 is the weight of the specimen after swelling, ρ_1 and ρ_2 are the densities of the solvent and polymer, respectively. Volume fraction of the polymer in the swollen gel (V_2) is given by eq. (6).

$$V_2 = \frac{1}{Q_V} \tag{6}$$

The sol–gel content was determined by solvent extraction of samples prepared with different NCO/OH ratios and cross-linker content. The sol fraction was calculated using the eq. (7).

$$\text{Sol fraction} = \frac{(W_1 - W_2)}{W_1} \times 100 \tag{7}$$

where W_1 is initial weight of sample and W_2 is the final weight of the sample after drying. Based on theory of elasticity by Flory,[26] relationships have been derived between the deformation of elastic networks during swelling and length of the polymer chain segments between crosslinks. This theory has been extended for derivation of expression for determination of molecular weight between crosslinks.[23,27] The equilibrium swell ratio as determined from the swelling experiments [eq. (5)] was used for the evaluation. The equilibrium swell ratio is related to the volume fraction of polymer in swollen gel (V_2) and is given by the eq. (6). The relation between V_2 and the molecular weight between crosslinks is given by Flory-Rehner equation[28–30] as shown below.

$$\mathrm{Mc} = -\mathrm{V}_1\rho\left(V_2^{1/3} - \frac{V_2}{2}\right)\Big/\left[\mathrm{Ln}(1 - V_2) + V_2 + \chi V_2^2\right] \tag{8}$$

where, V_1 is the molar volume of the solvent, ρ the density of the polymer network, and V_2 the volume fraction of polymer in the swollen gel as given in eq. (6). χ is the Flory- Huggins polymer–solvent interaction parameter. In this experiment, the value of χ (0.25 at 45°C) reported in Ref. 16 for GAP-THF system was taken for evaluation.

TABLE II
Compositions with TDI for Varying Cross-Linker Content (NCO/OH Ratio Is Unity for all Compositions and Catalyst Content Is 0.018%)

Cross-linker content (by weight % of binder)	Weight %	
	GAP	TDI
3	86.36	11.03
5	82.19	13.68
7	78.42	16.08
9	74.97	18.27

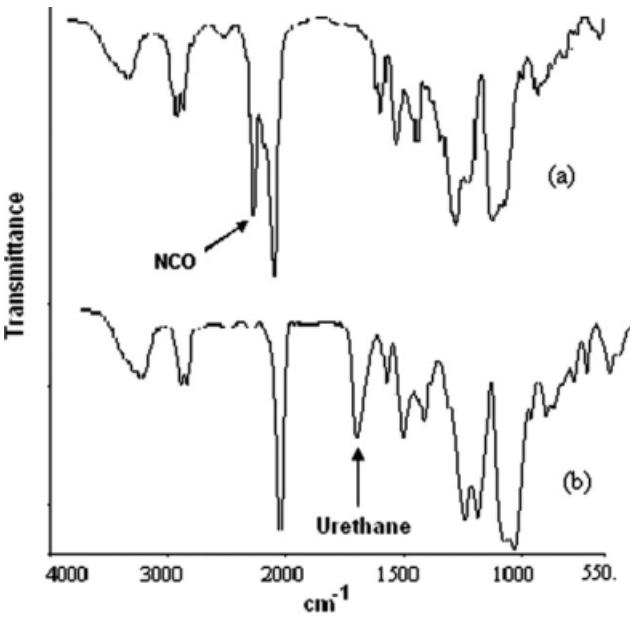


Figure 1 FTIR spectra of the DSC sample (a) immediately after mixing the ingredients and (b) after completion of cure cycle.

RESULTS AND DISCUSSION

Effect of cross-linker content and NCO/OH ratio on the gum-stock properties of cross-linked GAP network

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. This behavior is expected from GAP resin of functionality less than two. Hence, to achieve sufficient cross-link density, a minimum cross-linking agent content of 3% is necessary for NCO/OH ratio above 0.90. The test results show that increase in cross-linker content improves the tensile strength and reduces the strain capability due to increased cross-link density as expected.[9,10] Figure 2 shows 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.

