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Effect of the long chain extender on the properties of linear and castor oil cross-linked PEG-based polyurethane elastomers

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Abstract Polyurethane (PU) elastomers were elaborated from polyethylene glycol of high molecular weight (MW = 4,000), 1,6-hexamethylene diisocyanate and polyethylene glycol (PEG_{1500}) (MW = 1,500) as a long linear chain extender and/or castor oil as a cross-linker and were obtained in the form of transparent films. These poly(ether urethanes) elastomers are obtained by replacing the short-chain diol monomers with high molecular weight polyethylene glycols (PEG_{1500}). High molecular weight polyethylene glycol (MW = 4,000 and 1,500, respectively) have greater chain length thus producing networks with lower cross-linking densities and higher average molecular weight between two consecutive cross-links. The PU properties were investigated using Fourier transform infrared (FTIR) spectroscopy, differential scanning calorimetry, mechanical analysis and thermogravimetry. The results showed that the prepared polyurethanes (PUs) had very good tensile properties. The stress–strain data show that the PU elastomers obtained using a 60/40% $OH_{PEG1500}/OH_{castor\ oil}$ ratio have the best mechanical properties. The thermal degradation of the castor oil cross-linked PU elastomers starts at 280–300 °C, compared to the thermal degradation of linear PUs which begins at 220 °C. During storage at 25 °C, the morphology and mechanical properties of the elastomer films have been observed to change in time.

Introduction

Polyurethanes (PUs) have many industrial applications due to a wide range of properties. The variation in properties is determined by several factors such as the nature of the polyol and diisocyanate, the variation of hard segment concentration, the nature and ratios of the chain extenders and density of chemical cross-links [1–4]. There is an increasing interest in the development field towards designing materials consisting of both linear and cross-linked PUs having the design flexibility required for engineering applications. A large number of these PUs are biodegradable polymers with a wide variety of chemical and mechanical properties which make them useful in biomedical applications [5–10].

Recently, the production of PU elastomers with environment-friendly qualities has been linked to the replacement of petroleum-based raw materials with natural vegetable oils and especially with castor oil as it is also cost-efficient. Castor oil has a hydroxyl-containing fatty acid as a major constituent which can be directly used as a raw material for the preparation of PUs. Also, castor oil proved good compatibility with polyethylene glycol which may lead to improved properties in designing PU elastomers [11–15].

Polyethers are often used as flexible segments due to their low glass transition temperature and their good tensile properties. Among polyethers, poly(ethylene glycol) (PEG) is often used as a monomer or co-monomer for the soft segment of PUs. PEGs are hydrophilic and have non-toxic degradation products, being used in biomedical applications [16–18]. PEG segments have low-temperature flexibility, but it was found that an increase of the molecular chain length causes the melting temperature and crystallization to increase as well [19].

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Poly(ethylene glycol) (PEG) is known as a surface-modifying agent because it is a non-immunogenic and non-antigenic polymer. Thus, it prevents the binding of protein and cells to the surface. The PEG chain has low interfacial free energy, non-adhesive properties, and high mobility in its hydrated state which decreases the adhesion of the protein and cells [20–22]. Because PEG is only slightly affected by protein and bacterial adhesion it is often used in developing biomaterials—including PUs—through copolymerization and surface modification [23–25].

In this paper, we evaluate the effects of a long chain extender (PEG_{1500}) on new segmented PU elastomers by varying the ratios of chain extender and cross-linker. The low molecular diol commonly used as a chain extender was replaced by high molecular weight polyethylene glycols (PEG_{1500}). The results were found to vary with the change in the hard segment structure. The storage in time of these PU materials shows changes in morphology and mechanical properties.

Experimental

Materials

Poly(ethylene glycol) (MW 4,000 and 1,500) was obtained from Aldrich and dried under vacuum for 2 h before use.

1,6-Hexamethylene diisocyanate (HDI) was purchased from Fluka. The castor oil (CO) used in this study was supplied by Aldrich.

Preparation of the elastomers

Polyurethanes (PUs) were synthesized using a two-step bulk polymerization with a 1:2:1 M ratio of soft segment:diisocyanate:chain extender. The $OH_{diol}/OH_{castor\ oil}$ molar ratio was of 1/1 in each of the synthesized PU samples.

Typically, the synthesis of PU is performed by the following procedure and the ratios of the chain extenders are shown in Table 1.

