

Synthesis and Properties of Polyurethane Elastomers with Castor Oil as Crosslinker

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Abstract Castor oil–polyurethane elastomers were prepared by reacting poly (1,4-butane diol) (Terathane 1400) with aliphatic 1,6-hexamethylene diisocyanate. The prepolymers were chain-extended with bifunctional precursor chains and/or with castor oil as a trifunctional crosslinker at stoichiometric ratios. These resulted in a series of crosslinked polyurethane elastomers with different structures of the hard segment. The properties of the material were measured by differential scanning calorimetry, thermogravimetric analysis, atomic force microscopy, as well as tensile properties measurements. The effect of stoichiometric balance (i.e., OH/NCO molar ratio) on the final properties was evaluated. The formation of hydrogen bonds was observed by Fourier transform infrared spectroscopy. The measured properties were found to be strongly influenced by the molar ratio of chain extenders to the diisocyanate component. The glass transition temperatures (T_g) for the polyurethanes with $\text{OH}_{\text{polyol}}/\text{NCO}/\text{OH}_{\text{chain extender}}$ having molar ratios of 1:2:1 and 1:4:3 were found to be -70 and -57 °C, respectively. The polyurethanes networks with a OH/NCO molar ratio of 1:2:1 had excellent mechanical properties, indicating that this is the optimum ratio to be used in castor oil polyurethane elastomer formulations. The objective of this work was to study the effect of the castor oil crosslinker on the morphology of the resulting crosslinked polyurethanes and to correlate the morphology with the properties of these bio-based crosslinked polyurethanes.

Keywords Polyurethane elastomers · Castor oil mechanical properties · Thermal behavior

Introduction

In order to protect the environment and to reduce our dependence on fossil fuels, a great deal of research effort has been and is still being devoted to the development of innovative technologies using renewable resources [1].

Polyurethanes (PUs) are one of the most important classes of polymers with wide applications and properties, which can vary from linear polymers to thermosetting plastics. The structural-property relationships in PU depends on many factors that include the volume fractions of the soft and hard segments, the chemical compositions of these segments and distribution of each segment, as well as the degree of cross-linking. These factors influence the physical, chemical, and thermal properties of PUs and could be manipulated by varying the stoichiometric balance of the components [2].

Traditionally, PU is industrially produced by reacting petroleum-based polyols with isocyanates. Because oil resources are diminishing and are becoming expensive to produce, researchers have discovered new technologies to produce plastics from renewable resources [2–6].

Vegetable oils are one of the most abundant biological sources and important raw materials for the production of bio-based polyurethanes because of their numerous advantages: low toxicity, inherent biodegradability, and high purity [1, 7–9]. As a result of the hydrophobic nature of triglycerides, vegetable oils produce polyurethanes that have excellent chemical and physical properties such as enhanced hydrolytic tendencies, high tensile strength and elongation, high tear strength, and thermal stability [10, 11].

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Castor oil has been widely used to develop new materials for many different applications, because it is the main oil that is essentially composed of the triglycerides of a hydroxy acid, ricinoleic acid [12].

In this paper, we report on the properties of polyurethane elastomers, which present chemical crosslinking and grafting structure, prepared using castor oil as a crosslinker. The stoichiometric balance (OH/NCO molar ratio) of the hard segment was used to control the final properties of the material. The physical and thermal properties were studied using differential scanning calorimetry (DSC), thermogravimetric analysis (TGA), atomic force microscopy (AFM) and tensile properties measurements. Our research effort focused on the development of a novel synthesis method for polyurethane elastomers, which can constitute a potential candidate to replacing or partially replacing petroleum-based PUs.

Experimental Part

Materials

The polyether, poly (1,4-butane diol) (Terathane 1400) and 1,6-hexamethylene diisocyanate (HDI) were purchased from Fluka. Polyether diol (Terathane 1400) has an average molecular weight of 1,400 g/mol and a hydroxyl number 80. 1,4-butanediol (BD) was supplied by Aldrich. The castor oil (CO) used in this study was supplied by Aldrich. Polyether and chain extenders were dried under a vacuum before use.

