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Research paper

Designing a Highly Energetic PCL-GAP-PCL-based PU Elastomer; Investigation of the Effect of Plasticizers on Its Properties

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Abstract: Glycidylazide polymer (GAP) has potential interest for the development of high-performance energetic propellants. Although GAP is a well-known and promising energetic polymer, propellants based on it suffer from poor mechanical and low-temperature properties. In order to improve the mechanical and thermal properties of GAP a promising idea would be the preparation of a tri-block copolymer of it with a polymer having good mechanical and thermal properties, such as polycaprolactone (PCL). In this work, we report a detailed investigation of the glass transition temperature (T_g) and viscosity of PCL-GAP-PCL samples incorporated with energetic plasticizers, BuNENA, TMETN, and BTTN. The results demonstrated that the T_g of PCL-GAP-PCL is influenced by the type of plasticizer. PCL-GAP-PCL was cured with TDI and a mixed curing system (IPDI/N100). The elastomer prepared with the mixing curing system showed excellent mechanical properties with 2.64 MPa and 138% elongation. The effects of the energetic plasticizers on the mechanical properties of the elastomer were investigated. Finally, the plasticized tri-block copolymer showed enhanced mechanical and thermal properties.

Keywords: polyurethane elastomer, glycidylazide polymer, binder, energetic plasticizer, mechanical properties, thermal properties

Nomenclature:

GAP	Glycidylazide polymer
PCL	Polycaprolactone
PUE	Polyurethane elastomer
T_c	Crystallization temperature [°C]
T_g	Glass transition temperature [°C]
T_m	Melting temperature [°C]

1 Introduction

Polyurethane is a type of engineering polymer, well known for its useful properties. It is used in a broad range of commercial applications in many areas, such as binders, coatings, adhesives and medical devices [1-3]. Polyurethane elastomers (PUEs) are widely used because they can show quite interesting properties on changing the chemical structure of the starting materials [4]. PUEs are formed from soft segment and hard segment sequences. The soft segments are derived from a polyol, while the hard segments are derived from a di-isocyanate and a chain extender [5]. PUEs may be modified by various methods, such as using specific di-isocyanates, polyols and chain extenders, to provide new features.

The polymeric binders used in propellants are typically cross-linked elastomeric polyurethane networks, providing a matrix to bind the solids, such as oxidizers and metal fuels, with a plasticizer and other ingredients [6]. Among the cross-linked elastomeric polyurethanes, energetic polymer-based polyurethanes are unique. They have a positive effect on both the specific impulse and burning rate of solid composite propellants due to the decomposition of exothermic groups [7]. They are used as energetic binders in propellant and explosive formulations. Of the energetic polymers used as binders for solid composite propellants, glycidylazide polymer (GAP) is one of the most studied; its synthesis, performance, and applications have been reported in detail by many investigators [8-10]. GAP exhibits good properties, such as a high positive heat of formation, a higher density than other propellant binders, and compatibility with highly energetic oxidizers. Although the application of GAP as an energetic binder has many advantages, it suffers from weak thermal and mechanical properties. GAP contains bulky side groups in its structure and reduced backbone flexibility, resulting in the poor low temperature and mechanical properties [11]. Hence, GAP propellants need a high level of plasticizer to achieve the structural requirements. GAP-based propellants exhibit low stress and strain

capabilities [12]. The above mentioned disadvantages significantly restricts its application in solid propellants. To improve the mechanical and thermal properties of GAP a promising idea would be the preparation of a copolymer of it with a polymer exhibiting good mechanical and thermal properties, such as polycaprolactone (PCL) [13]. PCL is a semicrystalline, biodegradable polymer belonging to the aliphatic polyester family. It has been of more interest than other aliphatic polyesters because of its good properties for thermoplastic processing [14, 15].

