

Synthesis and Characterization of Energetic Thermoplastic Elastomers based on Carboxylated GAP Copolymers

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Abstract

Energetic thermoplastic elastomers (ETPEs) based on glycidyl azide polymer (GAP) and carboxylated GA copolymers [GAP-ETPE and poly(GA-carboxylate)-ETPEs] were synthesized using isophorone diisocyanate (IPDI), dibutyltin dilaurate (DBTDL), 1,4-butanediol (1,4-BD), and soft segment oligomers such as GAP and poly(GA-carboxylate). The synthesized GAP-ETPE and poly(GA-carboxylate)-ETPEs were characterized by Fourier transform infrared (FT-IR), gel permeation chromatography (GPC), thermogravimetric analysis (TGA), differential scanning calorimetry (DSC), universal testing machine (UTM), calorimetry and sensitivity towards friction and impact. DSC and TGA results showed that the introduction of carboxylate group in GAP helped to have better thermal properties. Glass transition temperatures of poly(GA-carboxylate)-ETPEs decreased from -31 °C to -33 °C compared to that of GAP-ETPE (-29 °C). The first thermal decomposition temperature in poly(GA_{0.8}-octanoate_{0.2})-ETPE (242 °C) increased in comparison to that of GAP-ETPE (227 °C). Furthermore, from calorimetry data, poly(GA-carboxylate)-ETPEs exhibited negative formation enthalpies (-6.94 and -7.21 kJ/g) and higher heats of combustion (46713 and 46587 kJ/mol) compared to that of GAP-ETPE (42,262 kJ/mol). Overall, poly(GA-carboxylate)-ETPEs could be good candidates for a polymeric binder in solid propellant due to better energetic, mechanical and thermal properties in comparison to those of GAP-ETPE. Such properties are beneficial to application and processing of ETPE.

Keywords: Solid propellant, Glycidyl azide polymer, GAP copolymer, Carboxylated GAP, Energetic thermoplastic elastomer

1. Introduction

The polymeric binders play an important role in solid propellants because it determines the shape and structural integrity of the propellants[1,2]. A variety of polymeric binders have been used to solid propellants. In the past, inert polymers such as hydroxy-terminated polybutadiene (HTPB), cellulose acetate butyrate (CAB) and Estane[®] have been used as polymeric binders[3,4]. These polymeric binders are cross-linked by chemical curing and cross-linking agents[5,6]. However, these inert binders have some drawbacks such as disposal, high mix viscosity and vulnerability to unplanned detonation[7,8]. To solve the problems, thermoplastic elastomers (TPEs) have attracted attention for

binder applications.

TPEs are consisting of short, glassy or crystalline hard segments and long, amorphous soft segments[9]. Hard segments such as polyurethane and polyester provide mechanical strength[10]. Soft segments such as polyether and macroglycol are flexible and elastomeric components [11,12]. Therefore, the microphase separation occurs between the two segment types because hard segments have reversible hydrogen bonding, while soft segments exhibit less interaction with each other and immiscible with hard segments[5,13]. In addition, above the melting or glass temperature of the hard segments, the physical crosslinks of hard segments are broken, allowing the TPEs to be mixed with other components and act like a thermoplastic, while TPEs behave like cross-linked elastomers at room temperatures[14]. The reversible physical crosslinks make it possible to recycle the TPEs, thereby solving the disposal problems of conventional crosslinked binders[15].

The mechanical and physical properties of TPEs such as hardness, stiffness and tensile strength are affected by type of chain extender, macroglycol and isocyanate, the degree of phase separation between hard and soft segments, hard to soft segment ratio as well as the conditions of synthesis reaction[16]. However, the TPEs based on inert polymers reduce the output energy and overall performance of an energetic formulation[17]. Therefore, these inert polymeric binders are

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being replaced with new energetic polymeric binders such as glycidyl azide polymer (GAP), poly[3,3-bis(3-azidomethyl)oxetane] [poly(BAMO)], and poly[(3-azidomethyl)methyloxetane] [poly(AMMO)] [18-20]. Among them, GAP contains azide groups as the energetic pendant groups that release heat due to the scission of the $-N_3$ bond structure to form N_2 [21]. In addition, it has increased performance at low oxidizer loading, low vulnerability, high energy, high specific impulse, and high burning rate [22,23]. Furthermore, GAP has chlorine-free propellant plumes with ammonium nitrate, which can avoid environmental pollution [18]. Thereby, GAP-based energetic thermoplastic elastomers (GAP-ETPEs) have been studied as solid propellant applications [24].

