



Design-properties relationships of polyurethanes elastomers depending on different chain extenders structures

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Abstract

In this study, the effect of the structure and amount of the chain extenders on the morphological image and physico-chemical properties of some new polyurethane elastomers has been investigated. To achieve this, three series of polyurethane elastomers based on poly(tetramethylene ether) glycol, hexamethylene diisocyanate and chain extenders with different structures (triethylene glycol, 3,6-dithia-1,8-octanediol, 1,6-hexanediol) were synthesized. The chain-extenders which introduce oxygen or sulfur atoms into the polyurethane backbone chains (hard domains) change the behavior of the properties compared to the corresponding polyurethanes chain-extended with aliphatic diols. The structures of the new polyurethane elastomers were examined by FTIR, X-ray diffraction analysis and by atomic force microscopy (AFM). They were also characterized for thermal and tensile properties. The polyurethanes with sulfur into their hard segment structure were found to exhibit improved thermal stability properties and equivalent mechanical properties with polyurethanes obtained with aliphatic diols. This is due to the extensive and many fold hydrogen bond network that characterizes polyurethanes with sulfur in their hard segment structure.

Keywords Polyurethane elastomers · Chain extenders · Mechanical properties · Thermal properties

Introduction

Polyurethanes represent one of the most used classes of polymers due to their broad spectrum of compositions, molecular architectures, properties and applications [1–4]. Polyurethanes are commonly produced by reacting diisocyanates, long-chain diols- usually, polyesters or polyethers - (soft segments) and short-chain diols (chain-extenders). Depending on the chain-extender structure (bifunctional or multifunctional), linear or crosslinked polyurethane structures can be obtained [5, 6]. The polyurethanes with a non-crosslinked structure are of particular interest because of their broad versatility and huge applicability from

producing useful elastomers to integration in biomedical devices [7–11]. Due to the possibility of obtaining some interesting combination of physical and mechanical properties from these polyurethanes, their structure-property relationships have so far been broadly studied. The physical linkages forming between their chains are generally mainly caused by the hydrogen bonding process and establish the microscopic and macroscopic properties of the polyurethanes [12].

Aside from the above-referenced polyurethanes that have been extensively studied for their low toxicity, biocompatibility and biodegradability, their sulfur analogues, polythiourethanes (containing -NH-CO-S-linkages) have also been studied because of their possible applicability in prolonged-release drugs [13]. Thus, studies have extensively covered the synthesis of polyurethanes using new dithiol chain-extendors such as bis [4-(mercaptomethyl) phenyl] methanone [14], methylenebis (1,4-phenylmethyleneethio) dialcanols [15], diphenylethane-derivative diols [16]. It was found that the introduction of sulfur into the urethane linkage improves the biodegradability,

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adhesion and refractive index of the obtained polymers. The presence of sulfur atoms in the polymer structure can have beneficial effects on their mechanical, electrical, and optical properties, and contributes to improving their resistance to heat, chemicals, radiation, and bacteria, as well as their biocompatibility [17–20].

By introducing high atomic weight atoms such as sulfur in the polyurethane structure, new types of optical polymers with highly refractive index and low chromatic dispersion have been obtained [21]. Introducing a thioether structure into the polyurethane macromolecular chain improves the flexibility and stability of the macromolecular chain due to the longer length of the C-S bond structure. Sulfur atoms also increase the selective absorption capacity of heavy and noble metals ions (Au^{3+} , Ag^+ , Cu^{2+}) [22].

The C-S bond is longer than the C-O bond and the polarity of the C-S bond is weaker than that of the C-O bond [23]. Nonetheless hydrogen bonds involving sulfur are generally considered to be weak hydrogen bonds compared to conventional ones, due to the lower electronegativity of S compared to O or N. But in the case of methionine-containing dipeptides, amide-NH...SH bonds are found to be even stronger than amide-N-H...O=CH bonds. This can be explained by the fact that sulfur can form a greater variety of hydrogen bonds because being a hydrogen bond acceptor it can also be a hydrogen bond donor or can form π -type linkages [24].

In the present study, three different chain extenders such as triethylene glycol, 3,6-dithia-1,8-octanediol, 1,6-hexanediol were used to obtain new polyurethane elastomers. One of the main objectives of this paper was to study the influence of the heteroatom (sulfur or oxygen) from the structure of the hard segment, on the thermo-mechanical properties and surface morphology of the obtained polyurethanes, compared to those of polyurethanes prepared with 1,6-hexanediol.

The aim of this study was to find the relationship between the chemical structure of the polyurethane and its properties behavior and we are also aiming to perform a future study of the antibacterial activity of polyurethanes which incorporate sulfur atoms versus polyurethanes which incorporate oxygen atoms into their hard domains.

Materials and methods

Materials

All materials used in this study were used as received from the suppliers, without any further purification. The polyether diol was poly(tetramethylene ether) glycol

(Terathane 1400, with an average molecular weight of 1400 g/mol) which was obtained from Fluka (Fluka Chemie AG, Buchs, Switzerland) and was dried under reduced pressure at 120 °C for 2 h, in order to eliminate any potential moisture. Hexamethylene diisocyanate (HDI) was obtained from Fluka. The chain-extenders, triethylene glycol (TEG), 3,6-dithia-1,8-octanediol (DTO), 1,6-hexanediol (HD) (Fig. 1) and dimethylformamide (DMF) - were obtained from Aldrich (Sigma-Aldrich Chemie GmbH, Taufkirchen, Germany).

Polyurethane synthesis

The polyurethane elastomers with different chain-extenders were obtained using a two-step route, according to the following typical procedure [25]. The polymers were synthesized with molar ratios of poly(ether)-diol/HDI/ chain extender diol of 1:2:1 and 1:3:2 (Table 1). In order to obtain linear polymers, the molar ratio of the NCO and OH groups was kept as 1:1.

The NCO-terminated prepolymer was prepared by reaction of dried Terathane 1400 and HDI in ratios as shown in Table 1, in a 250 mL glass reactor equipped with a mechanical stirrer, a drying tube connected to a vacuum pump and an oil bath, at 80 °C for 2 h.

The prepolymer was then chain-extended using the required amount of chain extender and 10 ml DMF used as a polymerization solvent, and kept at 80 °C for 2 h. No absorption band appeared at around 2270 cm^{-1} , indicating the complete reaction of the NCO functional groups. The resulting polyurethane solutions were then dry-cast onto cleaned glass plates and stored at 80 °C for 24 h in order to obtain flexible films. The films thus prepared were used for the determination of surface and thermo-mechanical properties.

Characterization

Fourier transform infrared (FTIR) spectra were recorded on a VERTEX 70 Instrument (Bruker, Germany) equipped with a Golden Gate single reflection ATR accessory. The spectra were recorded in the wavenumber range of $600\text{--}4000\text{ cm}^{-1}$ with a resolution of 4 cm^{-1} , averaging 32 scans for each sample.

Thermogravimetric experiments took place in air atmosphere through thermogravimetric analysis (TGA) using a DERIVATOGRAF Q-1500 D apparatus (Paulik, Paulik and Erdey, Budapest, Hungary). The heating rate of the TGA scans was of 10 °C /min . The initial weight of the samples was about 50 mg and the temperature range $30\text{--}700\text{ °C}$.

