

Structure and Mechanical Properties of Novel Composites Based on Glycidyl Azide Polymer and Propargyl-Terminated Polybutadiene as Potential Binder of Solid Propellant

Youzhao Ding,¹ Chong Hu,¹ Xiang Guo,^{1,2} Yuanyuan Che,¹ Jin Huang¹

¹College of Chemical Engineering, Wuhan University of Technology, Wuhan, Hubei 430070, China

²The 42nd Institute of the Fourth Academy of China Aerospace Science and Technology Corporation (CASC), Xiangyang, Hubei 441003, China

Correspondence to: X. Guo (E-mail: guoxiang06@tom.com) or J. Huang (E-mail: huangjin@iccas.ac.cn)

ABSTRACT: Instead of the traditional isocyanate curing system as the binder of solid propellant, a triazole curing system has been developed by the reaction of azide group and alkynyl group due to a predominant advantage of avoiding to the interference of humidity. In this work, the propargyl-terminated polybutadiene (PTPB) was blended with glycidyl azide polymers (GAPs) to produce new composites under the catalysis of cuprous chloride at ambient temperature. The triazole-crosslinked network structure was regulated by changing the molar ratio of azide group in GAP versus alkynyl group in PTPB, and hence various crosslinked densities together with the composition changes of GAP versus PTPB cooperatively determined the mechanical properties of the resultant composites. Furthermore, the formed triazole-crosslinked network derived from the azide group in GAP and alkynyl group in PTPB resulted in the slight increase of glass transition temperatures and α -transition temperatures, and improved the miscibility between GAP and PTPB. © 2013 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* **2014**, *131*, 40007.

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INTRODUCTION

Three-dimensional network-structured polymer can act as strong binder in solid rocket propellant.¹ Moreover, glycidyl azide polymer (GAP) and hydroxyl-terminated polybutadiene (HTPB) are the most common polymers for propellant binders, and generally crosslinked by diisocyanate according to the traditional isocyanate curing system.^{2,3} GAP is a unique binder with high energy, and its positive heat of formation is +117.2 kJ mol⁻¹. Furthermore, GAP shows a good compatibility with advanced oxidizer like ammonium dinitramide.⁴ At the same time, HTPB exhibits other excellent properties for the application of rocket propellant, such as low glass transition temperature, high flexibility, hydrolytic stability, and resistance to solvents.^{5,6} As a result, the polyurethane-type binder systems based on GAP and/or HTPB have been explored, and the crucial crosslinked structure and mechanical performances were optimized by changing the diisocyanate categories,⁷⁻⁹ applying chain extender and/or crosslinker of small molecular polyols,¹⁰ regulating the molar ratio of isocyanate group versus hydroxyl group,^{7,10} incorporating other polymer component,¹¹⁻¹⁴ and so on. To make full use of the advantages of GAP and HTPB, the

composites of GAP and HTPB had been attempted to develop. However, it is greatly inhibited by the poor compatibility between GAP and HTPB due to the presence of polar azido groups in GAP and nonpolar nature of HTPB.¹⁵ Therefore, the linkage of covalent bonds between GAP and HTPB was still expected to improve their compatibility, and so a new copolymer containing GAP and HTPB was synthesized. The as-synthesized copolymer showed two glass transition temperatures located at -74.03 and -35.84°C assigned to HTPB and GAP, respectively,¹⁶ whereas the decomposition of the components in copolymer was similar to that of their homopolymers. It suggested that the immiscibility nature between GAP and HTPB in this copolymer system did not obviously change in spite that the covalent bond integrated two segments of GAP and HTPB. Considering that the isocyanate curing systems of GAP and HTPB both depend upon the reaction between their terminal hydroxyl groups and isocyanates. As a result, the GAP and HTPB had been directly mixed, and then cured with various diisocyanates to produce the crosslinked GAP-HTPB network.¹⁷ The crosslinked GAP-HTPB composites containing higher than 30 wt % of GAP showed higher mechanical strength over the virgin GAP or HTPB crosslinked with

diisocyanates, and only single glass transition was observed. It indicated that no phase separation occurred in the isocyanate-cured GAP-HTPB composites when the GAP content was higher than 30 wt %. In this case, the diisocyanate-mediated crosslinked network played a key role to improving the miscibility between GAP and HTPB.

