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Synthesis of poly(urethane-urea)s based on novel macro-diamines: enhanced mechanical properties

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Abstract

Polyurethane elastomers are an important polymer in many applications which attach many interest. In this research, novel macro-diamines were synthesized successfully and used as chain extenders for the improvement of mechanical properties and thermal stability of poly(urethane-urea)s (PUUs). Structural characteristics of synthesized macro-diamines investigated by FT-IR. Also, thermal stability of prepared copolymers studied by DSC, TGA and DTG. As well, mechanical characteristics all of the PUUs investigated. Thermal melting (T_m) of copolymers hard segment appears in DSC curves. Furthermore, DSC curves don't show any peak in measured area; It's mean glass transition temperature (T_g) is less than (-80) °C. TGA curves displays that synthesized PUUs improvement thermal stability of polyurethane system. Mechanical test results show that mechanical properties of synthesized copolymers are improved.

Keywords: Polyurethane elastomer, macro-diamine, chain extender, poly(urethane-urea)s (PUUs).

1.Introduction

Engineering polymers are a group of synthetic polymers with special characteristics. Among various polymers, linear polymers have special importance, because there is ability of designation physical and chemical properties by changing in chemical composition, molecular weight, etc[1]. Thermoplastic elastomers are known as the best of new generation's copolymers in commercial field[2].

Polyurethane elastomers are a class of polymeric materials that because of their ideal physical and mechanical properties have various application in the industry. Polyurethane elastomers classify in various types that castable elastomers is the one of the most usable ones. Castable elastomers are systems that are completed their polymerization in final piece in the liquid phase. Improvement of mechanical and thermal properties of polyurethane have attracted a lot of attention, despite numerous studies that have been done on the synthesis and characterization of new polyurethane[3].

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Polyurethanes used in products such as coatings, adhesives, building materials, furniture, fabrics, colors[4] automobile manufacturing [5]. Polyurethanes are a class of polymers that have a urethane bond in their polymer’s chains[6]. Polyurethanes are formed from a reaction between isocyanates and polyols, also, diol and diamine chain extenders. By changing in the polyurethane component, can be designed the physical properties of the final polymer. Polyurethanes classified in thermoplastic elastomers[7]. The polyurethane’s chain consists of hard and soft segments [2]. Soft parts are formed from polyether, polyester or polycarbonate, while the hard part are produced via the reaction between diisocyanate with diol or diamine chains extender [8]. Hard segment has a less contribution in polymeric chain and act as a polymer domain organization. Hard segment via hydrogen bonding and van der waals intermolecular forces, causes crosslinking in polymer[3]. This polymer crosslinking improves the polymer’s thermal stability and mechanical properties[9]. Hard segments are dispersed in soft matrix also act as physical crosslinking and filler. Hard and soft segments are distributed random in the polymer chain. The micro phases are separated in polyurethanes due to the physical incompatibility of hard and soft domain[8]. Polymer consists of separate phases in the polymer chain structure with exceptional mechanical properties including high elongation, high stiffness and tensile strength[7]. Hydrogen bonding holds the hard segment together firmly and acts as a physical crosslink. These physical crosslink bonds are similar with chemical bonds and play a vital role in polyurethane elastomeric behavior[2]. Typical method for production of polyurethanes with high performance is chain extender creation with unique chemical structures in polymer’s chains.

Polyureas are another group of engineering polymers that attracted many interest of researcher in industrial applications. Urea groups formed from reaction between diisocyanate and diamine chain extender and forms the hard domain of polymer’s chain. Important advantage of using diamine as a chain extender is the creation urea phase in polymer’s chain[4]. The urea phase in contrast to urethane causes to more phase separation and resulting to the increases of modulus and good tensile strength in sample[10]. In the past decade, creation of urea bond in the structure of polyurethanes has been developed. In polymer synthesis process use from diol and diamine, resulting polymer calls urethane-urea copolymer (PUUs). PUUs copolymers are a wide range subset of polyurethanes which have many applications in industrial. Generally, thermal and mechanical properties of PUUs elastomers are superior compare to conventional polyurethane elastomers[11]. It has been confirming that the chain extender chemistry has significant influence on polymer properties. Chains extender and diisocyanate have influence on hard segment and physical properties of the final polymer’s properties[2]. Diamines react quickly with isocyanates and thus creates a hard segment with high density. Diamines used often to curing isocyanate’s pre-polymeric. the urea functional group is much stronger than polyurethane and provides better mechanical and thermal stability properties Due to strong hydrogen bond (double bond) and strong physical crosslink[12]. Increasing the physical crosslink force results to increase the crystallinity and rigidity and reduction of slippage of the chain[13]. This case effects on the polymer’s mechanical properties and increases the modulus and tensile strength[14].