However, GAP-ETPEs and GAP have poor low-temperature characteristics due to the presence of bulky and polar azide groups decreasing a flexibility of the backbone [25]. To improve these drawbacks, we have introduced some nucleophiles like long-chain carboxylates (butyrate, octanoate, 2-ethyl hexanoate, isononanoate, decanoate) in the GAP copolymers [poly(GA-carboxylate)] [18]. As a result, poly(GA-carboxylate) compounds exhibited better properties in comparison to GAP as a polymeric binder for solid propellants in terms of their energy and thermal properties.

Therefore, in the present work, our group selected poly(GA_{0.7}-butyrate_{0.3}) and poly(GA_{0.8}-octanoate_{0.2}) as prepolymers of ETPEs based on poly(GA-carboxylate) and synthesized poly(GA-carboxylate)-ETPEs to expect improvement of thermal properties of GAP-ETPEs as GAP copolymers. These poly(GA-carboxylate)-ETPEs are analyzed by Fourier transform infrared (FTIR), differential scanning calorimetry (DSC), gel permeation chromatography (GPC), friction and impact sensitivity, universal testing machine (UTM), calorimetry, and thermogravimetric analysis (TGA) in this paper.

2. Materials and Methods

2.1. Materials

Glycidyl azide polymer (GAP, $M_n = 1853$ g/mol) was supplied by J. CHEM. Inc. Poly(GA_{0.7}-butyrate_{0.3}) ($M_n = 2401$ g/mol) and poly(GA_{0.8}-octanoate_{0.2}) ($M_n = 2445$ g/mol) were synthesized as our previous publication [18]. Other chemicals such as isophorone diisocyanate (IPDI), 1,4-butanediol (1,4-BD), dibutyltin dilaurate (DBTDL) and ethyl acetate were purchased from Sigma Aldrich, and were used without further purification, unless specifically mentioned.

2.2. Synthesis of GAP-ETPE and poly(GA-carboxylate)-ETPEs (1-3)

GAP-ETPE and poly(GA-carboxylate)-ETPEs (1-3) were synthesized with isophorone diisocyanate (IPDI) and 1,4-butanediol (1,4-BD) by the solution polymerization in ethyl acetate. The synthetic process is presented in Scheme 1. Table 1 show the composition and molar ratio of GAP copolymers, IPDI, and 1,4-BD for the synthesis of GAP-ETPE and poly(GA-carboxylate)-ETPEs (1-3), respectively. GAP (0.1 mol) or poly(GA-carboxylate) (0.1 mol) dissolved in ethyl acetate (200 g) was added in a 2 L reactor equipped with a mechanical stirrer at room temperature. Dibutyltin dilaurate (DBTDL) as catalyst, IPDI and ethyl acetate (100 g) were added to the reaction mixture and stirred at 70

°C for 2 h. After that, the mixture was cooled as low as 60 °C and 1,4-BD as chain extender and ethyl acetate (500 g) were added to the reaction mixture. The completion of the reaction for each step was monitored by FTIR through the disappearance of the absorption band of -OH in diol and -NCO groups in diisocyanate at 3450 and 2270 cm^{-1} . Then, ethyl acetate was evaporated at 50 °C in Petri dish for film casting. The films of GAP-ETPE and poly(GA-carboxylate)-ETPEs (1-3) were analyzed by DSC, TGA, GPC, FTIR, and UTM.