Although polyurethane shows excellent mechanical properties and thus is widely applied as the binder of solid rocket propellant, it is sometimes inhibited by the moisture sensitivity of the isocyanate curing system. Usually, it should be required to eliminate moisture in both manufacture and storage surrounding.¹⁸ As a result, it is considered that the abundant azido groups in GAP act as the active species to react with the compound containing alkynyl groups via Huisgen 1,3-dipolar cycloaddition and hence fabricate three-dimensional network. The Huisgen 1,3-dipolar cycloaddition between azides and alkynes is one of the classical Click reactions, and has gained considerable attention due to the fact that it is a virtually quantitative, very robust, insensitive, general, and orthogonal ligation reaction.¹⁹ Furthermore, the process of Huisgen reaction between azides and alkynes shows an advantage of essentially chemical inert to reactive conditions, for example, oxidation, reduction, and hydrolysis.²⁰ It contributes to the readily formation of triazole linkages and largely avoids the possibility of side reactions in contrast with the isocyanate curing system.²¹ Therefore, it can be concluded that the Huisgen reaction between azides and alkynes might become a promising way to develop the binder of solid rocket propellant. The moisture-insensitive character of the Huisgen reaction resulted in no special precautions to inhibiting the moisture of surrounding and in the reactants in the manufacture and storage process.²² The triazole-crosslinked polymer based on GAP has been developed with bis-propargyl succinate (BPS) as a dipolarophile curing agent.²³ The curing process had been completed under 65°C for about 4 days. By varying the BPS amount, the mechanical performances could be adjusted. It is worth of note that the required amount of BPS for complete curing of GAP was lower than that of diisocyanate, and so confirmed a higher total energy content in the binder system. On the other hand, the BPS-cured systems gave higher glass transition temperatures than diisocyanate-based binder systems.²³ Moreover, many kinds of alkynyl-based curing agents, including aromatic and aliphatic types, were used to develop the isocyanate-free curing system of solid propellant binders.^{24,25} However, only the triazole curing system could not show enough good mechanical performances. When applying the dual curing system containing an isocyanate curing agent and an alkyne curing agent, the resultant GAP-based materials exhibited excellent mechanical properties for the requirement of the propellant. Because the terminal hydroxyl groups of the GAP are the reaction species for the isocyanate curing system and the azide groups in the side chains of GAP react with the alkyne compound in the triazole curing system, it is considered that the unsatisfactory mechanical performances of the GAP-based materials only cured by the alkyne compound were mainly ascribed to the

relatively shorter distance between two crosslinking points in the triazole curing system. Furthermore, the relatively higher rigidity of the GAP chain and the formed triazole structure might also inhibit the mechanical performances of the GAP-based materials only cured by the alkyne compound. As a result, the flexible polybutadiene (PB) with low glass transition temperature has been attempted to introducing the triazole curing system of GAP, and was expected to establish the curing system without isocyanate and achieve good mechanical performances. So far, it has not yet been reported that the Huisgen reaction acts as the curing and compatibilizing-integrated method to developing the composite binder based on GAP and PB.

In this study, HTPB was first reacted with propargyl bromide to produce a difunctional alkynyl polymer with PB as a backbone. Then, propargyl-terminated polybutadiene (PTPB) was blended with GAP, and subsequently cured by means of 1,3-dipolar cycloaddition reaction. The mechanical and thermal properties as well as crosslinking densities of the triazole-crosslinked GAP/PTPB composites with various molar ratios of N_3 versus $C\equiv C$ were investigated by tensile test, swelling test, differential scanning calorimetry analysis (DSC), and dynamic mechanical analysis (DMA). Furthermore, the fracture morphologies of the as-prepared composites were observed by scanning electron microscopy (SEM).

MATERIALS AND METHODS

Materials

HTPB with hydroxyl values of 0.84 mmol g^{-1} were purchased from Zibo Qilong Chemical Industry Co. (China) and purified by vacuum drying. Propargyl bromide (80 wt % in toluene, ca., 9.2 mol L^{-1}) and potassium tert-butoxide (99% pure) were purchased from J&K Scientific (China). GAP with molecular weight of 3400 $g\ mol^{-1}$ and hydroxyl value of 0.618 mmol g^{-1} was kindly provided from the 42nd Institute of the Fourth Academy of CASC. Cuprous chloride (AR), tetrahydrofuran (THF, AR), and acetic ether (EtOAc, AR) as well as anhydrous magnesium sulfate were purchased from Sino-pharm Chemical Reagent Co. (China). THF was refluxed over a mixture of Na and benzophenone ketyl under argon and distilled just before use.

Synthesis of PTPB

Figure 1 shows the schematical synthesis process of PTPB. First, a cooled (0°C) suspension of potassium tert-butoxide (2.07 g, 18.4 mmol) in THF (50 mL) was added into a solution of HTPB (10.96 g, hydroxyl value of 0.84 mmol g^{-1}) in THF (50 mL) under nitrogen atmosphere. Subsequently, the resulting mixture was added into a solution of propargyl bromide (2.0 mL, 80 wt % in toluene, ca., 9.2 mol L^{-1}) in 100 mL of THF in an ice-water bath under nitrogen atmosphere. After the reaction was mechanically stirred for an additional 44 h under ambient temperature, the reactants were diluted with 160 mL of 3 : 1 brine/water. The THF layer was separated, whereas the aqueous layer was extracted with EtOAc (3 × 100 mL). The combined organic layer was washed with 80 mL of 1 : 1 brine/water and 130 mL brine, and was dried