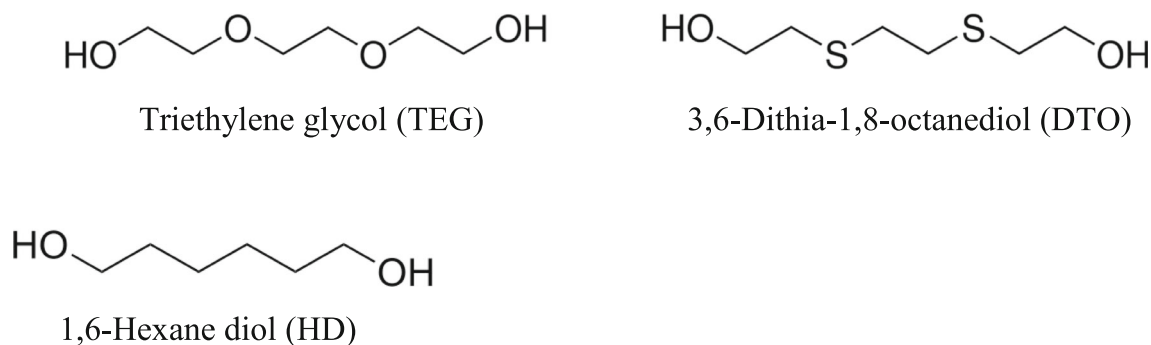


Fig. 1 Chemical structures of the chain extenders

The mechanical properties were determined using a Shimadzu EZTest (Japan), equipped with a 5kN load cell. Dumbbell-shaped specimens were prepared using dies ($75 \times 12.5 \times 4$ mm; ISO 37 type 2). The tests were performed at room temperature (23°C), with a cross-head speed of 50 mm/min. All the tests were conducted for five samples and their averaged values were reported. The standard deviation between the values obtained from all the performed tests was less than 10%.

Atomic force microscopy (AFM) measurements for the topography of the samples were performed at room temperature and under ambient pressure, using a Scanning Probe Microscope SOLVER PRO-M AFM, NT-MDT (Russia). The images of the film surfaces were taken using the tapping mode with a high resolution no-contact silicon NSG10 cantilever. In all AFM measurements the scan range was of 10 μm in the X-Y direction. Image acquisition and roughness parameters measurements were done with Nova 1.0.26.1443 software provided by NT-MDT.

Wide Angle X-Ray Diffraction (WAXD) was performed on a Diffractometer D8 ADVANCE (Bruker AXS, Germany), using the Cu-K α radiation ($\lambda = 0.1541$ nm), a parallel beam with a Gobel mirror and a Dynamic Scintillation detector. The working conditions were 36 kV and 30 mA. All the diffractograms were investigated in the range of 4–40 (2 theta degrees), at room temperature.

Results and discussion

FTIR study

Three series of the polyurethane elastomers containing ether (-C-O-C-), thioether (-C-S-C-) and aliphatic (-C-C-C-) moieties in their hard segment structures were synthesized.

The chemical structures of the polymers were confirmed by FTIR spectra. Figure 2 shows the FTIR spectra of the synthesized polyurethanes.

All the synthesized polyurethanes present an absorption band at 3322 cm^{-1} characteristic of the N-H groups from the urethane. The intensity of this absorption increases with the increase in hard segment content, except for the polyurethanes chain-extended with TEG (Fig. 2a). This behavior is also kept for the N-H bending vibration at about $1535\text{--}1538\text{ cm}^{-1}$.

Additionally, the absorption peak of the urethane carbonyl groups exhibits the same particular behavior, and the free (1720 cm^{-1}) and hydrogen-bonded (1684 cm^{-1}) urethane carbonyl groups have an approximately equal share within the structure of the polyurethanes obtained with TEG (Fig. 2a). On the other hand, the intensity of the absorption peak of the non-hydrogen-bonded urethane carbonyl groups (1720 cm^{-1}) is very low and almost disappears with the increase in hard segment content for polyurethanes synthesized with DTO and HD (Fig. 2b and c). The intensity of the absorption of the hydrogen-bonded urethane carbonyl groups (1681 cm^{-1} ,

Table 1 Designation and composition of the polyurethane elastomers

Sample	Terathane/HDI/Chain extender (molar ratio)	Chain extender
TEG1	1/2/1	Triethylene glycol
TEG2	1/3/2	Triethylene glycol
DTO1	1/2/1	3,6-Dithia-1,8-octanediol
DTO2	1/3/2	3,6-Dithia-1,8-octanediol
HD1	1/2/1	1,6-Hexanediol
HD2	1/3/2	1,6-Hexanediol

Fig. 2 FTIR spectra of the polyurethane elastomers obtained with **a** TEG, **b** DTO, **c** HD