2.3. Characterization

FTIR spectra were taken at room temperature with Alpha FTIR spectrometer from Bruker operating at a resolution of 4 cm^{-1} with scan number 24. Infrared measurements with a diamond ATR accessory were performed within the range 400–4000 cm^{-1} . The friction and impact sensitivity were determined according to MIL-STD-1751A, department of defense test method standards. The impact sensitivity was measured by NATO STANAG 4489. The friction sensitivity measurements were conducted using NATO STANAG 4487. The friction sensitivity apparatus utilizes a fixed porcelain pin and a movable porcelain plate that executes a reciprocating motion with an applied force varying from 5 to 360 N. The impact sensitivity was measured by NATO STANAG 4489.

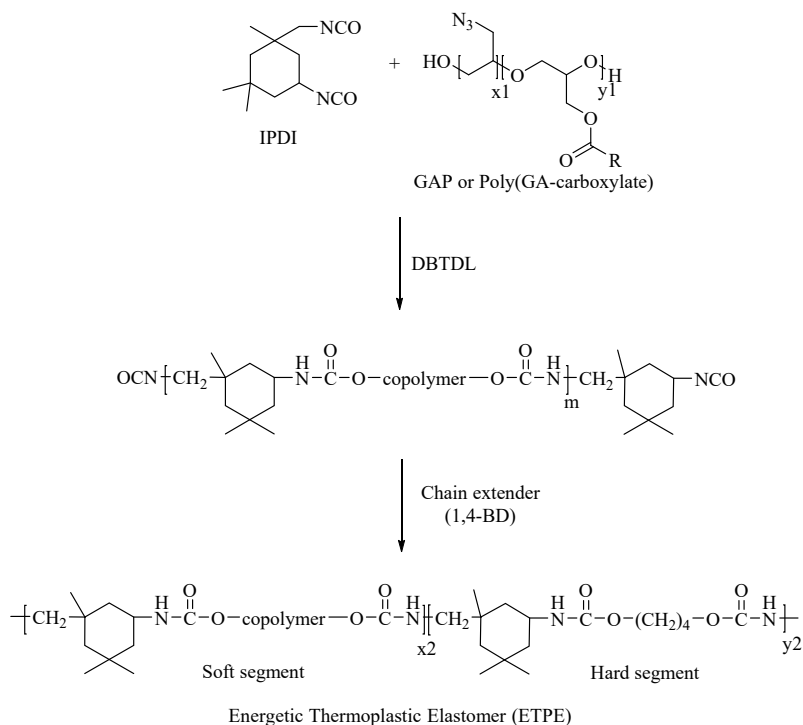
The thermal properties of polymers were analyzed by TGA and DSC. DSC was performed on a TA instruments DSC Q100 V8.2 Build 268 using aluminum pans at the heating rate of 5 °C/min under nitrogen flow, in the temperature range -90 °C to 100 °C. TGA was performed on a PERKIN ELMER TGA Q500 V6.2 Build 187 under nitrogen atmosphere using a heat rate of 3 °C/min, in the range room temperature to 500 °C. The molecular weights and molecular weight distribution of the materials were determined by GPC. GPC was performed on a WATERS 515, with the flow rate of 1.0 mL/min, using THF as the flow solvent. The heat of combustion was determined by the Parr Bomb Calorimeter 6200.

3. Results and Discussion

3.1. Synthesis and characterization of GAP-ETPE and poly(GA-carboxylate)-ETPEs (1-3)

As shown in Scheme 1, GAP-ETPE and poly(GA-carboxylate)-ETPEs (1-3) were synthesized by two step process called the 'prepolymer' method. Firstly, the prepolymer was produced by the reaction with IPDI, soft segment oligomers such as GAP and poly(GA-carboxylate) and DBTDL as catalyst. In the second step, GAP-ETPE and poly(GA-carboxylate)-ETPEs (1-3) were synthesized by the reaction with the prepolymer and 1,4-BD as chain extender.

The completion of the reaction for each step was monitored by FTIR. As the first step of reaction was completed, the absorption band of -OH groups in soft segment oligomers at 3450 cm^{-1} disappear, and N-H stretching band of urethane group at 3325 cm^{-1} and C=O stretching band of the urethane and ester groups at 1699 cm^{-1} were increased, while the absorption band of -NCO groups in diisocyanate at 2270 cm^{-1} decreased. After the completion of the final step in the reaction,



Scheme 1. The synthetic process of GAP-ETPE and poly(GA-carboxylate)-ETPEs (1-3).

