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ORIGINAL PAPER

Synthesis and characterization of new polyurethanes: influence of monomer composition

El Miloud Maafi · Lan Tighzert · Fouad Malek

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Abstract Different polyurethanes (PU) were synthesized from polycaprolactone diol, 1.6-hexamethylene diisocyanate and bis(2-hydroxyethyl)terephthalate, using a two- and one-step methods providing regular and random distributions of starting monomers in the polyurethane chains. Even with an identical molar monomer composition, the properties of obtained PU are different depending on the method of synthesis. The chemical structure of PU was characterized by ^{1}H and ^{13}C NMR spectroscopy, as well as by FTIR and UV–Visible spectroscopy. The thermo-mechanical and hydrophilic properties of synthesized PU were also studied demonstrating the influence of aromatic ring in the macromolecular chain.

Keywords Polyurethane · Poly(ε-caprolactone) · Biodegradable polymer · Thermo-mechanical properties

Introduction

The segmented polyurethanes (PU) can be considered as multiblock copolymers composed of flexible segments and tough, rigid segments. These two segments are

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E. M. Maafi · L. Tighzert (✉)
Groupe de Recherche En Sciences Pour l'Ingénieur/Laboratoire d'Etudes des Matériaux Polymères d'Emballage (GRESPI/LEMPE-EA 4301), Ecole Supérieure d'Ingénieurs en Emballage et Conditionnement (ESIEC), Esplanade Roland Garros, Pôle Henri-Farman, BP 1029,
51686 Reims Cedex 2, France
e-mail: lan.tighzert@univ-reims.fr

E. M. Maafi · F. Malek
Laboratoire de Chimie Organique, Macromoléculaire et Produits Naturels, Equipe: Chimie Bioorganique et Macromoléculaire, Faculté des Sciences, URAC, Université Mohamed Premier,
Bd Mohamed VI, BP 717, 60 000 Oujda, Maroc

thermodynamically immiscible, leading to a phase separation and the formation of rigid and flexible domains [1–5]. Many authors [6–14] have studied the morphology, thermal, mechanical and wetting properties of PU depending on the chemical composition of their structure, the type and molecular weight of soft segments and the method of synthesis. These materials have been used to obtain elastomers [3, 15–17], foams [18], coatings [19] and fibres [20].

Currently, biodegradable polyurethanes experience large growth due to their excellent physical properties, biocompatibility and biodegradability [10, 21–29]. They are widely used in the medical field as yards of sutures [30, 31], controlled release systems of active ingredients [32, 33], implants for orthopaedic surgery [21, 34] or in tissue engineering [35, 36]. Biodegradable polyurethanes are synthesized by incorporating flexible segments which are able to be hydrolysed such as poly (ε-caprolactone) (PCL), poly(lactide), poly(glycolide) and poly(alkyl adipate) [21–36]. The polyurethanes based on PCL have been widely studied. Indeed, PCL is linear aliphatic polyester, semi-crystallin, hydrophobic, biocompatible, bioresorbable, biodegradable and characterized by the degradation time in vivo which is remarkably long when compared to poly(lactide). In addition, PCL has a very mild inflammatory response with tissues [37].

PCL is also interesting in the field of packaging. However, this application remains restricted because the PCL suffers from a number of disadvantages, notably a limited service temperature induced by its low melting temperature and a low Young's modulus. According to the literature [38–41], the introduction of terephthalic units in the structure of polyester improves its physical properties. Poly(butylene adipate-co-terephthalate) is one of the copolyesters which has been widely studied and is marketed under the name of Ecoflex®. Witt et al [39] showed that this copolyester has good mechanical and thermal properties when the molar concentration of terephthalic acid is superior to 25%, but its rate of biodegradation declines sharply at a concentration higher than 50%. Therefore, the ratio of aliphatic and aromatic monomers must be chosen judiciously for syntheses. For a terephthalic acid molar concentration between 25 and 50%, the copolyesters reach a good compromise between biodegradability and properties of use.

bis(2-Hydroxyethyl)terephthalate (BHET) is a commercial low molecular weight diol with a terephthalic unit and can be used as a chain extender in the development of PU materials. Robin and co-workers [42] used BHET to synthesize polyurethanes miscible with PVC; the mixture of two polymers possesses good mechanical properties.

In this study, we planned to improve the performance of the PCL by synthesizing polycondensates, the structures of which contain urethane links and aromatic rigid segments in limited quantities to preserve the biodegradability of the polymers. During these syntheses, BHET was used as low molecular weight diol and the molar of the initial mixture [oligomers dihydroxy]/[diisocyanate] was varied. These conditions enabled us to obtain polyurethanes with different structures and properties. This article describes different synthesized polymers and their thermal, mechanical and wetting properties.