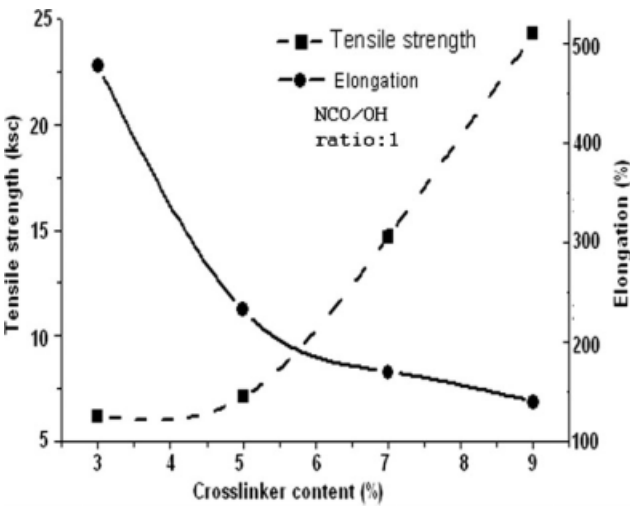


Figure 2 Variation of tensile strength and % elongation with cross-linker content.

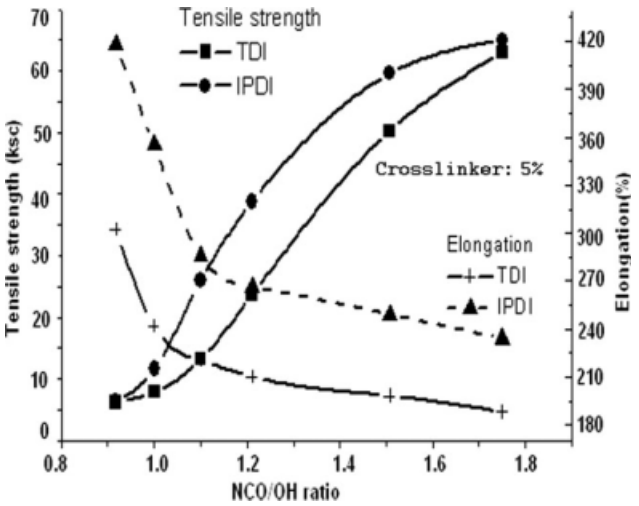


Figure 3 Variation of tensile strength and % elongation with NCO/OH ratio.

The influence of the NCO/OH ratio (*R* value) on the gum-stock properties of GAP matrix was investigated experimentally by varying the NCO/OH ratio in the range of 0.9 to 1.75 for a constant cross-linker content of 5%. This evaluation was also carried out with different curatives like TDI and IPDI. Figure 3 shows the variation of tensile strength and elongation with NCO/OH ratio of the cross-liked network with TDI and IPDI.

Samples prepared with NCO/OH ratio below 0.9 could not be tested as the slabs were found to be of too low strength. The increase in tensile strength and reduction in elongation with increase in NCO/OH ratio could be related to the increase in cross-link density of the network as reported earlier.[9,10] The results show that increasing the NCO content improves the tensile strength. Elongation is found to 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.

Swelling characteristics of cross-linked GAP network

The swelling ratios of the polymer prepared with different NCO/OH ratios show a similar pattern of variation in both THF and toluene. However, the swelling ratios were found to be higher in THF. The higher solubility in THF could be a result of higher

TABLE III
Equilibrium Swell Ratio for Various Formulations Used for the Study

Cross-linker content (by weight % of binder)	NCO/OH ratio	Equilibrium swell ratio		
		GAP-TDI in THF	GAP-TDI in toluene	GAP-IPDI in THF
5	0.9	8.74	1.56	12.20
5	1.0	8.07	1.54	10.62
5	1.2	5.60	1.59	6.68
5	1.5	4.89	1.49	5.18
5	1.75	4.60	1.45	4.78
3	1.0	10.14	1.59	
7	1.0	5.95	1.54	
9	1.0	5.09	1.44	

polarity of THF. Table III shows the equilibrium swelling ratio for GAP crosslinked with TDI with different NCO/OH ratios in THF, toluene and similar data generated for GAP crosslinked with IPDI in THF solvent.

