

Network Characterization of Energetic Poly(glycidyl azide)

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Energetic poly(glycidyl azide) (PGA) elastomers with different crosslink densities were prepared by varying the NCO/OH reactive-groups ratio from 0.8 to 1.0. In the preparation of the elastomers, PGA chains were end-linked with a mixture of hexamethylene diisocyanate (HMDI) and trimethylol propane (TMP) at a fixed TMP/PGA mole ratio. The number average molar mass between junction points of the network chains \bar{M}_c was calculated using data obtained from swelling and uniaxial tensile tests and the results were compared. For the mechanical characterization of the networks, Mooney-Rivlin plots were prepared and the values of the constants $2C_1$ and $2C_2$ of PGA networks having different crosslink densities were determined.

Introduction

Poly(glycidyl azide)-diol (PGA-diol) is a highly energetic and low-molar-mass ($\bar{M}_n \approx 2000$ g/mol) liquid prepolymer which was developed in the last decade for the preparation of highly energetic, high-burning-rate, chlorine-free smokeless solid rocket propellants. PGA-diol possesses hydroxy functional groups located at both ends of the chains and can be synthesized via the nucleophilic substitution reaction of its precursor, poly(epichlorohydrine)-diol, (PECH-diol), with sodium azide NaN_3)¹⁻⁸.

PGA-diol contains energetic pendant azidomethyl groups ($-\text{CH}_2-\text{N}_3$) on the polyether main chain and has a positive heat of formation (+957 kJ/kg)⁹. Therefore, this prepolymer has the ability to self-decompose exothermically even at relatively low temperatures and produce fuel-rich gases.^{9,10} The high energy potential and relatively low detonation-/sensitivity properties of this prepolymer means it is a superior replacement for nitroglycerine in both crosslinked and uncrosslinked composite modified double-base propellants. This leads to a greater degree of safety in the handling and storing of these types of propellants⁵. Aside from superior thermal properties, this polymer has excellent physico-chemical properties, such as low glass transition temperature ($T_g = -50^\circ\text{C}$), low viscosity and high density compared to other prepolymers widely used in rocket-propellant technology.

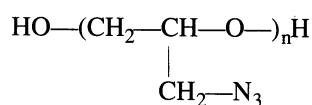
In a solid-propellant formulation a functionally active prepolymer is end-linked with a suitable low-

molecular reactive system in the presence of a solid oxidizer, fuel and other minor ingredients. Moreover, the mechanical strength and the solid loading capacity of the propellant network structure is greatly affected by the number average molar mass between junction points (\bar{M}_c). It is reasonable to expect that in the end-linking reaction of PGA chains, a great degree of chain extension causes the networks to have low mechanical strength resulting from a high (\bar{M}_c) value and low cross-link density. Therefore, the desired (\bar{M}_c) value of a network is obtained by the optimization of the reactive group ratio of two-function reactants to polyfunctional reactants in the network formulation. Hence, it is possible to control the reaction of the chain extension and end-linking reaction to some extent using di- or poly-functional reactants. The object of this study was to characterize highly energetic poly(glycidyl azide) networks through swelling, solubility and mechanical measurements.

Experimental

Materials and characterization

Poly(glycidyl azide)-diol (PGA-diol) was purchased from ICT-Germany. This liquid prepolymer had a number average molar mass (\bar{M}_n) of 1920, determined by vapour-phase osmometry (VPO). The OH equivalent of PGA-diol was determined to be 1.06-mEq/g (\approx Eq/mol), according to the method proposed by Dee et al.¹¹ using N-methyl imidazole as an acetylation catalyst. It was determined that the viscosity and density of PGA-diol at 24°C were 5.1×10^3 cP and 1.28 g/cm³, respectively. The chemical formula of PGA-diol is as follows:



(PGA-diol)

A mixture of hexamethylene diisocyanate (HMDI) (Fluka AG) and trimethylolpropane (TMP) (Aldrich) was used for end-linking PGA-diol chains. These reactants were used in the form in which they were received. Tetrahydrofuran (THF) was used as the solvent in the extraction and swelling experiments with PGA elastomers and was used without purification.

