

Study on Influence of Terminal Structure on Mechanical Properties of GAP Elastomers

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ABSTRACT: To improve mechanical properties of glycidyl azide polymer (GAP) elastomer, primary hydroxyl terminated GAP prepolymer (PH-GAP) has been synthesized by end-capping modification of GAP using carbamate reaction. FTIR, ¹³C-NMR, GPC results indicate that the functionality, molecular weight, and molecular weight distribution of PH-GAP are consistent with those of the original GAP. Mechanical tests indicate that mechanical properties of PH-GAP elastomer are much better than those of GAP elastomer. Swelling tests discover that the apparent molecular weight of the network chain in PH-GAP elastomer is much less than that of the original GAP elastomer, and PH-GAP elastomer has much perfect network structure. Network structure defect is the main factor causing inferior mechanical properties, and the GAP prepolymer terminal structure plays an outstanding role in the mechanical properties of its cross-linked elastomers. © 2012 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* 000: 000–000, 2012

KEYWORDS: glycidyl azide polymer; mechanical properties; network chain molecular weight; terminal structure

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INTRODUCTION

Since reported in 1970s, hydroxyl terminated glycidyl azide polymer (GAP) as a binder in a composite solid propellant formulation has been attracting considerable interest due to its positive formation enthalpy, high density, high oxygen balance, and low glass transition temperature.^{1,2} Unfortunately, the application of GAP is restrained because it suffers from poor mechanical properties, such as weak mechanical strength. The general structure of GAP is shown in Figure 1. It can be seen that the structure of GAP is characteristic of highly polar, bulky azidomethyl groups, and poor backbone flexibility³ as well as the terminal secondary-hydroxyl groups.

It is universally believed that the inferior mechanical properties of GAP result from its backbone flexibility with the rigid and conjugated azide side groups, and much effort has been made on the improvement of GAP mechanical properties. Bui⁴ and Mohan⁵ have prepared copolymers of glycidyl azide with ethylene oxide and tetrahydrofuran, respectively. The resultant copolymer elastomers exhibit good mechanical properties because of their improved backbone flexibility. In virtue of the flexibility of polybutadiene structure, Subramanian⁶ has synthesized a triblock copolymer polyglycidylazide-block-polybutadiene-block-polyglycidylazide (GAP-PB-GAP). Other than random copolymerization and block copolymerization, polymer blends or interpenetrating polymer network have also been

employed to increase the mechanical properties of GAP. For example, Min^{7,8} has applied composite curing agents and prepared GAP/polyethylene glycol and GAP/polycaprolactone interpenetrating network elastomers.

However, the aforementioned methods can typically deteriorate the energetic performance of GAP because of the incorporation of inert components. Aiming at maintaining the high energy while imparting superior mechanical properties, Brochu⁹ and Pisharath¹⁰ have synthesized an isotactic chiral GAP and a GAP-Poly(BAMO) [poly(bis(azidomethyl)oxetane)] copolymer, respectively, and tried to improve mechanical properties of GAP elastomer through polymer crystallization forming a micro-phase separation. Additionally, Anthony,¹¹ Jerald,¹² and Ampleman¹³ have patented higher molecular weight, primary-hydroxyl terminated GAPs, which, in comparison with lower molecular weight GAP, have improved GAP mechanical properties, but the mechanism were not presented clearly.

So far, the influence of terminal structure on mechanical properties of GAP elastomers has not yet been reported. In the present study, the prepolymer of primary-hydroxyl terminated GAP (PH-GAP) whose properties are very similar to original GAP was synthesized by an end-capping method. Through the performance comparison between GAP and PH-GAP, it was found that the terminal structure plays an important role in GAP elastomer mechanical properties.

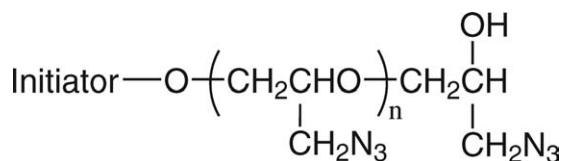


Figure 1. GAP general structure.

EXPERIMENTAL

Materials

The polymer used is secondary-hydroxyl bi-functionalized glycidyl azide polymer (GAP, hydroxyl value 0.48 mmol g^{-1} , 25°C density 1.28 g cm^{-3} , moisture content $< 300 \text{ ppm}$) and the curing agent is polyisocyanate N100 (\overline{M}_n 737, functionality 3.9), respectively.