The large difference in the equilibrium swell ratio of GAP in THF could be explained based on the polarity criteria. GAP being a polar system, a more polar solvent like THF is able to swell the polymer to a higher extent compared to less polar solvent, toluene. Also, moderately, hydrogen-bonded solvent like THF have a higher solubility parameter (δ = 19.6 $J^{1/2}$ $cm^{-3/2}$) compared with poorly hydrogen-bonded solvent, Toluene (δ = 18.2 $J^{1/2}$ $cm^{-3/2}$).[31] Higher polarity and solubility parameter associated with THF compared with toluene explains the difference observed in swelling characteristics.

The higher tensile strength and elongation and lower cross-link density observed for IPDI system compared with TDI could be explained based on the nature of the cross-linked network formed by the two systems. In the case of IPDI (aliphatic isocyanate) due to the low reactivity and "clean reaction" (lesser extent of side reactions compared with TDI which is an aromatic isocyanate), a systematic build up of the cross-linked network results. This helps to have more affine deformation for the system and more uniform distribution of stress, there by leading to better elongation and strength. Also, this leads to more polyurethane linkages compared with TDI system. Due to the higher reactivity of TDI (aromatic isocyanate) more side reactions are possible. Higher cross-link density of TDI system is the result of these side reactions and more number of incomplete network linkages compared with IPDI system. Better chemical compatibility of GAP and IPDI resulting from aliphatic nature could also contribute in this respect. The rigid nature of aromatic isocyanate based system could lead to lower stress bearing capability of the network. Table III also shows equilibrium swell ratio for different cross-linker content

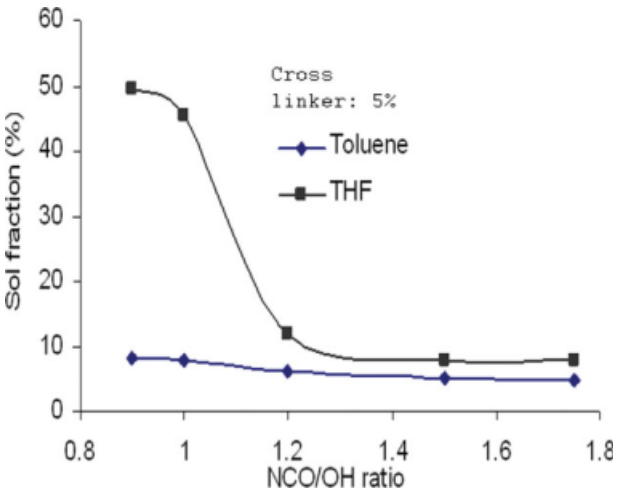


Figure 4 Variation of Sol fraction of cross-linked GAP with different NCO/OH ratio in THF and toluene. Variation of % elongation with NCO/OH ratio. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

for GAP–TDI system in THF solvent. The data show that the swell ratio decreases with increasing cross-linker content. This was found to be due to the increasing cross-link density making the network more solvent resistant.[22]

Effect of NCO/OH ratio on sol–gel ratio

The sol fraction determined for the cross-linked polymer show that the sol content decreases with increasing NCO/OH ratio or increase in cross-link density. This has been reported earlier.[16] The higher sol fraction seen at *R* value below 1.2 could be due to the low cross-link density, allowing solvent to easily swell the polymer chain and dissolve a higher