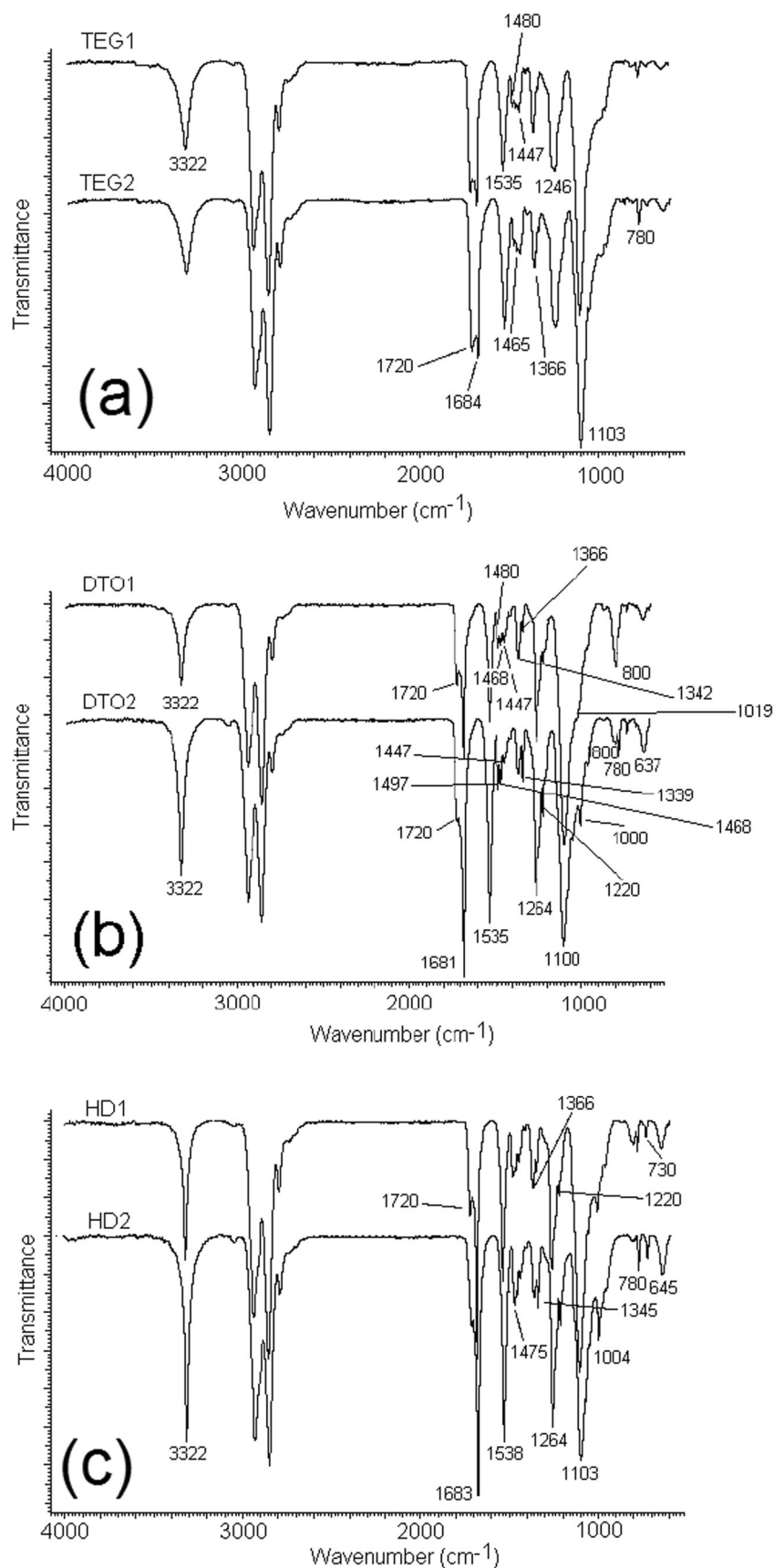


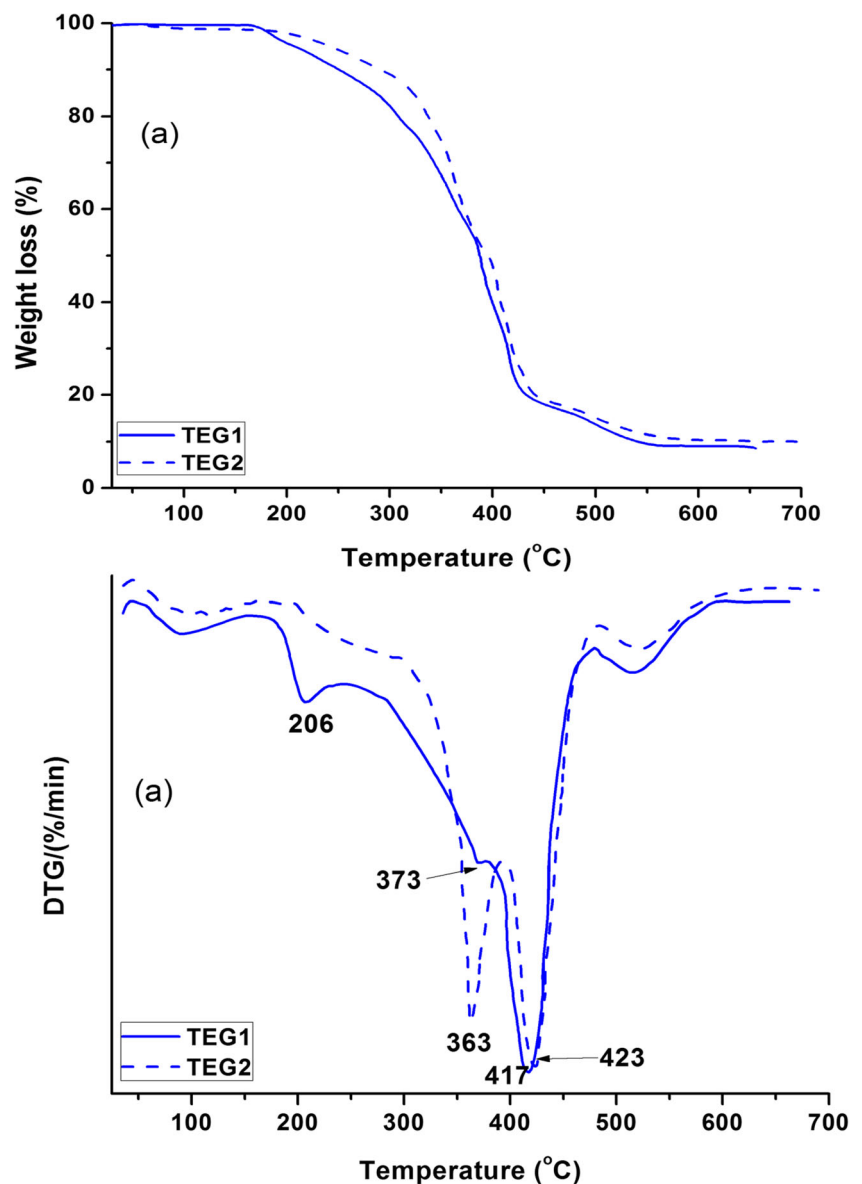
Table 2 Thermal properties of the polyurethane elastomers measured by TGA

Sample	T _{5%} (°C)	T _{10%} (°C)	T _{max} (°C)	W _{max} (%)	Char residue (%)
TEG1	207	250	373/417	43/73	8.57
TEG2	242	291	363/423	34/73	9.97
DTO1	288	316	398	54	4.72
DTO2	329	356	375/437	18/50	8.09
HD1	260	316	381/420/425	44/66/69	12.78
HD2	218	278	377/427	38/72	10

1683 cm⁻¹) is very significant and increases with the increase in hard segment content and therefore implicitly with the chain extender amount. This shows an increase in hydrogen bonds between the carbonyl groups and the N-H groups or sulfur components which have a higher versatility to form hydrogen bonds.

These results of the absorption stretching vibrations for the carbonyl groups in the polyurethanes matrix are a result of the different hydrogen bonds which can be achieved within the different structures of the hard urethane domains. The hydrogen bonds of the urethane N-H groups occur both with the urethane carbonyl as

Fig. 3 TG and DTG curves of the studied polyurethane elastomers obtained with **a** TEG, **b** DTO, **c** HD



well as with the sulfur (DTO) or oxygen (TEG) which belongs to the hard segment structure. All these hydrogen bonds are favored by the elasticity and the structural arrangement of the hard segments of the polyurethane matrix [26].

The bands at 1480, 1468, 1447, 1366, 1342 cm^{-1} are absorption of the various modes of the $-\text{CH}_2$ vibrations. The bands at 1264 cm^{-1} and 1246 cm^{-1} (TEG) are attributed to the aliphatic $-\text{R}-\text{NH}-\text{COO}-$ groups [27]. The band at 1100–1103 cm^{-1} is attributed to the C-O-C stretching vibrations of the ether group and the absorption band at about 790 cm^{-1} to the bending vibration of the carboxyl group [28].

Thermal properties

The thermal stability of the polyurethane elastomers was studied by TGA measurements, and the measurement values are shown in Table 2. The TG curves and TG derivative curves of the polyurethanes obtained with different chain extenders are shown in Fig. 3.

