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Novel glycidyl azide polymers containing aromatic diol units: synthesis and characterization for their application as energetic composite propellant binders

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As a widely known class of energetic binders, glycidyl azide polymers (GAPs) exhibit high-energy characteristics owing to the presence of azide groups (explosophores) in their backbone structure. However, GAPs are limited by their poor mechanical properties compared with inert binders, such as hydroxyl-terminated polybutadiene. Therefore, efforts to simultaneously enhance the thermal and mechanical properties of GAPs are still ongoing. In this study, novel glycidyl azide polymers containing different aromatic diol units (2-nitroresorcinol, catechol, 1,2-benzenedimethanol, and 1,3-benzenedimethanol) were successfully synthesized by a two-step methodology starting from epichlorohydrin. The structure and thermal behavior of the synthesized GAPs were fully characterized by spectroscopic analyses, dynamic mechanical analysis (DMA), thermogravimetric analysis (TGA), and differential scanning calorimetry (DSC). Two promising polymers, namely, GAP-NR and GAP-3BM, were further cured with N100/IPDI to form polyurethane-GAP three-dimensional crosslinked networks. The resulting PU-GAP-NR and PU-GAP-3BM elastomers exhibited good mechanical properties, thermal stability and acceptable glass-transition temperatures. Based on these results, GAP-NR and GAP-3BM might serve as potential energetic binders for composite propellants.

1 Introduction

In solid propellants, the polymeric binders play an important role in binding oxidizers, metallic fuels, and other additives into a stable, processable, and uniform solid mass. In addition, binders can influence combustion behavior, long-term aging and interfacial adhesion with solid phases.[1] Recently, interest in energetic binders for composite propellants has increased. Attention has been focused on replacing hydrocarbon-based, conventional, inert polymeric binders (hydroxyl-terminated polybutadiene (HTPB, Fig. 1), hydroxyl-terminated polyether, and hydroxy-terminated polyisoprene) with those bearing energetic groups such as azide, nitro, nitrate, nitramine, and nitrogen heterocycles (triazoles and tetrazoles) in the polymer backbones to improve the energetic output and overall performance of composite propellants.[2–4] Among these polymers, glycidyl azide polymers (GAPs, Fig. 1), hydroxy-terminated polyethers with azide groups attached on their polyether backbone structure, have been extensively studied as binders or plasticizers in various composites.[5] The formation of highly stable nitrogen molecules during the combustion of GAPs leads to a high positive heat of formation (+957 kJ kg^{-1} at 5 MPa),[6] which is equivalent to a 5% increase in specific impulse compared with that of HTPB. GAP are also found to enhance the burn rate, combustion temperature,[7,8] and processability during casting.[6,9,10] Owing to their low glass-transition temperature, low detonation sensitivity, thermal and mechanical stability, and good compatibility with oxidizers,[11,12] GAPs are considered

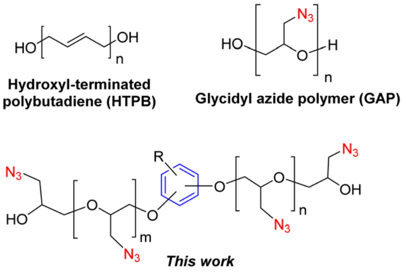

Fig. 1 Molecular structures of HTPB, GAP and the our targeted glycidyl azide polymers containing aromatic diol units.

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the most promising candidates to replace HTPB in composite propellants and explosives.

Despite their potential, the application of GAPs is restricted by inherent disadvantages, notably their insufficient mechanical performance, increased glass-transition temperature after curing due to low flexibility and the existence of methylene azido pendant groups in their molecular structures.[13,14] Owing to these limitations extensive research has been conducted on the structural modifications of the GAP backbone, including the modification of diol initiators, synthesis of branched GAPs, interactions with other materials, and the blending of GAPs with flexible chain polymers.[15–17] The diol moieties in the polyether chain of GAPs have a significant influence on their thermal stabilities, glass-transition temperatures and mechanical properties. The presence of aliphatic linear diols (such as ethylene glycol, 1,4-butanediol, and 2,2-bis(bromomethyl)1,3-propane diol) in the polyether backbone of GAPs provides high elasticity and low-temperature flexibility but lower thermal thresholds.[18–20] Recently, Hng *et al.* reported the synthesis of star-shaped GAPs using 2,2-diethyl-1,3-propanediol, trimethylolpropane (TMP) and pentaerythritol (PE) as diol initiators, and they found that TMP-GAP and PE-GAP with higher crosslinking densities showed better creep resistance and tensile strength, albeit with a reduced elongation at break.[21]

In the light of the aforementioned findings, this study is directed towards the development of novel energetic polymers with improved glass-transition temperatures, high heat of decomposition, and thermo-mechanical stability. In the present work, we attempted to synthesize precursor polyepichlorohydrins and glycidyl azide polymers containing aromatic diol (2-nitroresorcinol, catechol, 1,2-benzenedimethanol, 1,3-benzenedimethanol) (Fig. 1). The synthesized polymers were fully characterized *via* various spectroscopic techniques (IR, UV-vis, NMR, GPC), and we determined the glass-transition temperature (T_g) and thermal properties (TGA, DSC). The potential GAPs were cured with aliphatic isocyanate biuret (N100) and isophorone diisocyanate (IPDI) in the presence of catalyst triphenyl bismuth (TPB) to form three-dimensional crosslinked networks. These samples were then analyzed to evaluate their mechanical and thermal properties as important criteria to define the usefulness of the energetic binder.

2 Experimental

2.1 Materials

All the chemicals, namely epichlorohydrin (ECH); 2-nitroresorcinol (NR); 1,2-benzenedimethanol (2BM); 1,3-benzenedimethanol (3BM); catechol (CA); chloroform; acetone; dichloromethane (DCM); boron trifluoride tetrahydrofuran (BF_3 THF); ethylene glycol (EG); tert-butylammonium bromide (TBAB); *N*,*N*-dimethylformamide (DMF); ethylene glycol (EG); hexamethylene diisocyanate biuret trimer (Desmodur N100); isophorone diisocyanate (IPDI); and triphenyl bismuth (TPB), were obtained in synthetic grade and used without further purification.