Experimental part

Equipments and syntheses

Reagents

Poly (ε-caprolactone) diol (PCL) (number average molecular weight 2000 g/mol) and BHET were purchased from Aldrich and kept in a vacuum desiccator in the presence of P_2O_5. 1,6-Hexamethylene diisocyanate 98% (HDI), tetrahydrofurane (THF), chloroform ($CHCl_3$) and dibutyl tin dilaurate (DBTDL) were also supplied by Aldrich. All reagents were used without further purification.

Two-step synthesis of segmented polyurethane PU0

In a 250-mL reactor, equipped with a mechanical agitation and a supply of nitrogen, 20 g (0.01 mol) of PCL, 3.53 g (0.02 mol) of HDI and 15 mL of THF were introduced. The mixture was heated to 60 °C until all products fused. The catalyst, DBTDL (0.3 wt%), was then introduced to the reaction mixture. The reaction remained at this temperature for 2 h. 2.54 g (0.01 mol) of BHET in 10 mL of THF were added. After 3 h of reaction, the temperature was risen to 80 °C to remove THF. A solid polymer was obtained and polymer films were prepared by casting.

One-step synthesis of random polyurethane PUi

In a 250-mL reactor, equipped with a mechanical agitation and a supply of nitrogen, PCL, BHET, HDI and 20 mL of THF were simultaneously introduced. The mixture was heated to 60 °C until all products fused. The catalyst (DBTDL) was then introduced. After 5 h of reaction, the reaction mixture was heated to 80 °C to remove THF and films were prepared by casting using chloroform as a solvent according to the conditions described below. The molar ratios of reagents used are given in Table 1.

Table 1 Theoretical and experimental compositions of PU

PU	HDI/PCL/BHET	$(TU\%)_{the}$	% of PCL in PU	$(TU\%)_{exp}$	
				^{1}H-NMR	UV–visible
PU0	2/1/1	25	81.5	23	27
PU1	2/1/1	25	81.5	22.4	25.9
PU2	3/1/2	33.3	71.2	28.2	30.3
PU3	4/1/3	37.5	63.3	33.7	33.7
PU4	3/2/1	16.7	87.8	14.3	15.1
PU5	4/3/1	12.2	90.2	12.1	14.6

$TU\%_{the}$ theoretical value, $TU\%_{exp}$ experimental value

Preparation of films by casting

In a beaker, 10 g of polymer were introduced to 50 mL of chloroform. After complete polymer dissolution, the solution was poured into a petri dish. The solvent was evaporated at 30 °C for 2 h. Films were dried under vacuum for 48 h.

Techniques

Fourier Transform Infrared Spectroscopy (FTIR)

The IR spectra were recorded on an FTIR 8400 SHIMADZU between 4000 and 600 cm^{-1} with a resolution of 4 cm^{-1}. The number of scans was 20 for each sample. Samples were in film form.

Nuclear magnetic resonance

^{1}H and ^{13}C NMR spectra were recorded on a Bruker spectrometer 250 MHz, at room temperature. The solvent used was $CDCl_3$. Chemical shifts are given in ppm relative to TMS as an internal reference.

UV–visible absorption spectroscopy

Measurements were carried out using an UV–Visible absorption spectrometer UVIKON 932 with double beam, deuterium and tungsten lamps. It can operate on a range of wavelengths between 190 and 900 nm. Parallelepiped quartz cells with a length and width of 1 cm and a height of 5 cm were used. Dilute solutions (1 g/L) in chloroform were prepared and placed in measurement cells. The measurements were carried out within a wavelength range of 200–400 nm. The maximum absorption of BHET is at 285 nm. The terephthalic unit percentage in polyurethanes was calculated using a calibration curve performed with solutions of different concentrations in BHET (0.1, 0.2, 0.3 and 0.4 g/L) and the absorption intensity at 285 nm.

Size exclusion chromatography (SEC)

The size exclusion chromatograms were recorded on an IOTA2 apparatus supplied by JASCO with a PU-980 Intelligent HPLC pump. The columns employed were PLgel 5 μm MIXED-D 300 × 7.5 mm, VARIAN INC. The mobile phase was chloroform and the flow was 1 mL/min. Samples were injected using an injector of the Agilent 100 Series. Molar masses were determined in relation to monodisperse polystyrene standards.

Differential scanning calorimetry (DSC)

The DSC analyses were performed with a 204 F1 NETZSCH apparatus. Experiments were carried out under nitrogen with samples ranging from 15 to

20 mg. The temperature range was between −80 and 250 °C, with a heating rate of 10 K min^{-1}. Glass transition temperature was taken as the midpoint of heat capacity changed.