In present research, PUUs via the new macro-diamine synthesized successfully and thermal and mechanical properties of the synthesized copolymers were investigated. In the following, resulting data obtained from copolymer analysis,

2. Experimental

2.1 Materials

Commercial-grade of Toluene diisocyanate (TDI), 1,2-Diaminopropane, 1,3-Diaminopropane, (Polyethylene glycol (PEG400, M_n= 400 g/mol), Polyethylene glycol (PEG600, M_n= 600 g/mol), Polytetrahydrofuran (PTHF1000, M_n=1000 g/mol), Polytetrahydrofuran (PTHF1800, M_n=1800 g/mol), and 1,4-Dioxane were used in this research.

2.2 The polyurethane(PU) Synthesis

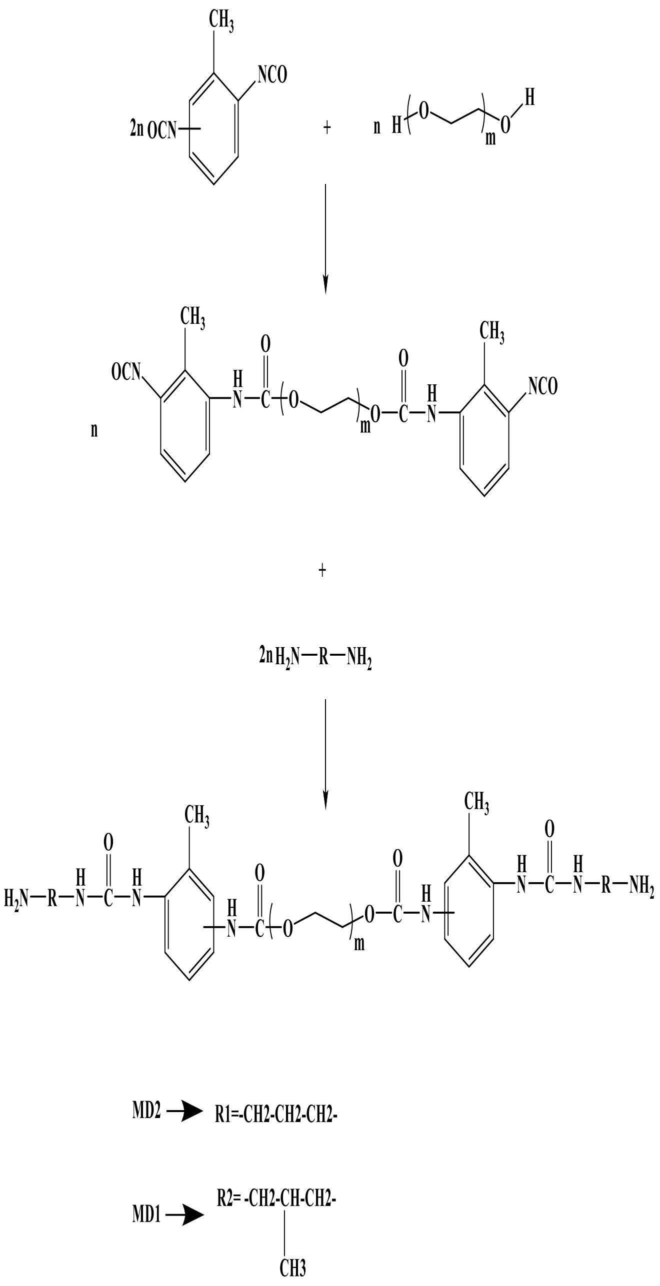
PU was synthesized by reaction of TDI with PEG (Mw = 400 g/mol). In order to synthesis of PU, PEG (2 g) was placed in a flask (100 mL) in ambient temperature. Then, TDI (1.74 g) was dissolved in 1,4-dioxane, added to the flask dropwise while stirred for 4 h. The reaction mixture was placed in an oven at 80°C for 2 h.

