

Degradation of Crosslinked Poly(ester-urethanes) Elastomers in Distilled Water: Influence of Hard Segment

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ABSTRACT: Polyurethane elastomers are frequently used in wet conditions. Crosslinked polyurethanes based on poly(ethylene adipate) diol, 4,4'-diphenylmethane diisocyanate, 1,6 hexane diisocyanate—with different hard-segment compositions but with the same molecular weight soft segment—were degraded in distilled water at 37°C, in a specific environment; in the dark without exposure to enzymatic conditions and under the continuous circulation of water. The incubation of polymer samples took place over a period of maximum 30 days. The degradation process was evaluated by the changes in mechanical properties and surface relief observed by optical microscopy. The changes in hydrogen bonding were collected through attenuated total reflectance infrared (ATR-FTIR) spectroscopy

which indicated that aliphatic diisocyanates allow for a better formation of hydrogen bonds. The mechanical properties of the degraded films show that the crosslinked polyurethanes containing aromatic diisocyanate suffer a decrease in tensile strength between 33 and 56% depending on the chain extender and hard segment content. The hydrolytic degradation behavior of crosslinked polyurethanes was found to be dependent on the diisocyanate and chain extender structure, as well as on the hard segment content and chemical crosslinks. © 2011 Wiley Periodicals, Inc. *J Appl Polym Sci* 124: 1059–1066, 2012

Key words: crosslinked polyurethane; hydrolytic degradation; mechanical properties; surface morphology

INTRODUCTION

The usage of polyurethane elastomers as polymer materials has noticeably increased in the areas of technical applications such as automotive, electric and electronic equipment, medical devices, aeronautics and the aerospace industry, fibers, artificial leathers, etc. These multiple applications are an indicator of their excellent mechanical properties, easy processing, and adaptability to industrial processes, resistance to abrasion and wear, to ozone and oils, flexibility at low temperatures, etc.^{1–6}

It can be generally said that polyurethanes are multiblock copolymers with a microphase separated structure consisting in a hard- and soft-domain. The hard segment domain gives dimensional stability to the polyurethane matrix by physical crosslinking through hydrogen bonding and by chemical crosslinks.^{7–10}

The changes in composition and distribution of the components lead to strong variation of the polyurethane morphology and properties. Thus, change in the structure of a chain-extender from the hard segments significantly affects the degree of segregation of the hard and soft domains and therefore the

properties of polymers.¹¹ The presence of a triol as a crosslinker within the hard segment increases the aggregation of the hard segments through covalent bonds crosslinking, but decreases the aggregation through hydrogen bonding.¹²

It is also known that polyurethanes have faster degradation rates under the influence of heat, ultraviolet radiation, humidity, etc.^{13,14} Thus, many applications require polyurethanes which maintain their mechanical stability even after exposure to water, water solutions, water dispersions, seawater, etc. Although poly(ester-urethane)s are not hydrolysis resistant due to their instable ester bond, many products have been synthesized so as to reduce the accessibility of water to ester groups. This can be achieved by increasing of the physical crosslinking degree through hydrogen bonding and by chemical crosslinking. The structure of the chain extenders plays an important role in the hydrolytic stability of the polyurethanes.^{15,16} In crosslinked polymers the chemical bond of the crosslink or the polymer backbones must be broken before any erosion of the polymer fragments can take place. The degradation rate of the crosslinked polyurethane can be controlled by the physical packing of the polymeric matrix and by the nature and density of the chemical crosslinks.^{17–19} Crosslinked polyurethanes may thus have high water-resistance and high mechanical strength which are required in many applications.^{20,21} There have also been studies focusing on

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the dependence of hydrolytic degradation on the nature of the polymeric chain, degradation which was conducted in buffered saline solutions^{22–24} or seawater.^{13,25,26}

The objective of this work is to analyze the effect of structural variation of the chemical crosslinked hard segments on the hydrolytic degradation behavior of the crosslinked polyurethanes that were subjected to degradation at 37°C in distilled water in a specific environment: in the dark without exposure to enzymatic conditions and under the continuous circulation of water. A selection of appropriate materials was subjected to the effect of distilled water and their physicomechanical properties were measured depending on the degradation time.