2.2 General procedure for the synthesis of polyepichlorohydrin containing aromatic diol units

To a 250 mL three-neck round-bottom flask equipped with a magnetic stir bar, a dropping funnel and a gas inlet tube, 0.01 mol of diol and 50 mL of chloroform (for 2-nitroresorcinol, catechol, 1,2-benzenedimethanol) or a mixture of chloroform/acetone (8 : 2, v/v) (for 1,3-benzenedimethanol) were added and stirred to obtain a homogeneous solution under an argon atmosphere. To this solution, boron trifluoride tetrahydrofuran (BF_3 THF) (2.5 mmol) was slowly injected and stirred for 30 min at room temperature. Afterward, the system was cooled to 0 °C using an ice-salt bath, and epichlorohydrin (20 g, 0.217 mol) was added dropwise for 1.5–2 h. The stirring was continued for 5 h at 0 °C and then overnight at room temperature under an argon atmosphere. Upon completion, the reaction mixture was quenched by adding a 100 mL aqueous solution of sodium bicarbonate (5 wt%) and vigorously stirred for 1 h. The organic phase was extracted with dichloromethane and washed several times with distilled water until the pH was neutral. The organic phase was dried over sodium sulfate, filtered, and evaporated under vacuum (100 mbar, 40 °C) to obtain pure polyepichlorohydrin (PECH) as a light-yellow to dark brown viscous oil in 85–94% yields.

2.3 General procedure for the synthesis of glycidyl azide polymers containing aromatic diol units

The mixture of ethylene glycol (62 g, 1 mol) and tetrabutylammonium bromide (161 g, 0.5 mol) was stirred at 120 °C until obtaining a colorless homogenerous liquid TBAB/EG solvent.[22] In a three-neck flask connected to a thermometer, condenser, and magnetic bar, polymer PECH (20 g) was dissolved in 50 mL of the TBAB/EG solvent. Sodium azide (15 g, 0.21 mol) was then added, and the reaction mixture was stirred at 100 °C for 5–8 h. Upon completion of the reaction (checked by IR analysis), water (50 mL) was added to the reaction mixture and stirred for 30 min at 100 °C. After separating the layers, the organic layer was washed twice with hot water. This procedure was repeated until the TBAB/EG solvent was completely removed (checked by IR analysis). The obtained organic layer was then dissolved in dichloromethane, dried over sodium sulfate, and concentrated under reduced vacuum to afford the pure products (GAPs) as yellow to dark-brown viscous oils in 90–95% yields.

2.3.1 Glycidyl azide polymer containing 2-nitroresorcinol unit (GAP-NR). ^{1}H NMR (600 MHz, $CDCl_3$) δ, ppm: 7.38 (Ph), 7.09 (Ph), 3.95 (m, OH), 3.66–3.62 (m, C**H**$_2$CHO), 3.42–3.34 (m, C**H**$_2$N$_3$). ^{13}C NMR (150 MHz, $CDCl_3$) δ 151.65, 137.26, 124.65, 111.74, 78.62 (CH_2CHO), 69.53 (CH_2CHO), 51.70 (CH_2N_3).

2.3.2 Glycidyl azide polymer containing catechol unit (GAP-CA). ^{1}H NMR (600 MHz, $CDCl_3$) δ, ppm: 6.93–6.89 (Ph), 3.90–3.87 (m, OH), 3.64–3.56 (m, C**H**$_2$CHO), 3.36–3.28 (m, C**H**$_2$N$_3$). ^{13}C NMR (150 MHz, $CDCl_3$) δ 148.43, 122.13, 114.73, 78.62 (CH_2CHO), 69.52 (CH_2CHO), 51.68 (CH_2N_3).

2.3.3 Glycidyl azide polymer containing 1,2-benzendimethanol unit (GAP-2BM). ^{1}H NMR (600 MHz, $CDCl_3$) δ, ppm: 7.36 (Ph), 7.31 (Ph), 4.52 (PhC**H**$_2$O), 3.89 (OH), 3.60–3.57 (C**H**$_2$CHO), 3.35–3.32 (C**H**$_2$N$_3$). ^{13}C NMR (150 MHz, CDCl$_3$) δ 135.50, 128.33, 127.62, 78.29 (CH$_2$CHO), 71.34 (PhCH$_2$O), 69.16 (CH$_2$CHO), 51.32 (CH$_2$N$_3$).

2.3.4 Glycidyl azide polymer containing 1,3-benzendimethanol unit (GAP-3BM). ^{1}H NMR (600 MHz, CDCl$_3$) δ, ppm: 7.35 (Ph), 7.31 (Ph), 4.53 (PhC**H**$_2$O), 3.94 (OH), 3.69–3.62 (C**H**$_2$C**H**O), 3.38–3.36 (C**H**$_2$N$_3$). ^{13}C NMR (150 MHz, CDCl$_3$) δ 138.10, 128.72, 127.18, 78.79 (CH$_2$CHO), 71.43 (Ph**C**H$_2$O), 69.66 (CH$_2$CHO), 51.79 (CH$_2$N$_3$).

2.4 Hydroxyl value estimation

The hydroxyl value (OHV) of the synthesized GAPs was determined using the acetylation method according to ASTM-E222-17.[23] In a typical experiment, 2–3 g each of the respective GAP was dissolved in 5 mL of the standard acetylating agent (prepared from 66 mL of pyridine and 33 mL of acetic anhydride) and heated at 95 °C for 1 h. Thereafter, 10 mL of water was added, and the reaction mixture was stirred at 95 °C for 10 min. A blank was prepared using the acetylating reagents alone and treated in the same way as the reaction mixture containing the GAP. Upon completion, the reaction contents were allowed to cool to room temperature and titrated against a 0.5 M ethanolic potassium hydroxide solution using a phenolphthalein indicator. The OHV of the GAPs was estimated using eqn (1):

$$\text{OHV(mg in KOH per g)} = 56.11 \times \frac{(B - V) \times N_{\text{KOH}}}{W_{\text{GAP}}}, \quad (1)$$

where B and V are the volumes (mL) of the KOH solution consumed by the blank and sample, respectively; N_{KOH} is the normality of the KOH solution, and W_{GAP} is the sample weight (g) used for the experiment.