Hexamethylene diisocyanate (HDI) was used without further purification. Bis(2,2-dinitropropyl)acetal/ bis(2,2-dinitropropyl)-formal (A3), 1,4-butanediol (BDO), trichloromethane (CHCl_3), tetrahydrofuran (THF), dibutyltin dilaurate (T12) were purchased and stored over 4 \AA molecular sieves.

Synthesis of PH-GAP

At room temperature, GAP (40 g, about 20 mmol hydroxyl), and HDI (11.76 g, 70 mmol) were added to 50 mL CHCl_3 in a three-necked 250 mL round-bottom flask, equipped with mechanical stirrer, thermometer, and reflux condenser. The mixture was kept at 60°C till hydroxyl group disappeared according to FTIR analysis *in situ*, then BDO (90 g, 1 mol) was added, and the mixture continued to be kept at 60°C till isocyanate group disappeared. The mixture obtained was successively washed with $4 \times 200 \text{ mL}$ of brine. The organic layer was separated and evaporated under reduced pressure to achieve primary-hydroxyl terminated GAP (PH-GAP) at a yield of about 28 g (25°C density 1.27 g cm^{-3} , moisture content $< 300 \text{ ppm}$). The synthesis scheme for PH-GAP is shown in Figure 2.

Preparation of GAP Elastomers

The elastomer compositions are listed in Table I. All components were mixed uniformly, degassed under vacuum, and cured at 50°C for 7 days, and the desired elastomers were obtained.

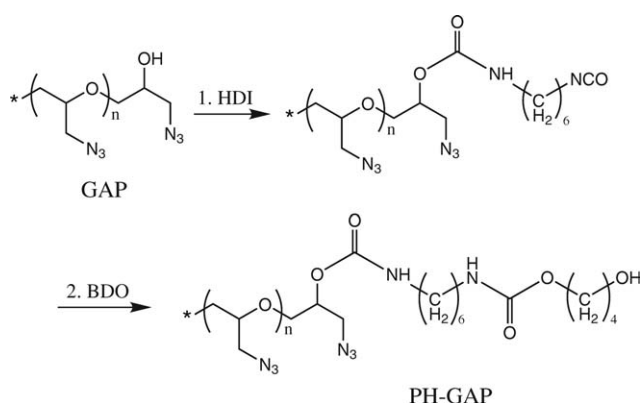


Figure 2. Scheme for preparation of primary-hydroxyl terminated GAP.

Table I. Mass Ratio of Elastomer Components

Elastomer	GAP	PH-GAP	A3	T12	N100
S1	10			0.0002	0.97
S2		10		0.0002	0.77
S3	10		5	0.0002	0.97
S4		10	5	0.0002	0.77

Swelling Test

Swelling measurements were carried out in THF at room temperature and the volume fractions of elastomers were determined gravimetrically. Small pieces of elastomers (about $10 \text{ mm} \times 5 \text{ mm} \times 2 \text{ mm}$) were immersed in THF, and the swollen gels were removed from solvent at different times, quickly blotted with dry filter paper, and weighed till the mass change was less than 0.01 g over the period of 30 min. The volume swelling ratio of the elastomers (q_v) can be calculated by assuming the additivity of volumes, using eq. (1).

$$q_v = 1 + (w/w_0 - 1)\rho_2/\rho_1 \quad (1)$$

wherein w_0 is the weight of the specimen before swelling, w is the weight of the specimen after swelling, and ρ_1 and ρ_2 are the densities of solvent and polymer, respectively.

Instrumentation

Infrared spectra were recorded on a Nicolet 8700 infrared spectrometer. The molecular weight of polymers were determined using a gel permeation chromatography WATERS1515 (solution concentration 0.1 mg mL^{-1} , column temperature 40°C , flux 1 mL min^{-1}). ^{13}C -NMR spectra were recorded on a Bruke 400 spectrometer (>500 scans) using gated decoupling, spectrum width 20 KHz , 25 s recycle delay, and a 90° pulse. Chemical shifts are quoted in ppm, relative to tetramethylsilane (TMS). At room temperature, the mechanical properties of the elastomers (specification $100 \text{ mm} \times 20 \text{ mm} \times 5 \text{ mm}$) were measured