The TGA curves from Fig. 3 show that the type and amount of chain extender influence the number of decomposition stages and the temperatures that occur at. In the TG curves, the main decomposition steps appeared in the range of 250 °C to 437 °C. The first decomposition step, the degradation of the urethane groups takes place between 250 °C and 356 °C,

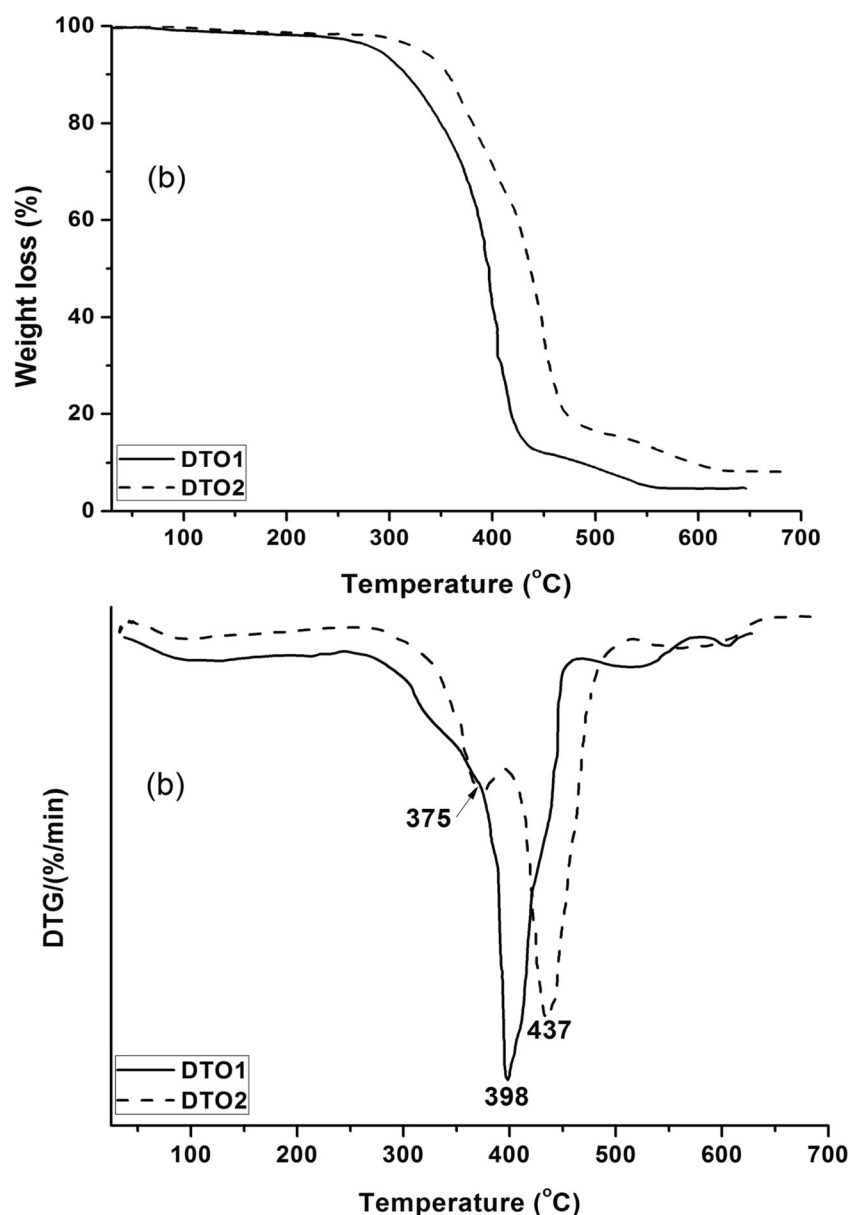


Fig. 3 (continued)

while the second stage of the degradation of the polyols was from 336 °C to 437 °C. The different behavior can be explained by the fact that the urethane groups are part of hard domains with different structures including heteroatoms such as oxygen or sulfur which more or less influence the thermal resistance of the hard domains which include the urethane groups.

Thus, the samples obtained with TEG present more stages of thermal decomposition (with maxim decomposition temperatures of 373 °C, 417 °C, (TEG1) and the increase in hard segment content leads to higher decomposition temperatures for TEG 2 (423 °C).

In comparison, polyurethanes obtained with a low content of DTO (DTO1) present a single maximum decomposition temperature peak at 398 °C (DTO1) while the polyurethanes with a higher DTO chain-extender

content (DTO2) exhibit not one, but two maximum decomposition temperature peaks at 375 °C and 437 °C. The improved thermal stability of DTO-based polyurethanes can be attributed to the presence of sulfur in the matrix of the hard segment which, through its structure and multiple hydrogen bonds, provides greater stability to the urethane groups. Polyurethanes synthesized with DTO easily form highly ordered physical cross-linked regions within the hard domains that strengthen the obtained polyurethane material. The stronger intermolecular interaction determines greater chain rigidity and the temperature needed for thermal motion is higher and thus thermal resistance increases [29].

As can be seen from Table 2, the polyurethanes obtained with DTO (DTO1 and DTO2) showed the highest degradation temperature for 5% weight loss ($T_{5\%}$;