The hydroxyl value of each polymer was estimated from three measurements, and the average value was calculated.

2.5 Curing method

Based on the estimated OHV of the GAP, the required amount of the isocyanate reagent for achieving the molar ratios $R = [\text{NCO}]/[\text{OH}]$ of 0.9 to 1.5 was calculated using eqn (2):

$$W_{\text{NCO}} = \frac{M_{\text{NCO}}}{f_{\text{NCO}}} \times \frac{\text{OHV}_{\text{GAP}}}{56100} \times W_{\text{GAP}} \times R, \quad (2)$$

where W_{NCO} is the weight of the curing reagent (g), M_{NCO} is the molecular weight of the curing reagent (g mol^{-1}), f_{NCO} is the functionality of the curing reagent, OHV$_{\text{GAP}}$ is the hydroxyl value of the GAP (mg in KOH per g), and W_{GAP} is the weight of the GAP used for curing (g).

The mixture of GAPs, curing agent N100/IPDI (1/1) and catalyst TPB (0.05 wt%) was stirred until homogeneity was achieved. The obtained mixtures were degassed under vacuum (5–20 mbar) for 20–30 min to remove air bubbles and then poured into a polypropylene plastic mold (5 × 10 cm^2). The samples were degassed again and cured at 60 °C for 7 days, and the mechanical properties were measured.

2.6 Characterization methods

IR spectra of the polymers were measured using a PerkinElmer Spectrum Two spectrometer in KBr pellets. ^{1}H NMR and ^{13}C NMR spectra were recorded in CDCl$_3$ using a Bruker Avance III spectrometer (600 and 150 MHz, respectively). UV-vis spectra were recorded using UV-Spectrophotometer SP-3000 Nano (Optima, Japan) over the wavelength range of 200 to 1100 nm. Gel permeation chromatography (GPC) measurements were carried out using a Varian Polymer PL-GPC 50 gel permeation chromatography system equipped with an RI detector and a mesopore column, employing chloroform as the eluent at a flow rate of 1.0 mL min^{-1} at 30 °C. The pressure over the column was 5.7 MPa. The average molecular weight (M_w and M_n) and polydispersity index (PDI) of the obtained polymers were determined using polystyrene (PS) standards. The total nitrogen content was determined according to the D5291 method measured on a CHN elemental analyzer.

The glass-transition temperature (T_g) of the polymers was recorded *via* the dynamic mechanical analysis (DMA) method using a PerkinElmer DMA 8000 at a heating rate of 5 °C min^{-1} from −80 °C to 25 °C.

Differential scanning calorimetry (DSC) analysis was carried out using a TA Instruments 2910 under nitrogen flow at a heating rate of 10 °C min^{-1}. The sample weighing around 3–4 mg was put in an aluminum cup with a pierced lid, and the test was carried out from 30 °C to 350 °C.

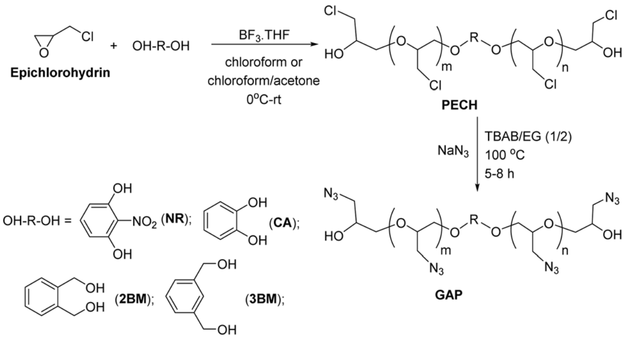
Thermogravimetric analysis (TGA) was performed using a LABSYS Evo STA Setaram instrument. Approximately 4–5 mg of the samples were used for each analysis, where the samples were heated from 30 °C to 700 °C at a heating rate of 10 °C min^{-1} under a 30 mL min^{-1} nitrogen flow.

The mechanical properties of the samples were measured using a Xilong equipment (model XL-T6T-5, China) and a hardness tester (type A, JIS, Shimadzu, Japan).

3 Results and discussion

3.1 Synthesis and characterization of glycidyl azide polymers containing aromatic diol units

Glycidyl azide polymers containing different aromatic diols (2-nitroresorcinol, 1,2-benzenedimethanol, 1,3-



Scheme 1 Synthesis of glycidyl azide polymers containing aromatic diol units.

benzenedimethanol, catechol) were successfully synthesized, as illustrated in Scheme 1. Initially, polyepichlorohydrins containing aromatic diol units were prepared by the cationic ring-opening polymerization of epichlorohydrin using aromatic diol as an initiator and borontrifluoride tetrahydrofuran (BF_3 THF) as a catalyst in chloroform at 0 °C to room temperature. Remarkably, owing to the poor solubility, the polymerization of epichlorohydrin with 1,3-benzenedimethanol was carried out in a mixture of chloroform and acetone (8 : 2, v/v). Polymerization reactions were carried out at a monomer/initiator ratio of 20 : 1 and the catalyst/initiator ratio of 0.23 to achieve a target GAP with an average molecular weight of about 2000 g mol^{-1}. The formation of polyepichlorohydrin (PECH) was confirmed by FT-IR analysis, as shown in Fig. S1. Characteristic absorption peaks were observed at 3500–3400, 2970–2868, 1190–1180 and 750–745 cm^{-1}, corresponding to OH, C–H, C–O–C, and CH_2Cl functional groups in the PECH polymer chain, respectively (Fig. 1).[24,25] There were small variations for the peaks corresponding to the aromatic ring system around 1500–1680 cm^{-1}. These polymers were obtained as yellow/dark reddish brown viscous liquids, having average molecular weights in the range of 1566–2522 g mol^{-1}, and the polydispersity index (PDI) ranged from 1.40 to 1.60 (Table S1).