A plasticizer is a homogenous unit within a solid propellant's binder system; plasticizers are firstly responsible for an improvement in the mechanical properties, making the propellant more flexible. They also assist in processing, and can function potentially as burning rate modifiers [16]. Energetic plasticizers contribute to the combustion mechanics by increasing the overall enthalpy [17, 18]. Therefore, to improve the performance and specific impulse of solid propellants a plasticizer should be added. Nitrate esters are important plasticizers in nitrate ester plasticized polyether (NEPE) propellants and other propellants. Incorporating a nitrate ester plasticizer into propellant formulations can improve their mechanical properties at low temperatures and make them safe to use [19, 20]. Experimental studies, using thermal and rheological techniques, may be useful in understanding the compatibility of a PCL-GAP-PCL binder with different plasticizers (Scheme 1) [21, 22], and also to gain a better insight in the selection of suitable plasticizers. Consequently, the present paper deals with the rheological behaviour and thermal properties of PCL-GAP-PCL blended with butanetriol trinitrate (BTTN), n-butyl nitroxyethylnitramine (BuNENA), and trimethylolethane trinitrate (TMETN) as energetic plasticizers, in order to make processable compositions with better solid loadings. It is thought that the PCL blocks might lead to better compatibility of these plasticizers with a binder, as well as enhancement in the thermo-mechanical properties. Polyurethanes based on PCL-GAP-PCL (polyol) with different curing agents, energetic plasticizers, and with tri-phenylbismuth as a catalyst, were prepared. The synthesized PUEs were characterized by spectroscopic methods and their mechanical properties were also investigated.

2 Experimental

2.1 Materials

ϵ -Caprolactone (Aldrich) was dried over CaH_2 and distilled at reduced pressure prior to use. Dibutyltindilaurate (DBTDL) with 96% purity, epichlorohydrin

(ECH), BF_3 -diethyl ether complex, sodium sulfate, and n-hexane were purchased from Merck. 1,4-Butanediol (BDO) was purchased from Fluka. Dimethyl formamide (DMF) and triphenylbismuth (TPB) were purchased from Sigma-Aldrich. Methylene chloride was purchased from Mojallali and was dried with CaH_2 (Merck) and distilled under reduced pressure. Isophorone di-isocyanate (IPDI) and toluene di-isocyanate (TDI) were purchased from Merck, and Desmodur polyisocyanate (N-100) from Bayer. The BuNENA, TMETN, and BTTN, used as plasticizers, were synthesized in the laboratory [23-25].

2.2 Instruments and measurements

The IR spectra were recorded with a Nicolet 800 spectrometer in the range $400\text{-}4000\text{ cm}^{-1}$. ^1H and ^{13}C NMR spectra were recorded with a Bruker DPX-250 instrument operating at 250.13 MHz, using CDCl_3 as the solvent; chemical shifts were reported in δ (ppm) from TMS. The glass transition temperature (T_g) measurements were performed using a DSC 200F3 under an N_2 flow of $20.0\text{ mL}\cdot\text{min}^{-1}$ and at a heating rate of $10\text{ }^\circ\text{C}\cdot\text{min}^{-1}$ from $-80\text{ }^\circ\text{C}$ to $50\text{ }^\circ\text{C}$. The T_g was computed as the midpoint of the heat capacity increase. Gel permeation chromatography (GPC) was conducted using $10\text{ }\mu\text{m}$ PL gel columns using a GPC Agilent 1100 (USA) instrument with a refractive index detector, and using an Agilent PL gel $5\text{ }\mu\text{m}$ mixed-C $300\text{ mm} \times 7.5\text{ mm}$ column. THF was used as the solvent ($1\text{ mL}\cdot\text{min}^{-1}$) and the sample was injected at $30\text{ }^\circ\text{C}$. The system was calibrated with polystyrene as standard. Tensile tests were performed with a Hiwa 200 instrument. All gauge sizes and shapes were compatible with the standard D638-02a (type IV) [26]. All tensile tests were performed at rates of $5\text{ mm}\cdot\text{min}^{-1}$ at room temperature. The effects of temperature on the polymer viscosities were investigated with a rotational rheometer under constant conditions with a shear rate of 10 s^{-1} and parallel plates with a 1 mm gap width (Physica MCR 300, Anton Paar, Germany).