The synthesis was carried out in a 250-mL glass reactor at normal pressure and under vigorous agitation. During first step, 1,6-hexamethylene diisocyanate was reacted with poly(ethylene glycol) (PEG_{4000}) at 80 °C for 2 h in order to yield an urethane pre-polymer. This pre-polymer was then reacted with the poly(ethylene glycol) (PEG_{1500}) chain extender and/or castor oil cross-linker at 80 °C for 10 min. The resulting transparent films were casted on a clean preheated glass at room temperature. Under these conditions the addition of catalysts was not necessary.

The obtained films were stored while being exposed to air at room temperature thus becoming more opaque and more rigid. These PU films were used for the determination of physico-mechanical properties and for the thermal resistance study which were performed after 5 days of storage.

Table 1 Formulations of the chain extenders ratios

Sample	Ratios of chain extenders
PU1	PEG
PU2	PEG 80% Castor oil 20%
PU3	PEG 60% Castor oil 40%
PU4	PEG 40% Castor oil 60%
PU5	PEG 20% Castor oil 80%
PU6	Castor oil

Characterization

Fourier transform infrared (FTIR) spectra were obtained at room temperature using a Bruker VERTEX 70 Instrument equipped with a Golden Gate single reflection ATR accessory. The spectra were recorded in the range of 400–4000 cm^{-1} with a nominal resolution of 4 cm^{-1}.

The *thermal stability* of the PUs was tested in an air atmosphere through thermogravimetric analysis (TGA) using a DERIVATOGRAF Q-1500 D apparatus (Hungary). The initial weight of the samples was of about 50 mg and tests were conducted in the temperature range of 30–700 °C and at a heating rate of 10 °C/min.

Differential scanning calorimetry (DSC) was performed on a DSC-7 Perkin-Elmer differential scanning calorimeter. The thermal transition behaviour was studied in a temperature range of -100 to 100 °C at a heating rate of 10 °C/min. Tests were conducted on samples of about 10 mg that were gradually heated in order to observe the glassy transition temperature (T_g). The DSC experiments were carried out with a liquid nitrogen cooler in a helium atmosphere.

Stress–strain measurements were performed on dumbbell-shaped samples cut from the obtained PU films. The tensile properties were evaluated at room temperature using a Shymadzu EZTest (Japan), equipped with a 5 kN load cell. The cross-head speed was of 50 mm/min. Four identical dumbbell-shaped specimens were tested for each sample and their average mechanical properties were reported.

Atomic force microscopy (AFM) measurements of the samples were achieved at room temperature and ambient pressure using a Scanning Probe Microscop SOLVER

PRO-M, NT-MDT (Russia). The film surfaces' morphology was investigated by AFM using the taping mode with silicon cantilever NSG10.

Contact angle measurement (CA) was performed at room temperature using de-ionized water and ethylene glycol. The contact angle of the samples was evaluated by static contact angle measurements using the sessile drop method on a Dataphysics Contact Angle System KSV Instruments LTD, Finland. The contact angle was measured with an accuracy of ±3°.

Results and discussions

We obtained PU elastomers with long soft-segment chains which bind to relatively long hard segment chains. In the hard domains the chain extender is a relatively long chain polyether (PEG_{1500}) which increases the distance between the hydrogen bonds which form between the urethane groups and the adjacent polymer chains. The mobility of the hard segments decreased with the increase in chemical cross-links generated by the castor oil. The absence of an absorbance at 2260 cm^{-1} indicated the formation of PU and also the absence of un-reacted isocyanate groups in the PU.

In order to study the PU infrared spectra, two main regions are widely researched: the N–H stretching vibration (3200–3500 cm^{-1}) and the C=O stretching vibration amide I region (1630–1750 cm^{-1}) [26–28].

The linear and cross-linked PUs were characterized by FTIR spectroscopy. Figure 1 shows the bands of the N–H stretching at 3300–3600 cm^{-1} for the urethane groups and carbonyl stretching bands at 1650–1760 cm^{-1} for the urethane groups combined with the ester carbonyl groups of the castor oil.