The azidation of polyepichlorohydrin using sodium azide is typically carried out in *N*,*N*-dimethylformamide (DMF) or dimethylsulfoxide (DMSO) at 100 °C.[26–28] However, the limitations of this procedure include a long reaction time and difficulty in removing DMF or DMSO from GAP cleanly, as well as the requirement of organic solvents (dichloromethane, ethyl acetate) to purify GAP. Recently, Shin J. A. *et al.* reported the facile synthesis of GAP in a tetrabutylammonium bromide (TBAB) and ethylene glycol-based deep eutectic solvent (DES).[22] Their approach minimized the use of organic solvents during both the synthesis and work-up and improved product yields; moreover, DES could be recovered and reused. Applying the method of Shin *et al.*,[22] in this study, GAPs containing aromatic diol units were synthesized starting from PECH and sodium azide using a deep eutectic solvent (TBAB/EG, 1/2 mole ratio) at 100 °C for 5–8 hours. These GAPs were obtained in yields of 90–95% as yellow/dark reddish brown viscous liquids, which are soluble in most organic solvents (dichloromethane, chloroform, ethyl acetate, DMF, DMSO, *etc.*).

The conversions of the nucleophilic substitution reactions of PECHs were confirmed by FT-IR analysis. The characteristic absorption peak for PECHs was observed at 750–745 cm^{-1} based on the C–Cl stretching vibration. As the reaction progressed, the intensity of the peak C–Cl band decreased. Meanwhile, the intensity of the CH_2N_3 band at 2110–2100 and 1286–1280 cm^{-1} increased, indicating the change of chloride groups into azide groups. After 5–8 h, the peak at 750–745 cm^{-1} disappeared, showing that the reactions had been completed (Fig. 2). The hydroxyl end-groups (3500–3400 cm^{-1}) remained intact throughout and after the azidation reaction, a critical feature for the subsequent crosslinking of GAP in solid propellant matrices. Furthermore, the formation of glycidyl azide polymers was confirmed *via* UV spectral analysis. Two absorption peaks were observed at 248 and 278 nm corresponding to the resonance of nitrogen bonds of the azide group in the polymeric chains,[19,29] whereas their precursor PECHs did not show any absorbance in the UV region (Fig. 3).

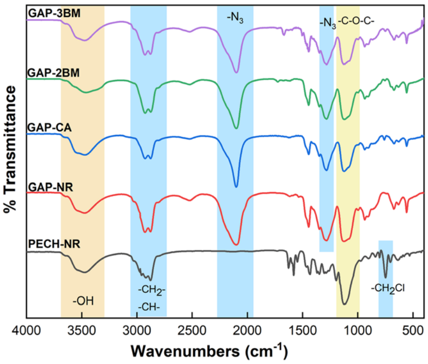


Fig. 2 IR spectra of the PECH-NR, GAP-NR, GAP-CA, GAP-2BM, and GAP-3BM polymers.

The chemical structures of the synthesized glycidyl azide polymers containing aromatic diols were identified by ^1H NMR and ^{13}C NMR spectroscopies. The signals at 3.69–3.56 ppm were assigned to the methyne and methylene protons of the polyether chain, and the signals at 3.42–3.28 ppm represented the methylene protons of azidomethyl groups. The peaks at 3.96–3.89 ppm were attributed to the hydroxyl group at the end of the chain. The signals of the aromatic protons of diol units resonated at 6.9–7.4 ppm. In the ^{13}C NMR spectrum, the characteristic resonance of the analyzed materials was as follows: 78.8–78.3 ppm (CHO), 69.7–69.2 ppm (CH_2O), 51.8–51.3 ppm (CH_2N_3), and 115–150 ppm (aromatic ring). In addition, the signals at 71.4–71.3 ppm were assigned to the methylene carbon connected to the aromatic ring in the case of GAP-2BM and GAP-3BM. The NMR spectral results were consistent with certain ref. 19, 20 and 30. The IR, UV, and NMR analyses confirmed the formation of glycidyl azide polymers containing aromatic diol units from their corresponding polyepichlorohydrins.

The GPC profiles of the synthesized polymers PECH and GAP using CA, 2BM or 3BM initiators displayed a monomodal peak, suggesting that low-molecular-weight by-products were not formed during the polymerization and azidation reactions.

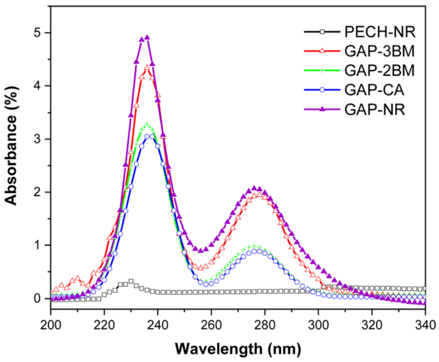


Fig. 3 UV-vis spectra of the PECH-NR, GAP-NR, GAP-CA, GAP-2BM, and GAP-3BM polymers.

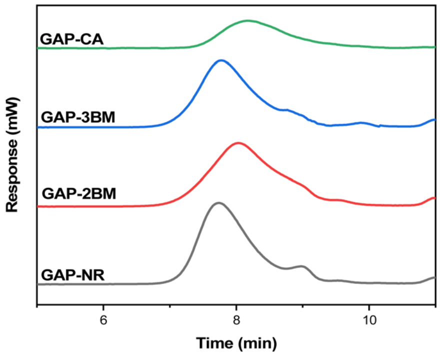


Fig. 4 GPC curves of the GAP-NR, GAP-CA, GAP-2BM, and GAP-3BM polymers in a chloroform eluent using polystyrene as the standard.