2.3 The polyurea(PUr) Synthesis

1.76 of TDI is placed in a round bottom flask with 100 mL capacity at room temperature. The 1,2-diaminopropane (0.74 g) dissolved in 1,4-dioxane was added dropwise into TDI by dropping funnel, while stirred for a period of 30 min. Then, the reaction mixture was maintained at 80 °C for 1 h.

2.4 Synthesis of macro diamines (chain extender)

Scheme 1 shows the synthesis of macro-diamines. were compared with net polyurethane and polyurethane.



Scheme 1. Synthesis of macro-diamines as chain extender.

The preparation route of both macro-diamines (MD_1 and MD_2) are similar. Here in, the preparation rout for one of the macro-diamine (MD_1) is given as an example.

First step: 4g of Polyethylene glycol (M_w = 400 g/mol) is placed in a round bottom flask with

100 mL capacity and was placed at room temperature. The TDI (3.48 g) dissolved in 1,4-dioxane was added dropwise into PEG400 by dropping funnel, while stirred for a period of 30 min. Then, the reaction mixture was maintained at room temperature for 2 h with continuous stirring to obtain an NCO capped polyurethane prepolymer (PP). The mentioned Prepolymer is synthesized using 2:1 mole ratios of TDI and PEG400, respectively.

Second step: Macro-diamines were synthesized using 2:1 mole ratios of different diamines and PU prepolymer, respectively. For this purpose, the PU prepolymer (synthesized in 1st step) reacted with two different diamines (1,2-diaminopropane and 1,3-diaminopropane), separately. Each of diamines dissolved in 1,4-dioxane and then added dropwise to the PU prepolymer under stirring for 30 min. mixtures were poured into Teflon molds and kept under room temperature for 24 h in order to evaporate all of the solvent to achieve Solid Macro-diamine. The labels and formulation of each macro diamines are given in table 1.

Table 1. labels and formulation of Macro-diamine as chain extenders.

Macro diamin	Pre polymer	Diamine
MD_1	PP	1,2-diaminopropane
MD_2	PP	1,3-diaminopropane

2.5 Synthesis of poly(urethane-urea)s (PUUs)

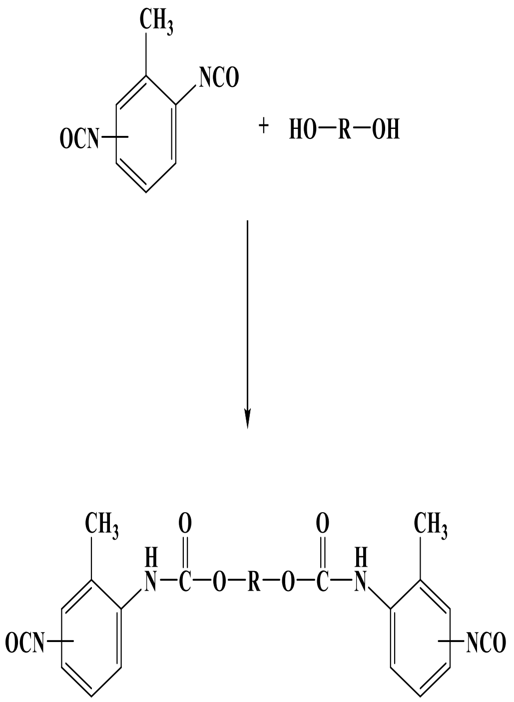
All polyurethane-urea (PUUs) were synthesized by a stepwise polyaddition reaction.

1st Step: prepolymers were synthesized by reaction of TDI with four different diols (PEG400, PEG600, PTHF 1000, PTHF 1800). The labels and formulation of prepolymers are given in table 2. Here in, the synthesis procedure for one of the prepolymers (PP4) is described as an example. In order to synthesis of PP4 prepolymer, PEG400 (4 g) was placed in a flask (100 mL) in ambient temperature. Then, TDI (1.74 g) was dissolved in 1,4-dioxane, added to flask dropwise while stirred (30 min). The reaction mixture was maintained at room temperature for 2 h with continuous stirring to obtain an NCO capped polyurethane prepolymer. The labels and formulation of each prepolymers are given in Table 2.