Instrumentation

The tensile testing experiments with PGA elastomers were performed using a TENSILON (Toyo Measuring Instruments Co. Ltd.) UTM II tester at room temperature with a crosshead speed of 5 mm/min. The number average molar mass and the polymer-solvent interaction parameter of the PGA diol-THF system (χ_1) were determined using a Knauer-type vapour-phase osmometer. The densities of both polymer and solvent were measured using a volume-calibrated pycnometer at 45°C. A Brookfield-type viscometer was used for measuring the viscosity of liquid PGA-diol prepolymer at 25°C.

Preparation of PGA elastomers

PGA-diol is a two-function hydroxyl-terminated prepolymer. Therefore, to prepare the elastomers, PGA-diol prepolymer was reacted with hexamethylene diisocyanate (HMDI) in the presence of trimethylol propane (TMP). In this study a mixture of TMP and HMDI was used as the polyfunctional reactant. Three different

elastomers with different \overline{M}_c values were prepared by varying the NCO/OH reactive-group ratio. The compositions of these elastomers are listed in Table 1.

Table 1. The composition of PGA elastomers

NCO/OH reactive group ratio	PGA-diol wt-%	HMDI wt-%	TMP wt-%
1.0	84.75	12.57	2.68
0.9	85.83	11.46	2.71
0.8	86.93	10.33	2.71

As it was anticipated that the crosslink density of the PGA elastomers would vary with varying amounts of TMP, in all the compositions the amount of triol (TMP) was chosen so that it would maintain the reactive/group ratio $\text{TMP}/(\text{TMP}+\text{PGA-diol})=0.4$, and so produce the best mechanical properties, as has been previously reported^{12,13}.

To produce clear and bubble-free elastomeric networks, liquid PGA-diol prepolymer was first degassed by mixing in a 200 mm Hg vacuum at 65°C and then mixed with carefully weighed TMP for 15 min at 65°C. After the addition of the amount HMDI calculated to obtain the desired NCO/OH ratio and following further mixing for 3 minutes, the mixture was transferred into a mold (coated with Teflon) so that a film of 0.7-1.0 mm thickness formed. The mold was kept in an oven in nitrogen atmosphere at 65°C for 24 hours.

Characterization of PGA elastomers

PGA elastomers were characterized through swelling, solubility and mechanical measurements. Swelling measurements were carried out gravimetrically using THF as the solvent at 45°C. Dry pieces of the test specimens (0.3-0.4 g) were weighed (w_1) and immersed in THF. After equilibrium was attained, the swollen specimens were quickly blotted with a dry filter paper as they were taken out, and then, they were weighed (w_2). The equilibrium-volume swelling ratio (q_v) of the test specimens and the volume fraction of the polymer in the gel at equilibrium (ν_{2m}) were calculated using the following equation,

$$1/\nu_{2m} = q_v = 1 + (w_2/w_1 - 1)\rho_2/\rho_1 \quad (1)$$

where w_1 and w_2 are the weight of the dry and swollen test specimens, respectively; and ρ_1 and ρ_2 are the densities of the solvent and polymer, respectively (at 45°C, $\rho_1=0.86$ g/cm³ and $\rho_2=1.27$ g/cm³). It has previously been reported that the polymer-solvent interaction parameter (χ_1) of a PGA-diol-THF system at 45°C was 0.25¹⁴. The equilibrium swelling values were further used for the calculation of the number average molar mass between the junction points of the PGA networks. These data are compiled in Table 2.

The sol-gel contents of the PGA elastomers were determined by extraction of the removable linear part of the specimens. Samples weighing 0.3-0.4 g from each PGA network (m_1) were immersed in THF for 24 hours and in chloroform for 24 hours and deswollen in an acetone-methanol mixture. The samples were then dried in a 200 mmHg vacuum at 50°C and weighed (m_2). The weights of the sol fraction of the PGA elastomers were calculated from the difference between m_1 and m_2 .¹⁴ The sol fraction values of the PGA elastomers are also listed in Table 2.