However, the GPC curve of GAP-NR showed a small peak corresponding to the formation of a low-molecular-weight by-product. This phenomenon may be attributed to the presence of the electron-withdrawing nitro group positioned between the two hydroxyl groups in the NR molecule. The inductive and mesomeric effects of the nitro groups reduced the nucleophilicity of NR, rendering its catalytic activation slightly less efficient, and subsequently generated by-products in the polymerization reaction. The GAP samples had retention time in the GPC chromatogram of about 6.42–7.10 min (Fig. 4) and comparable average molecular weights in the range of 1730–2522 g mol^{-1}, which falls within the suitable molecular weight range for energetic binder applications.[31] The polydispersity index (PDI) ranged from 1.38 to 1.80 (Table 1). As shown in Table 1, the M_n values of GAP-NR and GAP-2BM were lower than those of GAP-NR and GAP-3BM. This was likely because, in the polymerization of epichlorohydrin using diols CA and 2BM, steric hindrance arising from polyether chains at the ortho position of the benzene ring restricted the chain propagation of the resulting polymers GAP-CA and GAP-2BM.

The hydroxyl value (OHV), an important parameter indicating the polymer's functionality and capacity to cross-link with isocyanates, directly impacts the strength, flexibility, and cure properties of propellants. According to Table 1, the OHVs of GAP-NR and GAP-3BM are similar (61.2 and 60.8 mg in KOH per g), showing functionalities close to 2. Meanwhile, for polymers GAP-2BM and GAP-CA, the OHV increased to 98.1 and 98.9 mg in KOH per g, respectively, reflecting functionalities that were more than the theoretical functionality values. Besides, the nitrogen content of these glycidyl azide polymers ranged from 39.38% to 40.36% (Table 1). Apparently, the highest content found in the GAP-NR sample can be explained by the presence of nitro groups belonging to the diol unit in the polymer. The nitrogen content confirmed the high energy potential of the polymer and the efficiency of the azidation reaction.

3.2 Thermal studies of glycidyl azide polymers containing aromatic diol units

Polymeric binders play an important role in the combustion of solid propellants, and the glass-transition temperature (T_g) is a fundamental parameter of the physicochemical properties of binders that determines their in-service application.[32] The obtained single-point T_g values for the polymers suggested the homogeneity and thermodynamic compatibility of the polymer compositions.[13] The polymer with a low glass-transition temperature is beneficial for the manufacture of propellants. Meanwhile, a high glass-transition temperature may lead to brittleness when the propellant is applied at low temperatures.[33] Typically, the T_g value of a polymeric binder must be lower than the minimum service temperatures of solid rocket propellants (usually in a range of −54 °C to −40 °C, depending on the application).[34] The results of the DMA measurements are presented in Table 2. All the synthesized GAPs containing aromatic diol units possessed T_g values between −49 °C and −44.5 °C, approximately or lower than those of GAP based on ethylene glycol (−44.8 °C).[35] It can be observed that the incorporation of benzenediol or benzenedimethanol units into the GAP polyether backbone chain led to the desired plasticizing effect by lowering the T_g. Besides, GAP-NR and GAP-3BM have lower T_g values than GAP-CA and GAP-2BM. Based on the chemical structure of aromatic diol, this difference may be due to the higher flexibility of the polyether chains attached to the benzene or benzyl ring at the *meta* position compared to the chains linked at the *ortho* position, which facilitated greater segment movement within the polymer matrix. Moreover, high hydroxyl values lead to an increase in crosslinking density, resulting in an increase in the T_g.

In conjunction with a low glass-transition temperature, good thermal stability is an important characteristic of polymeric binders in the combustion of composite solid propellants. In that respect, thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) experiments were performed. The TGA thermogram of synthesized GAPs (Fig. 5) represented two major weight loss steps. The first decomposition stage started

Table 1 Yields, molecular weights, PDIs, nitrogen contents and hydroxyl value estimations of synthesized GAPs with different aromatic diol units

Entry	Sample	Yield (%)	M_n (g mol^{-1})[a]	M_w (g mol^{-1})[a]	PDI[a]	Nitrogen content (%)[b]	Hydroxyl values (OHV, mg in KOH per g)	Functionality of polymer[c]
1	GAP-NR	94	1714	2520	1.47	40.36	61.2	1.87
2	GAP-CA	92	1252	1730	1.38	39.62	98.1	2.19
3	GAP-2BM	95	1265	2040	1.61	39.38	98.9	2.23
4	GAP-3BM	90	1800	2522	1.40	39.89	61.8	1.98

[a] Determined by GPC. [b] Determined by elemental analysis. [c] Functionality of polymer = (M_n × OHV)/56 100.

Table 2 Thermal analysis of the synthesized GAPs

		TGA		DSC	
Sample	T_g (°C)	Onset decomposition temperature (°C)	Peak decomposition temperature (°C)	Peak decomposition temperature (°C)	Heat of decomposition (J g^{-1})
GAP-NR	−48.3	208.75	234.65	252.85	1949
GAP-CA	−47.1	212.59	233.81	243.03	1773
GAP-2BM	−44.5	211.39	244.62	251.60	1744
GAP-3BM	−49.0	213.84	241.12	250.96	1832

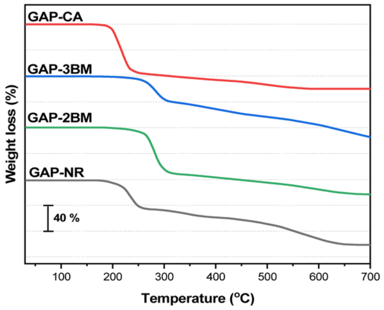


Fig. 5 TGA curves of GAPs containing different aromatic diol units.

around 210 °C and ended around 280 °C with an approximate mass weight loss of 40–45%. This stage corresponds to the typical exothermic nitrogen elimination from azido groups by intramolecular cyclization and intermolecular crosslinking, leading to the formation of acrylonitriles or imines in the polymeric chains (Scheme S1).[24,36,37] The second stage occurred between 280 °C and 450 °C, involving the decomposition of the polyether backbone. Upon reaching 600–650 °C, the decomposition is almost finished and a solid residue below 20 wt% was measured *via* TGA. There were no significant differences in the weight loss patterns among the synthesized GAPs, indicating that the different initiators did not influence their thermal decomposition behaviour. The thermal analysis of these polymers is detailed in Table 2.