Table 2. labels and formulation of prepolymer

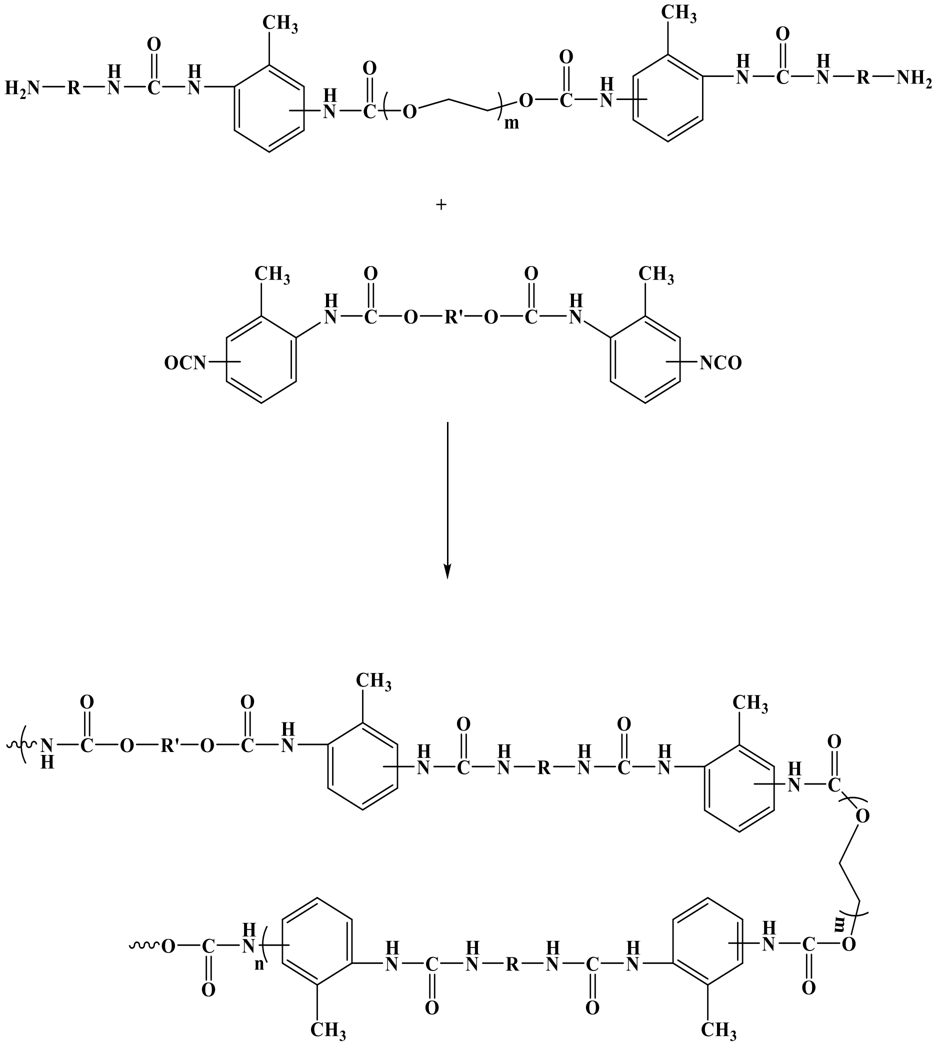
Pre polymer	Diisocyanate	Diol
PP_1	TDI	PTHF 1800
PP_2	TDI	PTHF 1000
PP_3	TDI	PEG 600
PP_4	TDI	PEG 400

The schematic of prepolymers synthesis reactions are shown in schem.2.



Scheme 2. Synthesis of prepolymer.

2st Step: each of the synthesized macro-diamines were added in each of the PU prepolymers under stirring (30 min). The reaction mixture was then maintained at 70°C for 1 h with continuous stirring to obtain a urethane-urea copolymers (PUUs). PUUs are prepared by mixing of MD and PU Prepolymer with molar ratio of 1:1. These mixtures were poured into Teflon molds and kept under room temperature for 24 h to evaporate the existence solvent and achieve the flexible PUUs films. In order to curing the PUUs films, the obtained films were kept in an oven at 60°C for 3 h. Schem.3 shows the synthesis of copolymers reaction schematically.



Scheme 3. Synthesis of copolymer.

All of the synthesized PUU systems, PU and PUr compositions are given in the Table 3.