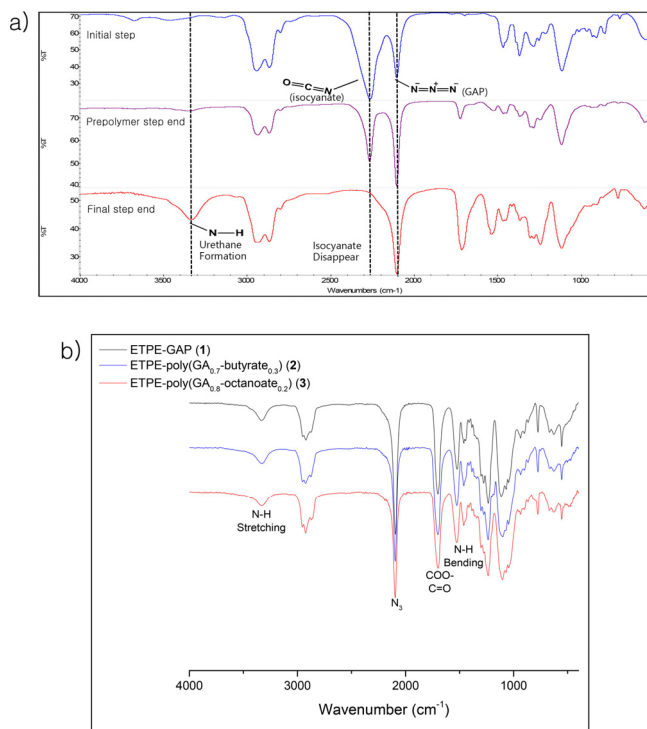


Figure 1. (a) FTIR spectra of GAP-ETPE according to reaction step (b) FTIR spectra of GAP-ETPE and Poly(GA-carboxylate)-ETPEs (1-3).

GAP-ETPE (1) did not reveal the absorption band of -NCO groups at 2270 cm^{-1} as shown Figure 1(a). Therefore, the completion of the reaction for each step was monitored by FTIR. Based on the reaction

condition of GAP-ETPE, the reactions of poly(GA-carboxylate)-ETPE proceeded, and IR spectrum after completion of the reaction was shown in Figure 1(b).

The structures of GAP-ETPE and poly(GA-carboxylate)-ETPEs (1-3) were identified by their FTIR spectra (Figure 1). N-H stretching band of urethane group at 3325 cm^{-1} and C=O stretching band of the urethane and ester groups at 1699 cm^{-1} were observed in GAP-ETPE and poly(GA-carboxylate)-ETPEs (1-3). Also, N-H bending band of the urethane group was revealed at 1524 cm^{-1} . The absorption bands at 2095 and 1236 cm^{-1} were attributed to azide N=N=N stretching band and C-O stretching band of the ester group. In addition, the GAP-ETPE and poly(GA-carboxylate)-ETPEs (1-3) have similar FTIR spectra.

3.2. Thermal properties

3.2.1. DSC thermograms

For the easy handling of ETPEs at low temperature, it would be better to have the lower glass transition temperatures (T_g). As mentioned earlier, our group introduced poly(GA-carboxylate) moiety into poly(GA-carboxylate)-ETPEs (2-3) to improve the thermal properties of GAP-ETPE (1). Thermal properties of GAP-ETPE and poly(GA-carboxylate)-ETPEs (1-3) were determined by differential scanning calorimetry (DSC) and were summarized in Table 1. Figure 2(a) shows the DSC thermograms of GAP-ETPE and poly(GA-carboxylate)-ETPEs (1-3). GAP-ETPE (1), poly(GA_{0.7}-butyratē_{0.3})-ETPE (2) and poly(GA_{0.8}-octanoatē_{0.2})-ETPE (3) have T_g at -29 , -31 , and $-33\text{ }^\circ\text{C}$, respectively [Figure 2(a)]. It indicates T_g of soft segments show at low temperatures, while T_g of hard segments do not show under $100\text{ }^\circ\text{C}$.