Preparation of the Elastomers

Polyurethane elastomers are block copolymers and their domain structure can be controlled through the selection of the materials and their relative proportions. The polymers were prepared in a two-step polymerization process. In this process, isocyanate-terminated pre-polymers are obtained by reaction of hydroxy-terminated polyether (Terathane 1400) with a low molecular weight diisocyanate (HDI). Low molecular weight diol and castor oil, as triols, are added as chain extenders to couple these prepolymers. In our investigation the hard-segment composition was controlled by the molar ratios of poly(ether)-diol/HDI/diol and triol used in the synthesis. The molar ratios of the OH group to the isocyanate (NCO) group chosen for the formulations were 1:2:1, 1:3:2–1:4:3. The $\text{OH}_{\text{diol}}/\text{OH}_{\text{castor oil}}$ molar ratio used was of 1/1 in each of the synthesized polyurethane samples.

Typically, synthesis of PU was done by the following procedure and the moles of added reagents for the various PU are shown in Table 1.

Table 1 Formulations and hardness of the polyurethanes obtained

Symbol of sample	Polyether/HDI/chain extenders molar ratio	Type of chain extenders	Hardness Shore A
PU1	1:2:1	Castor oil + BD	77
PU2	1:2:1	Castor oil	51
PU3	1:2:1	BD	90
PU4	1:3:2	Castor oil + BD	88
PU5	1:3:2	Castor oil	57
PU6	1:4:3	Castor oil + BD	89
PU7	1:4:3	Castor oil	63

The synthesis of PUs was performed in a 500-mL glass reactor at normal pressure and under vigorous agitation. The NCO/ $\text{OH}_{\text{polyol}}$ ratio of all formulations was 1.03–1.05. In the prepolymer procedure, polyether diol was reacted with a diisocyanate at 80 °C for 2 h, in order to yield a prepolymer that was mixed in the second step with chain extenders at 80 °C for 10 min. The progress of the reaction was monitored by measuring the infrared absorption of the isocyanate band at 2,200–2,300 cm^{-1} and the reaction was considered to be complete when this band had disappeared. The resulting material was poured into a mold and left to cure at 80 °C for 20 h. Under these conditions, the addition of catalysts was not necessary. The sheets of polyurethane containing castor oil were clear transparent, compared to those of polyurethane with BD content, which are opaque. Polyurethane sheets thus prepared were used for the determination of the physico-mechanical properties and for the thermal resistance study.

Methods

Fourier transform infrared (FTIR) spectra were recorded on a Bruker VERTEX 7 Instrument equipped with a Golden Gate single reflection ATR accessory. The spectra were recorded in the range of 600–4,000 cm^{-1} with a nominal resolution of 4 cm^{-1} .

The thermal stability of polyurethanes was tested in an air atmosphere through TGA using a DERIVATOGRAPH Q-1500 D apparatus (Hungary). The rate of TGA scans was 10 °C/min. The initial weight of the samples was about 50 mg and the temperature range 30–700 °C.

A DSC type DSC-7 Perkin-Elmer instrument was used for thermal analysis and was operated at a heating rate of 10 °C/min. The thermal transition behavior was studied over a temperature range of –100 °C to +50 °C. 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 polyurethane sheets obtained. The tests were performed at room temperature using a Shymadzu EZTest (Japan) instrument equipped with a 5kN load cell. The cross-head speed used was 50 mm/min. At least five identical dumbbell-shaped specimens were tested for each sample, and their average mechanical properties were reported.

AFM measurements of the samples were carried out at room temperature and ambient pressure, using a scanning probe microscope SOLVER PRO-M, NT-MDT (Russia). The film surface morphology was investigated by AFM using the tapping mode with a silicon cantilever NSG10.

Polyurethane hardness was measured on an Instron Shore Durometer using scale-A.

Results and Discussion

Fourier transform infrared spectroscopy was used to investigate the structural differences of polyurethanes based on castor oil with various hard segment structures.

The FTIR spectra of the PU series with different OH/NCO molar ratios are shown in Figs 1, 2, 3.

For characterization of the hydrogen bonding state of the polyurethanes two principal vibration regions were generally used: the N–H stretching vibration ($3,200\text{--}3,500\text{ cm}^{-1}$) and the carbonyl C=O stretching vibration in the amide I region ($1,690\text{--}1,730\text{ cm}^{-1}$). Polyurethanes are capable of forming several kinds of hydrogen bond, either hard segment–hard segment or hard segment–soft segment bonds [7, 13]. It is well-known that in hydrogen-bonded urethanes the N–H and C=O bands appear at lower wavenumbers than the bands that appear in urethanes free from hydrogen bonding [14]. The band centered around $1,700\text{ cm}^{-1}$ for polyurethane based on BD (PU3) had split

