

Energetic Polyurethanes from Branched Glycidyl Azide Polymer and Copolymer

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SYNOPSIS

Branched glycidyl azide polymer (GAP) and glycidyl azide-ethylene oxide copolymer (GEC) have been prepared by a degradation process using different polyols in the synthesis reaction. The azido homopolymers and copolymers were characterized by gel permeation chromatography and viscometry techniques. Energetic polyurethanes were then obtained from the curing of branched glycidyl azide polymers and copolymers using isophorone diisocyanate as a curing agent. The polyurethanes were characterized using thermomechanical analysis and tensile testing. The polyurethane copolymers have generally a higher elongation at break and a lower glass transition temperature than their GAP homopolymer counterparts. The polyol reactant used in the synthesis of GAP and GEC had an effect on the mechanical properties of the polyurethanes obtained from these polymers. © 1996 John Wiley & Sons, Inc.

INTRODUCTION

Glycidyl azide polymer (GAP) and glycidyl azide-ethylene oxide copolymer (GEC) are hydroxy-terminated aliphatic polyethers containing alkyl azide groups which could be used as energetic binders in low-smoke solid-rocket propellants, composite explosives, gun propellants, and pyrotechnics to enhance the energetic performance and stability, reduce the vulnerability, and improve the physicochemical properties of the energetic formulations.

GAP with molecular weight (MW 1000–6000) is currently produced in the United States^{1–5} according to a two-step process which requires two distinct reactions, polymerization and azidation. GAP of low MW (about 500), which could be used mainly as an energetic plasticizer, can be prepared through a single-step process^{6–8} developed at the Defence Research Establishment at Valcartier (DREV).

Branched GAP or GEC with variable MW (500–40,000) can also be prepared directly through a degradation process developed at DREV^{9–13} by reacting

a high MW rubbery polyepichlorohydrin (PECH) or its counterpart, polyepichlorohydrin-ethylene oxide copolymer (PEEC), with the epichlorohydrin (ECH) monomer and sodium azide (NaN_3). Recently, a novel degradation process was developed at DREV^{14–17} for the preparation of branched GAP or GEC with controlled and variable MW (1000–2,000,000), but without using any epoxide monomer such as ECH in the reaction. This process involves the single-step reaction of a high MW solid rubbery PECH or its counterpart, PEEC, with sodium azide in the presence of a basic cleaving agent and a polyol in a suitable organic solvent at elevated temperature. The MW, viscosity, equivalent weight, and hydroxyl functionality of the branched GAP and GEC products can be controlled and predetermined by the proper selection of the reactants types and by varying their relative proportions in the reaction mixture.

Branched GAP or GEC, when used as an energetic binder, should be transformed into a long-chain polyurethane, named energetic polyurethane (PU), after a curing reaction using a suitable isocyanate compound, such as hexamethylene diisocyanate (HDI), diphenylmethane diisocyanate (MDI), tolylene diisocyanate (TDI), or Desmodur N-100, which is a triisocyanate based on HDI. For a given

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GAP or GEC sample, the various isocyanates used should yield PU products with different mechanical properties—namely, the elongation at break and the tensile strength. Usually, these two properties vary inversely. For instance, an aliphatic diisocyanate such as HDI gives rise to PU with a lower tensile strength but a higher elongation at break than the one produced from a diisocyanate containing an aromatic ring, such as TDI or MDI.¹² Recently, another isocyanate compound, called isophorone diisocyanate (IPDI), was used for the curing of branched GAP, and this compound seemed to yield PU products with a better mechanical performance than the other cited isocyanate compounds.¹⁸

The purpose of this work is to synthesize and characterize some branched GAP and GEC samples and then to carry out the curing of these azido homopolymers and copolymers using IPDI as the curing agent. Finally, the energetic PU products obtained will be characterized using thermomechanical analysis (TMA) and the tensile test. These testings allow one to assess and to compare the performances of branched GAP and GEC as well as to determine the effects of some main synthesis parameters on the mechanical properties of the polyurethanes obtained from these polymers.

EXPERIMENTAL

Materials

The branched GAP and GEC samples used in this study are listed in Table I. GEC is a copolymer containing 70% GAP and 30% ethylene oxide. The homopolymers and copolymers were prepared accord-

ing to the improved process described in refs. 14–17. The chemical reaction involves the simultaneous degradation and azidation of a commercial rubbery PECH or PEEC with NaN_3 and a basic cleaving agent in the presence of a polyol at 120°C in a polar organic solvent.