Among them, GAP-ETPE (1) revealed the highest T_g at $-29\text{ }^\circ\text{C}$. In

Table 1. Composition and Thermal Properties of GAP-ETPE and Poly(GA-carboxylate)-ETPEs (1-3)

Composition	Copolymer : IPDI : 1,4-BD molar ratio	HS (wt%)	M _w (10 ³ g/mol) ^a	T _g (°C) ^b	T _{dec} (°C) ^c
GAP-ETPE (1)	1.0 : 6.0 : 4.8	40	146	-29	227
Poly(GA _{0.7} -butyrate _{0.3})-ETPE (2)	1.0 : 6.0 : 4.8	40	10	-31	227
Poly(GA _{0.8} -octanoate _{0.2})-ETPE (3)	1.0 : 8.6 : 8.1	40	70	-33	242

^a Determined by GPC, ^b measured by DSC, ^c measured by TGA.

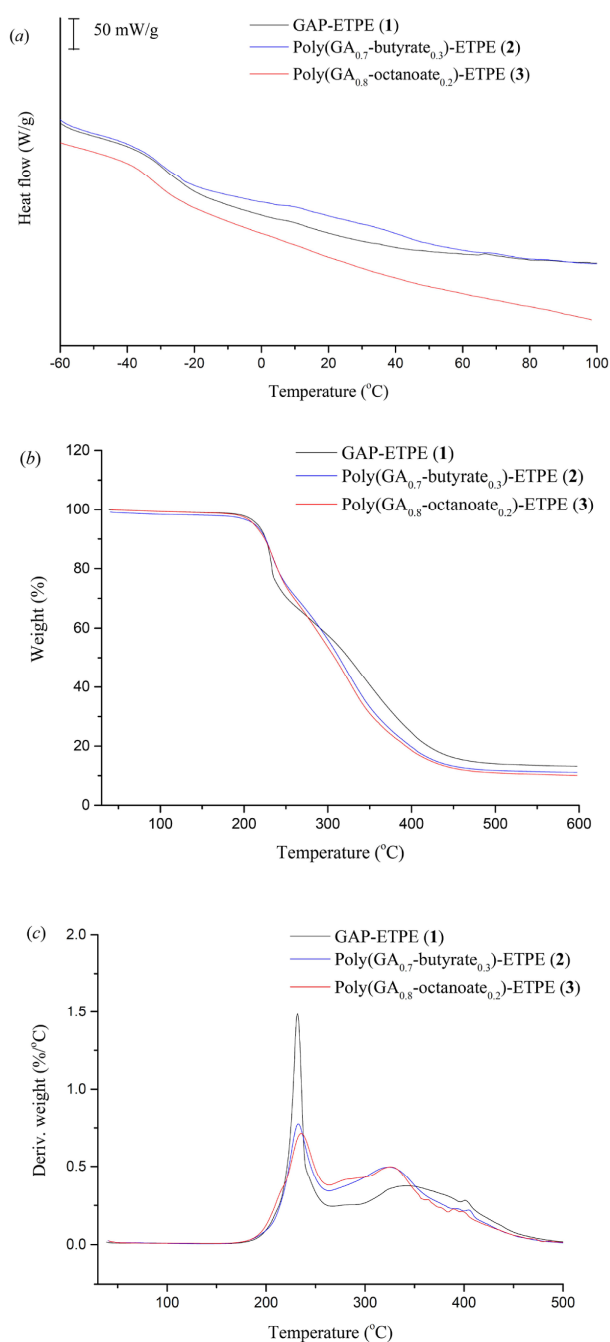


Figure 2. (a) DSC curves of GAP-ETPE and poly(GA-carboxylate)-ETPEs (1-3) (b) TGA curves of GAP-ETPE and poly(GA-carboxylate)-ETPEs (1-3) (c) DTG curves of GAP-ETPE and poly(GA-carboxylate)-ETPEs (1-3).

other poly(GA-carboxylate)-ETPEs (2, 3), the glass transition temperatures were lower than GAP-ETPE (1) that is a characteristic of a micro-phase-separated ETPE by the longer non-polar alkyl chain. It suggested that the soft segments of poly(GA-carboxylate)-ETPEs (2, 3) moved more freely than that in GAP-ETPE (1). In addition, the longer alkyl chain of carboxylate group, the more decrease the glass transition temperatures of poly(GA-carboxylate)-ETPEs (2, 3). Therefore, poly(GA_{0.8}-octanoate_{0.2})-ETPE (3) revealed the lowest glass transition temperature (-33 °C) because it has the longest alkyl chain among them.