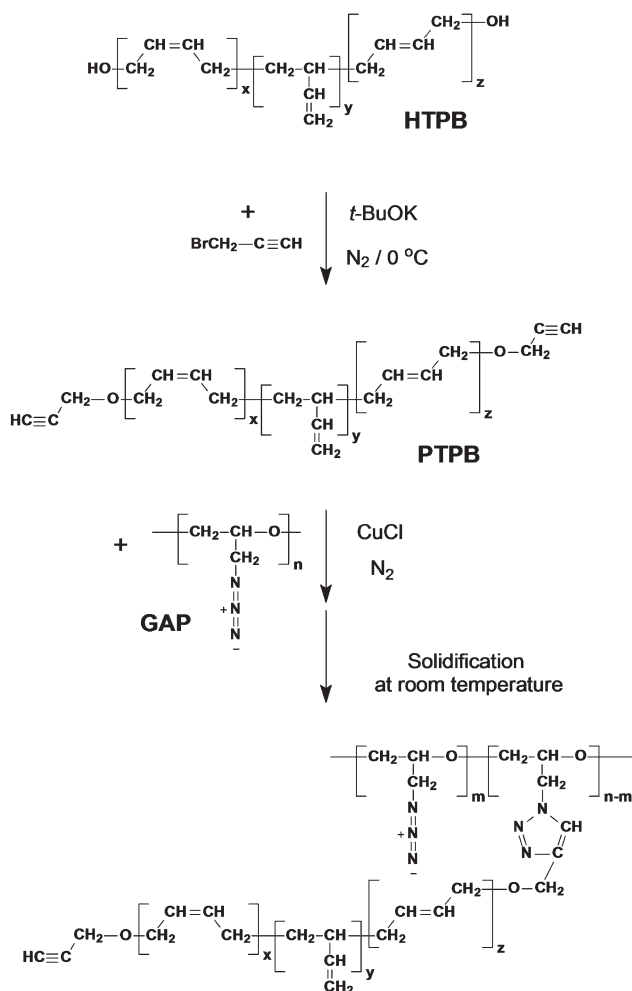


Figure 1. Schematic illustration for the reaction between HTPB and propargyl bromide, and the subsequent reaction between PTPB and GAP.

over anhydrous MgSO₄. Finally, the PTPB in a yellow oily liquid state (11.16 g, yield 98.6%) was obtained through filtration and after solvent evaporation.

Preparation of the GAP/PTPB Composites via 1,3-Dipolar Cycloaddition

The preparation of the GAP/PTPB composites is schematically depicted in Figure 1. The desired amount of GAP and 11.16 g of PTPB were added into a THF solution under mechanical stirring to produce a mixture solution. After 0.45 g of cuprous chloride as a catalyzer was added into the mixture solution, the reaction was mechanically stirred under nitrogen atmosphere at the ambient temperature for 12 h in the dark. Then, the reaction mixture was filtered to remove CuCl, and condensed by rotating evaporation. The condensed reaction solution was cast into a Teflon mold, and solidified by the evaporation of the THF solvent at ambient temperature for 48 h. Finally, the solidified film was vacuum dried and kept in a desiccator containing phosphorus pentoxide. According to the molar ratios of N₃ versus C≡C in the GAP/PTPB composites, the resultant films were, respectively, coded as GAP/PTPB-1.0, GAP/PTPB-1.5, GAP/PTPB-

2.0, GAP/PTPB-2.5, and GAP/PTPB-3.0, where the Arabic numerals represented the theoretical molar ratio of N₃ versus C≡C.

CHARACTERIZATION

Fourier transform infrared spectroscopy (FTIR) spectra of the oily liquid HTPB, PTPB, and GAP as well as the GAP/HTPB composites, were recorded on an FTIR 5700 spectrometer (Nicolet, Madison, WI) in the range of 4000 ~ 400 cm⁻¹.

¹H-NMR spectra of HTPB and PTPB were recorded on a Bruker 600 MHz spectrometer at ambient temperature. Tetramethyl silicane was used as internal standard and CDCl₃ as solvent. Chemical shifts were referenced relative to the corresponding residual solvent signals (δ 7.26).

DSC analysis was performed on a PYRIS 1 DSC TALAB SYSTEM (Perkin Elmer Company, U.S.) under a nitrogen atmosphere with a heating or cooling rate of 20°C min⁻¹. About 15 mg composites as well as PTPB and GAP were placed in hermetically sealed DSC crimp pans, which were tested over a range of -150–40°C.

DMA was performed on a DMA 242C dynamic mechanical analyzer (Netzsch, Hanau, Germany) with a dual cantilever device at a frequency of 3 Hz. The temperature range was from -150 to 75°C with a heating rate of 3°C min⁻¹. The dimensions of the test specimens were 30 mm × 10 mm.