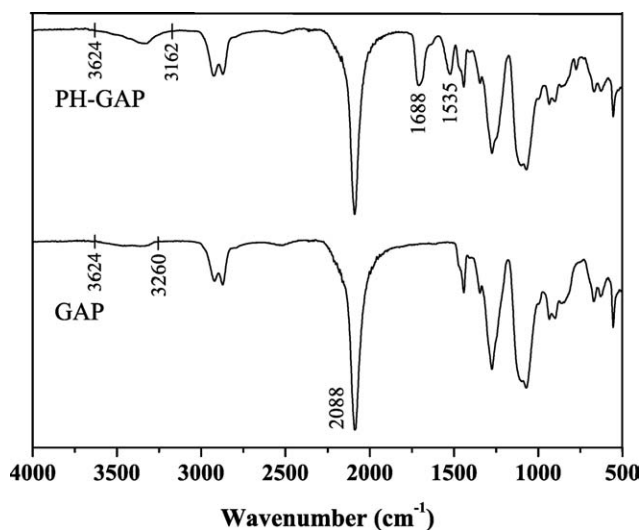


Figure 3. FTIR Spectra for prepolymers.

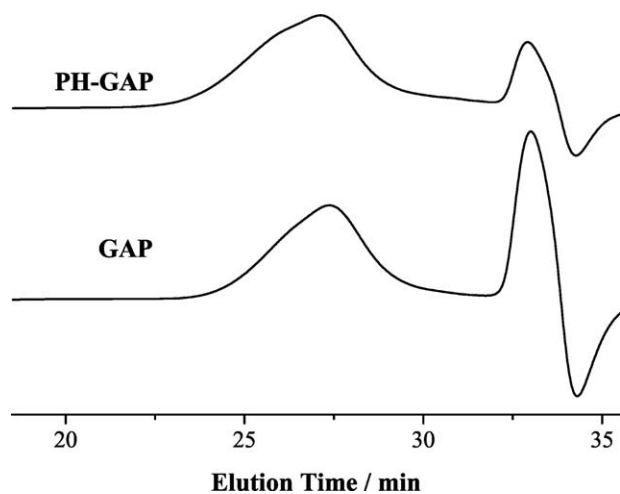


Figure 4. GPC traces for prepolymer GAP and PH-GAP.

on an mechanical tester Instron 6022 at a crosshead speed of 100 mm min⁻¹.

RESULTS AND DISCUSSION

Structure Characterization

FTIR spectra for GAP and PH-GAP are shown in Figure 3. GAP is characteristic of major vibrations like azide group at 2088 cm⁻¹, secondary-hydroxyl group at 3624–3260 cm⁻¹ and others. In comparison with GAP, PH-GAP also has carbonyl group at 1688 cm⁻¹, 1535 cm⁻¹ due to the formation of carbamate resulted from the reaction between hydroxyl and HDI, besides original GAP characteristic peaks. Additionally, a wide absorbent band at 3624–3162 cm⁻¹ caused by the peak overlapping of primary-hydroxyl and amido also appears.

The GPC traces of GAP and PH-GAP are shown in Figure 4. Prepolymer GAP and PH-GAP traces are very similar to each other. The parameters of the prepolymer GAP and PH-GAP evaluated by GPC are listed in Table II. It is shown that the number average molecular weight of GAP is 4431 g mol⁻¹, and that of PH-GAP is 5290 g mol⁻¹, which is close to the theoretical value 4947 g mol⁻¹ ($M_{GAP} + M_{HDI} \times 2 + M_{BDO} \times 2$). Moreover, the polydispersity index of PH-GAP (1.66) is also close to that of GAP (1.48). These suggest that few chain extension reactions happened and GAP was turned into PH-GAP only through the end-capping modification. The hydroxyl value of resultant PH-GAP was tested 0.39 mmol g⁻¹, referring to the method described in Ref. 14.