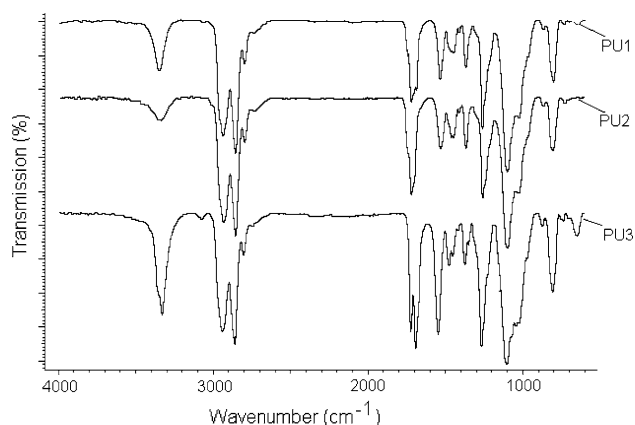


Fig. 1 FTIR spectra of polyurethane elastomers synthesized with molar ratio 1:2:1. See Table 1 for PU formulas

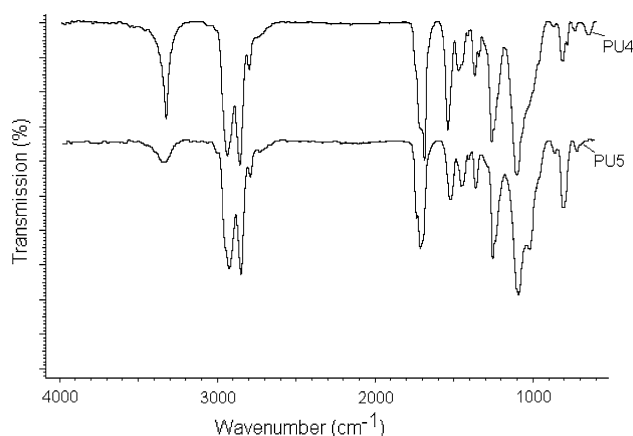


Fig. 2 IR spectra of polyurethane elastomers synthesized with molar ratio 1:3:2. See Table 1 for PU formulas

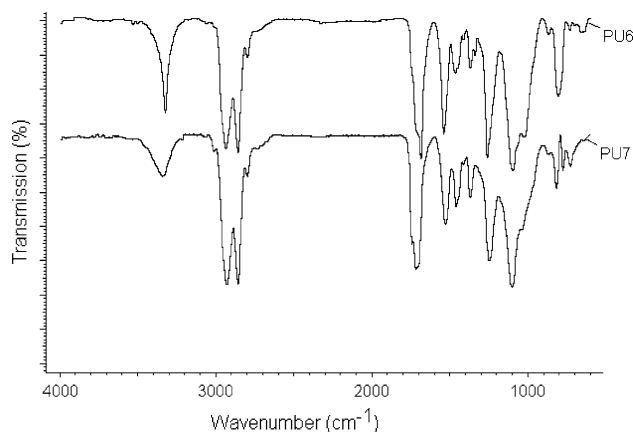


Fig. 3 IR spectra of polyurethane elastomers synthesized with molar ratio 1:4:3. See Table 1 for PU formulas

into two branched peaks, indicating the presence of hydrogen-bonded urethane carbonyl (C=O) groups [7, 15]. Also, for cross-linked polyurethanes based on castor oil and BD (PU1) a shoulder appears for the band centered at $1,700\text{ cm}^{-1}$ indicating some hydrogen-bonded urethane carbonyl (Fig. 1). The intensity of the vibration region (around $3,300\text{ cm}^{-1}$) for the N–H groups is higher for samples with BD in formulations (PU1, PU3, PU4, PU6). This suggests more urethane linkages, consequently more hydrogen bonds may have been formed. This improves the mechanical properties of the crosslinked polyurethane elastomers. In the case of the polyurethanes based only on castor oil, the intensity of the absorption band at $3,300\text{ cm}^{-1}$ is smaller. This is due to a steric hindrance effect caused by the large amount of dangling chains generated by the usage of castor oil, which blocks the formation of hydrogen bonds [1].

Polyurethanes have relatively low thermal stability, mainly because of the presence of urethane bonds.