SEM observations were carried out on a VEGA 3 LMU scanning electron microscope (TESCAN, Czech Republic). All the GAP/PTPB composites were frozen in liquid nitrogen and then immediately snapped. The fracture surfaces of the sheets were sputtered with gold, and then observed and photographed.

The mechanical parameters, including tensile strength (σ_b), elongation at break (ϵ_b), and Young's modulus (E), of all the GAP/PTPB composites were measured on a CMT6503 universal testing machine (SANS, Shenzhen, China) with a tensile rate of 50 mm min⁻¹. The testing sheets were cut into strips with a width of 10 mm and a distance of 30 mm between testing marks. The testing strips were kept at 0% humidity for 7 days before measurement. A mean value of five replicates from each sheet was taken.

Crosslinking density, defined as moles of effective chains per cubic metre, was generally obtained from volume fraction of the swollen polymer in a solvent. The testing specimens of the GAP/PTPB composites were placed in toluene for 7 days and the solvent were changed every day to keep fresh. The specimens were then removed from the solvent, and weighed after gently wiping out the solvent attached the specimen surface. Subsequently, the absorbed solvent was driven off by placing the specimen in a vacuum oven at 60°C for overnight, and then the weight of the deswollen specimen was measured. From the weights of the initial (m_0), swollen (m_1) and deswollen (m_2) specimens, the volume fraction of the polymer (φ) in the swollen specimen could be calculated as following^{26,27}:

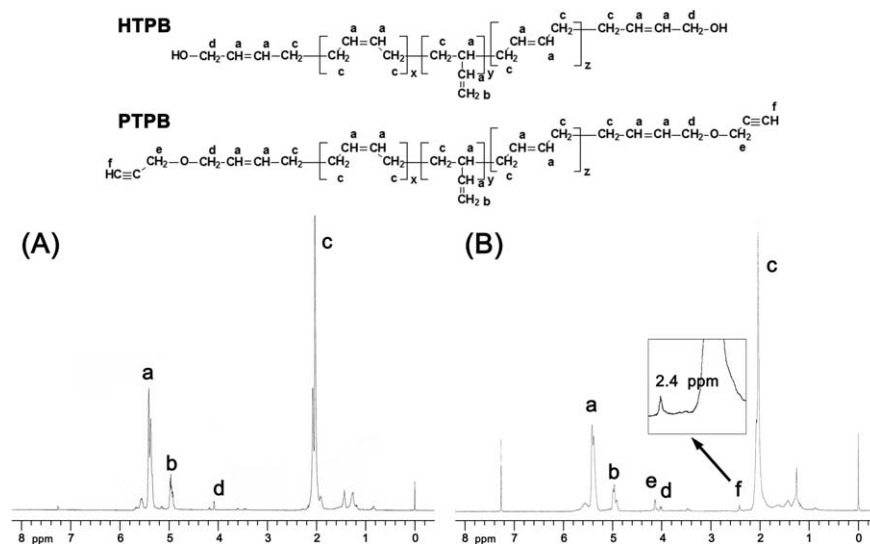


Figure 2. $^1\text{H-NMR}$ spectra of HTPB (A) and PTPB (B).

$$\varphi = \frac{m_0/\rho_2}{m/\rho_1 + m_0(1/\rho_2 - 1/\rho_1)} \quad (1)$$

where ρ_1 and ρ_2 are the densities of solvent (0.80 g cm^{-3}) and the composites (0.96 g cm^{-3}), respectively.

In addition, the gel fraction of the swollen polymer (ω) can be defined as:

$$\omega = \frac{m_1}{m_0} \times 100\% \quad (2)$$

Finally, the crosslinking density (γ) can be obtained from the parameters of φ and ω :

$$\gamma = \varphi^{5/3} \times \omega \quad (3)$$

RESULTS AND DISCUSSION

Synthesis of PTPB

In this present study, it is reported for the first time that the alkyne functionalized PB was synthesized in a single step reaction, namely HTPB, was directly condensed with propargyl bromide using potassium tert-butoxide as a condensation reagent in the THF solvent. The structure of the as-synthesized PTPB was confirmed by $^1\text{H-NMR}$ and FTIR. Figure 2 shows the $^1\text{H-NMR}$ spectra of HTPB and PTPB, whereas Figure 3(A,B) depicts the FTIR spectra of HTPB and PTPB, respectively. In the $^1\text{H-NMR}$ spectra of Figure 2, except for the conventional peaks of HTPB [can be also seen in Figure 2(A)] located at 2.0 ppm (c), 4.0 ppm (d), 4.9 ppm (b), and 5.6 ppm (a),^{28,29} there were the peaks observed at 2.4 ppm (f) and 4.1 ppm (e) in Figure 2(B) of PTPB, which were assigned to proton resonance in $\equiv\text{CH}$ and $-\text{CH}_2$ of the propargyl group of PTPB. On the other hand, the FTIR spectrum of PTPB in Figure 3(B) showed the predominant peak located at 3307 cm^{-1} , which is obvious different from the FTIR spectrum of HTPB in Figure 3(A). At the same time, the absorption around 3350 cm^{-1} assigned to O—H stretching of HTPB almost disappeared because the terminal

hydroxyl groups in HTPB were condensed with propargyl bromide. The results mentioned above indicated the success of terminal alkylation from HTPB.