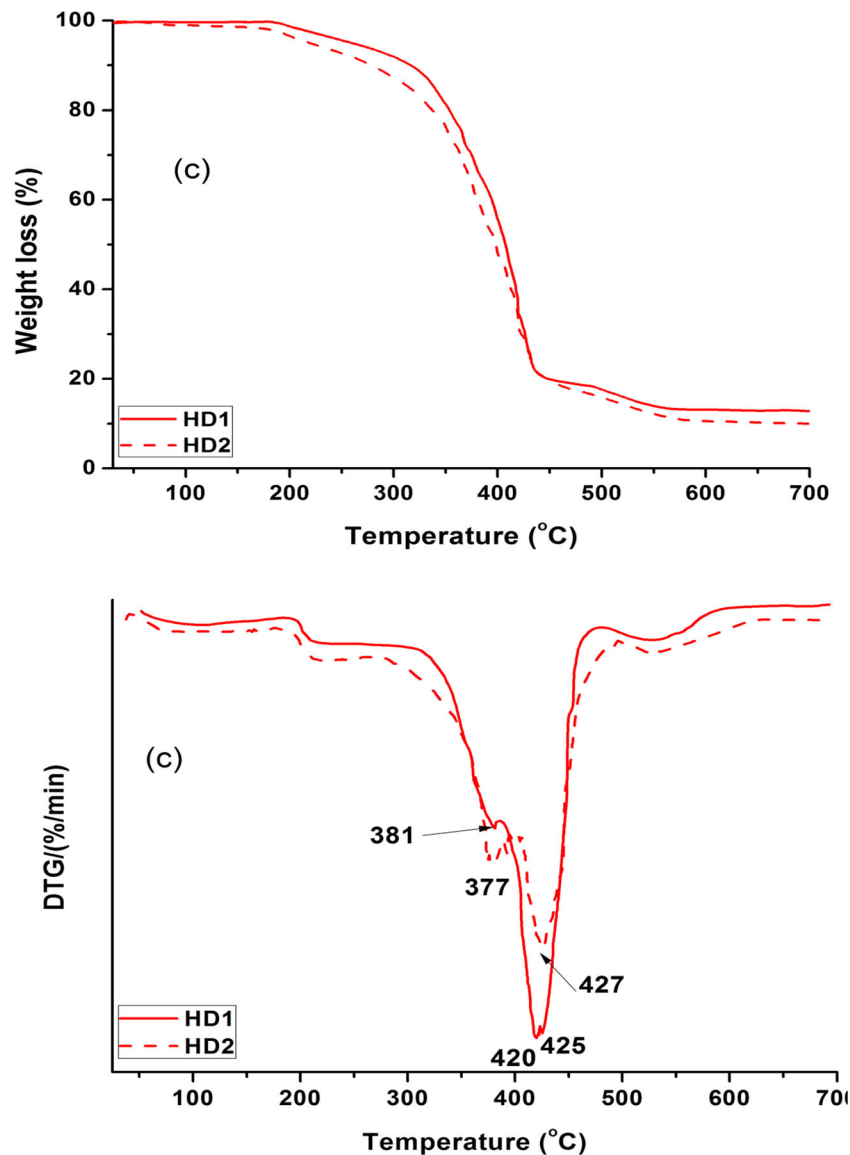
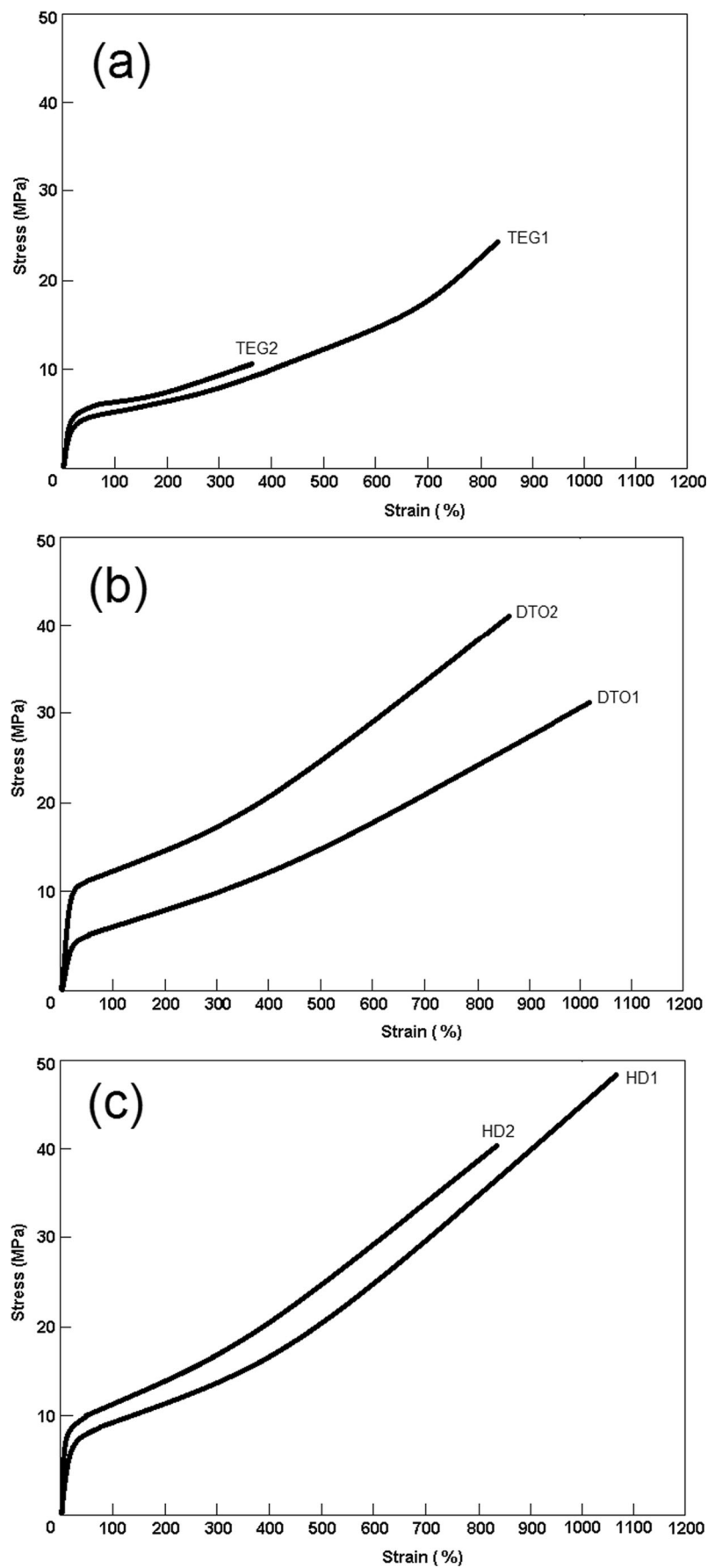
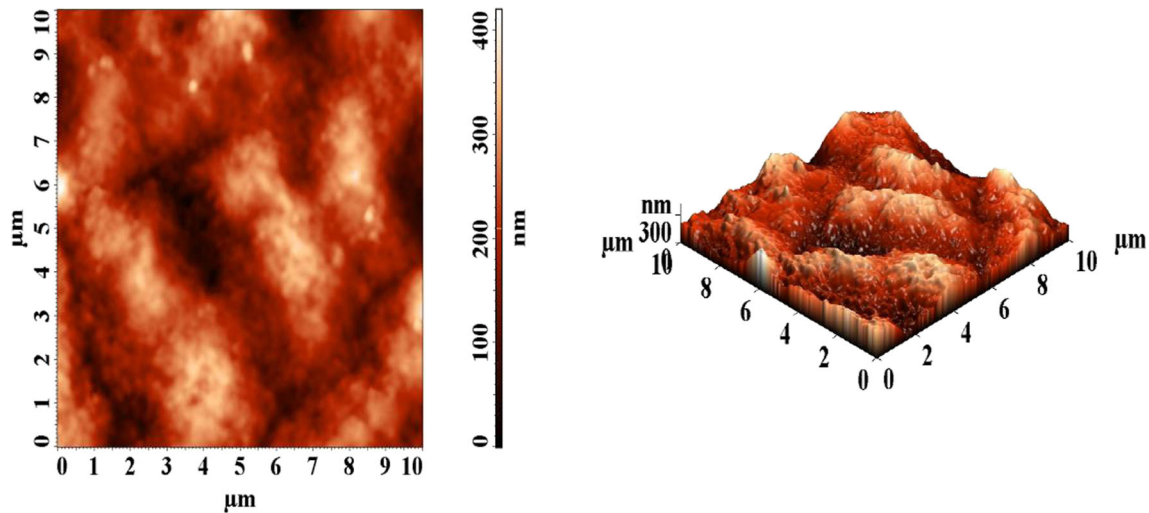