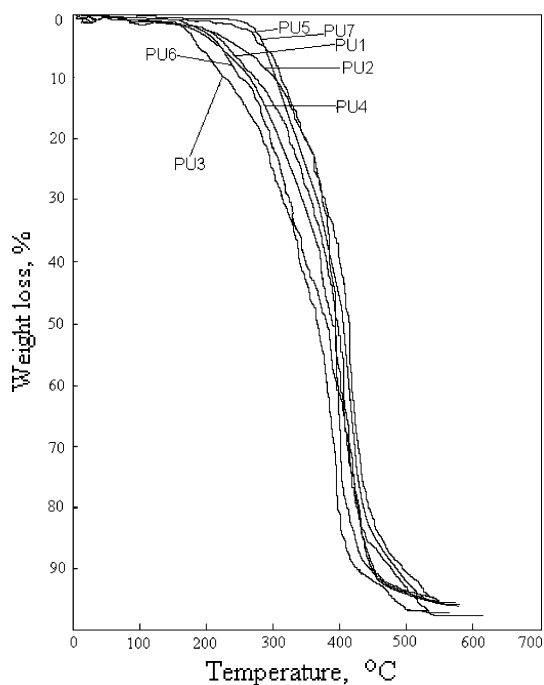


Fig. 4 TGA curves of castor oil-based polyurethane elastomers

TGA curves of the PU elastomers with various OH/NCO molar ratios are shown in Fig. 4. There were two distinct stages of decomposition in the curves. In the first stage, polyurethane elastomers decomposed slowly until 300 °C, which accounted for the first 10–15% of the weight loss. Weight loss was very rapid in the temperature range of 300–500 °C. The main degradation process can be observed at temperatures around 450 °C.

The weight loss of the polyurethane elastomers increases when the hard segment content increases, a fact which is in accordance with the existence of a higher number of weaker urethane bonds. The first stage of degradation is dominated by urethane bond decomposition [1, 16].

The DSC curves of the PU elastomer sheets with different molar ratios are shown in Figs. 5, 6.

All the PU samples were prepared using the same number of soft segments. T_g of soft segments increases with the concentration of hard segments and with of the number of crosslinks added. The increase in T_g of the soft segments is due to the hindrance local motion of the polymer segments throughout the formation of physical and chemical crosslinks between molecular chains.

Thus, the glass transition temperature of the castor oil-based polyurethanes is influenced by its crosslinking density and chemical structure. For the castor oil-based polyurethanes with molar ratios of 1:2:1 and 1:4:3, the values of T_g were -70 and -57 °C, respectively (Fig. 5). The difference in T_g values arises from several factors including the crosslinking density of the castor oil-based network and higher content of HDI in crosslinked polyurethanes [6].

The T_g increases (by 13 °C) when the molar ratio increases from 1:2:1 to 1:4:3. The high hard segment content coupled with an increased chemical crosslinks may immobilize the chains to some extent and reduce the aggregation of the hard segments into domains. The crosslinks can make hard segments disperse into the continuous soft segments. The T_g transition may be related to the movements of the main chain containing the urethane group that is attached to the crosslinker [17].

Fig. 5 The DSC scan plots for castor oil-based polyurethanes elastomers (-100 , -20 °C)