Table 3. Composition of synthesized elastomers

Polymer	Diol	Diisocyanate	Chain extenders	Molar ratio Diol:Diisocyanate:CE
PUU-1	PTHF1800	TDI	MD_1	1:2:1
PUU-2	PTHF1000	TDI	MD_1	1:2:1
PUU-3	PEG600	TDI	MD_1	1:2:1
PUU-4	PEG400	TDI	MD_1	1:2:1
PUU-5	PTHF1800	TDI	MD_2	1:2:1
PUU-6	PTHF1000	TDI	MD_2	1:2:1
PUU-7	PEG600	TDI	MD_2	1:2:1
PUU-8	PEG400	TDI	MD_2	1:2:1
PU	PTHF1800	TDI	-	1:1
PUr	-	TDI	1,2-Diaminopropane	1:1

3. Results and discussion

In order to evaluate of the chemical structural properties of macro-diamines, Fourier-transform infrared spectroscopy was done.

Fig. 1 shows the FT-IR spectrum of the synthesized macro-diamines. As can be seen, in MD_1 and MD_2 spectrums, two peaks are appearing at about 2860 cm^{-1} and 2910 cm^{-1} which, related to symmetrical and asymmetrical CH_2 stretching[15]. Also, the peaks at about 1240 cm^{-1}, 1640 cm^{-1}, 1690 and 1700 assigned to ether linkage, aromatic C-H stretching bonds, amorphous and crystalline urea and urethane carbonyls, respectively[16, 17].In the Crystalline (urethane/urea) N–H stretching vibration region from 3303 to 3318 cm^{-1}[18]. The FTIR spectra obtained confirmed the formation of the specific urea linkage by the presence of the N-H stretching vibrations around 1100 cm^{-1} and carbonyl stretching band at 1655 and 1105 cm^{-1}.[19]. As well as, disappear of NCO peak at about 2244 cm^{-1} in FTIR spectrum, indicate that synthesis of the Macro-diamines has been successful. According to the Fig. 1(MD1 and MD2), a peak at about 1680-1690 cm^{-1} correspond the carbonyl group of urea linkages.

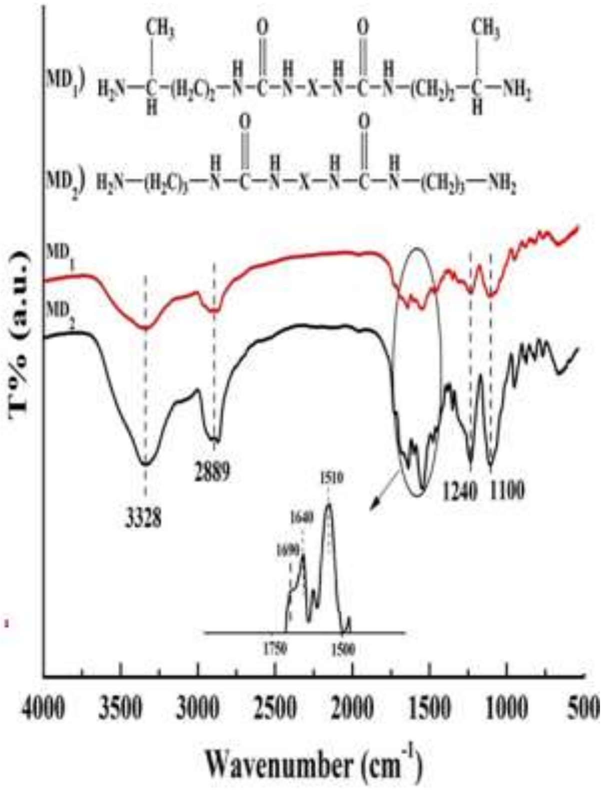


Fig 1. FT-IR spectra of synthesized macro-diamines.

3.1 Thermal analyses

Thermal stability of the prepared PUU elastomers that synthesized by MD1 and MD2, were evaluated by TGA and DSC analysis. Fig. 2 shows the TGA thermogram of polyurethane and polyurea as reference sample and also the synthesized PUUs which, prepared by MD1 (Fig. 2 (a)) and MD2 (Fig.2 (b)).

TGA curves of synthesized PUUs by using MD1 (Fig. 2 (a)) shows a main weight loss that occurs at 268–419°C temperature range. This weight loss has occurred due to the degradation of the hard segments. According to the Fig. 2 (a), from the comparison of synthesized PUUs with PU and PUr, it can be concluded that the presence of urea bond improved thermal properties of synthesized copolymers. In addition, with increasing the molecular weight of diols thermal stability has been improved. Therefore, using of PTHF is better than PEG.