The ¹³C-NMR spectra for GAP, PH-GAP are shown in Figure 5. It is clear that carbon atom 1, 2, 3 in GAP molecule are attrib-

Table II. Parameters of Prepolymer GAP and PH-GAP

Prepolymer	\overline{Mn} (g mol ⁻¹)	\overline{Mw} (g mol ⁻¹)	$\overline{Mw}/\overline{Mn}$	Hydroxyl value (mmol g ⁻¹)
GAP	4431	6570	1.48	0.48
PH-GAP	5290	8791	1.66	0.39

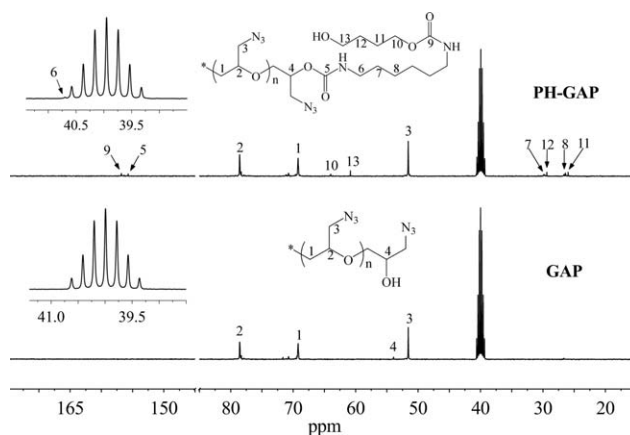


Figure 5. ¹³C-NMR spectra for GAP and PH-GAP.

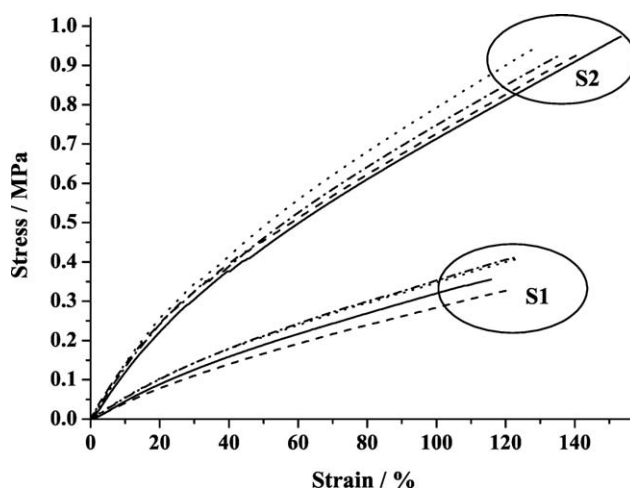


Figure 6. Stress–strain curves of elastomer S1 and S2 (without plasticizer, S1 made from GAP and S2 made from PH-GAP).

uted to the peaks at 69, 78, and 51 ppm, respectively, as is in good agreement with the reports in Refs. 15 and 16. In addition, the peak at 54 ppm is resulted from the secondary-carbon atom

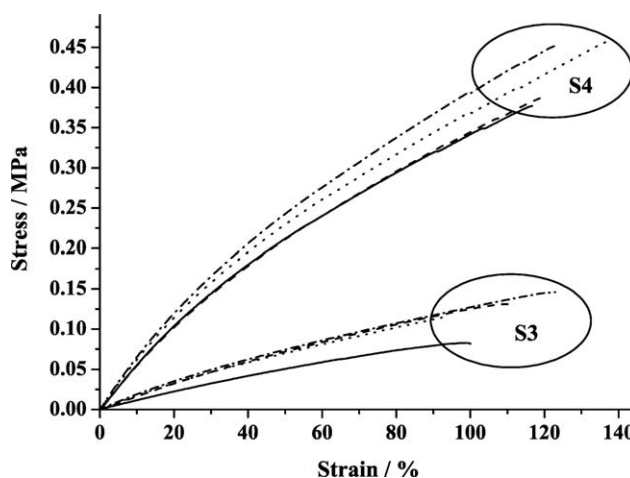


Figure 7. Stress–strain curves of elastomer S3 and S4 (with plasticizer A3, S3 made from GAP and S4 made from PH-GAP).

Table III. Mechanical Properties for Elastomer S1–S4

Mechanical properties	Elastomer examples			
	S1	S2	S3	S4
Strain at break (ϵ_b /%)				
1	116	153	100	117
2	121	142	111	120
3	123	129	92	137
4	123	136	123	124
Average	121 \pm 3	140 \pm 10	107 \pm 13	125 \pm 9
Stress at break (σ_b /MPa)				
1	0.36	0.97	0.08	0.38
2	0.33	0.93	0.13	0.39
3	0.41	0.94	0.12	0.46
4	0.41	0.93	0.15	0.45
Average	0.38 \pm 0.04	0.94 \pm 0.02	0.12 \pm 0.03	0.42 \pm 0.04
Young's modulus (E/MPa)				
1	0.49	1.19	0.11	0.55
2	0.41	1.27	0.17	0.53
3	0.54	1.35	0.19	0.59
4	0.52	1.28	0.18	0.62
Average	0.46 \pm 0.06	1.27 \pm 0.07	0.16 \pm 0.04	0.57 \pm 0.04