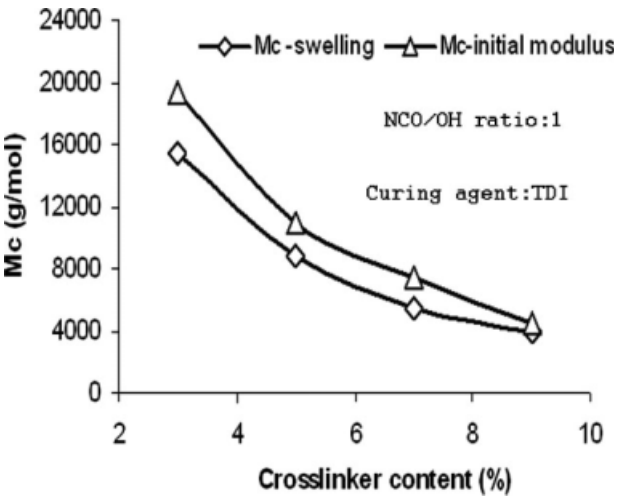


Figure 5 Effect of cross-linker content on the Mc values of cross-linked GAP-TDI system determined from swelling and initial modulus data.

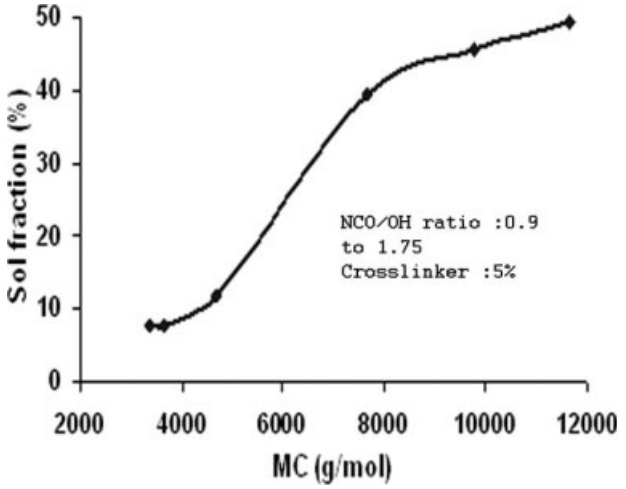


Figure 6 Variation of Mc values with Sol fraction for GAP crosslinked with TDI, using THF as solvent.

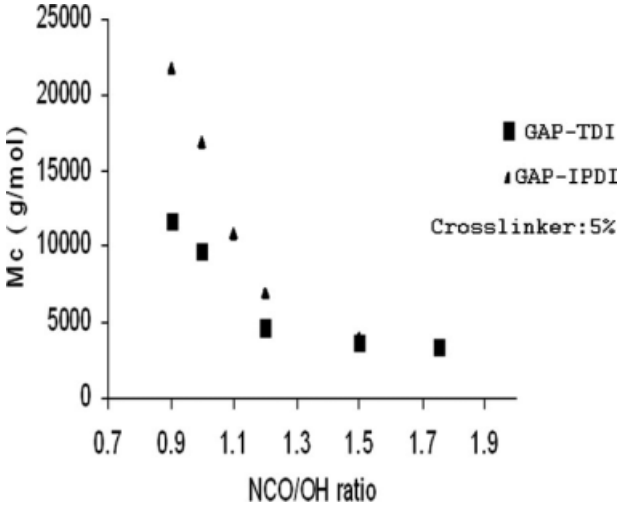


Figure 7 Variation of Mc values with NCO/OH ratio for GAP crosslinked with TDI and IPDI.

fraction.[16,22] The reason for difference in sol fraction in THF and toluene is same as seen for higher equilibrium ratio in THF. The equilibrium swell ratio was found to be higher in THF than in toluene for cross-linked GAP. The difference in equilibrium swell ratio was found to decrease for higher NCO/OH equivalent ratios. Figure 4 shows variation of sol content of GAP-TDI system with NCO/OH ratio in Toluene and THF. The sol–gel studies proved that THF is a better solvent compared with toluene for cross-linked GAP networks.