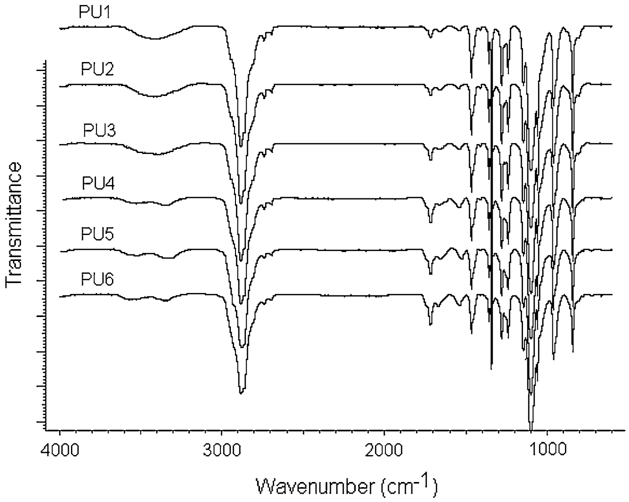

Fig. 1 FTIR spectra of linear and cross-linked polyurethanes

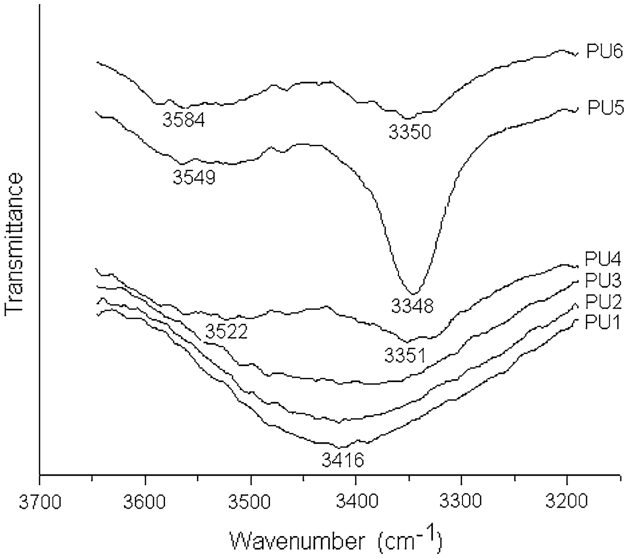

Fig. 2 FTIR spectra for the NH stretching regions of polyurethanes

Figures 1, 2 and 3 show the differences present in the NH and C=O stretching regions due to the structural differences of the hard segments of each PU. Along with the increase in castor oil content a clear splitting of the NH peak appears, which indicates an increase of the free N–H stretching vibrations (Fig. 2). The free N–H peak shifts from 3522 cm^{-1} to 3584 cm^{-1} and its intensity also modifies with the increase in castor oil content in the PU formulations. The H-bonded NH stretching vibrations peaks appear around 3350 cm^{-1}. Also, the free carbonyl stretching peaks (1716–1717 cm^{-1}) become higher with the increase in the amount of castor oil within the PU formulation. The usage of castor oil as cross-linker causes the apparition of an ester carbonyl stretching peak at

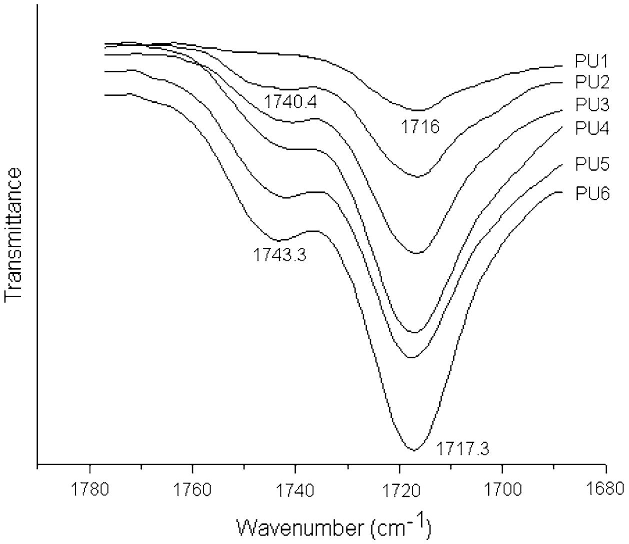

Fig. 3 FTIR spectra for the C=O stretching regions of polyurethanes

1740 cm^{-1} (Fig. 3). This ester carbonyl stretching peak shifts to a higher wave number (1743 cm^{-1}) for PUs obtained using only castor oil as chain extender (PU6). This indicates that weak hydrogen bonds have formed between the N–H and C=O due to the existence of chemical cross-links and due to the hindering effect of the castor oil exerted upon the dangling chains.