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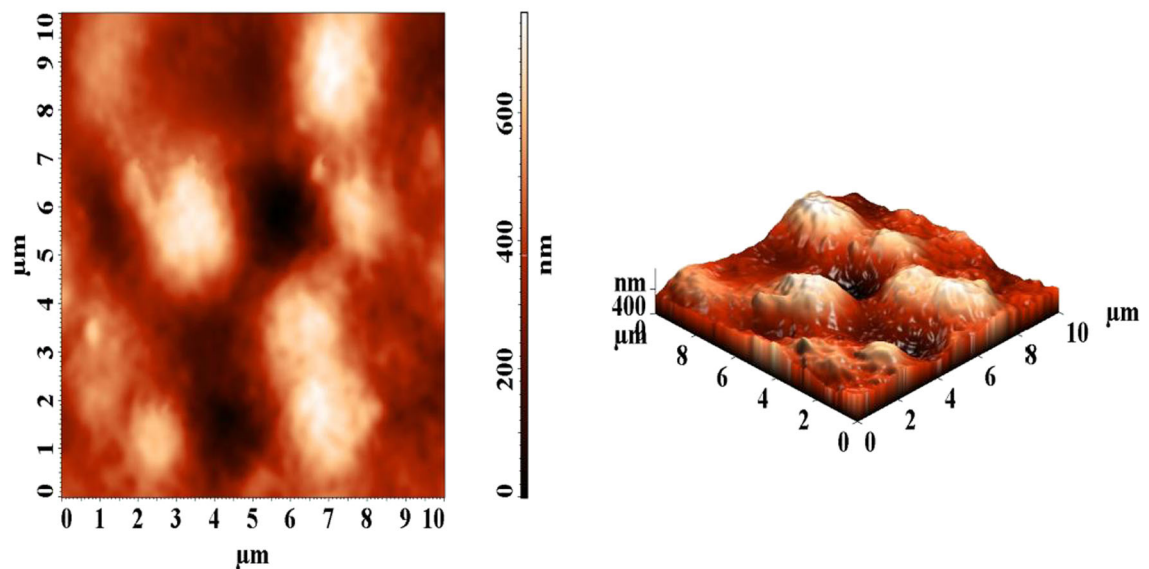
Fig. 4 Stress-strain curves of the obtained polyurethanes synthesized with **a** TEG, **b** DTO, **c** HD



(a)



TEG1



TEG2

Fig. 5 AFM images of the obtained polyurethanes with **a** TEG, **b** DTO, **c** HD

288 °C for DTO1 and 329 °C for DTO2). The polyurethanes with DTO in their content also exhibit higher values of the other parameters, namely temperature for 10% weight loss ($T_{10\%}$) and temperature of the maximum rate of the weight loss (T_{\max}) when compared with polyurethanes obtained with TEG and HD.

All samples obtained with HD had a certain degree of separation in the microphase. The increase in hard

segment content resulted in a decrease of the flexibility of the molecular chains that prevented the tight packing of the chains so that the degree of separation in the microphase has decreased and thermal properties have worsened. Also, the increase in the number of urethane groups leads to an increase in the number of centers of initiation of decomposition so that the thermal stability of these polyurethanes decreases.

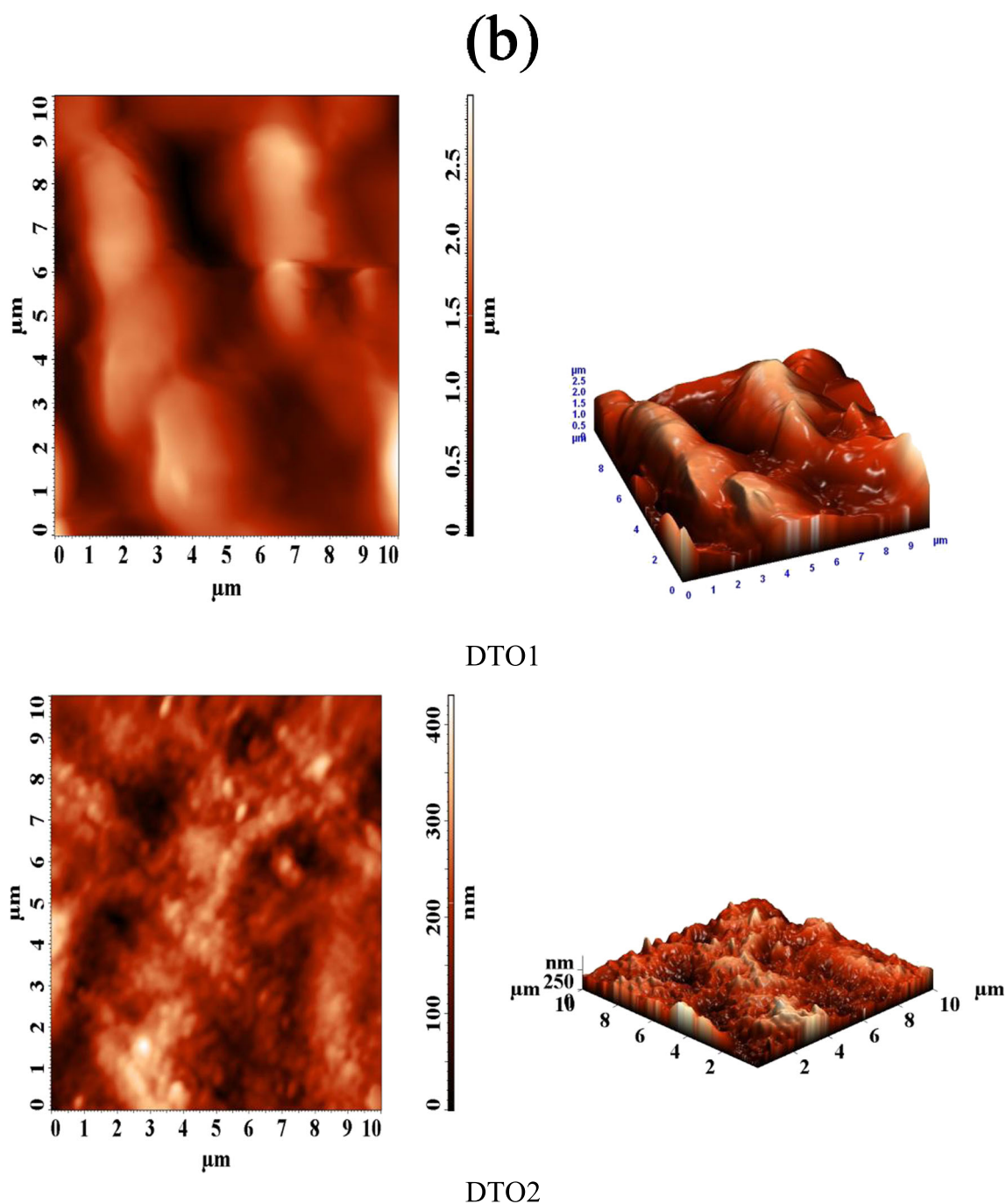


Fig. 5 (continued)

The synthesized polyurethanes were obtained from compounds in which the ratio of monomers was constant, while only the chain extender was different for each material. The various chain extenders have a strong effect on the structure of the hard segment, and consequently on the thermal and mechanical behavior.

The different structure of the radicals resulting from the decomposition of the urethane groups will result in

combinations with the radicals of the thermal decomposition products of other bonds, thus the differing resulting products will influence the final thermal stability of the polyurethanes [30].