All the GAP and GEC samples were prepared in dimethyl sulfoxide (DMSO) using lithium methoxide (CH_3OLi) as the cleaving agent in a weight ratio ($\text{CH}_3\text{OLi}/\text{Rubber}$) = 0.03–0.04. All the polymers were synthesized with a reaction time of 7–20 h at the laboratory scale in lots of 50 g. The following polyol reactants were used in the synthesis: glycerol (GOL), trimethylol propane (TMP), and pentaerythritol (PE). The purification method, mostly aimed at removing the solvent used from branched GAP or GEC products, is described in ref. 19.

The curing agent, IPDI, was obtained from Aldrich Chemicals Ltd. and was used as received without further purification.

Molecular Weight Determination

The average molecular weights of all branched GAP and GEC samples were determined by combining gel permeation chromatography (GPC) and viscometry techniques according to the universal calibration method, based on the hydrodynamic volume concept described in ref. 20.

Gel Permeation Chromatography

The chromatograph used was a Waters model ALC 200 series instrument operating at room temperature using high-performance liquid chromatography

Table I Solution Properties of Branched GAP and GEC Samples

Polymer	Sample	Polyol ^a	$[\eta]$ (dL/g)	M_w	M_n	(M_w/M_n)	M_e
GAP homopolymer	HG-1	GOL	0.122	18,100	10,600	1.70	2510
	HG-2	GOL	0.163	28,800	15,200	1.90	2870
	HT-1	TMP	0.125	18,500	11,000	1.68	2550
	HT-2	TMP	0.140	22,500	14,000	1.60	2790
	HP-1	PE	0.141	22,700	11,400	2.00	2585
GEC copolymer	CG-1	GOL	0.185	20,900	10,400	2.01	2280
	CG-2	GOL	0.181	20,000	9,500	2.10	2250
	CT-1	TMP	0.216	28,500	14,700	1.94	2980
	CT-2	TMP	0.201	24,700	13,600	1.82	2600
	CP-1	PE	0.186	21,200	10,800	1.96	2300
	CP-2	PE	0.183	20,400	11,600	1.76	2270

^a Type of polyol reactant used in the synthesis of GAP and GEC.

(HPLC)-grade tetrahydrofuran (THF) as a solvent with a constant flow rate of 1.0 mL min⁻¹. A multipore ultrastyrigel column was used with an effective MW range from 1000 to 1 × 10⁶. A refractive index detector Shodev SE-51 was used. Data were analyzed using a computer. The GPC calibration was performed with six polystyrene standards ranging from 4000 to 600,000 by plotting log MW versus elution volume. The conversion of PS MW to GAP or GEC MW was done as reported in refs. 16 and 17 by combining the hydrodynamic volume ($[\eta]M_w$) concept²⁰ with the Mark-Houwink relation ($[\eta] = KM_w^a$).

The Mark-Houwink relations reported in the literature²¹ for PS in THF and for branched GAP or GEC in THF^{16,17} are, respectively,

$$[\eta]_{\text{PS}} = 9.1 \times 10^{-5} M_w^{0.746} \quad (1)$$

$$[\eta]_{\text{GAP}} = 2.8 \times 10^{-4} M_w^{0.62} \quad (2)$$

$$[\eta]_{\text{GEC}} = 12.8 \times 10^{-4} M_w^{0.50} \quad (3)$$

For a given elution volume, both PS and GAP (or GEC) have the same hydrodynamic volume $[\eta]M_w$. By combining the Mark-Houwink [Eqs. (1) and (2)] for branched GAP and Eqs. (1) and (3) for branched GEC, the following relations were obtained:

$$M_{\text{GAP}} = 0.51 M_{\text{PS}}^{1.075} \quad (4)$$

$$M_{\text{GEC}} = 0.17 M_{\text{PS}}^{1.164} \quad (5)$$

Therefore, by using Eqs. (4) and (5), respectively, the PS calibration curve could be transposed to give the calibration curves for branched GAP and GEC, from which the MW averages of the GAP and GEC samples could be computed.

Viscometry

The viscosity measurements of branched GAP and GEC solutions in THF were carried out at 25°C using a modified Ubbelohde viscometer, model 50/104. The Gallenkamp viscometer bath was controlled within ±0.02°C and the flow times of solutions were measured using a Wescan automatic timer at better than ±0.01 s. The flow-time data were first used for the calculations of the relative viscosity, η_r , and the specific viscosity, η_{sp} , of the solutions. The intrinsic viscosity, $[\eta]$, was then obtained by a linear regression of both $(\ln \eta_r)/c$ and (η_{sp}/c) versus c , where c is the concentration of solutions varying from about 1.700×10^{-2} g cm⁻³ to 0.400×10^{-2} g cm⁻³. The

correlation coefficients were higher than 0.980 for all GAP and GEC samples.

Curing of Branched GAP and GEC Samples

For the purpose of making the most reliable comparison between the performances of branched GAP and GEC samples, both of them were cured by exactly the same procedure, with all experimental conditions being identical.