Fourier transform infrared (FTIR) was used to observe the morphologic changes occurring in the PU segments after various periods of storage. The obtained films were kept in air at room temperature (1–8 days) and became more opaque and more rigid. The FTIR spectra from Fig. 4 show the effect of time on the morphology of the PU films.

Figure 4 shows the infrared spectra for the linear PU (PU1). During the first few days that follow the casting, the H-bonded urethane carbonyl peak from 1660 cm^{-1} is predominant. If the storage time increases the H-bonded carbonyl peak from 1660 cm^{-1} decreases and the free carbonyl peak from 1717 cm^{-1} increases. The long chain length obtained from both the soft and hard segments enables the formation of a well-organized micro-domain structure. This is due to the increased chain flexibility of PEG which eases the orientation of disordered chains which are not subjected, in this case, to the constraints imposed by the chemical cross-links. The polymer crystallization controls the macroscopic structure and the properties characteristic to long chain molecular materials. As for PEG blends with other polymers, the ageing at ambient temperature manage to induce only a slow crystallization of PEG [29, 30]. In these cases the phase separation was obtained by excluding soft segments from the crystalline hard segment by extend of hydrogen bonding of the urethane carbonyl [31].

Usually, the crystallization of the hard segments is a major factor in phase separation, but the present system differs in terms of hard segment chemical structure, because it contains relatively long, flexible PEG$_{1500}$ chain. This hard segment structure and also the presence of a long and highly mobile ether chain (PEG$_{4000}$) from the soft segment results in competition between the urethane interchain hydrogen bonds and the increased amount of hydrogen bonded from the PU N–H to ether oxygen bond. At the same time the hydrogen bonded of the urethane N–H to urethane carbonyl decreases which results in a decrease of the H-bonded carbonyl peak from 1660 cm^{-1} (Fig. 4). Thus, the high molecular weight of the segments and their high mobility makes them capable of forming new ordered phase-separated domains. A similar behaviour was observed for PU–urea in blends with PEG when most of the PU N–H groups in these blends were hydrogen bonded to ether oxygen, as opposed to some other distribution of carbonyl groups [32].

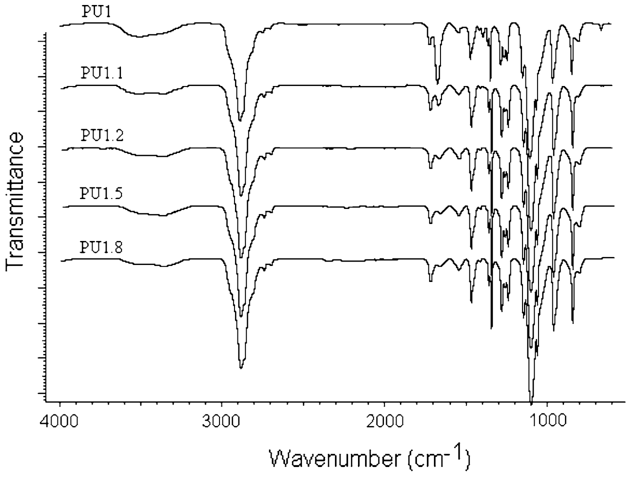

Fig. 4 FTIR spectra of the linear polyurethane (PU1) during storage for 1, 2, 5, 8 days

Figure 5 presents the thermograms for the PEG-based PU elastomers.

As can be seen from the thermograms, the initial decomposition temperature increases with the increase in castor oil content, this being a result of the chemical cross-linking effect. This effect occurs within samples that have a maximum of 60/40 as ratio between the OH$_{PEG}$/OH$_{castor\ oil}$ from the chain extender (PU1–PU3). Thus, the sample that has only PEG$_{1500}$ as a chain extender (PU1) presented a