In previous publication, poly(GA_{0.7}-butyrat_{0.3}) and poly(GA_{0.8}-octanoate_{0.2}) have T_g at -51 and -55 °C, while GAP has higher T_g at -49 °C. Therefore, poly(GA-carboxylate) compounds exhibited better properties in comparison to GAP as a polymeric binder for solid propellants in terms of thermal properties[18].

In the present work, T_g of poly(GA-carboxylate)-ETPEs (2-3) decrease in comparison to GAP, that is a general phenomenon observed in ETPE.

3.2.2. TGA thermograms

Thermal decomposition temperatures (T_{dec}) is important property of polymeric binders in solid propellants because of safety, thermal stability and performance predictions. Therefore, the T_{dec} of GAP-ETPE and poly(GA-carboxylate)-ETPEs (1-3) were measured by thermogravimetric analysis (TGA) for the estimation of their thermal stability (Table 1).

As shown in Figure 2(b), GAP-ETPE and poly(GA-carboxylate)-ETPEs (1-3) were decomposed by two exothermic decomposition steps. The first weight loss steps of GAP-ETPE and poly(GA-carboxylate)-ETPEs (1-3) resulted from the decomposition of the azide group in the soft segments with the release of nitrogen gas at 227–242 °C. The second weight loss steps were attributed to the polyurethane segments, the polyether main chain of GAP and poly(GA-carboxylate), and the ester groups at 284–334 °C [23].

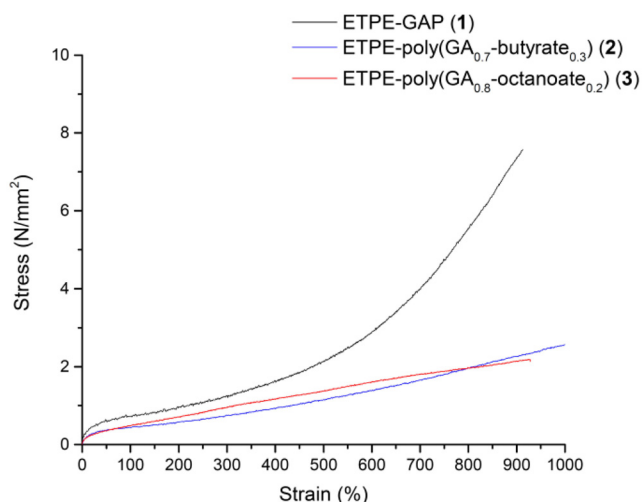
Figure 2(b) and Figure 2(c) shows the TGA thermograms and DTG thermograms of GAP-ETPE and poly(GA-carboxylate)-ETPEs, respectively (1-3). Especially, the first exothermic decomposition of poly(GA_{0.8}-octanoate_{0.2})-ETPE (3) starts at 242 °C. It indicates that poly(GA_{0.8}-octanoate_{0.2})-ETPE (3) is thermally stable up to this temperature, which is the highest first decomposition temperature of all compounds. Therefore, it is more stable than GAP-ETPE and poly(GA_{0.7}-butyrat_{0.3})-ETPE (1, 2) in terms of thermal stability. As a result, poly(GA_{0.8}-octanoate_{0.2})-ETPE (3) have better processability in comparison to the GAP-ETPE (1).