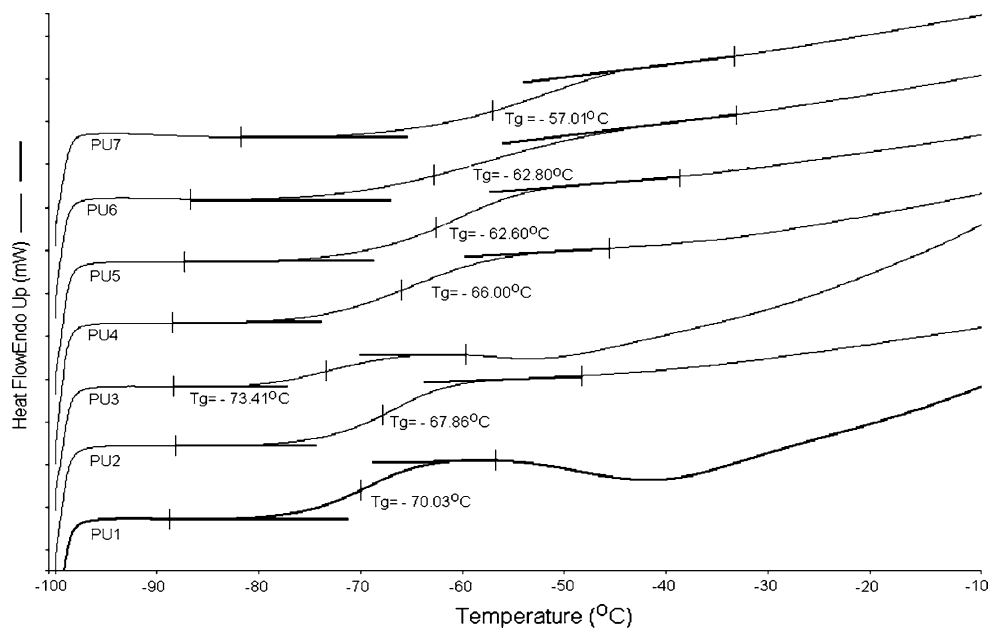


Fig. 6 The DSC scan plots for castor oil-based polyurethanes elastomers (−20, 100 °C)

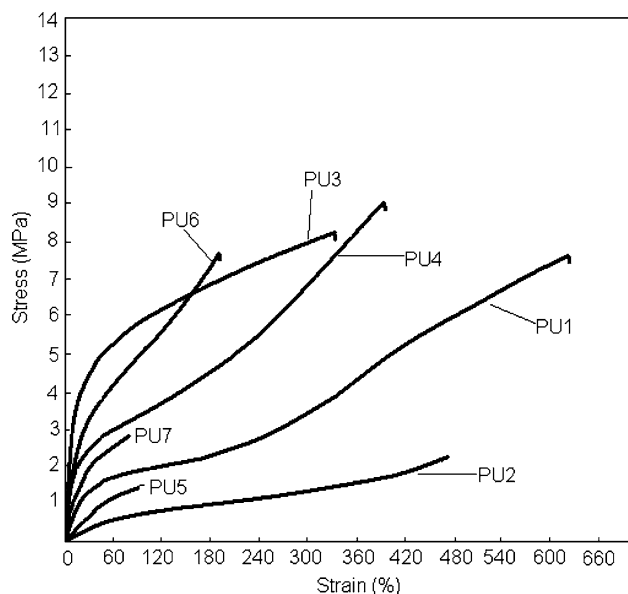
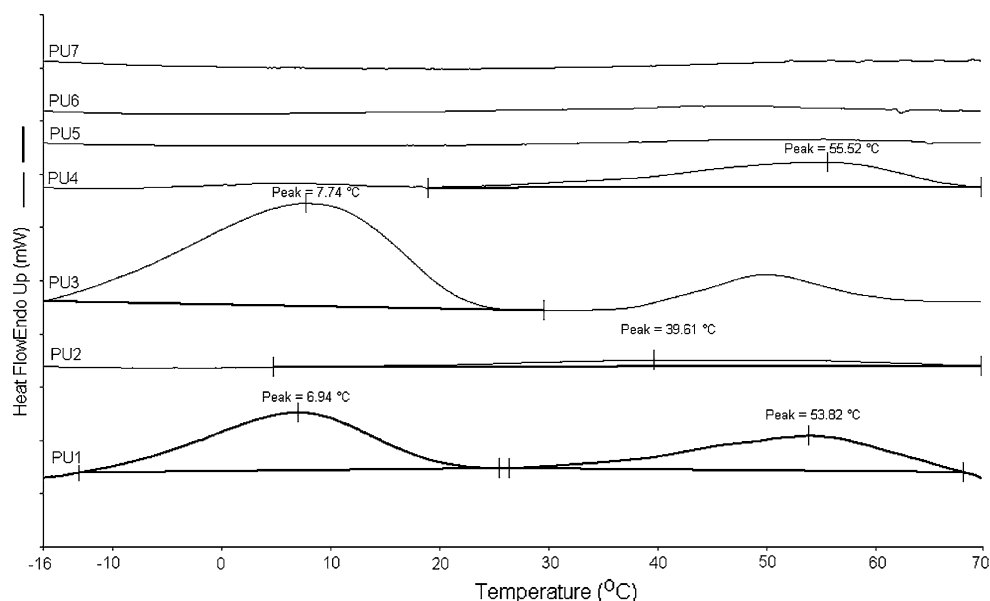


Fig. 7 Stress vs strain curves for the castor oil polyurethane

As indicated in Fig. 6, for two of the PUs with 1:2:1 PU formulas (PU1 and PU3), there were two endothermic peaks at about 5–7 °C and 53–55 °C, but for PU formulas of 1:2:1 containing solely castor oil (PU2) only one peak appears at 40 °C. It shows that the restriction of chain mobility resulted from the interlocking of the chains in PU films due to an increase in the chemical cross-linking density and thus an increase in the melting temperature of the hard segments. This must be due to the disruptions of H-bonds of long-range ordering and microcrystalline hard segments and the re-ordering of hard segment into short-range ordering domains by the incorporation of castor oil crosslinkers.