The DSC curves of GAPs (Fig. 6) showed similar decomposition behavior compared to pure GAP with a single strongly exothermic peak.[24,25] This exothermic peak is caused by the elimination of nitrogen from the azido groups in the polymer chain. As shown in Table 2, the peak decomposition temperatures of the synthesized polymers were slightly higher than that of pure GAP.[25] This thermal behavior might be explained by the presence of aromatic diol units restricting the mobility of the polymer main chains and the azide pendant groups, requiring higher temperatures to initiate degradation.[19] Furthermore, heat of decomposition in this stage were recorded in the ranging from 1744 to 1949 J g^{-1} (Table 1), meanwhile pure GAP had the heat of decomposition of about 1828 J g^{-1},[25] pointing that the beneficial values of aromatic diol units in the polymer chains. The enthalpy of the first decomposition step depends on the number of azido groups in the polymer and is therefore proportional to the nitrogen content. Obviously, GAP-NR exhibited the highest value of heat of decomposition (1949 J g^{-1}), which is ascribed to the presence of an energetic functional nitro group in the aromatic diol units.

The thermal analysis confirmed that the GAP binders exhibited consistent thermal degradation and exothermic energy release behaviour.

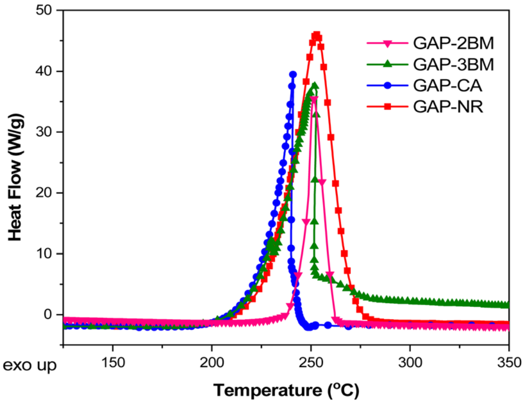
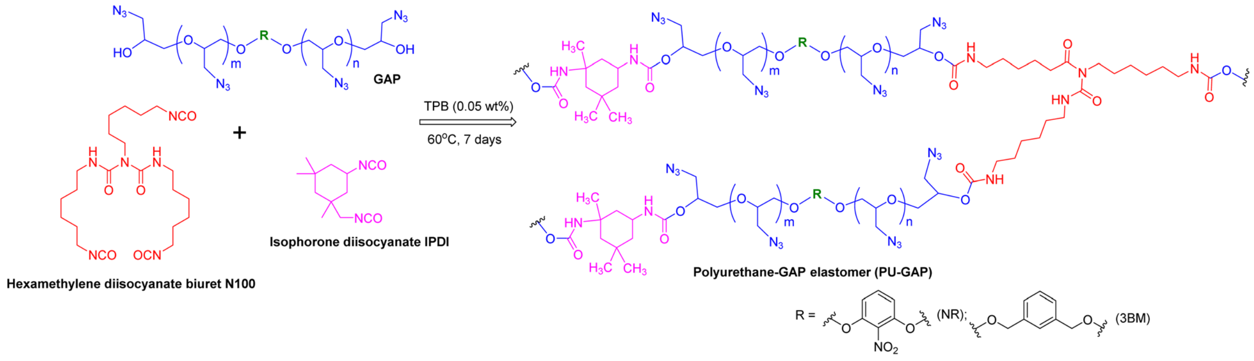


Fig. 6 DSC curves of GAP-NR, GAP-CA, GAP-2BM, and GAP-3BM.

3.3 Synthesis and characterization of polyurethane-GAP elastomers

Similar to HTPB, GAPs need to be cured to improve their mechanical properties and render them suitable as propellant binders. So far, the most important curing method for GAPs is treatment with aromatic or aliphatic multifunctional isocyanates to form three-dimensional crosslinked polyurethane networks.[38,39] Choosing an appropriate curing agent is one of the main factors affecting the mechanical and thermal properties of the polyurethane matrix. Non-volatile isocyanates, such as hexamethylene diisocyanate biuret (Desmodur N100), isophorone diisocyanate (IPDI), and Desmodur N3300, are preferable because of their low toxicity and decreased reactivity, allowing for an adequate pot-life and concomitant propellant processing. Among these isocyanates, a dual curing system N100/IPDI at a 1 : 1 ratio is typically employed in order to adjust chain extending and crosslinking reactions during the curing process.[40] With the characterized samples available, the two potential polymers GAP-NR and GAP-3BM, exhibiting the highest decomposition energy and lowest glass-transition temperatures, were chosen for curing, and their mechanical properties were evaluated. The curing process was carried out with an equivalence ratio R = [NCO]/[OH] ranging from 0.9 to



Scheme 2 Synthesis route of polyurethane-GAP elastomers.

1.5 in the presence of 0.05 wt% catalyst triphenyl bismuth (TPB) relative to the GAP. The schematic of this reaction is shown in Scheme 2. The structures of the copolyurethane elastomers were characterized by FTIR spectroscopy. As shown in Fig. 7, the broad absorption band related to the hydroxyl terminals of GAP-NR and GAP-3BM at 3500–3400 cm^{-1}, as well as the characteristic peak of isocyanate groups (N=C=O) at 2270 cm^{-1}, disappeared. The characteristic absorption peaks of polyurethane were observed at 3338–3342 cm^{-1}, 1700–1690 cm^{-1} and 770–760 cm^{-1}, corresponding to –NH stretching, C=O stretching and C–N–H bending vibration, respectively, indicating that the cross-linking reaction was completed.[13,36,41]

3.4 Mechanical properties of polyurethane-GAP elastomers

The mechanical properties of the polymeric network are known to be strongly dependent on the structure of the elastic network. To study the influence of the elastomer network on the mechanical properties, a series of uniaxial tensile tests was carried out on elastomers PU-GAP-NR and PU-GAP-3BM at room temperature. Fig. 8 shows the tensile properties at different curing ratios ([NCO]/[OH]). In general, the tensile strength and Shore A hardness of these elastomers gradually increased with an increase in the *R* value from 0.9 to 1.4 and then decreased until the *R* value continuously increased up to 1.5. Meanwhile, the elongation at break for both elastomers exhibited a decreasing trend with an increase in the *R* value from 0.9 to 1.5. As the [NCO]/[OH] ratio of the composites increased to 1.5, the significant excess NCO groups remaining in the cross-linked network might form allophanate cross-linked moieties and can