Reaction Between GAP and PTPB in the Composites

FTIR was used to trace the reaction between azide groups in GAP and alkyne groups in PTPB. The FTIR spectrum of the GAP/PTPB composite [Figure 3(D)] was similar to that of GAP [Figure 3(C)]. At the same time, the characteristic peak located

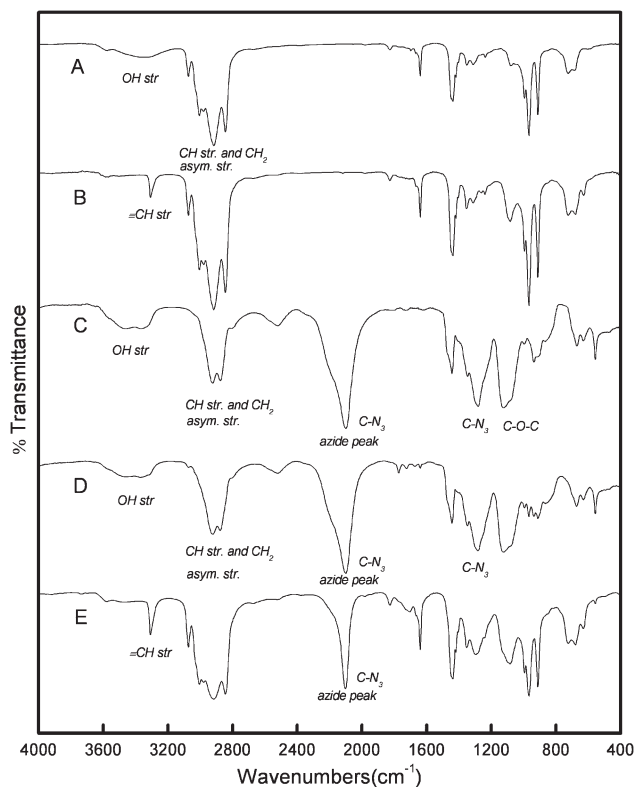


Figure 3. FTIR spectra of HTPB (A), PTPB (B), GAP (C), cured GAP/PTPB composite (D), and the blend of GAP and PTPB (E).

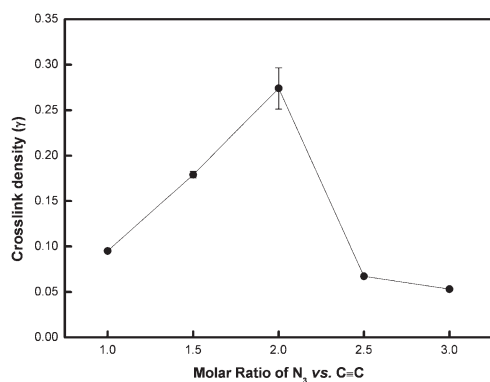


Figure 4. Effect of the molar ratio of N₃ versus C≡C on the crosslink densities of the GAP/PTPB composites.

at 3307 cm⁻¹, which was assigned to the —CH stretching of alkynyl in PTPB [can be seen in Figure 3(B)], was absent in Figure 3(D) of the GAP/PTPB composite. It indicated that the composites consisted of GAP and PTPB while the C≡C in PTPB reacted with the N₃ in GAP to form the triazole structure as the crosslinking point. Furthermore, the FTIR spectrum [Figure 3(E)] of the GAP/PTPB blend, which was obtained without the process of catalysis, could be seen as the complexation of the FTIR spectra of GAP and PTPB. The —CH peak of alkynyl in PTPB located at 3307 cm⁻¹ in Figure 3(E) suggested that there was no reaction between the C≡C in PTPB and the N₃ in GAP on the lack of catalysis condition. It further proved that the triazole structure formed in the GAP/PTPB composite.

Crosslinking Densities of the GAP/PTPB Composites

Figure 4 shows the dependence of the crosslinking densities (γ) of the GAP/PTPB composites upon the molar ratios of N₃ versus C≡C. The crosslinking densities firstly increased up to the maximum value of 0.27 with an increase of the molar ratio of N₃ versus C≡C from 1.0 to 2.0, and then decreased until the molar ratio of N₃ versus C≡C continuously increased up to 3.0. In theory, the crosslinking densities should continuously increase with a decrease of the molar ratio of N₃ versus C≡C. However, when the molar ratio of N₃ versus C≡C was lower than 2.0, the decrease of the crosslinking densities might be ascribed to the fact that the initial formed triazole structure became the steric hindrance to inhibit the subsequent reaction between the neighboring N₃ groups and the C≡C in PTPB. When the molar ratio of N₃ versus C≡C decreased and tended to equivalent, the steric hindrance of the initial formed triazole structure might make only one terminal C≡C group in one PTPB chain participate the reaction with the N₃ groups in GAP, and hence resulted in the decrease of crosslinking densities.