2.3 Synthesis of tri-block copolymer PCL-GAP-PCL

The tri-block copolymer PCL-GAP-PCL was synthesized in two stages, the first stage being the synthesis of GAP, and the second stage being the synthesis of PCL-GAP-PCL from GAP [13]. In the first stage, 1,4-butanediol (BDO) (2.7 g , 0.0299 mol) in methylene chloride (50 mL) was added to a 100 mL three-necked flask fitted with a thermometer and nitrogen inlet. BF_3 -diethyl ether complex (0.7 mL) was injected into the reaction mixture and stirred at room temperature for 30 min . After cooling the reaction vessel to $0\text{ }^\circ\text{C}$ using an ice-salt mixture, epichlorohydrin (ECH; 25 g , 0.2161 mol) was added

dropwise to the reaction mixture over a period of 4 h. The mole ratio of BDO to ECH was 1:9. After the addition of the ECH, the reaction was continued for a further 12 h at room temperature. Thereafter, the organic phase containing PECH was added to distilled water and washed several times until neutral pH was obtained. The washed organic phase was dried over sodium sulfate, filtered and the solvent evaporated under vacuum to obtain PECH (24.85 g, 89.7% yield). Then, PECH (20 g) in DMF (100 mL) was added to a 250 mL three-necked flask fitted with a thermometer, nitrogen inlet, and water condenser. The reaction mixture was heated, with stirring, to 60 °C in an oil bath. Sodium azide (20 g, 0.2768 mol) was added to the mixture over a period of 20 min, then the reaction mixture was heated to 110 °C and the reaction was continued for a further 24 h. Thereafter, the unreacted azide and salted out sodium chloride were filtered off and the solvent was evaporated under vacuum. The resin obtained was dissolved in methylene chloride (50 mL) and washed several times with distilled water until neutral pH. The washed organic phase was dried over sodium sulfate, filtered, and the solvent was evaporated under vacuum. GAP (17.12 g, 85.6% yield) was obtained and characterized:

- **GPC analysis:** – $M_w = 1036$ g/mol; – $M_n = 1006$ g/mol, – $PDI = 1.2$,
- **$^1\text{H NMR}$** (CDCl_3 , 250 MHz, ppm) δ : 3.4, 3.66, 2.31, 1.65, 1.41, 4.06,
- **$^{13}\text{C NMR}$** (CDCl_3 , 250 MHz, ppm) δ : 78.6, 70.14, 51.5,
- **FTIR** (cm^{-1}) ν : 3450, 2101, 2925, 2868, 1281, 1121.

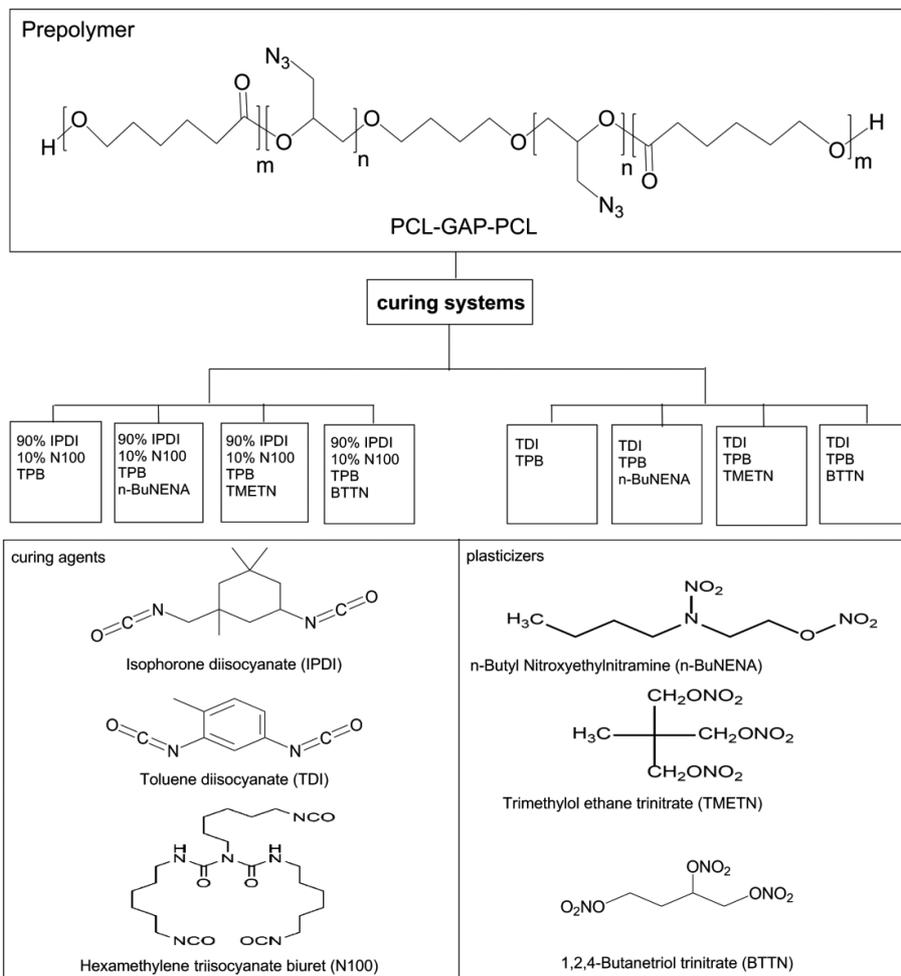
In the second stage, GAP (5 g) of low molecular weight ($M_n = 1006$ g/mol) obtained from the previous reaction, was added to a 250 mL three-necked flask fitted with a thermometer and nitrogen inlet. DBTDL (0.01 g) was injected into the reaction mixture and stirred for 60 min at 60 °C in an oil bath. Thereafter, the reaction mixture was heated to 100 °C and ϵ -caprolactone (7.5 g, 0.06 mol) was added dropwise to the reaction mixture over a period of 30 min. After the addition of the ϵ -caprolactone was complete, the reaction was continued for a further 19 h at 100 °C. The reaction was then cooled to room temperature and a solid polymer was formed. The resulting solid was dissolved in dichloromethane to obtain a viscous solution. This solution was added to a well-stirred flask containing cold methanol (200 mL) and the precipitated polymer was then filtered off, washed with cold methanol and dried under vacuum at room temperature to obtain PCL-GAP-PCL (11.78 g, 94.28% yield). PCL-GAP-PCL analysis:

- **$^1\text{H NMR}$** (CDCl_3 , 250 MHz, ppm) δ : 4.06, 3.66, 3.4, 2.31, 1.65, 1.41,
- **$^{13}\text{C NMR}$** (CDCl_3 , 250 MHz, ppm) δ : 173, 78.6, 64, 34, 28.8, 25.4, 24.5,
- **FTIR** (cm^{-1}) ν : 3450 (w), 2943 (m), 2866 (s), 2101 (vs), 1724 (vs), 1100 (m).

2.4 Synthesis of pure and plasticized polyurethane elastomers

In order to synthesize the polyurethane elastomers, the PCL-GAP-PCL tri-block copolymer, as the prepolymer, was first synthesized. Thereafter, an appropriate amount of PCL-GAP-PCL was placed in a single-necked flask in an oil bath and heated to 60 °C under vacuum for 2 h to remove solvent and dissolved air. Equivalent amounts of the curing agent and catalyst were then added. The solution was agitated for a further 15 min under the same conditions. The final mixture was poured into an aluminum mold and cured in a hot-air circulating oven at 60 °C to form a uniform sheet. The cured samples were stored for 1 week at room temperature before further characterization and measurement. To synthesize the plasticized polyurethane elastomers, n-BuNENA, TMETN, and BTTN were added to the polyol mixture in the prepolymer stage before the addition of the curing agent. All of the other stages and reaction conditions were the same as for the preparative procedure for the pure polyurethane elastomer.

The main purpose of this research was to study the effect of the PCL block on the mechanical and thermal properties of GAP and GAP-based polyurethane elastomers, and also on the compatibility and effects of energetic plasticizers on the PCL-GAP-PCL as a prepolymer. A schematic illustration of the chemical routes for the synthesis of the polyurethane elastomers is shown in Scheme 1.



Scheme 1. Overview of the curing systems, curing agents, and plasticizers for PCL-GAP-PCL diol

3 Results and Discussion

3.1 Thermal study

In order to study the thermal effect of energetic plasticizers on PCL-GAP-PCL, mixtures of PCL-GAP-PCL and 20 percent of BuNENA (G2), TMETN (G3), and BTTN (G4) were prepared. The DSC curves of PCL-GAP-PCL with these

plasticizers are shown in Figure 1, and their glass transition temperatures (T_g), melting temperatures (T_m), and crystallization temperatures (T_c) are listed in Table 1.