TGA curves of synthesized PUUs that prepared by MD2 shown in fig. 2 (b). According to the fig. 2 (b), a significant weight loss occurred at 272–451°C temperature range which, related to hard segment of synthesized PUUs. As can be seen, the synthesized PUUs copolymers by using of MD2 extender have same thermal properties with the synthesized PUUs copolymers that prepared by MD1.

As a result, can be say by increasing the molecular weight of diols the thermal characteristics of synthesized PUUs copolymers were improved than the net polyurethane. As well as, among the PTHF and PEG diols, PTHF has better effect on thermal stability of synthesized copolymers than PEG. In addition, by comparison of the TGA thermograph of copolymers that prepared by MD1 and MD2, thermal stability of the synthesized copolymers which, prepared by MD2 are better than the synthesized copolymer that prepared by MD1. Therefore, can be say that the 1,3-diaminopropane had more effect on copolymers thermal stability than 1,2-diaminopropane.

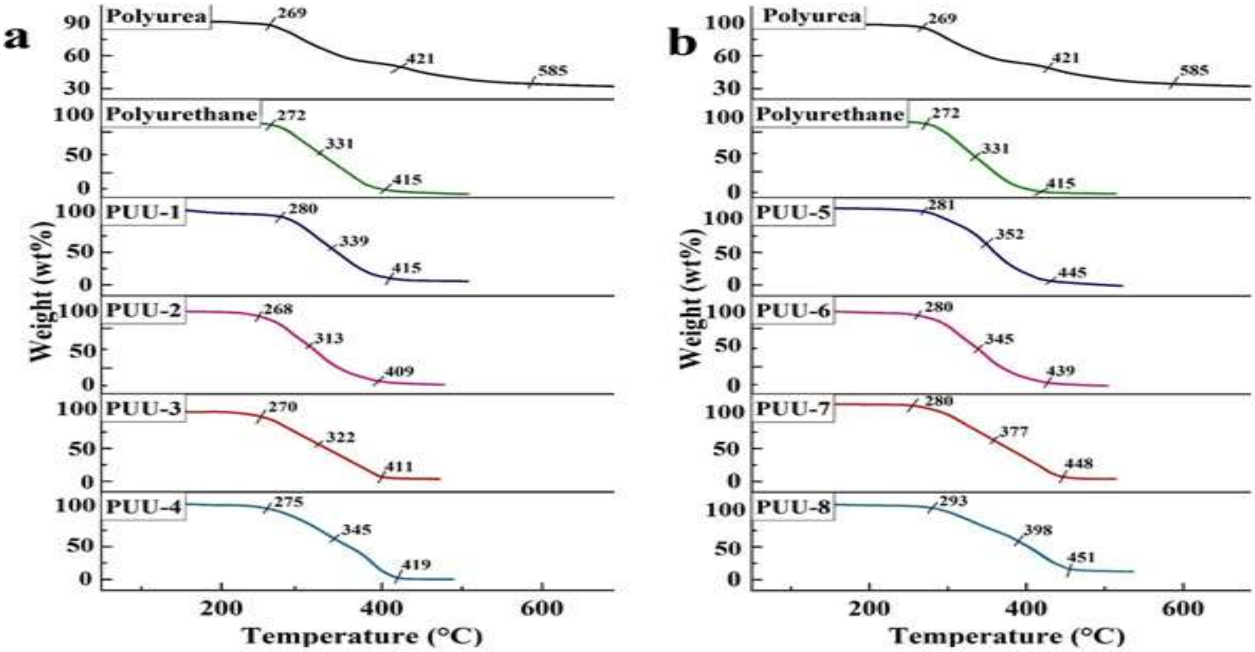


Fig 2. TGA curves of synthesized PUUs copolymers by using (a) MD1 and (b) MD2.

3.2 Differential scanning calorimetry (DSC)

The DSC curves of the synthesized PUUs copolymers, net polyurethane and polyurea in ambient temperature to 500°C are shown in Fig. 3. As can be seen in Fig. 3 (a and b), melt temperatures (Tm) of the synthesized PUUs copolymers are increased than net PU and decreased than net PUr. It should be noted that the first weight change of T_m corresponded to soft segment of PUUs copolymers and second weight change of T_m is related to hard segment of PUUs copolymers[3]. According to the Fig. 3 (a and b), it is clear that by increasing the molecular weight of diols, thermal stability is improved. In addition, thermal stability of the PUUs copolymers which, prepared by PTHF is better than the PUUs copolymers that prepared by PEG.