Mechanical Properties of the GAP/PTPB Composites

Figure 5 shows the dependence of the mechanical parameters, including tensile strength (σ_b), elongation at break (ε_b), and Young's modulus (E), of the GAP/PTPB composites upon the molar ratios of N₃ versus C≡C. The tensile strength and Young's modulus of the GAP/PTPB composites gradually increased with an increase of the molar ratio of N₃ versus C≡C from 1.0 to 2.0, and then decreased until the molar ratio of N₃ versus C≡C continuously increased up to 3.0. When the molar

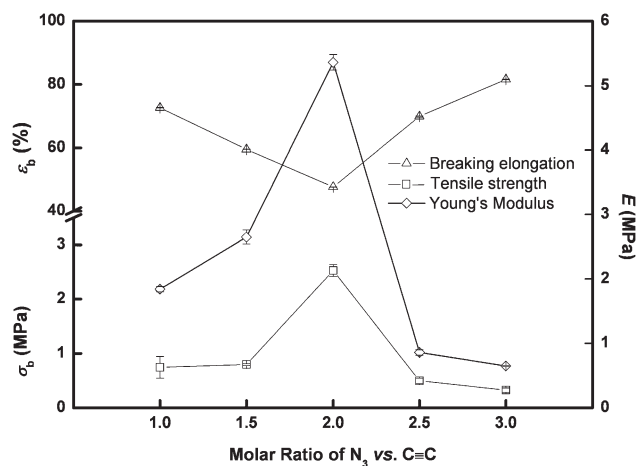


Figure 5. Effect of the molar ratio of N₃ versus C≡C on the σ_b, ε_b, and E for the GAP/PTPB composites.

ratio of N₃ versus C≡C was 2.0, the σ_b and E of the GAP/PTPB-2.0 reached the maximum values of 2.53 and 5.36 MPa, respectively. Meanwhile, the effect of molar ratios of N₃ versus C≡C on breaking elongation was just opposite to that on E. The ε_b value firstly fall down to the minimum (47.6%) with an increase of molar ratio of N₃ versus C≡C from 1.0 to 2.0, and then increased up to the maximum (81.6%) when the N₃ versus C≡C molar ratio continuously increased the up to 3.0.

In general, higher crosslinking density results in higher tensile strength and Young's modulus, and lower elongation at break. On the other hand, the flexibility of main chains of the GAP component is inhibited by the azido groups of side chains, whereas the PTPB component favored improving the elongation. The elongation of the GAP/PTPB composites tended to decline with an increase of the GAP content. As a result, the mechanical performances strongly depended upon the synergistic effect of the compositions and crosslinking densities of the GAP/PTPB composites. With an increase of the molar ratio of N₃ versus C≡C, the GAP content in the composites increased. When the molar ratio of N₃ versus C≡C increased from 1.0 to 2.0, the simultaneous increase of crosslinking densities and GAP content in the composites resulted in the decrease of elongation. Although higher content of GAP in the composites did not favor the enhancement of elongation when the molar ratio of N₃ versus C≡C was higher than 2.0, the sharp decrease of crosslinking density determined the increase of elongation.

Thermal Properties of the GAP/PTPB Composites

Figure 6 shows the DSC thermograms of the GAP/PTPB composites as well as the PTPB and GAP, whereas Table I summarizes the glass transition temperature (T_g) and the increment of heat capacity (ΔC_p) obtained from the DSC thermograms. The T_{g,PTPB} values located at low temperature, which was assigned to PTPB of the GAP/PTPB composites, were slightly higher than that of neat PTPB. At the same time, when the molar ratio of N₃ versus C≡C was higher than 2.5, the glass transition assigned to GAP was observed at high temperature due to the increasing content of the GAP component in the composites. Furthermore, the T_{g,GAP} values of GAP/PTPB-2.5