Thermogravimetric analyses (TGA)

To assess the thermostability of polymers, TGA were performed. These tests provide the mass loss of a sample during heating. The TGA tests were performed on a TG 209 F3 NETZSCH 51 apparatus. About 15 mg of the sample was put in a ceramic pan and heated from 30 to 600 °C under nitrogen purge, with a temperature ramp of 10 K min^{-1}.

Contact angle analyses

Contact angles were measured on a Dataphysics—Contact Angle System OCA. A drop of water was deposited on films. The contact angle θ_i was measured after stabilization of the drop spreading by means of a camera connected to a software image analysis. The contact angle values were obtained from the average of tests on ten drops.

Mechanical properties

Mechanical tests were carried out with a machine of type MTS Adamel Lhomargy-DY35XL equipped with a load cell of 500 N, on shaped dumbbell-type H3 samples (ISO 37, 34 mm of length and 4 mm of width). The tensile speed was 10 mm/min, at room temperature. The curves obtained enabled us to access the Young's modulus, tensile strength and elongation at break. For each sample, the mechanical properties at break of the material were obtained from the average of tests on ten specimens.

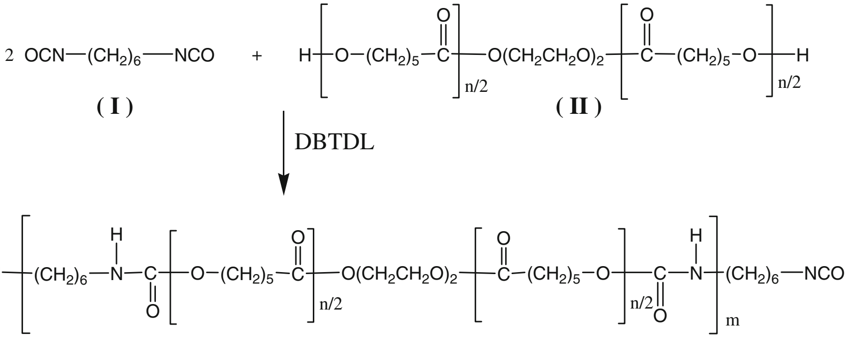
Results and discussions

Preparation and characterization of PU films

PU synthesis in two steps

To control the distribution of PCL and BHET along the polymer chain, a segmented polyurethane (PU0) was initially synthesized by the process of prepolymers. The first step in this synthesis was the condensation between the α,ω-dihydroxy oligomers of PCL and HDI (Scheme 1). The initial molar reagent ratio [HDI]/[PCL] was 2:1. The excess of HDI enables a prepolymer with NCO groups at both chain ends to be obtained.

The FTIR spectrum of the prepolymer obtained (Fig. 1) shows the formation of urethane groups by the presence of absorption peaks at 3319 and 1531 cm^{-1} due to the valence and deformation vibrations of the N–H bond, respectively. Moreover, a



Scheme 1 Structure of prepolymer obtained by reaction of a diisocyanate (HDI) and a diol (PCL)

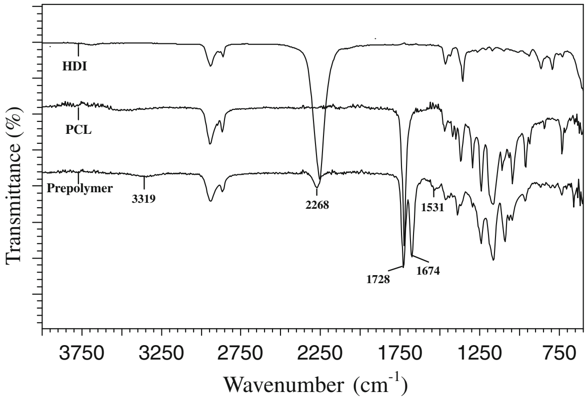


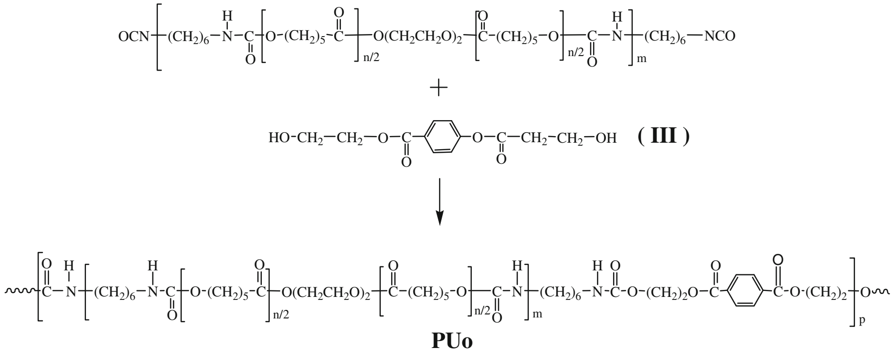
Fig. 1 FTIR spectrum of diisocyanate (HDI), diol (PCL) and prepolymer obtained by their reaction