By comparison of DSC thermoghraph of PUUs copolymers which, synthesized by MD1 (Fig. 3 (a)) and PUUs copolymers that synthesized by MD2 (Fig. 3 (b)), can be conclude that the 1,3-diaminopropane (MD2) had better effect on the copolymer's thermal properties than 1,2-diaminopropane (MD1). This effect is due to the presence of (-CH_3) groups in the PUUs copolymer skeleton.

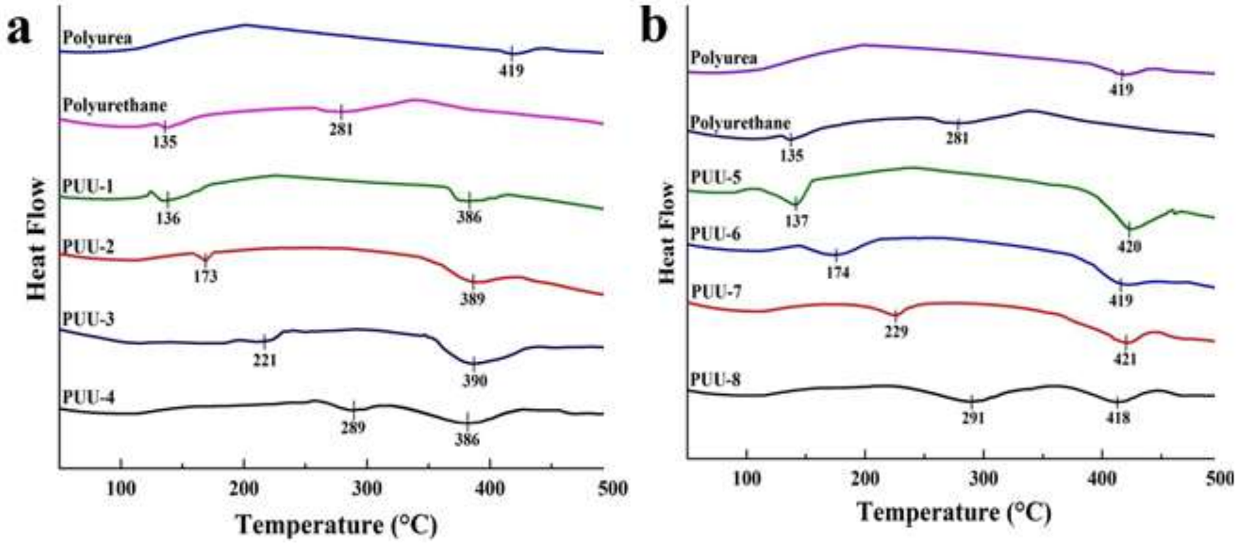


Fig 3. DSC curves of synthesized PUUs copolymers by using (a) MD1 and (b) MD2 in ambient temperature to 500°C.

Fig. 4 shows the DSC cooling curve in -80°C to 20°C of some PUUs copolymers which synthesized by MD1 and MD2. By investigation of copolymer's DSC cooling curve, not observed the Tg temperature in measured temperature range. It's mean that the glass transition temperature (Tg) is less than -80°C.

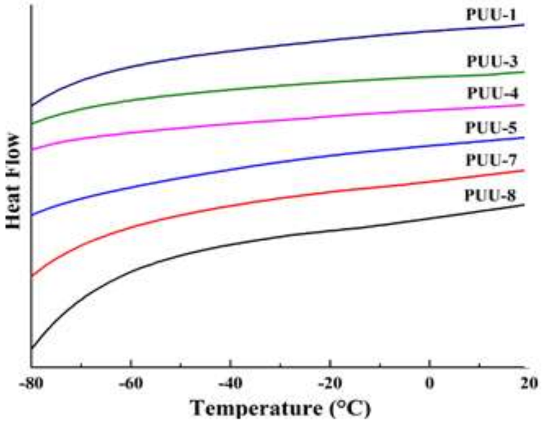


Fig 4. DSC cooling curve in -80°C to 20°C of some PUUs copolymers which synthesized by MD1 and MD2.