The curing was performed at 60°C using IPDI as the curing agent. The oil bath and the vacuum oven were set and preheated at 60°C prior to the curing process. The exact amount of branched GAP or GEC was weighed in a 50-mL beaker and then introduced into the vacuum oven, where a high vacuum was applied for at least 1 h in order to remove traces of impurities such as water and solvent. Then the beaker was installed in the oil bath before adding the desired quantity of IPDI to satisfy a fixed NCO/OH ratio. The mixture was stirred for about 3 min and then transferred into the molds (at least three for each set of curing) made of Teflon, according to the ASTM 638 standard for plastic-elastomeric materials. The molds were also preheated to 60°C in order to prevent any temperature fall in the reaction mixtures. A vacuum was then applied for about 15 min in order to remove all air bubbles from the samples. However, due to the high viscosity of the curing media, there were some small voids still hidden inside the cured samples. The molds were kept overnight in the oven at 60°C and then about 1 h at 100°C to complete the curing reaction.

Thermomechanical Analysis of Cured Samples

To determine the glass transition temperature, T_g , of the energetic PU obtained, TMA was applied to some typical PU samples. This technique, previously used for the polyurethanes based on castor oil,²² is based on the principle that there is an abrupt change in the coefficient of expansion of the sample when it passes through the softening temperature or T_g under a constant heating. This manifests itself as that temperature at which the regression line before the break intersects that after the break.

TMA was performed using a Mettler TA-4000 with a TMA 40 measuring cell. The approximate sample dimensions were 3 mm thick in the direction of measurement and 6 mm in diameter. Measurements were carried out in the range of -100–50°C. A low-temperature accessory was used with liquid nitrogen as refrigerant. The heating rate was 10°C

Table II Properties of Energetic Polyurethanes from Branched GAP

Sample	Polyol ^a	σ_u (MPa)	ξ_b (%)	T_g (°C)
HG-1	GOL	0.25	230	-23
HG-2	GOL	0.24	290	-26
HT-1	TMP	0.43	160	-26
HT-2	TMP	0.34	155	-22
HP-1	PE	0.36	155	-20

^a Type of polyol reactant used in the synthesis of GAP.

min⁻¹ and the constant probe force applied to the sample was 0.02N.

Tensile Test

The most significant evaluation of energetic polyurethane is certainly the tensile test. This was performed on cured samples using an Instron Tester, model 4206, where the force applied to the sample as well as its elongation during the test were automatically recorded by the control board of the tester. The tensile load cell has a capacity of 5 kg or 50N. A suitable grip for elastomeric materials was used for correctly holding the sample in place without slipping. The crosshead speed used was 10 cm min⁻¹. Prior to testing, the width and thickness of the gauge region of each test specimen was measured to an accuracy of $\pm 0.5 \mu\text{m}$ using an electronic micrometer. Usually, the gauge dimensions were approximately (25 × 6 × 3) mm. All specimens were drawn at ambient temperature.

RESULTS AND DISCUSSION

Solution Properties of Polymers

The intrinsic viscosity $[\eta]$ values measured for branched GAP and GEC samples are listed in Table I along with the hydroxyl equivalent weight (M_e) and the MW averages. The M_e values for all the polymers studied were determined by infrared (IR) absorption spectroscopy according to the method and relationships reported in refs. 16 and 17. This method²³ permits the determination of the hydroxyl concentrations in branched GAP and GEC samples from the IR absorption band of tetrahydrofuran-associated hydroxyl groups.

As shown in Table I, the weight average molecular weight (M_w) of the GAP and GEC samples were in the range 18,100–28,800; the number average molecular weight (M_n) values were in the range 9500–

15,200; and M_e varied between 2250 and 2980. The polydispersity index (M_w/M_n) is between 1.60 and 2.10; this type of MW distribution may be considered relatively low for polymers resulting from a degradation process. As shown in Table I, GEC has a higher viscosity than GAP with a similar MW. This may be attributed to the presence of ethylene oxide groups in the copolymer chain.

Tensile Properties of Energetic Polyurethanes

The main tensile properties of interest in this work are defined as follows²⁴:

$$\begin{aligned} \text{Elongation at break } (\xi_b) &= (\text{gauge length at break}/ \\ &\quad \text{initial gauge length}) \times 100\% \quad (6) \end{aligned}$$

$$\begin{aligned} \text{Tensile strength } (\sigma_u) &= (\text{ultimate tensile force} \times \xi_b)/ \\ &\quad (\text{original cross-sectional area}) \quad (7) \end{aligned}$$

These two quantities were directly produced by a computer using the software provided by the Instron Company, and they may be checked by the extension and the load recorded on the keyboard control of the Instron system.