band at 1674 cm^{-1}, characteristic of the valence vibration of C=O bond in the urethane group, is observed. The band at 1728 cm^{-1} characterizes C=O bond of ester groups. The FTIR analysis also reveals the presence of a band at 2268 cm^{-1} corresponding to the isocyanate function. These results confirm that NCO terminated polyurethane prepolymers have been obtained.

In the second step, BHET was used as a chain extender (Scheme 2). At the time when BHET was added, the solution became slightly cloudy, probably due to phase segregation in the material [7].

On the FTIR spectrum of PU0 (Fig. 2), the characteristic band of isocyanate groups at 2266 cm^{-1} disappears completely. The appearance of two intense bands 3310 and 1541 cm^{-1}, characteristic of valence and deformation vibrations of the N–H bond, respectively, is also noted. Moreover, a band at 727 cm^{-1} characteristic of aromatic C–H bond deformations of BHET moieties is clearly observed.

In Figs. 3 and 4, ^{1}H and ^{13}C NMR spectra of PU0 and the assignation of different peaks are shown. All expected signals of protons and carbon atoms are present, thus confirming the structure of PU0 illustrated in Scheme 2.



Scheme 2 Structure of prepolymer extended with BHET diol

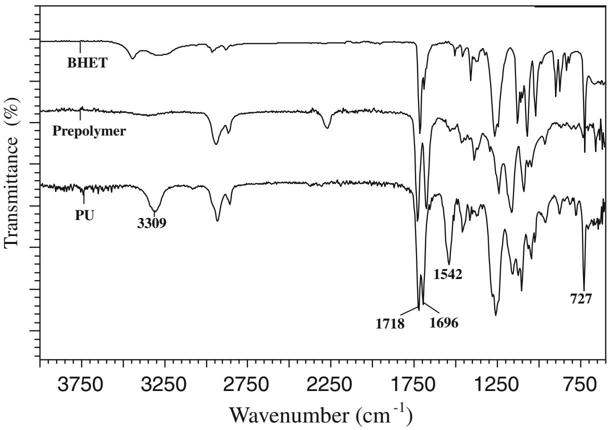


Fig. 2 FTIR spectrum of prepolymer, BHET and PU0

From the ^{1}H NMR spectrum, we assessed the composition of terephthalic units (TU%) in polymers from the peak integration of aromatic protons (8.02 ppm), 4 methylene protons in α of urethane group (3.08 ppm) and 4 central protons of PCL (3.62 ppm). After calculation according to Eq. 1, the TU% value found for PU0 is 23%.

$$\mathrm{TU\%} = \frac{I_{8.02}}{I_{8.02} + I_{3.08} + I_{3.62}} \times 100 \tag{1}$$

where I_x is the integration value of the signal located at x ppm.

The TU% of PU0 was also determined by UV–visible spectroscopy from the absorption intensity at 285 nm, the value obtained is 27% (Table 1). It is consistent with the theoretical value (25%) and the value determined by ^{1}H NMR (23%). Moreover, the number average molecular weight determined by SEC, using polystyrene standards, is 39200 g/mol with a polydispersity index equal to 1.57. All results obtained show a good coherence among themselves and the synthesis was successful for obtaining polyurethane with low molar mass distribution.