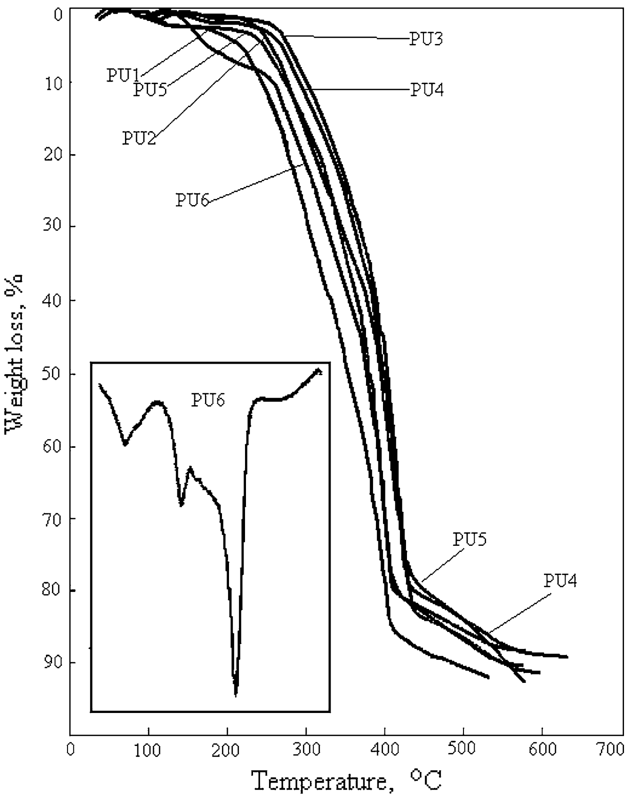

Fig. 5 TGA curves for the obtained polyurethanes

T_{onset} of 200 °C, while the sample prepared with a blend of PEG_{1500} and castor oil as chain extender (PU3) presented a T_{onset} of 300 °C.

For PUs with ratios of above 60/40 in $OH_{PEG}/OH_{castor\ oil}$, the increase in castor oil content from the chain extender formulation leads to a decrease in T_{onset}. This is a consequence of the plasticizing effect caused by the high amount of dangling chains from the castor oil.

Polyurethane (PU) elastomers based only on castor oil as a chain extender (PU6) have a three-step degradation profile which can be clearly distinguished in the DTG curves. The initial thermal decomposition occurs within the hard segments (urethane linkages). The second stage of degradation occurs within the castor oil segments and the last stages occur in the soft segments formed by the polyol [33].

Differential scanning calorimetry (DSC) analysis provided the information on glass transition, crystallization melting endotherms and also on the microphase separation of polymers [34]. The glass transition temperatures (T_g) and the melting endotherms of the linear and cross-linked PUs are shown in Fig. 6.

The soft segment glass transition temperature appears at −67 °C for linear PUs and increases for PUs with castor oil up to −53 °C (Fig. 6a). PUs with only PEG_{1500} as a chain extender showed lower T_g (−67 °C) and melting