conjunctive to hydroxyl group. In the ^{13}C -NMR spectrum of PH-GAP, the typical peaks of GAP such as peaks at 69, 78, and 51 ppm still exist, also other carbon atoms are clearly assigned, except carbon atom 4 (at about 71 ppm, theoretically). It should be emphasized that the peak at 54 ppm has disappeared thoroughly and the peak attributing to the primary-carbon atom connected to hydroxyl group emerges at 60 ppm in PH-GAP spectrum. Meanwhile, the peaks at about 156 ppm are attributed to carbon atom 9, 5, respectively. These indicate that no allophanate group exists in PH-GAP molecular structure and few branching reactions have happened. The functionality of prepolymer PH-GAP is 2, which is consistent with that of GAP.

Mechanical Properties

The stress–strain curves of elastomer S1–S4 are shown in Figure 6 and 7. It can be seen that elastomer S2 and S4 made from PH-GAP have superior mechanical properties, in comparison with elastomer S1 and S3 made from GAP, respectively.

The mechanical data of elastomer S1–S4 are listed in Table III. Without plasticizer, the strain ϵ_b , stress σ_b and modulus E of sample S2 made from PH-GAP are 140% \pm 10%, 0.94 \pm 0.02 MPa, and 1.27 \pm 0.07 MPa, respectively, significantly higher than those of sample S1 made from GAP (ϵ_b 121% \pm 3%, σ_b 0.38 \pm 0.04 MPa, E 0.46 \pm 0.06 MPa). Although the hydrogen bonding existing in the hard segments region of polyurethane elastomers helps to enhance mechanical properties,¹⁷ under the condition of plasticization by A3 which can disrupt the hydrogen bonding,¹⁸ the mechanical properties of sample S4 made from PH-GAP (ϵ_b 125% \pm 9%, σ_b 0.42 \pm 0.04 MPa, E 0.57 \pm 0.04 MPa) are still superior to those of sample S3 obtained from GAP (ϵ_b 107% \pm 13%, σ_b 0.12 \pm 0.03 MPa, E 0.16 \pm

0.04 MPa). These suggest that the improvement in the stress and modulus of PH-GAP elastomer is not related to the content of carbamate, which can form the hard segments region in PH-GAP elastomer. As to the higher strain of PH-GAP elastomer, it is originated from higher molecular weight of prepolymer PH-GAP. In addition, it also indicates that the addition of plasticizer A3 has evidently decreased the stress and modulus of GAP and PH-GAP elastomers.

Network Structure

The volume swelling curves of elastomer S1 made from GAP and elastomer S2 made from PH-GAP are shown in Figure 8. It

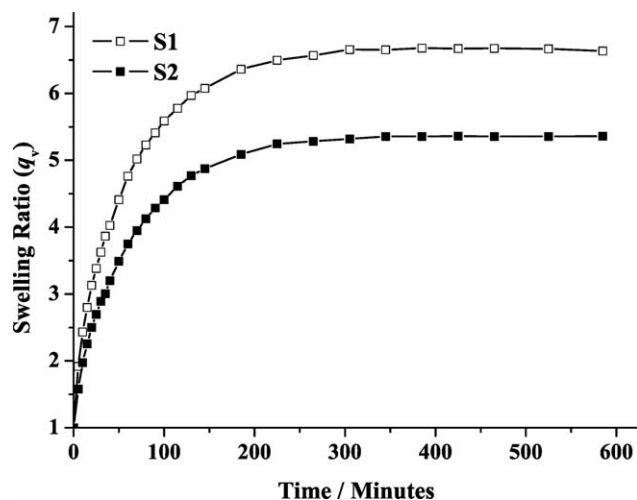


Figure 8. Swelling ratio curves for elastomer S1 and S2 (without plasticizer, S1 made from GAP and S2 made from PH-GAP).