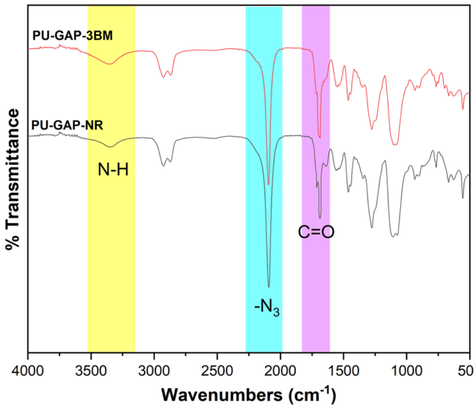


Fig. 7 FTIR spectra of the PU-GAP-NR and PU-GAP-3BM elastomers.

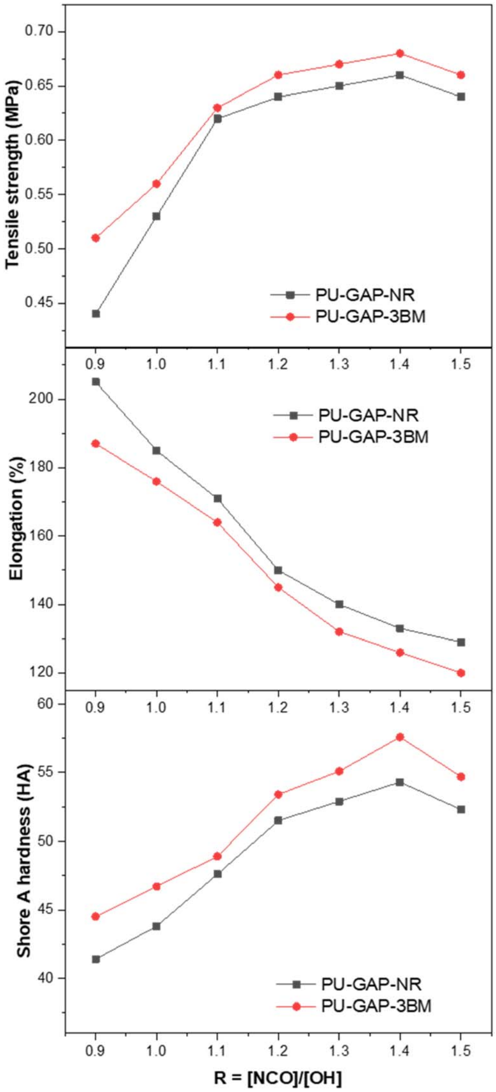


Fig. 8 Mechanical properties of polyurethane-GAP elastomers.

react with moisture, causing the material to become porous and phase-separated, leading to reduced mechanical properties.[42]

In all cases, PU-GAP-3BM elastomers showed higher tensile strength and Shore A hardness values but lower elongation at break values than those of PU-GAP-NR elastomers. We believed that the presence of sterically unhindered 1,3-benzenedimethanol units and the higher OHV of GAP-3BM led to an enhanced degree of crosslinking, which restricted the extensibility of the polyurethane network. In summary, the PU-GAP-NR and PU-GAP-3BM elastomers (curing ratio $R = 1.2$) achieved the best mechanical properties with a tensile strength of 0.64–0.66 MPa, an elongation at break of 150–145% and a Shore A hardness of 51.5–53.4 HA. These results revealed that the PU-GAP-NR and PU-GAP-3BM elastomers exhibited mechanical properties comparable to or slightly better than those of conventional GAPs.[13,21,40] The presence of rigid aromatic rings within the polymer backbone facilitates the formation of a more robust polyurethane network compared to flexible linear diols. The elastomers prepared at a curing ratio of 1.2 were chosen for further investigation.

3.5 Dynamic mechanical analysis of polyurethane-GAP elastomers

The storage modulus of polyurethane-GAP elastomers (curing ratio $R = 1.2$), measured *via* DMA, is shown in Fig. 9A. Both samples displayed a clear transition from the glassy to the rubbery state, marked by a decrease in storage modulus. At low temperatures (under −45 °C), all the copolyurethane networks were in the glassy state with an E' value of approximately 1000 MPa. The onset temperature of PU-GAP-3BM is slightly higher (T_{onset} about −39.8 °C) than that of PU-GAP-NR (T_{onset} about −43.5 °C), suggesting that as the polymer functionality increased, GAP binders can maintain their glassy moduli at higher temperatures.[21] The storage modulus values of these samples gradually decreased with an increase in temperature, and a rapid decrease was observed near the glass-transition temperature. At high temperatures (from −20 °C), the storage modulus of both samples reached a rubbery plateau. Fig. 9B shows the loss factor (tan δ) curves of the PU-GAP-NR and PU-GAP-3BM elastomers. It could be seen that both elastomers exhibited only one loss factor peak corresponding to the glass transition temperature (T_g), indicating the homogeneous nature of copolyurethane networks. Moreover, the curing process caused a further increase in the glass transition temperatures of both synthesized elastomers.[35] The PU-GAP-3BM elastomer recorded a higher T_g (−23.3 °C) than the PU-GAP-NR elastomer (−29.5 °C). This behavior might be attributed to the polyether chains attached to the sterically unhindered 1,3-benzenedimethyl core in GAP-3BM, which promoted the more complete and rigid network of the PU-GAP-3BM elastomer, leading to an increase in its T_g.[21]

3.6 Thermal stability analysis of polyurethane-GAP elastomers

It is necessary to understand the thermal properties of the obtained elastomers as they are important parameters that