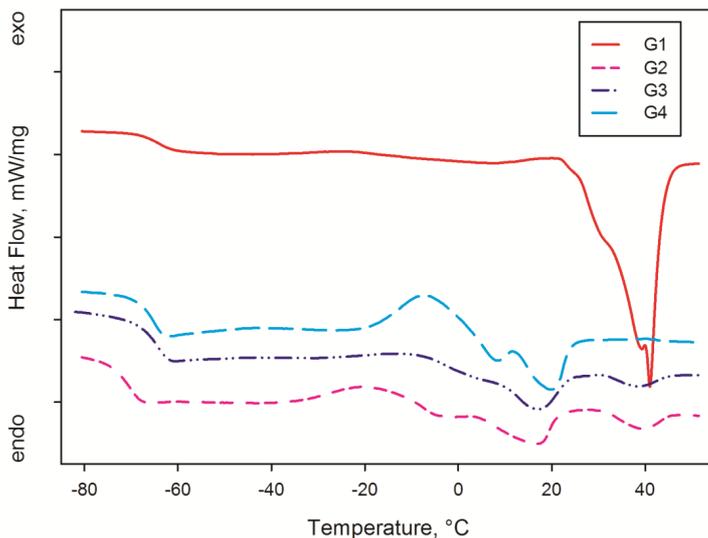


Figure 1. DSC curves of PCL-GAP-PCL and plasticized PCL-GAP-PCL with three types of plasticizer

Table 1. Thermal properties of PCL-GAP-PCL tri-block copolymer, with and without three types of energetic plasticizer

Sample	Plasticizer	T_g [°C]	T_m [°C]	T_c [°C]
G1	–	–64.3	41.0	–
G2	Bu-NENA	–71.7	39.5	–20.3
G3	TMETN	–65.6	35.5	–13.1
G4	BTTN	–65.6	20.2	–7.5

In the PCL-GAP-PCL tri-block copolymeric binder system, in the presence of plasticizers, we observed that the T_g of the binder network had decreased, also that the T_g of the tri-block copolymer is dependent on the type of plasticizer. According to the free volume theory [27, 28], the addition of low molar mass plasticizer molecules into the polymer involves an increase in free volume and consequently more chain flexibility and ease of movement. In addition, a plasticizer with lower molar mass such as BuNENA has a higher number of chain end groups, which creates many more movement possibilities than

in chain groups. Furthermore, BuNENA has a relatively long non-polar aliphatic chain (n-butyl), which increases the mobility and free volume in the polymer, allowing more conformational change and movement.

As shown in Figure 1, the tri-block copolymer mixed with a plasticizer exhibited a single T_g . This indicates that PCL-GAP-PCL and the plasticizer segments are compatible and that the two segments are well-dispersed and blended within the network. The PCL-GAP-PCL with plasticizer therefore consists of one-phase.

G1 exhibited a single melting peak ($T_m = 41\text{ }^\circ\text{C}$) and no crystallization peak, but PCL-GAP-PCL samples mixed with plasticizers exhibited an exothermic peak, due to cold crystallization, occurring before the endothermic melting peak. The areas under the crystallization and melting peaks are almost the same. This means that nearly all of the crystallites that melt were produced during cold crystallization, and thereafter the endothermic melting peak of PCL-GAP-PCL is observed. The results showed that the melting peaks of the tri-block copolymer for the three samples are same, but in the case of G4, the melting peak was decrease ($T_m = 20\text{ }^\circ\text{C}$).

3.2 Mechanical studies

3.2.1 Rheological studies

The viscosities of GAP, PCL-GAP-PCL, and mixtures of PCL-GAP-PCL with plasticizers, as a function of temperature are plotted in Figure 2. These results indicate that the viscosity of the samples depends on the temperature and type of plasticizer. The viscosity decreases with increase in temperature and *vice versa*, but the viscosity of PCL-GAP-PCL and mixtures of PCL-GAP-PCL with plasticizer is more dependent on the temperature than GAP, due to an increase in free volume and chain mobility at temperatures above $40\text{ }^\circ\text{C}$. The ability of the plasticizers to lower the viscosity of the polymer was measured on mixtures of PCL-GAP-PCL with 20 percent plasticizer. It was demonstrated that the maximum lowering of the viscosity at temperatures above $40\text{ }^\circ\text{C}$ was observed with the addition of BuNENA to PCL-GAP-PCL, but at lower temperatures, BTTN is more effective than the others. Therefore, BTTN ranks highest in reducing the viscosity at temperatures lower than $35\text{ }^\circ\text{C}$ because it causes loose binding interactions between segments of the polymeric binder PCL-GAP-PCL.