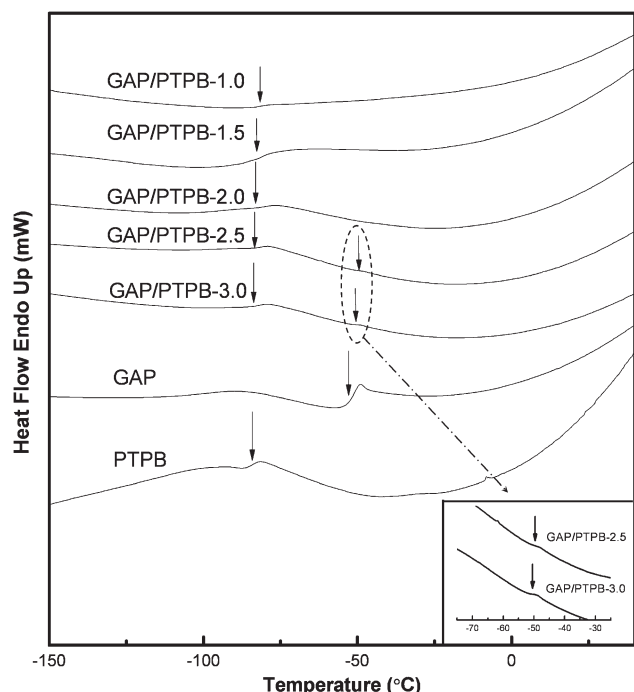


Figure 6. DSC thermograms of the GAP/PTPB composites with various molar ratios of N_3 versus $C\equiv C$ as well as PTPB and GAP.

and GAP/PTPB-3.0 were also slightly higher than that of neat GAP. However, on the whole, the $T_{g,PTPB}$ values and the $T_{g,GAP}$ values of the GAP/PTPB composites almost kept a constant level independent upon the changes of the crosslinking densities and the compositions, which resulted from the increase of the molar ratio of N_3 versus $C\equiv C$. It indicated that the motion of the segments in PTPB was almost not affected by the crosslinked network and the GAP component in the composites. Except for the immiscibility nature between PB and GAP, this was also ascribed to the fact that the PTPB component was a relatively long chain and only a small fraction of segments close to the triazole structure located at the ends of PTPB might be restricted by the crosslinked network.

Figure 7 shows the curves of loss factor versus temperature of the GAP/PTPB composites from the DMA test, whereas Table I summarizes the results of the α -relaxation tempera-

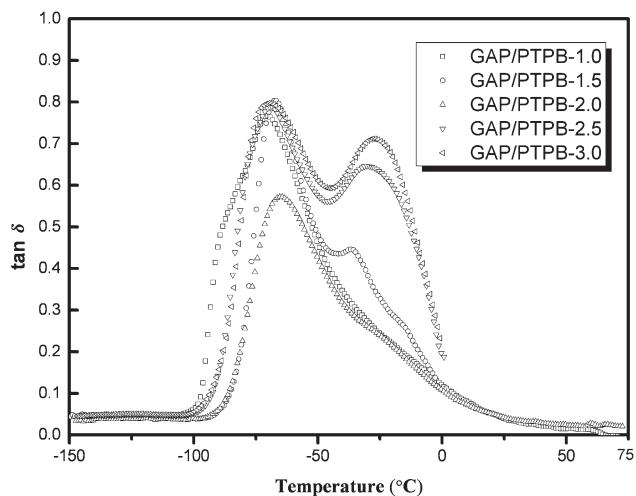


Figure 7. $\tan \delta$ —temperature curves for the GAP/PTPB composites with various molar ratios of N_3 versus $C\equiv C$.

ture (T_{α}) and loss factor ($\tan \delta$). Compared with the segmental motion at domain scale revealed by the specific heat increment of glass transition from the DSC test, DMA is a more sensitive technique to study initial motion of frozen polymer segments through α -relaxation at molecular scale. As a result, all the GAP/PTPB composites showed two regions of mechanical loss located at about -70 and -30°C , respectively, in Figure 7. The $T_{\alpha 1, \max}$ located at low temperature was assigned to the PTPB component, whereas the other loss region located at high temperature was assigned to the GAP^{10,12} while the GAP/PTPB-2.5 and GAP/PTPB-3.0 gave the $T_{\alpha 2, \max}$ values. The change tendency of $T_{\alpha 1, \max}$ was in agreement with that of crosslinking density, namely, the $T_{\alpha 1, \max}$ first increased to -65.4°C of GAP/PTPB-2.0 and then decreased with an increase of the molar ratio of N_3 versus $C\equiv C$. From the DMA results, the inhibition of the crosslinked network on the segmental motion could be revealed at molecular scale.

Fracture Morphologies of the GAP/PTPB Composites

Figure 8 shows the SEM images of the fracture morphologies of the GAP/PTPB composites. With an increase of the molar ratios of N_3 versus $C\equiv C$, the fractured stripes became few and

Table I. DSC and DMA Data of the GAP/PTPB Composites with Various Molar Ratios of N_3 Versus $C\equiv C$ as well as Neat PTPB and GAP