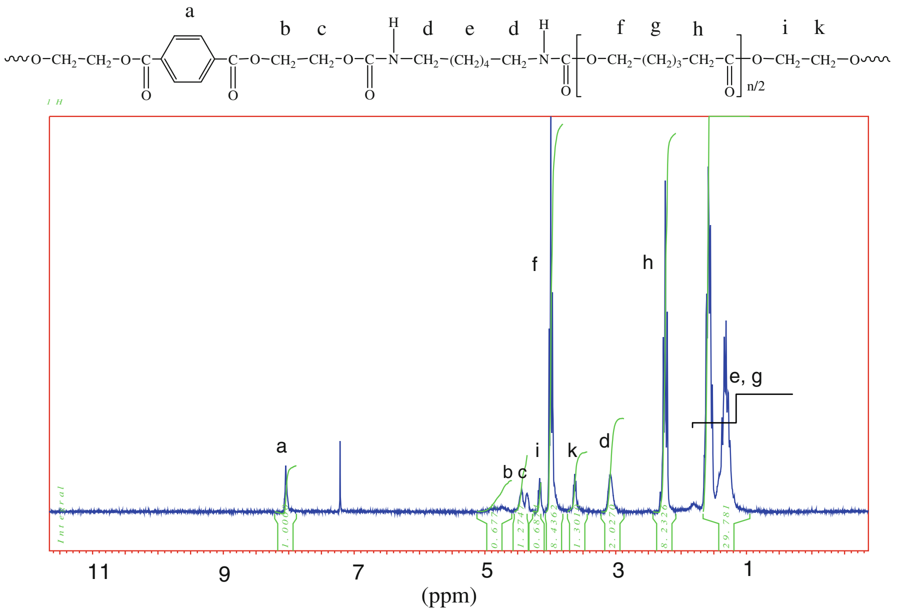


Fig. 3 ^{1}H-NMR(250 MHz, $CDCl_3$) spectrum of PU0

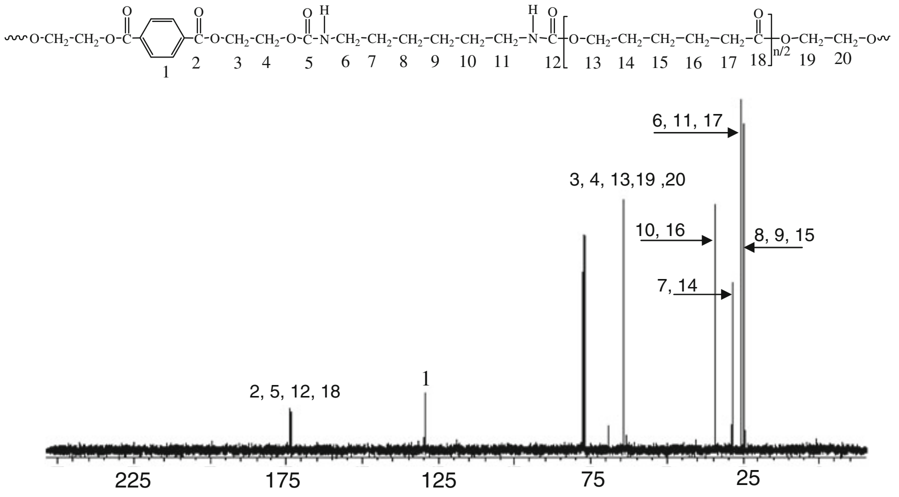


Fig. 4 ^{13}C-NMR ($CDCl_3$) spectrum of PU0

PU synthesis in one step

To elaborate these materials, the strategy of synthesis illustrated in Scheme 3 was adopted. In order to obtain PU with different structures and properties, different initial molar mixtures of PCL (II), BHET (III) and 1,6-hexamethylene diisocyanate (I) were used.

$(x + y)(\mathbf{I}) + x(\mathbf{II}) + y(\mathbf{III}) \longrightarrow$ Polyesters-urethane of various properties according to the values of x and y

Scheme 3 Synthesis of PU*i*

FTIR, ^{1}H and ^{13}C-NMR spectra of the obtained PU are identical to those previously recorded for PU0, the same signals were found at the same wavelengths and chemical shifts. From the peak integration of different ^{1}H-NMR spectra, the value of TU% in polyurethanes was calculated according to Eq. 1. In Table 1, we report the used initial molar reagents, the composition of polyurethanes obtained in TU% determined by ^{1}H-NMR and UV–visible spectroscopy. These values show that the polycondensation reactions were quantitative. For each PU*i*, the TU% determined by ^{1}H-NMR and UV–visible is almost equal to the theoretical percentage of BHET initially introduced in the reaction. We can therefore conclude that the strategy of introducing terephthalic units to the PCL structure is effective.

Table 2 gathers the values of number average molar mass M_n, weight average molar mass M_{w} and the polydispersity index (I_w) of all PU obtained. All samples possess a relatively narrow molar mass distribution. In fact, their polydispersity index is inferior to 2.