All the PU samples were prepared and tested using the same procedure and techniques. The only variables were the (NCO/OH) ratio and the sample type, in order to study the effects of the GAP homopolymer or copolymer and the polyol reactant used in the polymer synthesis on the mechanical properties of the resulting PU. The (NCO/OH) ratio varied from one sample to another in order to optimize the mechanical properties. Representative results of the tensile properties of PU obtained from branched GAP and GEC samples synthesized with different polyols are presented, respectively, in Tables II and III. The optimum mechanical properties

Table III Properties of Energetic Polyurethanes from Branched GEC

Sample	Polyol ^a	σ_u (MPa)	ξ_b (%)	T_g (°C)
CG-1	GOL	0.16	285	-39
CG-2	GOL	0.23	315	-39
CT-1	TMP	0.11	510	-42
CT-2	TMP	0.13	540	-41
CP-1	PE	0.28	700	-38
CP-2	PE	0.34	515	-38

^a Type of polyol reactant used in the synthesis of GEC.

of the PU were obtained at a (NCO/OH) ratio of 1.0–1.4.

The mechanical properties reported in Table II indicate that PU products obtained from samples HG-1 and HG-2 have higher ξ_b (230–290%) but lower σ_u (0.24–0.25 MPa) than the PU of samples HT1, HT2, and HP1 ($\xi_b = 155$ –160%, $\sigma_u = 0.34$ –0.43 MPa). Consequently, a branched GAP homopolymer synthesized with glycerol will lead to a PU with a higher elongation at break but a lower strength compared to a PU obtained from a polymer prepared with TMP or PE.

The mechanical properties reported in Table III indicate that PU products obtained from GEC samples synthesized with TMP and PE have higher elongation ($\xi_b = 510$ –700%) than those produced from copolymers prepared with glycerol ($\xi_b = 285$ –315%). On the other hand, PU of GEC samples prepared with TMP have a relatively lower strength ($\sigma_u = 0.11$ –0.13 MPa) compared to the ones produced from copolymers synthesized with PE and glycerol ($\sigma_u = 0.16$ –0.34 MPa).

A comparison of the results listed in Tables II and III shows that PU produced from GAP and GEC samples synthesized with glycerol have about the same mechanical properties. However, the PU products obtained from GEC samples prepared with TMP have higher elongation but lower strength than their GAP counterparts. On the other hand, PU produced from GEC samples synthesized with PE have higher elongation but similar strength compared to their GAP counterparts. The presence of ethylene oxide ($-\text{O}-\text{CH}_2-\text{CH}_2-$) groups in the GEC chain likely causes a greater flexibility in the resulting PU, which is responsible for their relatively high elongation at break.

The results of Tables II and III indicate that the polyol reactant used for the synthesis of GAP and GEC has a significant effect on the mechanical properties of the PU obtained from these polymers. As reported in refs. 15–17, a portion of the polyol

included in the synthesis reaction of GAP and GEC is grafted on the polymer, and, depending on the type of polyol used, additional primary and/or secondary alcohols (originating from the polyol) are thus incorporated into the polymer molecular structure. This will have a noticeable effect on the curing reaction of GAP and GEC with the isocyanate and, consequently, on the resulting PU mechanical properties.

Class Transition Temperature

The T_g values obtained from TMA technique for some PU specimens based on branched GAP are presented in Table II, while those for PU specimens from branched GEC are shown in Table III together with their tensile properties. The T_g values for PU products from branched GEC ($T_g = -40 \pm 2^\circ\text{C}$) are much lower than those resulting from branched GAP ($T_g = -23 \pm 3^\circ\text{C}$). This, in good agreement with the tensile properties results, is certainly caused by the great flexibility contribution provided by the ethylene oxide groups in the branched GEC molecules. It is also noted that the T_g values for PU based on branched GEC are very close to the ones for PU based on castor oil previously reported.²²

CONCLUSIONS

Various GAP homopolymers and GEC copolymers were synthesized by a degradation process with different polyol reactants. The GEC copolymer has a higher viscosity than the GAP homopolymer with similar MW. The curing of branched GEC using IPDI yielded polyurethanes with lower T_g but generally higher elongation at break compared to the PU products obtained from the GAP homopolymer. These differences in the properties of polymers and resulting PU products observed between GAP and GEC could be attributed to the presence of ethylene

oxide groups in the copolymer chains, which give them a higher flexibility.

The polyol reactant used in the synthesis of GAP and GEC has a significant effect on the mechanical properties of the PU obtained from these polymers.

The authors wish to thank the Defence Research Establishment at Valcartier (DREV) for granting a research contract to carry out this project at the Royal Military College of Canada, Kingston, Ontario.

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Received December 18, 1995

Accepted March 4, 1996