Table 2. Elastic Modulus and Elongation at Break Point of GAP-ETPE and Poly(GA-carboxylate)-ETPEs (1-3)

	GAP-ETPE (1)	Poly(GA _{0.7} -butyrate _{0.3})-ETPE (2)	Poly(GA _{0.8} -octanoate _{0.2})-ETPE (3)
100% modulus (N/mm ²)	0.76	0.40	0.49
300% modulus (N/mm ²)	1.24	0.69	0.96
Elongation at break (%)	910	>1000	920

Table 3. Friction and Impact Sensitivities of GAP-ETPE and Poly(GA-carboxylate)-ETPEs (1-3)

	GAP-ETPE (1)	Poly(GA _{0.7} -butyrate _{0.3})-ETPE (2)	Poly(GA _{0.8} -octanoate _{0.2})-ETPE (3)
Friction sensitivity (N)	> 360	> 360	> 360
Impact sensitivity (J)	50	50	30.7

**Figure 3. Stress-strain curves of GAP-ETPE and poly(GA-carboxylate)-ETPEs (1-3).**

3.3. Tensile modulus and breaking elongation at break

The mechanical properties of propellants are determined by the mechanical properties of ETPEs. In this study, the tensile strength and breaking elongation at break were measured for the mechanical properties of GAP-ETPE and poly(GA-carboxylate)-ETPEs (1-3) using universal testing machine (UTM). 100% modulus, 300% modulus and breaking elongation at break of the GAP-ETPE and poly(GA-carboxylate)-ETPEs (1-3) are presented in Table 2 and the stress-strain curves of them in Figure 3.

GAP-ETPE (1) has 0.76 N/mm² at 100% modulus, 1.24 N/mm² at 300% modulus and tensile elongation at break point was 910%. In other poly(GA-carboxylate)-ETPEs (2, 3) have 0.4~0.49 N/mm² at 100% modulus, 0.69~0.96 N/mm² at 300% modulus and tensile elongation at break point over 920%. With the introduction of carboxylated GAP copolymer, the elastic modulus of poly(GA-carboxylate)-ETPEs (2, 3) decreased and tensile elongation at break point increased in comparison to GAP-ETPE (1). It results from a microphase separation in ETPE between soft and hard segments. The long non-polar alkyl chain of carboxylate in soft segments enhance immiscibility with hard segments. Therefore, the elastic modulus of poly(GA-carboxylate)-ETPEs (2, 3) decreased as the soft segments of poly(GA-carboxylate)-ETPEs (2, 3)

moved more freely than that in GAP-ETPE (1). This property makes it easier to handle the reaction in processing owing to better elastic mechanical properties.

3.4. Energy properties

3.4.1. Sensitivity

The impact and friction sensitivity is an important property of polymeric binders that determines their application. The friction and impact sensitivities were measured by NATO STANAG 4487 and NATO STANAG 4489, respectively. As shown in Table 3, GAP-ETPE and poly(carboxylate)-ETPEs (1-3) were insensitive to friction (> 360 N). Also, GAP-ETPE (1) and poly(GA_{0.7}-butyrate_{0.3})-ETPE (2) have the same friction and impact sensitivity. However, poly(GA_{0.8}-octanoate_{0.2})-ETPE (3) have lower impact sensitivity than GAP-ETPE (1). Therefore, poly(GA-carboxylate)-ETPEs (2, 3) as a polymeric binder in solid propellants revealed similar or lower sensitivity with GAP-ETPE (1).

3.4.2. Heats of combustion and formation

The energies of combustion (ΔU_{comb}) of GAP-ETPE and poly(GA-carboxylate)-ETPE (1-3) were determined by a Parr Bomb Calorimeter 6200. Then, the combustion enthalpies (ΔH_{comb}) were calculated at 25 °C by using the combustion energies [$\Delta H_{\text{comb}} = \Delta U_{\text{comb}} + \Delta nRT$, $\Delta n = \Delta n_{\text{i}}$ (product, g) - Δn_{i} (reactant, g)]. The enthalpies of formation ($\Delta_f H^\circ$) can be obtained by using the following equation: $\Delta_f H^\circ$ (ETPE) = $a\Delta_f H^\circ(\text{CO}_2) + 0.5b\Delta_f H^\circ(\text{H}_2\text{O}) - \Delta_c H^\circ(\text{ETPE})$ (for the composition C_aH_bN_cO_d). It is based on the Hess thermochemical cycle at 25 °C with the combustion reactions of the repeating unit. Herein, the heat of formation of H₂O (L) is -286 kJ/mol, and for CO₂ (g), is -394 kJ/mol [26].