At this stage of syntheses, we can compare different polyurethanes obtained. PU0 and PU1 have the same chemical molar composition (Table 1), but differ in the methods of synthesis. PU0 was synthesized using the two-step method and has average molar masses M_n and M_{w} which are about three times inferior to those of PU1 which was synthesized using the one-step method (Table 2). This result could be explained, on the one hand, by the lower reactivity of NCO groups at both chain ends of the prepolymer obtained in the first step, in comparison with the reactivity of NCO groups in the HDI molecule. On the other hand, the reactivity of OH groups in BHET molecule is higher than that of PCL. Thus in the second step, the consummation of NCO groups of prepolymer could be incomplete, OH groups of BHET could promptly react leading to short chains. Consequently, the molar masses of PU0 are much lower than those of PU1. In comparison with PU2, PU3 contains more HDI and BHET (Table 1), this difference leads to the decrease in average molar masses which are divided by two (Table 2). This could be explained as follows. The molar masses of HDI and BHET are much lower than those of PCL. As a result, their high concentration in the case of PU3 leads to the formation of low molar weight polycondensates. A post-polycondensation should be carried out to

Table 2 Number and mass average molar weights and polydispersity index of PU

PU	$\overline{M_n}$ (g mol^{-1})	$\overline{M_w}$ (g mol^{-1})	I_w
PU0	39,200	61,500	1.57
PU1	126,400	200,700	1.59
PU2	101,600	155,200	1.53
PU3	49,000	80,900	1.65
PU4	51,600	104,200	2.02
PU5	97,300	174,800	1.80

obtain high polymers. To apply the same reasoning to other samples, the average molar masses of PU5 are higher than those of PU4, this result is due to its larger concentration in PCL.

Property characterization

Analysis by DSC

Table 3 collects the glass transition temperatures T_g of various PU and PCL determined during the second scan and the melting temperature of flexible segments during the first scan, as well as their melting enthalpies.

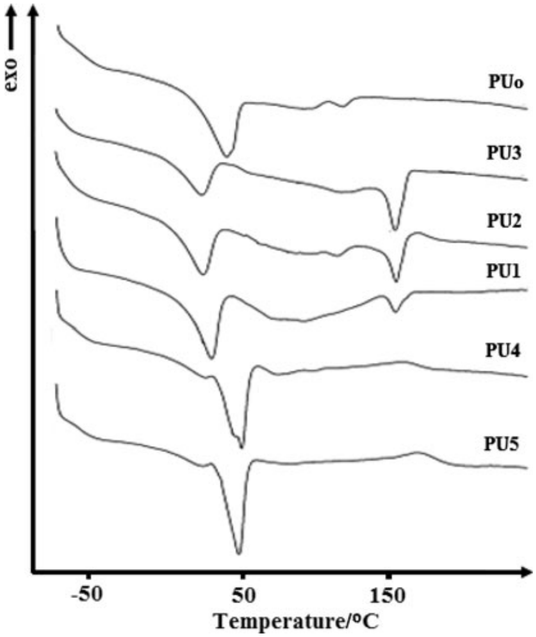
Figure 5 represents the DSC thermograms obtained during the first scan. The melting peak of flexible segments shifts to low temperatures, from 29.4 °C (PU1) to 23.9 °C (PU2) and 24.1 °C (PU3) when the composition of hard segments increases. In the same way, the melting enthalpy of flexible segments (ΔH_{mfs}) increases as the number of hard segments decreases and the PCL percentage increases (Fig. 6). While pure PCL has a melting enthalpy of 98.64 J/g, PCL in PU becomes more amorphous. Indeed, the melting enthalpy of PCL soft segments decreases and stabilizes at around 20 J/g for PU samples with PCL percentage inferior to 80%. Moreover, the hard segments influence the glass temperature transition of polyurethanes. In fact, for PU1, PU2 and PU3, there is an increase in T_g of flexible segments as the number of hard segments increases (Table 3). For example, the T_g of PU1 of −48.7 °C shifts to −29 °C for PU3. Some authors [1, 3] explained this phenomenon by increased interaction between flexible segments and hard segments. Moreover, we can propose the following hypotheses. First, the observed T_g below room temperature associated with PCL soft segments depends strongly on their miscibility with the hard domains. Secondly, the increasing number of hard segments, formed from HDI and BHET and containing highly polar urethane linkage, acts as thermally reversible and multifunctional crosslinks between the soft domains. Indeed, other samples with low TU%, such as PU4 and PU5, have low

Table 3 Contact angle, melting temperature T_m, glass transition temperature T_g, and enthalpies of crystallization (ΔH_c) and fusion (ΔH_m) during the first and the second scan of PU

PU	T_g (°C)	T_m (°C)	ΔH_1 (J/g)		ΔH_2 (J/g)		Contact angle (°)
			ΔH_{mfs}	ΔH_{mhs}	ΔH_c	ΔH_{mfs}	
PCL	−65.7	59.2	98.7	–	0	81.7	–
PU0	−50.9	40.9	26.7	0	7.4	6.3	93.6 ± 1.9
PU1	−48.7	29.4	19	7.1	3.7	6.1	103.8 ± 4.2
PU2	−37.5	23.9	20.5	23.9	4.1	0	111.2 ± 3.3
PU3	−29	24.1	19.2	28.3	4.5	0	104.2 ± 1.3
PU4	−51.8	52.2	29.8	0	0	33.3	97.9 ±2.0
PU5	−50.7	48.6	34.5	0	0	42.9	85.0 ± 2.4