Table IV. Parameters Evaluated on Elastomer S1 and S2

Elastomer	q_v	v_{2m}	ρ (g cm ⁻³)	χ_1	M_c (g mol ⁻¹)	N_0 (mmol cm ⁻³)
S1	6.665 ± 0.015	0.1500 ± 0.0003	1.32 ± 0.01	0.25 ²²	6984 ± 1182	0.19 ± 0.03
S2	5.354 ± 0.014	0.1868 ± 0.0005	1.36 ± 0.02	0.25 ^a	4670 ± 837	0.29 ± 0.05

^aAssuming that χ_1 of S2 system is the same as χ_1 of S1 system.

can be seen that firstly, the volume swelling rate of elastomer S1 is faster than that of S2, and after 300 min the volume swelling ratios (q_v) of S1, S2 come to the equilibrium.

On the basis of the volume swelling ratios after 300 min, the equilibrium swelling ratios are gotten, and the volume fractions (v_{2m}) of polymer can be evaluated using eq. (2). The apparent average molecular weights (M_c) of network chains of the elastomer S1 and S2 are further calculated according to Flory-Rehner Equation (see eq. 3).^{19,20} In addition, the apparent densities of network chains (N_0) of elastomers can also be calculated using eq. (4).

$$v_{2m} = 1/q_v \quad (2)$$

$$M_c = -V_1\rho\left(v_{2m}^{1/3} - v_{2m}/2\right) / \left[\ln(1 - v_{2m}) + v_{2m} + \chi_1 v_{2m}^2\right] \quad (3)$$

$$N_0 = \rho/M_c \quad (4)$$

wherein V_1 denotes the molar volume of solvent THF (80.99 mL mol⁻¹), ρ denotes the density of elastomer, χ_1 denotes the Flory-Huggins interaction parameter of the polymer-solvent system.

The evaluated parameters of elastomer S1, S2 are listed in Table IV. Contrasting Table II and IV, it can be seen that M_c of elastomer S1 made from GAP is 6984 g mol⁻¹, higher than the theoretical value 4431 g mol⁻¹, while M_c of elastomer S2 made from PH-GAP is 4670 g mol⁻¹, less than the theoretical value 5290 g mol⁻¹. These indicate that the chemical cross-link inside elastomer S1 is not complete so that the apparent average molecular weight M_c is much higher than the theoretical value, while elastomer S2 possesses not only perfect chemical cross-link but also lots of effective chain entanglements, and the M_c of elastomer S2 is less than the theoretical value. As a result, elastomer S1 made from lower molecular weight GAP gives the higher M_c , while elastomer S2 made from higher molecular weight PH-GAP gives the lower M_c . Correspondingly, N_0 of elastomer S1 (0.19 mmol cm⁻³) is also much lower than that of S2 (0.29 mmol cm⁻³). Elastomer S2 is in possession of more perfect network structure than elastomer S1.

The stress, modulus of cross-linked elastomer are proportional to the density of network chains N_0 .²¹ In comparison with elastomer S1, elastomer S2 is bound to be of higher modulus and stress in theory, as is in good agreement with the result of mechanical test (see Table III). Thus, it can be drawn that PH-GAP elastomer possesses consummate network structure, higher density of network chains, and exhibits superior mechanical properties, while the imperfect network structure gives lower network chain density, causes GAP elastomer lower stress and modulus.

All of the molecular weight, polydispersity index, and hydroxyl functionality of PH-GAP are very close to those of GAP, and the predominant cross-link reaction in the preparation process of elastomer S1, S2 is still the carbamate reaction between hydroxyl and isocyanate,^{23,24} so it can be deduced that the difference in mechanical properties between elastomer S1 and S2 merely results from their terminal structures. Meanwhile, in virtue of higher reactivity of primary-hydroxyl than that of secondary-hydroxyl,²⁵ it can be concluded that the higher reactivity of primary-hydroxyl of PH-GAP makes its elastomer possess more perfect network structure and gives better mechanical properties, while lower reactive secondary-hydroxyl causes the defect of the network structure and weakens mechanical properties of elastomer GAP.

CONCLUSIONS

Primary-hydroxyl terminated GAP (PH-GAP), whose molecular weight, the polydispersity index, and the hydroxyl functionality are very close to those of the original GAP, has been prepared from secondary-hydroxyl terminated GAP by end-capping modification. PH-GAP elastomers excel GAP elastomers in mechanical properties. Terminal structure plays a predominant role in GAP elastomer mechanical properties. The higher reactivity of the terminal primary-hydroxyl imparts the PH-GAP elastomer more perfect network structure and much superior mechanical properties. Network structure defect is the main factor to weaken mechanical properties of elastomer GAP.

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