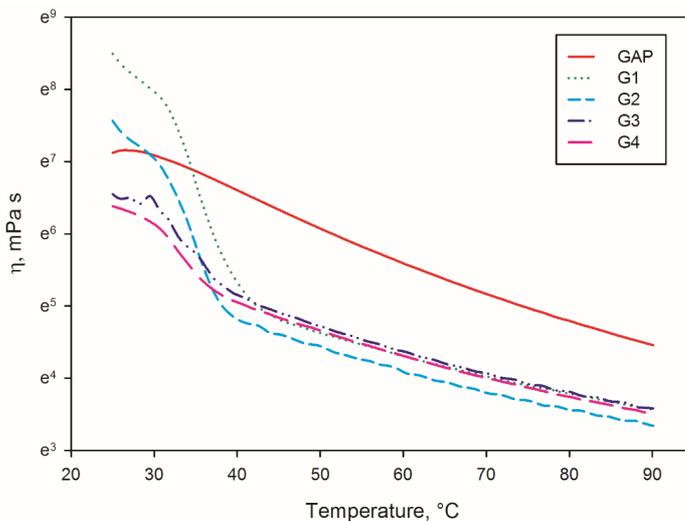


Figure 2. Viscosity vs. temperature of GAP, PCL-GAP-PCL, and mixtures of PCL-GAP-PCL with energetic plasticizers

3.2.2 Curing of PCL-GAP-PCL diol with isocyanate curing systems

GAP-based polyurethanes show low tensile strength and elongation at room temperature. Improvement in the mechanical properties of GAP-based binders had already been studied by blending GAP with linear, flexible polymers such as PCL [6, 29]. It was anticipated that copolymerization of GAP and PCL, and the incorporation of a plasticizer in a mixture of PCL-GAP-PCL as the polyol, could reduce these problems.

The tensile stress-strain curve is a tool to gain some data about the tensile strength, Young's modulus and elongation at break. The synthesized PUEs showed extensive mechanical properties depending on the curing agent and plasticizer. All of the PUEs displayed elastic stress-strain behaviour due to the specific domain structure formed by microscopic phase separation, in which the hard segments act as filler-like reinforcements [30-32]. The various curing mechanisms, curing systems, curing agents, and plasticizers for PCL-GAP-PCL diol that are discussed in this work are summarized in Scheme 1.

Four samples of PCL-GAP-PCL, cured with N100 and IPDI, were prepared and subjected to tensile testing. Three samples were mixed with equal amounts of BuNENA (GP1), TMETN (GP2), and BTTN (GP3) and a fourth sample was cured without a plasticizer (GP1). In addition, four samples of PCL-GAP-PCL, cured with TDI, were prepared and subjected to tensile testing. Three samples were mixed with equal amounts of BuNENA (GT1),

TMETN (GT2), and BTTN (GT3) and a fourth sample was cured without a plasticizer (GT1). IPDI and TDI work as chain extenders, while N100 cross-links the mixture to an elastomer.

In our earlier research, it was confirmed that the mechanical properties of GAP-based binder networks could be improved by the copolymerization of linear, flexible polymers such as PCL. Moreover, the effect of PCL blocks on the mechanical properties was much greater with a mixture of N-100 and IPDI (1:9, wt. ratio) than TDI as the curing system, because of the crosslinked network structure of the polyurethane on the GP samples. Proposed polyurethane network structures of GP and GT samples are shown in Figure 3. The elongation of the networks is increased by adding plasticizers in the curing system. The mechanical properties of polyurethane elastomers based on PCL-GAP-PCL as the polyol were influenced differently by different curing agents and plasticizer types. This is attributable to different network topologies. The effect of the curing agent and plasticizer on the tensile strength and elongation at break can be followed in Figure 3 and Table 2. When a plasticizer is added, it remains between the polymer chains, separating them and acting to provide more glide and less interaction and mobility restrictions, improving the flexibility and free volume. As a consequence, the addition of a plasticizer should increase elongation and strain capability, with the enhanced slipping between the chains.