Effect of NCO/OH equivalent ratio and cross-linker content on average molecular weight between crosslinks (Mc)

The Mc values were determined from swelling data and stress–strain relationship for cross-linked GAP prepared with varying cross-linker content and NCO/OH ratios. The Mc values of cross-linked GAP were found to decrease with increase in NCO/OH ratios as reported earlier for similar experiment.[22] Figure 5 shows the variation of Mc values with cross-linker content, determined from swelling studies and stress–strain data.

The sol fraction was found to increase with increase in Mc values. The variation of Mc values with sol fraction for different formulations is shown in Figure 6. Increase in cross-linker content was found to have a negative effect on Mc values of the cross-linked network as in the case of NCO/OH ratio.[16] It was noted that the Mc values of GAP-IPDI system were always higher than the Mc values for GAP-TDI system for all NCO/OH ratios. Figure 7 shows variation of Mc with NCO/OH ratio for GAP-TDI and GAP-IPDI systems.

Correlation between gum-stock properties and Mc

The Mc values determined for GAP-TDI system by both mechanical and swelling methods given in Table IV show a decreasing trend with increasing NCO/OH ratios as expected.[22] The difference in the Mc values by the two methods could be due to the basic difference in the methods of determination.

TABLE IV
Comparison of Mc Values Determined by Mechanical and Swelling Methods for GAP Crosslinked with TDI. NCO/OH Ratio

NCO	Mechanical method			Swelling method		
OH ratio	Initial modulus (ksc)	Mc (initial modulus) (g/mol)	Cross-link density (Mol/m^3)	Mc (swelling) (g/mol)	Sol fraction (%)	Cross-link density (Mol/m^3)
0.9	5	19396.3	65.9	11654.6	49.5	109.8
1.0	8.9	10896.8	117.5	9760.3	45.5	131.1
1.1	10	9698.1	131.9	7668.4	39.3	166.9
1.2	12	8081.8	158.4	4668.7	11.9	274.2
1.5	25	3879.3	329.9	3675.1	7.9	348.3
1.75	48	2020.5	633.5	3366.6	7.8	380.2

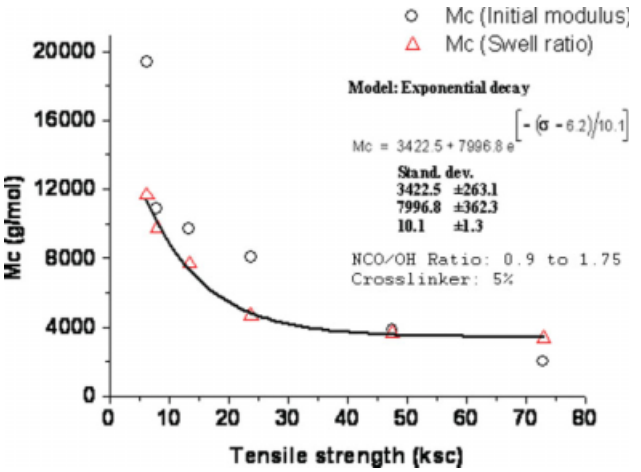


Figure 8 Correlation between Mc and Tensile strength with best fit. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

The basic molecular dynamics of the methods differ considerably. The visco-elastic process in stress–strain measurements leading to dissipation of energy in the polymer network could affect results which may be totally absent in the case of swelling experiments. Also, the Mc values depend on the time scale of the method.[20] The higher Mc values seen in mechanical methods could be a result of the network defects leading to fast disentaglement.[22]

The Mc values for GAP-TDI system determined from the swelling study with THF were correlated with the gum-stock properties of GAP-TDI system prepared with same NCO/OH ratios. The cross-linker content was maintained at 5% by weight with respect to binder in the experiments. The correlative equations could be employed to predict the tensile properties of the cross-linked network system when used as binder for propellant applications. Tensile strength and elongation were correlated with Mc values. The correlations were determined by selecting a best fit for the data. Different fits were attempted using computational software, Microcal Origin Version 5.0, and the best fit was selected. The relationship between tensile strength and Mc values were best described by a second-order exponential function as given by expression 9, and the fit was found to be as shown in Figure 8.

$$\mathrm{Mc} = 3422.5 + 7996.8\, e^{[-(\sigma-6.2)/10.1]} \qquad (9)$$

where Mc is in g/mol and σ is the tensile strength in ksc.