Table 2 Mechanical properties of polyurethane elastomers at various chain extenders molar ratios

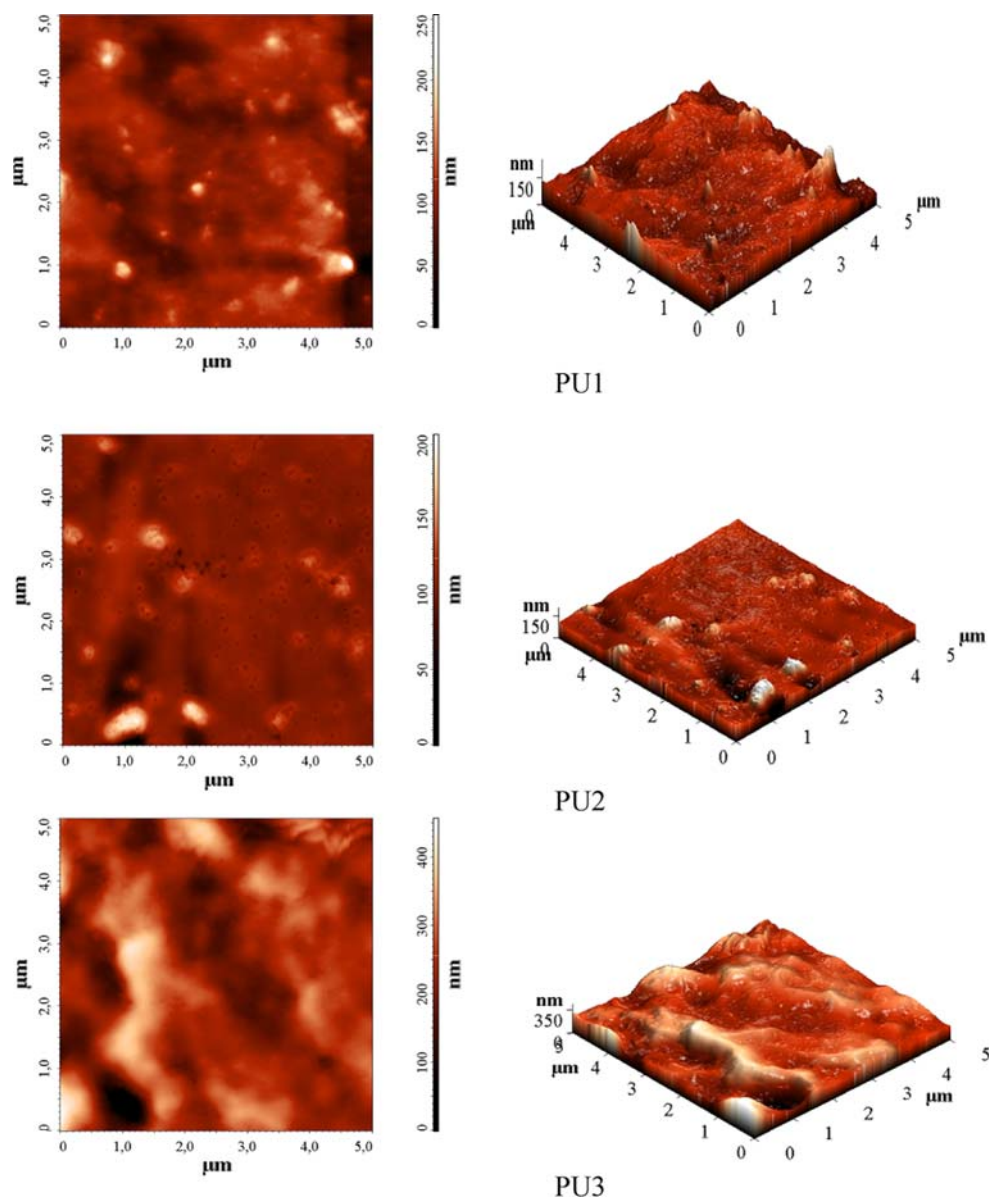
Symbol of sample	Young's modulus (MPa)	Strength at break (MPa)	Strain at break (%)
PU1	9.8 ± 0.5	7.6 ± 0.3	630 ± 15
PU2	2.9 ± 0.1	2.2 ± 0.2	480 ± 10
PU3	14.8 ± 0.5	8.3 ± 0.4	340 ± 7
PU4	10.4 ± 0.4	9 ± 0.3	398 ± 13
PU5	3.8 ± 0.3	1.5 ± 0.2	100 ± 10
PU6	11.7 ± 0.4	7.5 ± 0.1	190 ± 12
PU7	5.7 ± 0.3	2.8 ± 0.2	85 ± 5