Mechanical properties

One of the purposes of the present research was to study the changes of the physical properties of the obtained

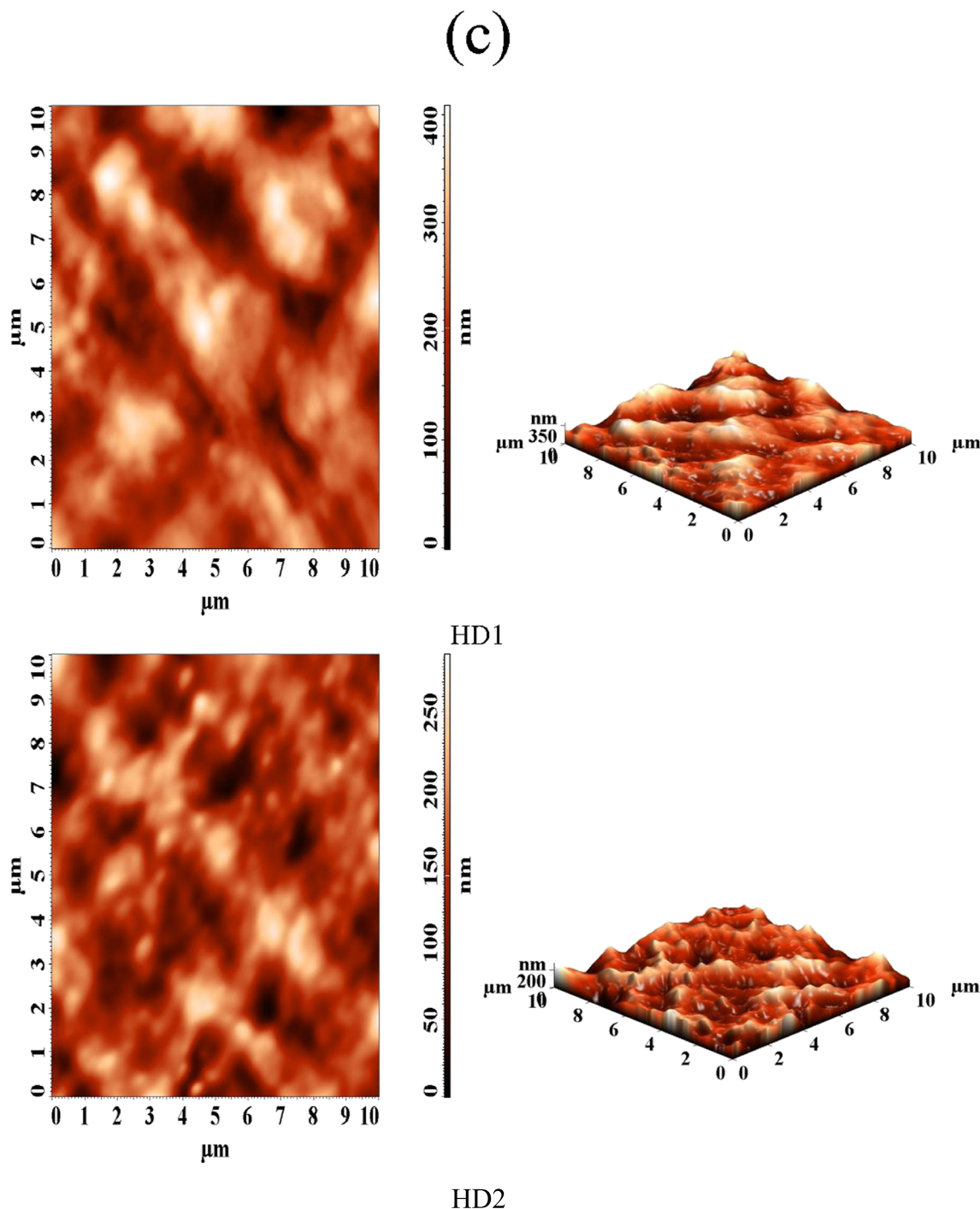


Fig. 5 (continued)

polyurethanes based on the chemical structure of the chain extender. The mechanical properties behavior of the obtained polyurethanes is plotted in Fig. 4.

The polyurethanes with higher DTO content (DTO2, Fig. 4b) present a tensile strength of 43 MPa and elongation at break of 850%. These values are close to the ones for polyurethanes obtained with conventional aliphatic chain extenders (HD2, Fig. 4c), which have a tensile strength of

42 MPa and elongation at break of 850%. The very good mechanical properties of the DTO-based polyurethanes are a result of the intermolecular interactions of the sulfur, which create multiple hydrogen bonds within the hard segment domains [31]. We also have to mention that all the synthesized polyurethanes have the same type of soft segments, which means that the results have not been influenced by the composition of the soft segments.

Table 3 Roughness analysis for the polyurethane films

Sample	<i>Sa</i> (nm)	<i>Sq</i> (nm)
TEG1	52.9	64.7
TEG 2	115	143
DTO1	55	65
DTO2	51.3	63.8
HD1	51	63.9
HD2	34	42.7

Sa – Average roughness, *Sq* - root mean square

By comparison, polyurethanes chain-extended with TEG have lower tensile strength values and any increase in chain-extender content has the effect of decreasing the tensile strength from 25 MPa (TEG1) to 10 MPa (TEG2) and elongation at break values from 850% (TEG1) to 370% (TEG2) (Fig. 4a). This can be explained by the fact that the hard domain of the TEG polyurethanes no longer has the same amount of connections, but there are more connections between the soft and hard segments. This is because there is a competition to form hydrogen bonds between the ether oxygen from the hard segment and the ether oxygen from the soft segment whose macromolecular chains present a high degree of mobility. This mobility also increases the likelihood of forming intra-molecular hydrogen bonds.

The obtained results show that the mechanical properties are dependent on the design of the hard segment (given by the kind of chain extender employed), as well as on the particularities of the hard segment structure and content. An additional factor which has influenced the behavior of the mechanical properties was the type of heteroatom belonging to the chain-extender, which determines the nature and strength of the intermolecular interactions.

Surface characterization by AFM

The surface morphologies of the obtained polyurethane series were investigated using Atomic Force Microscopy (AFM) and the micrographs and the topography of the samples are shown in Fig. 5. The roughness parameters such as average roughness (*Sa*) and root mean square (*Sq*) are given in Table 3.

In the case of DTO-based polyurethanes, the continuous polymer matrix appears to have developed clear globular domains due to the extensive molecular chains interconnection. The average roughness (*Sa*) values are situated approximately in the range of 51–55 nm and the root mean square (*Sq*) values are in the range of 63–65 nm, indicating the preservation of a more uniform surface compared with the other studied samples. This behavior is also confirmed by values of the roughness maximum peak heights, generated on a 3D nanoscale profile, which are in the range of 200–250 nm.

In the case of polyurethanes chain-extended with TEG, the morphological separation is no longer so clear, while the dispersed phase no longer has a clear shape and the inter-phases are diffuse, which shows a degree of miscibility of the phases. Additionally, the roughness of the TEG-based polyurethanes increases with the increase in TEG content as *Sa* increases from 53 nm (TEG1) to 115 nm (TEG2) (Table 3), the root mean square, *Sq*, values increase from 64 nm (TEG1) to 143 nm (TEG2) and the maximum peak heights are in the range of 300–400 nm.