A second-order polynomial was found to be the best fit for relationship between Mc values and elongation as shown in Figure 9. The mathematical relationship between Mc values and percent elongation was given by expression 10, which is true for all positive values of ε.

$$\mathrm{Mc} = -0.7\,\varepsilon^2 + 441.2\,\varepsilon - 54,314.7 \qquad (10)$$

where ε is the % elongation.

The variation of tensile strength and elongation with Mc as given by the expressions 9 and 10, respectively, are found to be in agreement with reported literature on polyurethane networks.[9,22,32] The decrease in tensile strength and increase in elongation with increasing Mc values and the plateau observed in the curve at higher values of Mc agrees well with experimental observations.

CONCLUSIONS

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 cross-linked GAP networks. The type of curing agent was also found to affect the curing and gum-stock properties. Aliphatic diisocyanate(IPDI) curing agent was found to improve the mechanical properties of cross-linked GAP more readily than aromatic(TDI) curing agent even though the latter exhibited higher cross-link density. This could be explained based on the observation that more systematic and complete polyurethane network structure formed by less reactive aliphatic isocyanate helps to have more uniform distribution of stress in the network structure. Better chemical compatibility resulting from the aliphatic nature of binder and curative could also contribute to this effect.

The swelling studies carried out showed that swelling behavior is strongly influenced by the

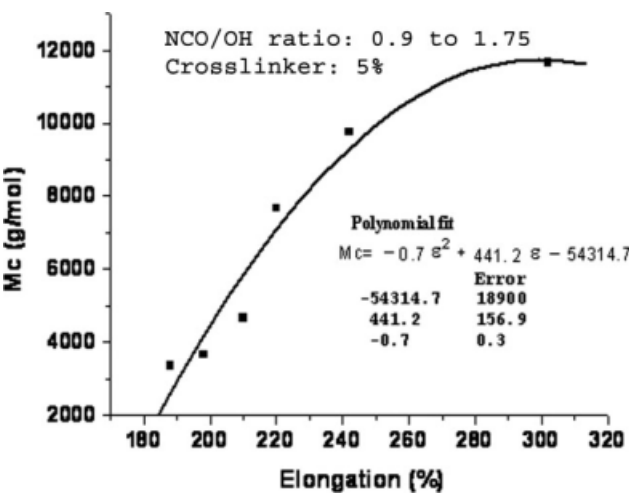


Figure 9 Correlation between Mc and elongation with best fit.

NCO/OH ratio. Between THF and toluene, THF was found to be a better solvent for the GAP network. GAP crosslinked with IPDI showed higher swell ratio compared with GAP crosslinked with TDI. The data showed that the swell ratio decrease with increasing NCO/OH ratio and also with increase in cross-linker content. The molecular weight between crosslinks was determined from swelling data and initial modulus. The Mc values determined by both the methods were found to show decreasing trend with increasing NCO/OH ratios. An exponential correlation was found to describe the relationship between tensile strength and Mc values determined by swelling whereas for elongation, a second-order polynomial was found to be best suited. The correlation derived between data generated from swelling experiments and mechanical measurements can be used for evolving a structure property relationship for GAP network.

The authors are very thankful to Mr. C.V. Mohandas, Rocket Propellant Plant, VSSC for mechanical testing of the specimens thank Director, VSSC for granting permission to publish this work.