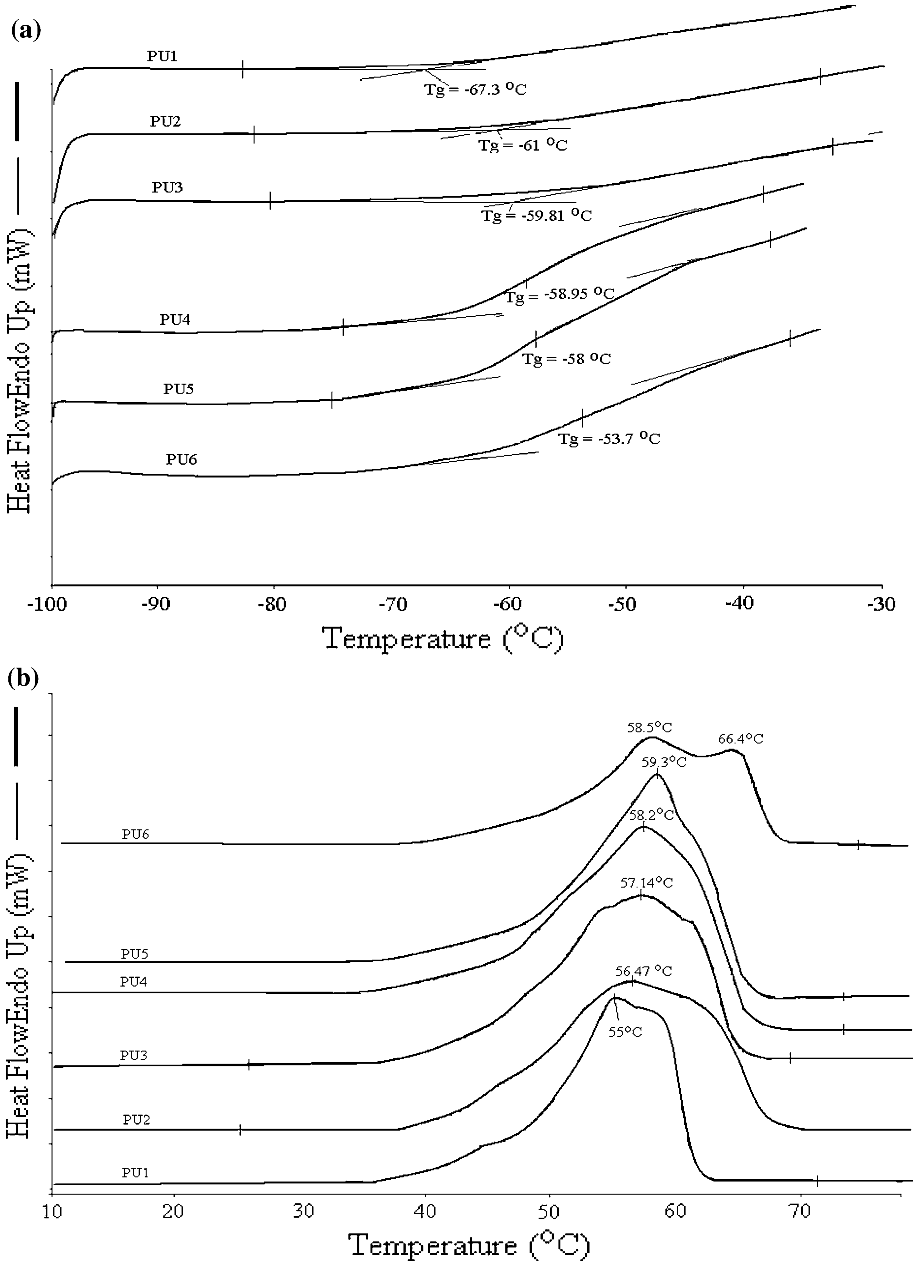

Fig. 6 DSC thermograms of polyurethanes for the T_g (**a**) and melting endotherm (**b**)

endotherm (55 °C). The addition of castor oil to the PU formulations shifts the T_g to higher values and thus T_g becomes more defined and broader.

The soft segment glass transition temperature increases with the increase in castor oil content. The tri-functional nature of the castor oil causes the hard domain morphology to be determined by the rate of chemical cross-linking that impedes mobility and phase separation thus leading to an increased T_g for PU6. The melting temperature of the soft segment is situated in the temperature range of 55–60 °C (Fig. 6b). The modified degree of phase separation can very well be used to explain the observed changes.

Mechanical properties including tensile strength, modulus and elongation at the break were evaluated according to the stress–strain curves (Fig. 7) and the data is tabulated in Table 2.

The ratio of NCO/OH_{polyol} remained unchanged in all PU samples. The linear polyurethane (PU1) has an average tensile strength because the higher molecular weight of the chain extender (PEG_{1500}), which is linear in nature, leads to the formation of a weaker physical network. This is explained by a low physical cross-link density and by the non-uniform distribution of the load throughout the network due to the longer length of the chain extender.

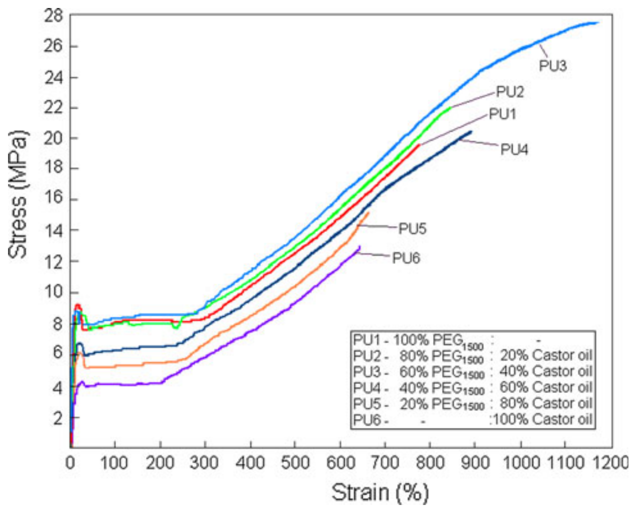

Fig. 7 Stress–strain curves of the polyurethane elastomers

The data shows a gradual increase in all mechanical properties with the increase in chemical cross-links in the hard segments, up to the PU with a 60/40 ratio of $OH_{PEG1500}/OH_{castor\ oil}$ within the chain extender. This formulation has a stress at the break of 27.5 MPa and a strain at the break of 1180%. With the increase in castor oil content, the tensile strength and elongation decrease due to the increased cross-linking and plasticizing effect of the dangling chains from the castor oil.