ΔH_1 enthalpy during the first scan, ΔH_2 enthalpy during the second scan, ΔH_c crystallization enthalpy, ΔH_{mfs} melting enthalpy of flexible segments, ΔH_{mhs} melting enthalpy of hard segments

Fig. 5 DSC analysis of different PU during the first scan



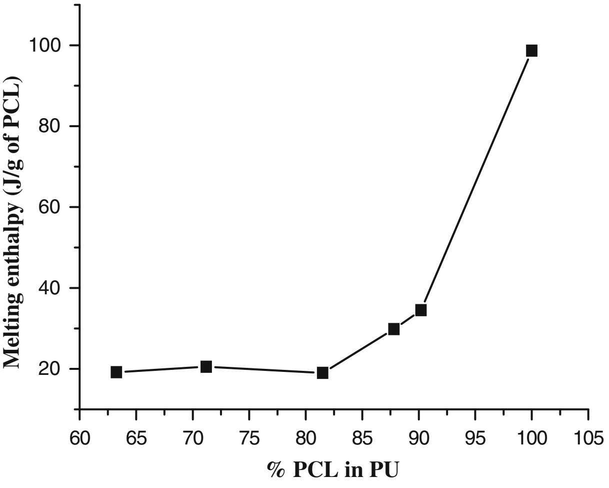


Fig. 6 Melting enthalpy of PCL soft segments versus PCL percentage in PU

values of T_g at −51.8 and −50.7 °C, respectively. A melting peak also emerges at 156 °C due to hard segments of PU containing more than 25% of TU. The melting enthalpy (ΔH_{mhs}) of this peak increases proportionally with the number of hard segments (Table 3).

By comparing the thermal transitions of PU0 and PU1, both contain the same composition in TU% and in flexible segments, have almost the same T_g value, but

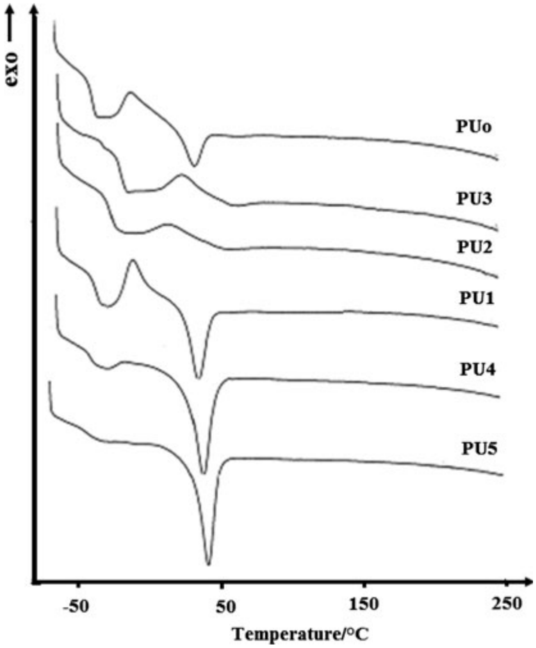


Fig. 7 DSC analysis of different PU during the second scan

the melting of flexible segments in PU0 takes place at a higher temperature, 40.9 °C instead of 29.4 °C. Moreover, the absence of the endothermic melting of hard segments in PU0 is observed (Fig. 5). Thus the thermal properties of PU are strongly influenced by the method of synthesis which could lead to various polymer morphologies.

After rapid cooling, the samples underwent a second rise in temperature. We can see on the thermograms obtained that the (Fig. 7) flexible domain is no longer pure, it contains rigid segments (HDI–BHET) which have not had time to separate more fully because of the rapid cooling applied to the sample. In fact, the endothermic melting peaks of flexible segments and hard segments of PU containing more than 25% of BHET are absent (PU2 and PU3). Moreover, exothermic crystallization takes place for PU containing 25% or more of BHET. The area of these exothermic peaks (ΔH_c) remains almost constant with the increasing percentage of rigid segments in the PU samples (PU1, PU2 and PU3). Besides, PU0 and PU1, both having an identical molar composition, present a similar behaviour during the second DSC scan. PU0 and PU1 present a crystallization peak at −21.9 and −16.1 °C followed by fusion at 24.7 and 33.7 °C, respectively.