3.3 Mechanical test

In PUU elastomers the concentration of the hard segments and nature of soft segments play the important role in their mechanical properties. In order to investigation of chain extender effect (MD1 and MD2) on mechanical characteristics of synthesized copolymers and comparison of them with net polyurethane and polyurea, tensile tests were done on the PUU-4, PUU-8, net polyurethane and polyurea. Fig. 5 shows the stress-strain curves of the PUU-4, PUU-8, net polyurethane and polyurea. According to the Fig. 5, mechanical properties of synthesized copolymers (PUU-4 and PUU-8) are better than net polyurethane and polyurea. As well as, among the investigated copolymers (PUU-4 and PUU-8), PUU-8 has better mechanical properties than PUU-4, relatively. Then, can be say that the (-CH_3) groups which, exist in 1,2-diaminopropane has more important role than 1,3-diaminopropane on mechanical properties.

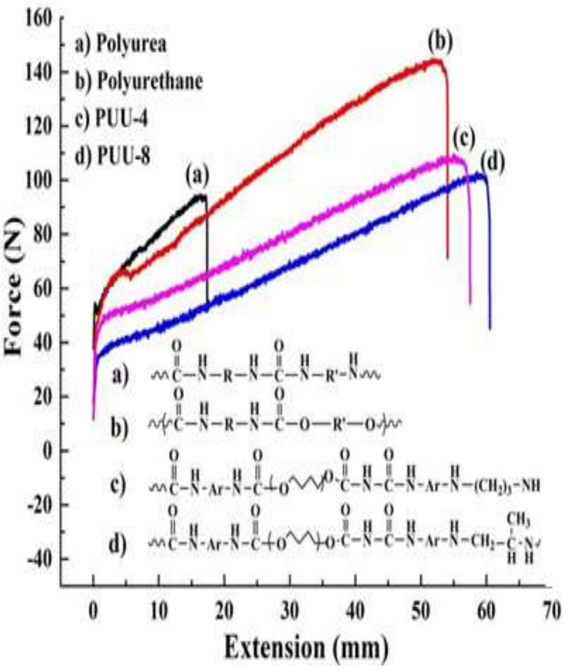


Fig 5. stress-strain curves of PUr, PU, PUU-4 and PUU-8

The results of the stress-strain measurements are given in Table 4. According to the obtain results from table 4, the PUU-4 modulus is 1.24 Mpa and it increased to 2.8 MPa for PUU-8 copolymer. It can be say the modulus increased with increase the hard segment concentration. In other word, between the concentration of hard segments and mechanical properties is a direct relationship. The tensile strength test is desirable for the PUU copolymers that are flexible[13]. The best elongation and elongation to break was obtained for the PUU copolymer that synthesized by 1,2-diaminopropane (PUU-8). Because the presence of the (-CH_3) groups causes the more flexible in the polymer chain. Among the PUU-4 and PUU-8 copolymers, the PUU-4 has more modulus and less flexibility than PUU-8. It can be concluded that the 1,3-diaminopropane results to the more urea groups creation and subsequently copolymer flexibility is decreased. In contrast, the presence of polyurethane groups in copolymer chain causes the increase the copolymer chain flexibility.

Table 4. Mechanical properties of PUr, PU, PUU-4 and PUU-8

Polymer	Elongation	Elongation to break	Modulus
Polyurea	324	328	2.4
Polyurethane	413	1043	1.73
PUU-4	635	1101	1.24
PUU-8	720	1170	1.1

4. Conclusions

Different urea/urethane copolymers were synthesized successfully by using reaction between two different of synthesized macro diamines (MD_1 and MD_2) and different prepolymer that prepared by PTHF and PEG with various molecular weight. Thermal analysis results indicated that the synthesized copolymers had better thermal stability than net polyurethane and weaker than net polyurea. Also, by increasing the molecular weight of diols the thermal properties of synthesized PUUs copolymers were improved than the net polyurethane. As well as, among the PTHF and PEG diols, PTHF has better effect on thermal stability of synthesized copolymers. In addition, by comparison of the thermographs of copolymers that prepared by MD1 and MD2, thermal stability of the synthesized copolymers which, prepared by MD2 are better than the synthesized copolymer that prepared by MD1. As a matter of fact, can be conclude that the 1,3-diaminopropane had more effect on copolymers thermal stability than 1,2-diaminopropane. The mechanical tests results indicated that the flexibility of copolymers were improved than net polyurethane and polyurea. By comparison between PUU-4 and PUU-8, resulted that the used of the 1,2-diaminopropane (PUU-8) had more effect on copolymer’s flexibility.

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