Table 2. Results of extraction, swelling and mechanical measurements of PGA elastomers prepared with mixture of HMDI and TMP as the reactive system

Run no	Reaction system	NCO/OH Reactive group ratio	Sol fraction wt. (%)	q_v	Elongation at break (%)	Ultimate tensile stress (MPa)	Young's modulus (MPa)	$\overline{M}_c^{(a)}$ (g/mol)	$\overline{M}_c^{(b)}$ (g/mol)	$2C_1$ (MPa)	$2C_2$ (MPa)
1	HMDI/TMP	1.0	5.43	5.33	86.7	0.68	1.46	4200	7750	0.409	0.051
2	HMDI/TMP	0.9	10.04	6.08	94.6	0.54	0.91	5550	10500	0.297	0.015
3	HMDI/TMP	0.8	24.88	8.06	132.6	0.24	0.27	9700	27000	0.114	0.000

^a Calculated from the Flory-Rehner equation using swelling data obtained in THF

^b Calculated from the Mooney-Rivlin plot

Uniaxial tensile testing of the PGA elastomers was performed for the determination of tensile strength, elongation at break and initial modulus values. Test samples were punched from the cured slab using a die prepared in accordance with ASTM D 412-68. Six sample of each composition, having different NCO/OH ratios were measured and the results were averaged. From the data obtained from tensile-test measurements, Mooney-Rivlin plots of the elastomers were prepared and the \overline{M}_c values were calculated.

Results and Discussion

In this study three types of PGA elastomers with different \overline{M}_c values were prepared via the network-forming reaction between reactive groups of PGA-diol and a polyfunctional reactive system (a mixture of HMDI and TMP). It is evident that the number average molar mass between the junction points of a network is significant characterizing parameter, which serves as a reference in describing a network structure. \overline{M}_c values of the PGA networks were determined from the swelling and mechanical measurements of the networks and the results were compared. Different equilibrium swelling degrees were observed, depending on the value of the NCO-to-OH ratio of the PGA networks. As shown in Table 2, the equilibrium-swelling values of the networks increased with the decreasing of the NCO/OH ratio. From the equilibrium-swelling degrees, the \overline{M}_c values of the networks were calculated by means of the Flory-Rehner equation^{15,18}

$$\overline{M}_c = -v_1\rho_2(\nu_{2m}^{1/3} - 2\nu_{2m}/\Phi)/[\ln(1 - \nu_{2m}) + \nu_{2m} + \chi_1\nu_{2m}^2] \quad (2)$$

where v_1 is the molar volume of the solvent, ρ_2 is the density of the PGA networks, Φ is the network functionality (due to TMP, $\Phi = 3$). The calculated \overline{M}_c values of the PGA networks, using equation 2 for $\chi_1=0.25$, are collected in Table 2. As can be seen from Table 1, the \overline{M}_c and the sol-fraction values of the networks were strongly influenced by the NCO/OH reactive-group ratio. Both \overline{M}_c and sol fraction values increased with the decreasing of the NCO/OH ratio of the networks. The tendency for an increase in the sol fraction with increasing \overline{M}_c , and elongation at break values of the networks are in the same order. This can be explained by the fact that, as the NCO/OH ratio decreases, number the of PGA-network chains that are unreacted, reacted at only one end and extended increases. These results imply that the longer the chain length between junction points, the greater the elongation at breaks and the greater the quantity of the sol fraction. The minimum \overline{M}_c value obtained from the swelling measurements was about 4200 for the network at a NCO/OH ratio of 1.0, which is about double the \overline{M}_c of PGA-diol prepolymer (for PGA-diol prepolymer $\overline{M}_n=1920$). This indicates that in the network-forming reaction, much of the PGA-diol prepolymer chain becomes end-linked rather than intermolecularly linked. Chain extension may be minimized by increasing the amount of TMP in the reactant mixture.

Figure 1 illustrates the stress-strain curves of the PGA networks. A considerable increase in tensile strength at break and modulus values was obtained as the NCO/OH ratio of the networks increased while elongation at break values decreased. For the quantitative evaluation of stress-strain data, the following

Mooney-Rivlin equation is frequently used (19,21)

$$f^* = f/(\lambda - \lambda^{-2}) = (2C_1 + 2C_2\lambda^{-1}) \quad (3)$$

where f^* is the reduced stress, f is the tensile stress (which is based on the cross-section area of the unstretched dry sample), λ is the elongation (l/l_0 , which is the ratio of the final length to the original length of the test specimen), and $2C_1$ and $2C_2$ are the Mooney-Rivlin constants. A plot of the reduced stress, f^* , as a function of reciprocal elongation, λ^{-1} , gives a straight line, whose intercept with the ordinate and the slope give us $2C_1$ and $2C_2$, respectively. The Mooney-Rivlin plots of the samples are shown in Figure 2 and the values of the constants $2C_1$ and $2C_2$ of the PGA networks are shown in Table 2.