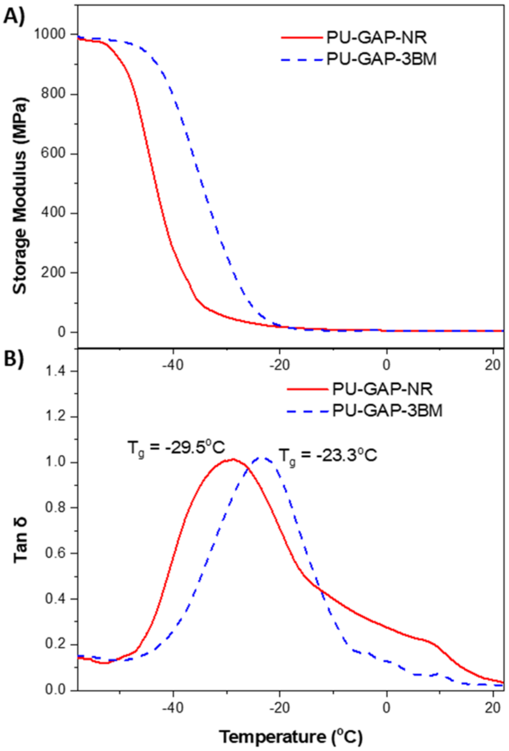


Fig. 9 Storage modulus (A) and tan δ (B) curves of polyurethane-GAP elastomers ([NCO]/[OH] value = 1.2).

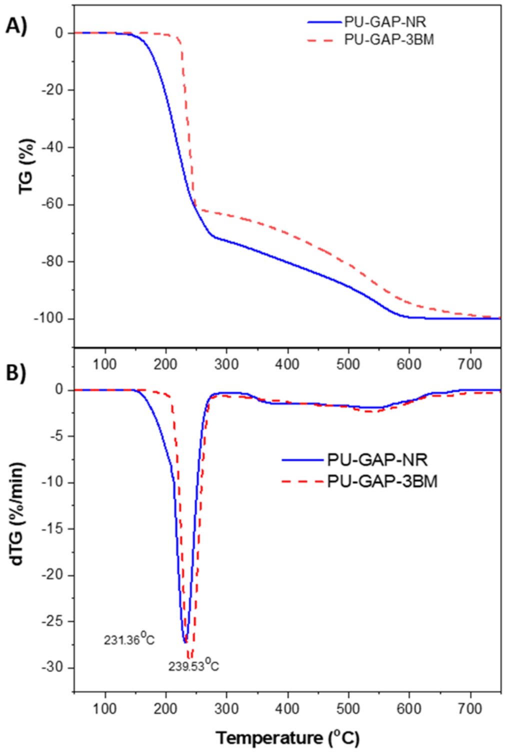


Fig. 10 TG (A) and dTG (B) curves of polyurethane-GAP elastomers ([NCO]/[OH] value = 1.2).

indicate the application potential of these materials. In the TG-dTG analysis (Fig. 10), a two-step degradation behavior was observed. For the PU-GAP-3BM elastomer, the first-stage weight loss of 64% was observed between 179.82 °C and 296.49 °C with a peak of 239.53 °C, resulting from the main breakage of the polyether backbone. The second-step weight loss of 36% was observed between 300 °C and 750 °C, with a peak of 532.91 °C on account of the carbamate and part of the hard segment molecular chain. For the elastomer prepared using prepolymer GAP-NR, the max decomposition temperatures were recorded at 231.36 °C and 545.35 °C with an approximate mass weight loss of 70% and 30%, respectively. The maximum decomposition temperatures ($T_{\max}$) of these elastomers were slightly lower than those of the prepolymers of GAPs, which could be due to the reduction in the density of azide in the molecules upon the grafting of diisocyanates.[35]

4 Conclusions

In summary, a special category of glycidyl azide polymers, containing different aromatic diol units (2-nitroresorcinol, catechol, 1,2-benzenedimethanol, 1,3-benzenedimethanol), was successfully synthesized through the cationic ring-opening polymerization of epichlorohydrin, followed by azidation with sodium azide in a TBAB/EG solvent. The synthesized GAPs exhibited comparable average molecular weights in the range of 1730–2522 g mol^{-1} with hydroxy values ranging from 60.8 to 98.9 mg in KOH per g. All the synthesized GAPs showed slightly lower glass-transition temperatures (−49.0 °C to −44.5 °C) and higher heat of decomposition (up to 1949 J g^{-1}) than conventional GAPs. Their thermal stability was studied, and a similar behavior at a decomposition point of 243–253 °C was observed. The polyurethane elastomers PU-GAP-NR and PU-GAP-3BM were prepared and characterized *via* FTIR spectroscopy and tensile tests. According to the mechanical analysis, $R = 1.2$ was the optimal curing ratio, at which the PU-GAP-NR and PU-GAP-3BM elastomers achieved better mechanical properties (tensile strength = 0.64–0.66 MPa, elongation at break = 150–145% and Shore A hardness = 51.5–53.4 HA). TGA and DMA measurements revealed that these PU-GAP elastomers exhibited thermal stability and acceptable glass-transition temperatures (−29.5 °C to −23.3 °C). All the above analyses revealed that GAP-NR and GAP-3BM can be considered as potential energetic binders for the composite propellant.

Author contributions

Giang Le-Nhat-Thuy: methodology, investigation, data curation, conceptualization, project administration, writing – original draft, review & editing. Dang Thi Tuyet Anh: investigation: characterization of polymers. Vu Quang Hung: methodology, investigation, characterizations of polymers, formal analysis. Hoang Thi Phuong: Investigation: synthesis of polymers. Nguyen Ha Thanh: investigation: synthesis of polymers. Nguyen Thi Quynh Giang: investigation: synthesis of polymers. Nguyen Tuan Anh: investigation: preparation of elastomers. Dang Thi Mai: investigation: preparation of elastomers. Nguyen Van Tuyen: methodology, conceptualization.

Conflicts of interest

There are no conflicts of interest to declare.

Data availability

The datasets supporting this article have been uploaded as part of the supplementary information (SI). Supplementary information is available. See DOI: https://doi.org/10.1039/d6ra00798h.

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