The polyurethanes obtained with HD present rod-like features which are more densely distributed throughout the continuous phase. The polyurethanes with a higher content of HD present a less roughness surface (*Sa* = 34 nm and *Sq* = 42 nm for HD2) compared with the other polyurethane samples. These polyurethanes also exhibit lower values of the maximum peaks height in the range of about 200 nm. The polymers obtained with HD show a less roughness surface due to the aliphatic structure of the chain extender. Having an even number of CH₂ groups, such as 1,6 hexane diol, the chain extender exhibits a completely extended conformation. This allows for the binding by hydrogen bonds in both directions perpendicular to the macromolecular chain, which result in an ordered structure of the hard domains. Thus, these polymers can crystallize more easily in extended conformations with better phase separation and better elastomeric properties [32]. The strong interaction between the hard segments and the elasticity of the aliphatic chain determine a better packaging of the macromolecular domains, which results in surfaces with less roughness and improved mechanical properties.

X-ray study

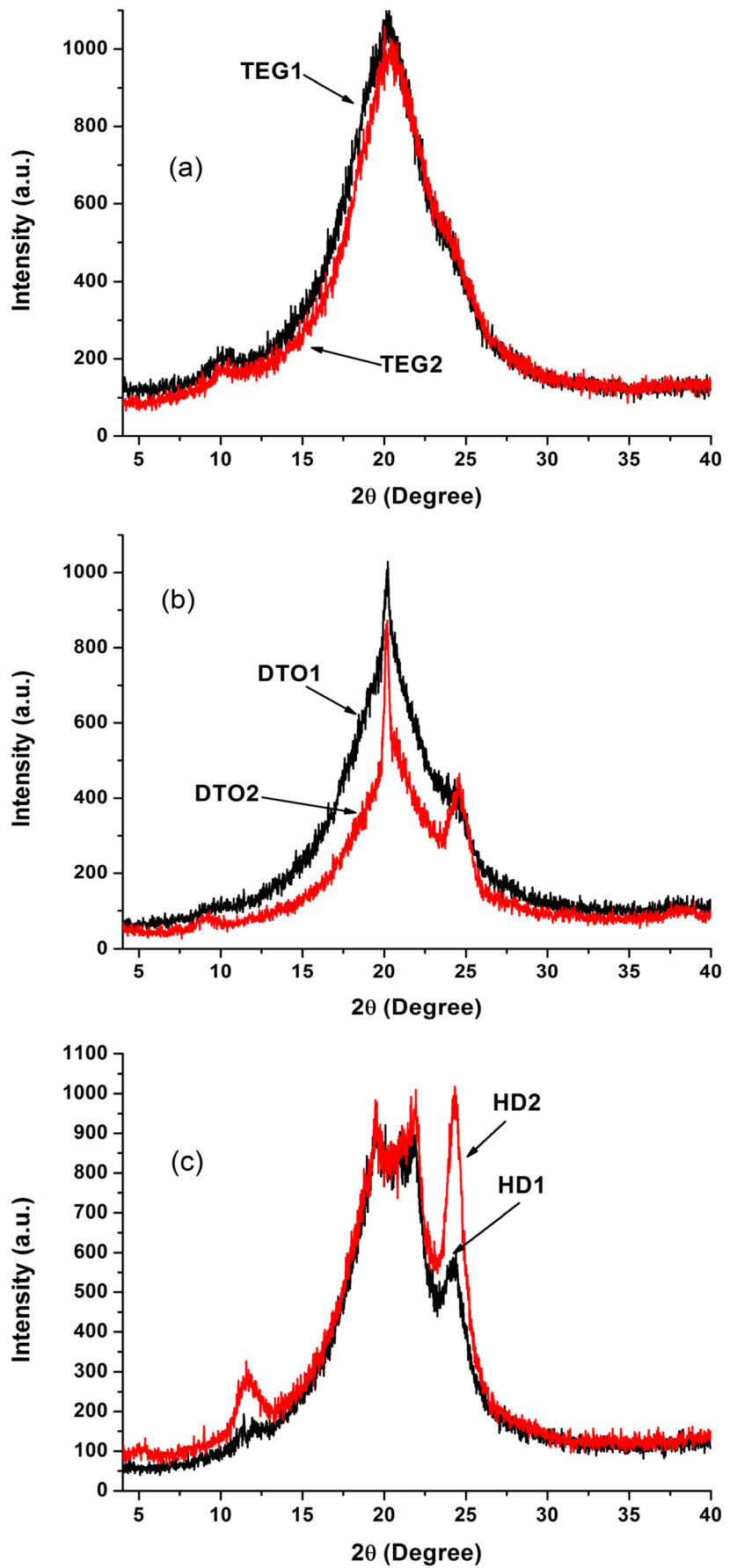
The X-ray diffraction curves of the investigated polyurethane samples are shown in Fig. 6.

The X-ray diffraction experiment revealed that with polyurethanes obtained with TEG, only one peak appeared at a 2 θ angle of about 20° for both samples with different content of the hard segment. This value shows that the content of hard segment (and, by default, TEG content) does not have a great influence on the crystallization process of these polyurethanes.

In the case of polyurethanes chain-extended with DTO, it was found that the polyurethane with a higher content of hard segment (DTO2) presented a second peak at 25° aside from the one at 20°. The appearance of this peak can be considered an effect of the crystalline phase which can form an extensive hydrogen-bonded structure within the hard segment domain.

The polyurethanes chain-extended with HD present multiple peaks at 13°, 18°, 23°, 26°. The increase in HD content resulted in a higher ordering inside the macromolecular structure which caused an increase in the intensity of the peak from 26°. This behavior can suggest that the HD chain-extender allowed for the formation of a more crystalline structure

Fig. 6 X-ray diffraction patterns of the prepared polyurethanes with **a** TEG, **b** DTO, **c** HD



compared with other chain extenders which contain oxygen (TEG) or sulfur (DTO) in their chemical structure. This is a result of the aliphatic structure of the chain-extender, which allows for some degree of freedom of movement within the polyurethane matrix [10] which in turn determines a better packaging of the macromolecular domains.

The results of the performed measurements have highlighted the strong correlation between the chemical structure of the chain-extendors and the morphological, surface and physical properties of the synthesized polyurethanes.

Conclusions

New polyurethane elastomers were synthesized by using chain extenders such as triethylene glycol(TEG) and 3,6-dithia-1,8-octanediol (DTO), which were then compared with conventional polyurethanes chain-extended with 1,6-hexanediol. The paper has studied the effects of these different structures and of the amount of the chain extenders on the morphological design, surface, thermal and mechanical properties of the selected polyurethanes.

The tensile strength and elongation values of the polyurethane films with DTO are close to the values for polyurethanes obtained with HD. The polyurethanes, chain-extended with TEG, present weaker physical properties. The TGA results show that the thermal degradation for DTO-based polyurethanes occurred in multiple stages and demonstrate their improved thermal stability compared with TEG-based polyurethanes. The DTO-chain-extended polyurethane exhibits multiple hydrogen bonds of the sulfur atom from DTO, thus generating a better ordering of the hard segment domains, as confirmed by XRD analysis. The XRD shows that polyurethanes chain-extended with TEG exhibit a partially crystalline structure.

Compliance with ethical standards

Conflict of interests The authors declare that there is no conflict of interest regarding the publication of this paper.

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