The mechanical behavior of the crosslinked polyurethane elastomers is dependent on the structural differences between polyurethanes based on castor oil which were caused by changing the hard segment content, crosslinking density and intermolecular interactions between their hard segments. The stress versus strain curves for the castor oil-based PU sheets with different hard segment molar ratios are shown in Fig. 7. The mechanical properties of PU elastomers obtained with castor oil for various hard segment molar ratios are summarized in Table 2.

Young's modulus and tensile strength at break increased with increasing the molar ratios of the formulations for both of the polyurethanes (obtained only with castor oil and those obtained with the mixture of castor oil and BD). Elongation decreases dramatically along with increasing molar ratios, especially in the case of polyurethanes obtained only with castor oil.

The best stress–strain properties were obtained from PU elastomers based on castor oil and BD, which have a

Fig. 8 Topographic and three dimensional AFM images of castor oil polyurethane elastomers



tensile strength at break of 8–9 MPa and elongation of 400–630%. The PU sheet with a molar ratio of 1:4:3 is more rigid, having a tensile strength at yield of 7.5 MPa and elongation at break of 190%. Again, this is probably due to an excess of hard segment content in this series. The strength and strain values of the vegetable oil based PU elastomers are similar to those of the commercial PU elastomers [18]. The polyurethane elastomers based only on castor oil have a lower strength (1.5–3 MPa) and less elongation (85–480%).

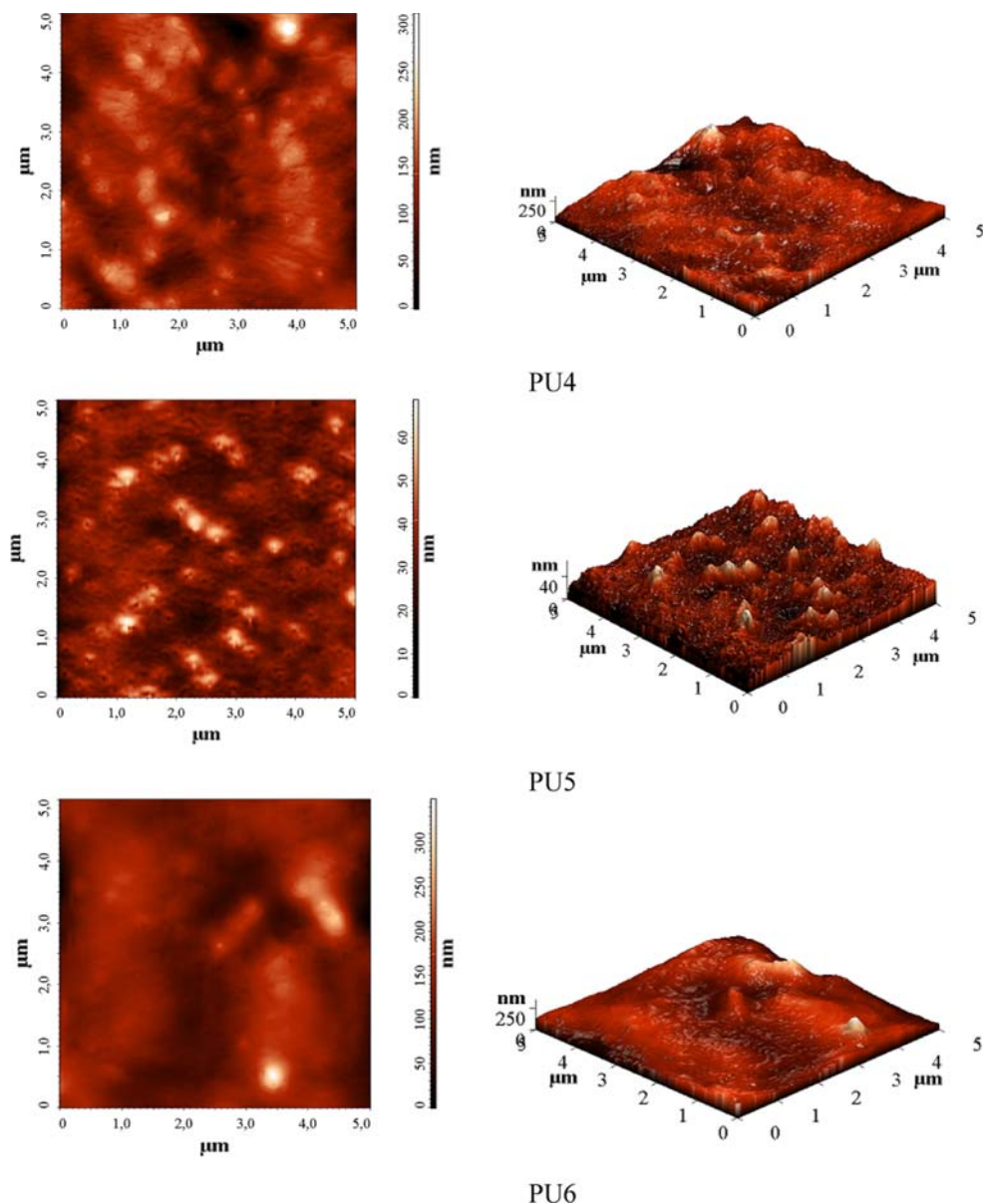
In the first case, the higher strength is caused by high hydrogen bond content and crosslinks, while the lower strength of the polyurethane elastomer based solely based on castor oil as a chain extender is a result of the large number of dangling chains that are present, which represent