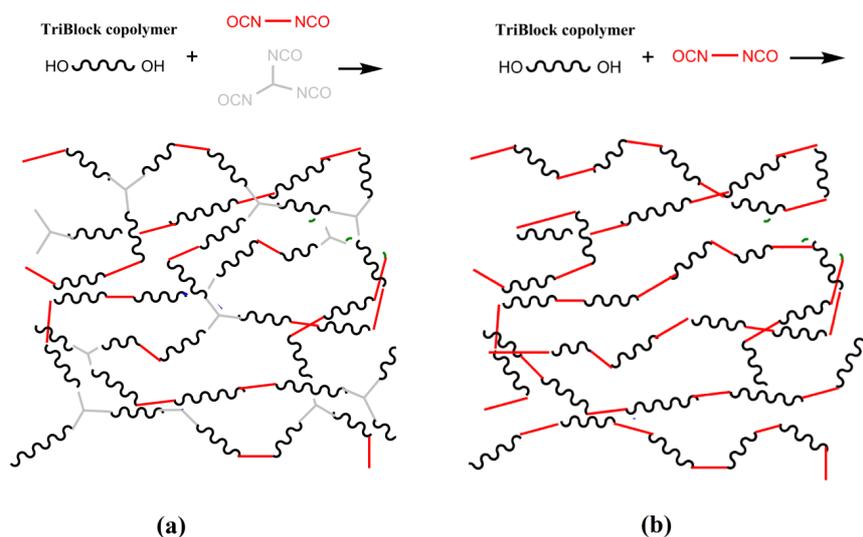


Figure 3. The conceptual models of (a) GP samples, and (b) GT samples

Table 2. Mechanical properties of the prepared polyurethane elastomers with the curing system of IPDI and N100

Sample	Plasticizer	Tensile strength [MPa]	Young's modulus [MPa]	Elongation [%]
GP1	–	2.64	2.65	138
GP2	BuNENA	1.97	1.48	257
GP3	TMETN	1.51	0.95	241
GP4	BTTN	1.12	0.80	288

In case of the GP samples, the initial elastic modulus and tensile strength increased dramatically with the incorporation of plasticizers to the polyurethane elastomers, in comparison to the GP1 sample which was composed of only PCL-GAP-PCL as a polyol. Addition of plasticizers as a portion of the curing system was accompanied by an increase in soft domain order binder, which was earlier confirmed by DSC and viscosity analysis. Additionally, the tensile strength and modulus decreased on changing the plasticizer type in GP2 to GP4 samples, compared to the GP1 sample, which can be attributed to increased interaction and mobility restrictions of GP1 [29]. The effect of the plasticizers on the tensile strength and elongation at break of the samples can be followed in Figure 4 and Table 2. The GP2, GP3, and GP4 samples showed higher tensile strength and lower modulus, and also a considerable increase in elongation, compared to the GP1 sample.

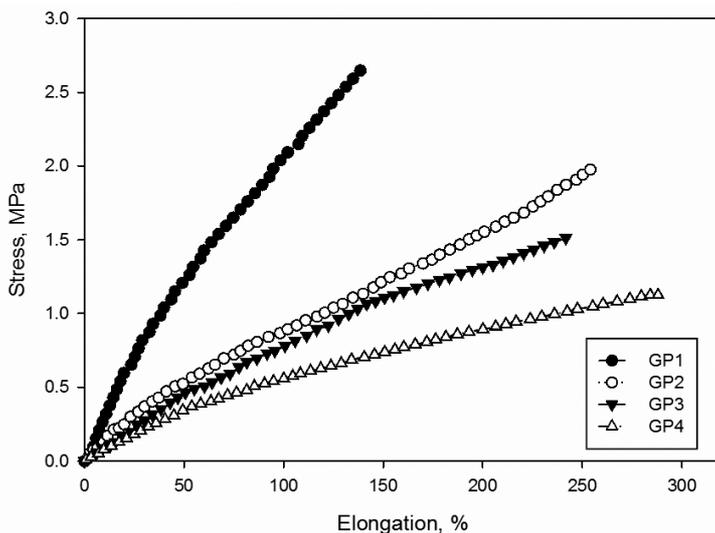
**Figure 4.** Tensile test results of PCL-GAP-PCL with the IPDI and N100 curing system