Firstly, the enthalpies of formation of GAP-ETPE and poly(GA-carboxylate)-ETPEs (1-3) are negative because contributions of CO₂ and H₂O terms in the equation of the enthalpies of formation increase beyond the $\Delta_f H^\circ$ term[27]. The negative formation enthalpies of GAP-ETPE and poly(GA-carboxylate)-ETPEs (1-3) indicate formations of products are thermodynamically favorable. In addition, the combustion enthalpies are always negative because combustion is an exothermic reaction (Table 4). A comparison of the combustion enthalpies show that poly(GA-carboxylate)-ETPEs (2, 3) have more negative values than GAP-ETPE (1) because they have larger repeating units

Table 4. Energetic Characteristics of GAP-ETPE and Poly(GA-carboxylate)-ETPEs (1-3)

	GAP-ETPE (1)	Poly(GA _{0.7} -butyrate _{0.3})-ETPE (2)	Poly(GA _{0.8} -octanoate _{0.2})-ETPE (3)
Formula (repeating unit)	C _{91.8} H _{159.4} N _{14.6} O _{23.2}	C _{92.7} H _{160.9} N _{13.7} O _{23.8}	C _{93.2} H ₁₆₂ N ₁₄ O _{22.8}
FW (repeating unit)[g/mol]	1,838.96	1,848.28	1,843.60
-ΔU _{comb} [J/g]	22,954	25,245	25,240
-ΔH _{comb} [kJ/mol]	42,262	46,713	46,587
Δ _f H _{m,o} [kJ/mol]	-16,701	-12,819	-13,300
Δ _f Ho [kJ/g]	-9.08	-6.94	-7.21

(greater molar mass) and $|\Delta U_{\text{comb}}|$. It suggests that poly(GA-carboxylate)-ETPEs (**2**, **3**) release higher energies during the combustion process than GAP-ETPE (**1**). Therefore, the introduction of poly(GA-carboxylate) can improve the energy output of the GAP-ETPE (**1**).

4. Conclusion

GAP-ETPE and poly(GA-carboxylate)-ETPEs (**1-3**) were synthesized via two step reaction with IPDI, soft segment oligomers such as GAP and poly(GA-carboxylate), DBTDL and 1,4-BD in ethyl acetate. The synthesized GAP-ETPE and poly(GA-carboxylate)-ETPEs (**1-3**) were characterized by FTIR. As a results, the GAP-ETPE and poly(GA-carboxylate)-ETPEs (**1-3**) have similar FTIR spectra. The molecular weights were measured by GPC. The thermal properties were measured by DSC and TGA. Based on the DSC results, the poly(GA-carboxylate)-ETPEs (**2**, **3**) had lower T_g in comparison to that of GAP-ETPE (**1**). In addition, poly(GA_{0.8}-octanoate_{0.2})-ETPE (**3**) has higher T_{dec} than other materials. Therefore, poly(GA-carboxylate)-ETPEs (**2**, **3**) have thermal properties in terms of T_g and thermal stability. The mechanical properties were analysed by UTM. The energetic properties were determined by friction and impact sensitivity, and heats of combustion and formation. Results from heats of combustion and formation showed poly(GA-carboxylate)-ETPEs (**2**, **3**) have negative formation enthalpies and higher heats of combustion than GAP-ETPE (**1**). In addition, compared to GAP-ETPE (**1**), poly(GA-carboxylate)-ETPEs (**2**, **3**) have lower tensile modulus and higher breaking elongation at break. Consequently, poly(GA-carboxylate)-ETPEs (**2**, **3**) could be good candidates for a polymeric binder in solid propellant due to better energetic, mechanical and thermal properties in comparison to GAP-ETPE (**1**). These properties are very beneficial to application and processing of ETPE.

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