Poly(ethylene glycol) (PEG) has a regular structure and crystallizes easily [19] thus a high yield point is detected for the first three samples. A higher crystallization of PEG, in linear or lower cross-linked PUs, lead to a higher initial modulus in these samples. After the yield point follows a plateau when the material begins to deform plastically and then follows an increase in stress that starts at a 200–300% strain.

Poly(ethylene glycol) (PEG) is a water soluble polymer and wettability studies have revealed that surfaces become hydrophilic through the segregation of the PEG segments at the polymer–water interface. The hydrophilic–hydrophobic balance can be controlled through the variation of the hard segment structure and weight fraction [35]. The contact or wetting angle has a particular value for each material and is determined by the interactions of the three interfaces as described by Young's equation: [36]

$$\gamma_{SV} = \gamma_{SL} + \gamma_{LV}\cos(\theta) \tag{1}$$

where γ_{SV}, γ_{SL} and γ_{LV} represent the interfacial tension of the solid/vapour, solid/liquid and liquid/vapour interfaces. The equilibrium contact angle is represented by θ.

Also, Owens and Wendt [37] showed that the surface energy (γ_{SV}) is a result of disperse interactions and polar interactions.

$$\gamma_{SV} = \gamma_s^d + \gamma_s^p \tag{2}$$

Polar interactions contain Coulomb interactions between permanent dipoles as well as interactions between permanent and induced dipoles. Dispersive interactions are caused by fluctuations in time of the charge distribution within the molecules [36].

Table 2 Tensile test results of the polyurethane films

Sample	Stress at break (MPa)	Initial modulus (MPa)	Strain at break (%)	Yield point (MPa)
PU1	19.5	86	780	9.7
PU2	21.7	84	885	8.9
PU3	27.5	85	1180	9
PU4	20	66	900	7
PU5	13.5	44	670	6
PU6	11.5	42.5	660	4.3

Table 3 Contact angle (θ) and work of adhesion (W_a) values of the PEG-based polyurethane films surfaces

Sample	Water		Ethylene glycol	
	θ (°)	W_a (mN/m)	θ (°)	W_a (mN/m)
PU1	63.2	91.3	76.3	59.3
PU2	68.8	99.1	83.0	53.8
PU3	73.4	93.6	83.3	53.6
PU4	80.5	84.8	81.2	55.3
PU5	94.4	67.3	81.03	55.5
PU6	104.7	54.2	93.7	44.8

Table 4 Interfacial tension for a solid–liquid system (γ_{SL}) in PEG-based polyurethanes

Sample	λ_{SV}^{p} (mN/m)	λ_{SV}^{d} (mN/m)	γ_{SL} (mN/m)	
			Water	Ethylene glycol
PU1	9.2	6.7	7.3	3.4
PU2	24.6	9.1	7.5	5.9
PU3	15.1	9.8	12.9	5.3
PU4	46.1	0.12	25.3	8.8
PU5	2.9	21.0	29.5	7.6
PU6	1.3	16.7	36.5	12.1

p polar, *d* disperse

The water contact angles were obtained by static contact angle measurements for the various PEG-based PUs by using two liquids: water and ethylene glycol.

The cross-linking of high-molecular weight PEG (PEG_{4000} and PEG_{1500}) PUs makes the surface less hydrophilic with the increase in castor oil content, as opposed to PUs obtained with only PEG_{1500} as chain extender. Thus, the water contact angles increased from 63° for linear PUs (PU1) to 104.7° for PUs with only castor oil as a chain extender, (PU6) (Table 3). The values of the surface energy obtained from contact angles using Owens–Wendt method are shown in Table 4.

The explanation for the difference observed between the values of the contact angles could be found in the interaction of water with the large number of ethylene glycol segments per repeat unit of PEG-based PU found in linear chains. In contact with water, the PEG segments migrate to the surface thus lowering the PU interfacial tension with water phenomenon occurring only for those segments that are not hindered by the chemical cross-links.

For these PUs to degrade in biological environments it is necessary to have a higher amount of water penetrate into the bulk of the polymer. The lower hydrophilicity of the PU surface obtained through a higher amount of castor oil can be explained by the high cross-linking density and the hydrophobic nature of castor oil. The increase in surface energy can be explained by the introduction of polar functional groups provided by the castor oil. The values of the contact angles may have varied due to differences in the surface chemical composition, but also due to differences in surface structure [38].