Sample	DSC data				DMA data			
	$T_{g,PTPB}$ ($^{\circ}\text{C}$)	$\Delta C_{p,PTPB}$ ($\text{J g}^{-1} \text{ } ^{\circ}\text{C}^{-1}$)	$T_{g,GAP}$ ($^{\circ}\text{C}$)	$\Delta C_{p,GAP}$ ($\text{J g}^{-1} \text{ } ^{\circ}\text{C}^{-1}$)	$T_{\alpha 1, \max}$ ($^{\circ}\text{C}$)	$\tan \delta$	$T_{\alpha 2, \max}$ ($^{\circ}\text{C}$)	$\tan \delta$
GAP/PTPB-1.0	-81.5	0.21	—	—	-70.2	0.77	Convexity	
GAP/PTPB-1.5	-82.7	0.55	—	—	-67.8	0.8	Convexity	
GAP/PTPB-2.0	-83.0	0.12	—	—	-65.4	0.57	Convexity	
GAP/PTPB-2.5	-83.1	0.16	-49.6	0.03	-69.3	0.79	-29.3	0.65
GAP/PTPB-3.0	-83.8	0.21	-50.5	0.03	-69.8	0.80	-29.8	0.71
PTPB	-84.2	0.18	—	—	n.d.	n.d.	n.d.	n.d.
GAP	—	—	-52.6	0.34	n.d.	n.d.	n.d.	n.d.

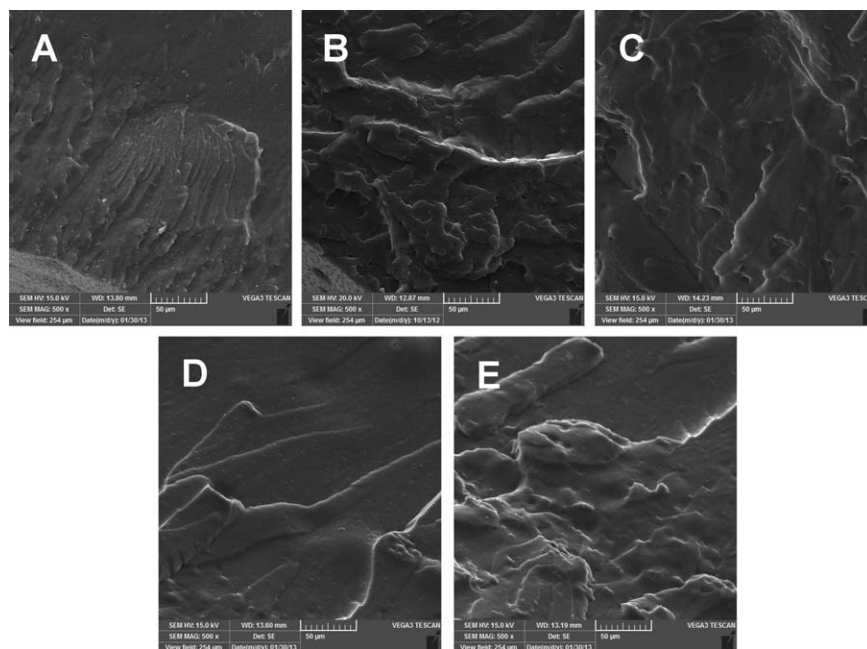


Figure 8. SEM images for the fracture surface of the composites of GAP/PTPB-1.0 (A), GAP/PTPB-1.5 (B), GAP/PTPB-2.0 (C), GAP/PTPB-2.5 (D), and GAP/PTPB-3.0 (E).

scattered while the fractured surface gradually became smooth. Due to the immiscibility nature between GAP and PB, the GAP/HTPB blends cured with diisocyanate³⁰ showed the morphologies of the spherical phase dispersed into the other continuous phase, and two phases were assigned to GAP and HTPB, respectively.³⁰ However, in this work, there was no obvious two-phase structure observed in the GAP/PTPB composites. It indicated that the reaction between N_3 and $C\equiv C$ forcibly combined the GAP and the PTPB in the composites and hence resulted in no great-scale phase separation, namely the miscibility of GAP and PTPB was improved to some extent.

CONCLUSIONS

In this work, HTPB was first modified via alkynylation, and subsequently a series of triazole-linked composites based on (GAPs) and PTPB were prepared. The mechanical performances of the resultant GAP/PTPB composites can be regulated by changing the molar ratios of N_3 versus $C\equiv C$. Both the cross-linking density and the composition in the composites cooperatively determined the mechanical performances. The reaction between N_3 and $C\equiv C$ forcibly combined the GAP and the PTPB in the composites, and hence the miscibility of GAP and PTPB was improved to some extent. The composites with the molar ratios of N_3 versus $C\equiv C$ as 3.0 showed the highest elongation at break (ϵ_b) of 81.6% for, and the corresponding tensile strength (σ_b) and Young's modulus (E) were 0.33 and 0.65 MPa, respectively. When the molar ratio of N_3 versus $C\equiv C$ was 2.0, the composites had the maximum of σ_b and E as 2.53 and 5.36 MPa, respectively, and the ϵ_b kept as 47.6%. In comparison with the excellent polyurethane binder in solid propellant areas, the GAP/PTPB composites based on the triazole linkage showed a great potential by virtue of their predominant advantages of

moisture insensitivity, regulated mechanical performances, compatibility with other high-energy ingredients in propellant, and so on.

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