imperfections in the final polymer network, that do not support stress when the network is under load. The use of the aliphatic diisocyanate (HDI) also limits the strength and elongation at break [1, 19, 20].

The surface topography of the castor oil-based polyurethanes was examined by AFM (Fig. 8). AFM was utilized to study the phase-segregated morphology of polyurethane with various hard segment structure and concentrations. AFM investigations were conducted on the surface of the polymer, with a scanning area of $5 \times 5 \mu\text{m}$.

Topographical heterogeneity is observed in the images of the castor oil polyurethane, which may reflect the existence of ordering tendencies in the polymer structure. In these images, by convention, the hard and soft micro-phases appear as bright and dark regions, respectively. By

Fig. 8 continued



increasing the hard segment concentration, changes were observed in the surface morphology. The presence of bright and dark regions indicates the presence of microphase morphology.

AFM images of polyurethane films that have castor oil in the molecular formulas have an extended smoother surface area compared to the structural formations observed in the BD-polyurethane film (PU3).

The light-colored spots represent hard domains which are grouped into compact areas. These are dispersed all over the matrix which is formed by the soft domains while in the case of polyurethane with BD in their molecular formula (PU3) the hard segment domains group themselves together and appear as thick regions.

Inclusions or even agglomerates of hard segments can be seen in some limited areas. This could be explained by the possibility that those areas benefitted from a better ordering.

The effect of the various polyurethane microstructures on their macroscopic behavior was reflected in their hardness. Table 1 shows shore A hardness of crosslinked polyurethane films with different amounts of hard segment content. BD-based polyurethanes turned out to be harder (90 Shore A) than those based on only castor oil (51–63 Shore A) across the whole composition range studied. These results show that hydrogen bonding, phase segregation, crosslink density and the plasticizer effect of castor oil dangling chains affect the polyurethanes

hardness. A higher number of crosslinked hard segments leads to an increase in the hardness of the polyurethane materials.

Conclusion

Polyurethane elastomer films have been prepared by reacting polyols with aliphatic diisocyanate. The prepolymer was chain-extended with bifunctional precursor chains and/or with castor oil as a trifunctional crosslinker at stoichiometric ratios. The sheets of polyurethane containing castor oil are clear transparent, compared to those of polyurethane with BD content, which are opaque.

The increased hard segment molar ratio and dangling chains present in the triglyceride structures that act as plasticizers increasing T_g by about 13 °C for polyurethane with an increased content of castor oil. This polyurethane displayed a relatively low glass transition temperature (of -70 to -57 °C) and a tensile strength of maximum 9 MPa and elongation at break of 630%. The properties of PU sheets were mainly governed by the stoichiometric balance of the components in the reaction and the degree of crosslinking.

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