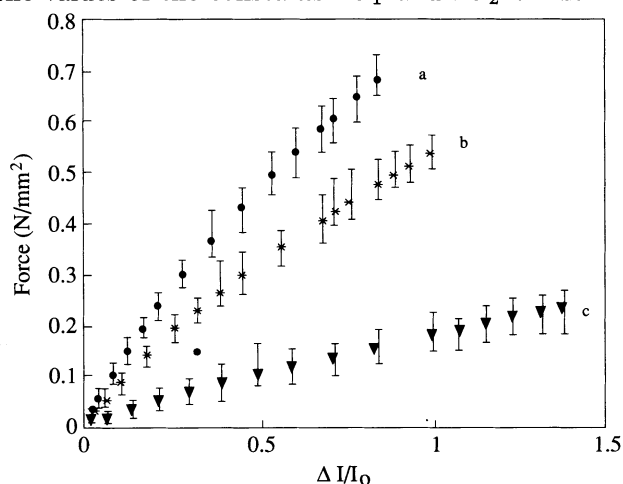


Figure 1. Stress-strain curves of PGA elastomers with different NCO/OH reactive-groups ratios a) 1.0, b) 0.9, c) 0.8

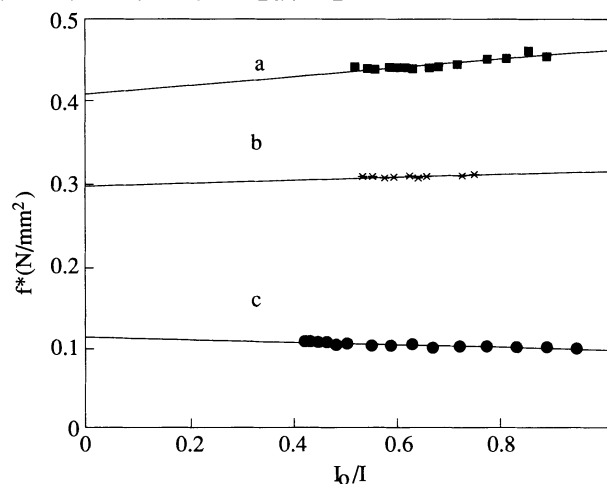


Figure 2. Mooney-Rivlin plots of PGA elastomers with different NCO/OH reactive groups ratios a) 1.0, b) 0.9, c) 0.8

The constants $2C_1$ and $2C_2$ are parameters, which are independent of λ^{20} . $2C_1$ is a measure of the \overline{M}_c value and this can be taken as an estimate of the high-deformation modulus of a network (the phantom network model limit). The constant $2C_1 + 2C_2$ can be considered an estimate of the low-deformation modulus (the affine network model limit) and thus $2C_2$ is a measure of the increase in nonaffinity of the deformation as the elongation increases and can be considered to be a measure of the interchain entanglements of a network. A lower value of the constant $2C_2$ means there is a lower degree of entanglements in a network. As can be seen from Table 2, the increase in the $2C_1$ and $2C_2$ values with increasing NCO/OH ratio reflects the increase in the junction-point density of networks (or decrease in \overline{M}_c). In PGA networks, $2C_2$ values increase as the NCO/OH reactive-groups ratio of the PGA network increases. These results mean that the nonaffinity of PGA elastomers increases with increases in the NCO/OH ratio. The \overline{M}_c values of PGA-network chains can be calculated from the $2C_1$ value using the following expression:

$$2C_1 = \frac{\rho_2 RT}{\overline{M}_c} \quad (4)$$

where R is the gas constant and T is the temperature (25°C). The calculated \overline{M}_c values of the network chains using equation 4 are listed in Table 2. The \overline{M}_c values of the elastomers determined through tensile stress-strain measurements are nearly double the values calculated from the swelling measurements. This inconsistency seems to be quite reasonable since the network defects (i.e. loops and entanglements) play

a minor role in the stress-strain behavior of the elastomers²². However, it is well known that the swelling behavior of networks is more sensitive to network irregularities.

Conclusion

Three different PGA networks were prepared by end-linking PGA-diol chains with a mixture of HMDI and TMP at three different NCO/OH reactive-group ratios. The \bar{M}_c values of these networks were determined using the swelling and tensile stress-strain data. The \bar{M}_c and sol-fraction values of these networks were strongly influenced by the small change in the NCO/OH reactive-group ratio. The \bar{M}_c values of the networks calculated from the stress-strain data were found to be higher than the values calculated from the swelling experiments.

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