Thermogravimetric analysis

The thermogravimetric curves obtained (Fig. 8) show that all PU samples decompose with a same mechanism, they are stable up to 260 °C, after that the first stage of degradation starts. This step most likely corresponds to the degradation of flexible segments. The second stage begins at 340 °C and depends on the

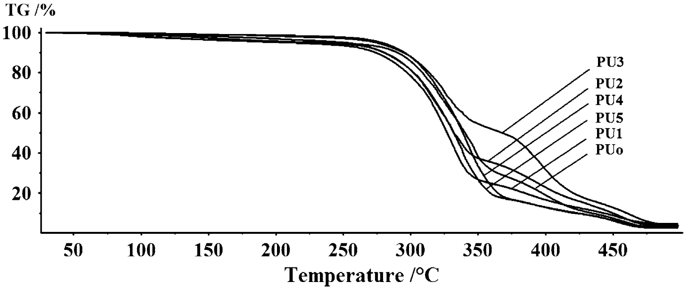


Fig. 8 TGA analysis of polyurethanes

composition of PU in terephthalic units. This step is absent in samples containing more flexible segments, such as PU4 and PU5. Moreover, with an increasing percentage of hard segments, the decomposition rate becomes slower towards elevated temperatures. Thus, the presence of terephthalic units gives polymer material thermal stability. Effectively, PU3 is the most thermally stable.

Contact angle

The hydrophobic nature of PU was determined by their contact angle with water. The values obtained (Table 3) show that the polyurethanes become more hydrophobic as the percentage of BHET increases. In fact, it notes that the hydrophilic character of the film decreases as BHET increases in PU1, PU2 and PU3, with a contact angle superior to 100°. Moreover, the hydrophilic character decreases sharply in the case of ordered polyurethane PU0 ($\theta = 93.6°$) in comparison with random polyurethane PU1 ($\theta = 103.8°$). This result is probably due to the hydrophobic nature of aromatic rings which are randomly distributed on the polymer chain of PU1 and are easily agglomerated together. Therefore, this structure induces a more important hydrophobicity in PU1 than in PU0, in spite of the fact that their composition in BHET is identical.

Mechanical properties

The stress–strain curves of all polyurethanes give the numerical values of mechanical characteristics collected in Table 4. All curves show the resilience of the sample at break. They have three types of behaviour. The first, at low deformation, is attributed to the elastic deformation which characterizes the elastomers [43]. The second, for plastic deformation between 300 and 500%, characterizes all materials studied and is due to shear-induced crystal fragmentation. In the last, for strains higher than 500%, there is a regular rise of stress which can be attributed to the crystallization of flexible segments. Similar results were found in the case of PCL-based polyurethanes [12].

PU0 and PU1, despite their identical chemical composition, do not have the same mechanical properties. PU1, with a random distribution of flexible and hard segments in the macromolecular chains, has tensile strength and elongation at break

Table 4 Mechanical properties of PU

	Deformation at break (%)	Young's modulus (MPa)	Stress at break (MPa)
PU0	1043 ± 211	47.8 ± 8.4	10 ± 1.2
PU1	1709 ± 321	5.4 ± 0.6	29.7 ± 3.5
PU2	1595 ± 374	11.4 ± 1.6	31.5 ± 10.7
PU3	481 ± 58	23.9 ± 1.7	10.7 ± 0.9
PU4	1955 ± 75	19.2 ± 3.3	23.3 ± 7.2
PU5	1850 ± 180	12.9 ± 2.3	32 ± 6.2

superior to those of PU0, which has a regular distribution. Moreover, the Young's modulus of PU0 is about nine times superior to that of PU1. This is logical owing to higher molar masses of PU1. For other samples, the tensile strength and elongation at break decrease as terephthalic units increase and soft segments decrease. These results confirm well the rigidity of aromatic rings and the softness and flexibility of PCL. In fact, PU3 having the highest TU% and the lowest percentage of PCL, has the lowest elongation at break.

Conclusion

The syntheses of PU were implemented in two ways. The first is a two-step synthesis giving polyurethane with an ordered and regular distribution of three components HDI/PCL/BHET. While, the second synthesis, a one-step method, yields a random copolymer. Even with an identical molar composition of monomers, having two methods of synthesis produces two polyurethanes with different properties, such as molar masses, mechanical properties, etc. The ^{1}H and ^{13}C NMR spectra confirm the expected structures of all PU, as well as the FTIR and UV–visible spectroscopy. The thermal and mechanical characterizations highlight the influence of hard segments. They contain a highly polar urethane linkage and hence play an important role in reinforcing fillers thus providing both dimensional stability and good mechanical properties. The improvement of properties is therefore most likely due to the increased interaction occurred in PU because of the increase in hard segments.

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