The morphology of PUs depends on the polyol soft segment chain length, the compatibility of the soft and hard segments and the mobility of the hard segments inside the soft domain [39]. In perspective of potential biomedical applications not only surface hydrophilicity plays an important role in cell adhesion surface but also surface roughness. Cell adhesion increases with the increase in surface roughness [40].

The surface of the PU samples was observed by AFM and is shown in Fig. 8.

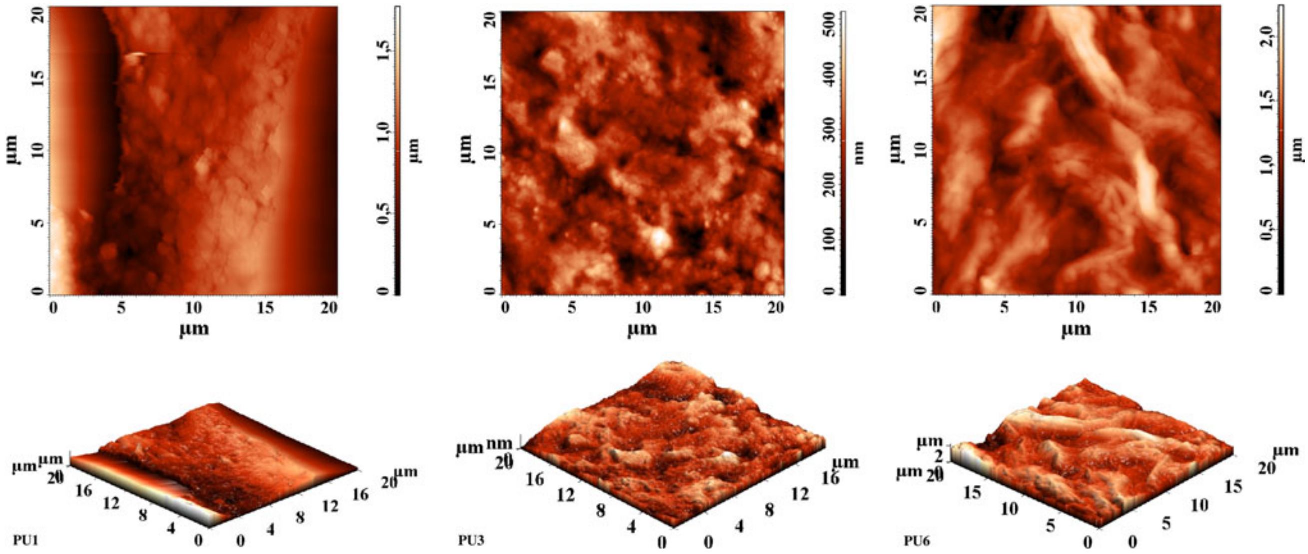

Fig. 8 AFM surface and profile images of the polyurethane films

The linear PUs (PU1) have a more granular surface as a result of the PEG crystallization. In the case of the castor oil cross-linked PUs the homogeneity and flatness characteristics of the surface are improved (PU3).

The average roughness decreases from 235 nm for the linear PU (PU1) to 54 nm for the PU with a 60/40 ratio of the $OH_{PEG}/OH_{castor\ oil}$ from the chain extender (PU3). Further increasing the amount of castor oil from the formulations makes the average roughness gradually increase to 218 nm (PU6).

Conclusions

PU elastomers with long soft segment chains and with relatively long chain extenders were obtained. The high molecular soft segment domain increases soft-segment flexibility and in time favours the crystallization of the material.

The thermogravimetric analysis results showed an increase in thermal stability with the addition of castor oil up to a 60/40 ratio of $OH_{PEG}/OH_{castor\ oil}$, followed by a decrease in T_{onset} with the increase in castor oil content. When comparing linear PUs (PU1) with the castor oil cross-linked PUs, the tensile strength increases for PUs up to the one with a 60/40 ratio of the $OH_{PEG}/OH_{castor\ oil}$ from the chain extender (PU3), then decreases with the additional increase in castor oil content. This trend that is contrary to the effect of the chemical cross-linking is given by the plasticizing effect of the dangling chains from the castor oil.

The surface contact angle data confirmed that using a high molecular chain PEG for the soft and hard segments of the PU maintains a high level of hydrophilicity that decreases with the increase in castor oil content. The surface modification was also confirmed by AFM which showed changes in the morphology of the various formulations. Future studies will be needed in order to examine the performance of these materials from an environmental degradation point of view.

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