Table 3 and Figure 5 show the mechanical properties of PCL-GAP-PCL samples cured with TDI. The results showed that the modulus decreased on adding plasticizers. On the other hand, the elongation was variable and a considerable increase in elongation was observed. This observation is due to the plasticizing effect of the freely moving and displaced isocyanate-ended chains. The type of plasticizer has a marked influence on elongation. The GT2, GT3, and GT4 samples showed higher tensile strength and lower modulus and also a considerable increase in elongation compared to the GT1 sample, with the GT3 sample showing the highest tensile strength. In terms of elongation (%), the pure PCL-GAP-PCL-based polymer reached 91%, while the maximum obtained with the BTTN plasticizer was 176% elongation.

Table 3. Mechanical properties of the prepared polyurethane elastomers with the TDI curing system

Sample	Plasticizer	Tensile strength [MPa]	Young's modulus [MPa]	Elongation [%]
GT1	–	0.34	7.142	91
GT2	BuNENA	0.28	4.26	142
GT3	TMETN	0.21	3.66	174
GT4	BTTN	0.19	2.18	176

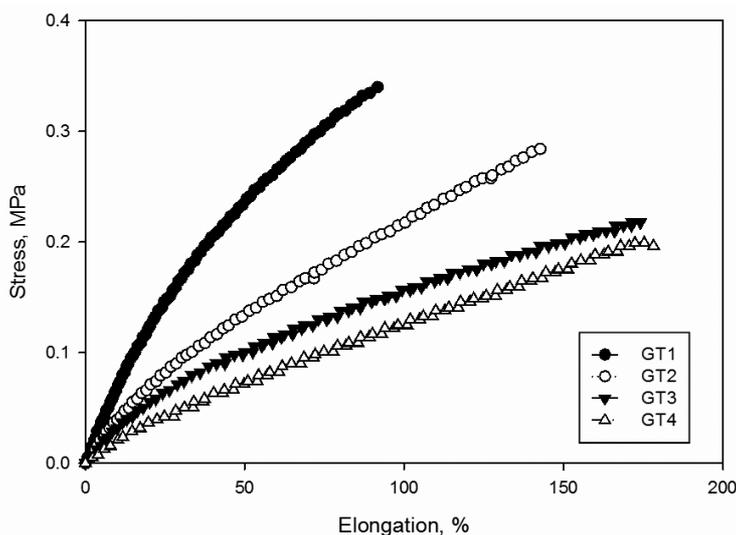


Figure 5. Tensile test results of PCL-GAP-PCL with the TDI curing system

4 Conclusions

Linear PCL-GAP-PCL diol was synthesized as a binder. The viscosity and glass transition temperature of GAP were found to be significantly influenced by the PCL blocks and plasticizers. The effects of the addition of three different energetic plasticizers, BuNENA, TMETN and BTTN, to the energetic binder, PCL-GAP-PCL, have been studied in detail, employing thermal and rheological techniques. The lowering of T_g was observed in all cases. BuNENA lowers T_g to a maximum extent (-71.7 °C), whereas BTTN and TMETN reduce it to a lower degree (-65.6 °C). Similarly, a maximum increase in the lowering of viscosity at temperatures above 40 °C was observed on addition of BuNENA. The relative ability of plasticizers to reduce the viscosity of the resultant plasticizer/binder blend was in the order TMETN < BTTN < BuNENA. Two series of polyurethane elastomers based on PCL-GAP-PCL tri-block copolymer as polyol with energetic plasticizers were synthesized with IPDI/N100 and TDI curing systems. Isocyanate curing using mixed IPDI and N100 is superior to curing with TDI. Synchronous curing, employing N100 and IPDI, gave samples with many improved properties in comparison with those from TDI curing.

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