References

1. Frankel, M. B.; Flanagan, J. E. U.S. Pat. 4,268,450 (1981).
2. Frankel, M. B.; Witucki, E. F.; Woolery, D. O., II. U.S. Pat. 4,379,894 (1983).
3. Mul, J. A.; Korting, P. A. O. G.; Schoyer, H. F. R. ESA J 1990, 14, 253.
4. Frankel, M. B.; Grant, L. R.; Flanagan, J. E. J Propul Power 1992, 8, 560.
5. Selim, K.; Ozkar, S.; Yilmaz, L. J Appl Polym Sci 2000, 77, 536.
6. Hori, K.; Kimura, M. Propellants Explosives Pyrotech 1996, 21, 160.
7. Hunter, R.; Manzara, T. In 30th International Annual Conference of ICT; Federal Republic of Germany: Karlsruhe, 1999; p 54 (1–5).
8. Manu, S. K.; Varghese, T. L.; Joseph, M. A.; Shanmugam, K.; Mathew, S. In 35th International Annual Conference at ICT; Federal republic of Germany: Karlsruhe, 2004; p 98 (1–13).
9. Manjari, R.; Somasundaram, U. I.; Joseph, V. C.; Sriram, T. J Appl Polym Sci 1993, 48, 279.
10. Hocaoglu, O.; Ozbelge, T.; Pekel, F.; Ozkar, S. J Appl Polym Sci 2002, 84, 2072.
11. Mark, J. E. Rubber Chem Technol 1982, 55, 762.
12. Kusano, T.; Tamura, S.; Murakami, K. J. Polym Sci Polym Symp 1974, 46, 251.
13. Dusek, K. Polymer Networks; Springer-Verlag: New York, 1982.
14. Oikawa, H.; Murakami, K. Rubber Chem Technol 1987, 60, 579.
15. Seneker, S. D.; Born, L.; Schmelzer, H. G.; Eisenbach, C. D.; Fischer, K. Colloid Polym Sci 1992, 270, 543.
16. Erogulu, M. S.; Guven, O. Polymer 1998, 39, 1173.
17. Jain, S. R.; Sekkar, V.; Krishnamurthy, V. N. J Appl Polym Sci 1993, 48, 1515.
18. Ramarao, M.; Scariah, K. J.; Ravindran, P. V.; Chandrasekharan, G.; Alwan, S.; Sastri, K. S. J Appl Polym Sci 1993, 49, 435.
19. Sekkar, V.; Ramarao, M.; Krishnamurthy, V. N.; Jain, S. R. J Appl Polym Sci 1998, 62, 2317.
20. Sekkar, V.; Narayanaswamy, S.; Scariah, K. J.; Nair, P. R.; Sastri, K. S.; Ang, G. H. J Appl Polym Sci 2006, 101, 2986.
21. Sekkar, V.; Narayanaswamy, S.; Scariah, K. J.; Nair, P. R.; Sastri, K. S.; Ang, G. H. J Appl Polym Sci 2006, 103, 3129.
22. Erogulu, M. S. J Appl Polym Sci 1998, 70, 1129.
23. Eisele, U. Introduction to Polymer Physics; Springer Verlag: Berlin, 1990.
24. Mooney, M. J. Appl Phys 1940, 11, 582.
25. Slade, P. S., Jr.; Jenkins, L. T. Technics and Methods of Polymer Evaluation; Marcel Dekker Inc.: New York, 1970; Vol. 2, p 130
26. Flory, P. J. Principles of Polymer Chemistry; Cornell University press: Ithaca, New York, 1953.
27. Treolar, L. R. G. The Physics of Rubber Elasticity; Clarendon press: Oxford, England, U.K., 1975.
28. Flory, P. J.; Rehner, J. J. Chem Phys 1943, 11, 521.
29. Bell, J. P. J Polym Sci 1970, 2, 417.
30. Erman, B.; Flory, P. J. Macromolecules 1986, 19, 2342.
31. Van Krevelen, D. W.; Hoftyzer, P. J. Properties of Polymers, 2nd ed.; Elseiver Scientific Publishing Company: Amsterdam, 1976; p 144.
32. Haska, S. R.; Bayramli, E.; Pekel, F.; Ozkar, S. J Appl Polym Sci 1997, 64, 2347.