EXPERIMENTAL

Materials

Two different diisocyanates were used: 1,6-hexane diisocyanate (HDI), a linear aliphatic diisocyanate and 4,4'-methylene diphenyl isocyanate (MDI) which were purchased from Fluka. Poly(ethylene adipate)-diol (PEA)(MW = 2000 g mol⁻¹) end-capped with hydroxyl groups was purchased from Fiberx SA, Savinesti, Romania. The 1,4-butanediol (BD), 1,6-hexanediol (HD), and glycerin (Gly) were purchased from σ -Aldrich (σ -Aldrich Chemie GmbH, Germany) and were used as received.

Synthesis of crosslinked polyurethanes

Crosslinked polyurethanes were synthesized as was described in previous work.²⁷ The compositions that were used and their hardness are shown in Table I.

In a 500-mL four-necked cylindrical vessel, which was equipped with a mechanical stirrer, a thermometer, heating oil bath, and a drying tube connected to the vacuum pump, required amounts of diisocyanate and PEA were added while stirring at 80°C for 2 h to obtain the NCO end-capped prepolymer. The 1,4-butanediol or 1,6-hexanediol and glycerin were added to the reaction mixture according to the MDI/PEA ratios and were stirred at 80°C for 120 min. Polyurethane films were obtained by casting the melted polymers on clean glass, being subsequently left to cure at 80°C for 24 h. The polyurethane films thus prepared were used for the determination of water degradation behavior.

Hydrolytic degradation

For hydrolytic degradation, similar dumbbell-shaped samples were cut from the dried films. The degradation of polyurethane samples was performed in laboratory conditions: in distilled water, in the dark,

TABLE I
Formulations of the Crosslinked Polyurethanes

Samples	Molecular ratios of polyester/diisocyanate/chain extenders	Diisocyanate	Chain extenders glycerin +
PU1	1: 2: 1	MDI	BD
PU2	1: 2: 1	HDI	BD
PU3	1: 2: 1	MDI	HD
PU4	1 : 2 : 1	HDI	HD
PU5	1 : 3 : 2	MDI	BD
PU6	1 : 3 : 2	MDI	HD
PU7	1 : 3 : 2	HDI	BD
PU8	1 : 3 : 2	HDI	HD

under continuous recirculation in a B. Braun Mel-sungen apparatus (Germany). Sodium azide (0.195 g NaN₃/1000 mL) was added to the distilled water to exclude the activity of microorganisms in evaluating the resistance of the polymers to hydrolysis. The polyurethane samples were incubated at 37°C in distilled water for 10, 20, and 30 days. This study consists in the fact that the chemically crosslinked poly(ester urethane) with different structures of the hard segment are subjected to degradation in distilled water in a specific environment: in the dark and under the continuous circulation of water. First of all, conducting experiments in the dark eliminates the influence of light on degradation. Also, the use of a dynamic system through the continuous recirculation of water eliminates the unfavorable conditions created by the long period of stagnation of water around the sample.

Measurements

Fourier transform infrared (FTIR) spectra were recorded on a Bruker VERTEX 70 Instrument equipped with a Golden Gate single reflection ATR accessory. The spectra were recorded in the range of 600–4000 cm⁻¹ with a nominal resolution of 4 cm⁻¹.

The mechanical properties were determined using a Shimadzu EZTest (Japan) equipped with a 5-kN load cell. Dumbbell-shaped specimens were prepared using dies (75 × 12.5 × 4 mm³; ISO 37 Type 2). The test specimens that were cut from the samples were no more than 0.5-mm thick. The specimens were prepared so as to be free of surface roughness, fabric layers, etc. The tests were performed at room temperature (23°C) with a cross-head speed of 50 mm min⁻¹.

The effects of the hydrolytic degradation on the polyurethane surface relief were evaluated by optical microscopy (Leica DM2500M). The images of the surface of nondegraded and degraded samples were obtained using a microscope digital camera in ambient temperature.

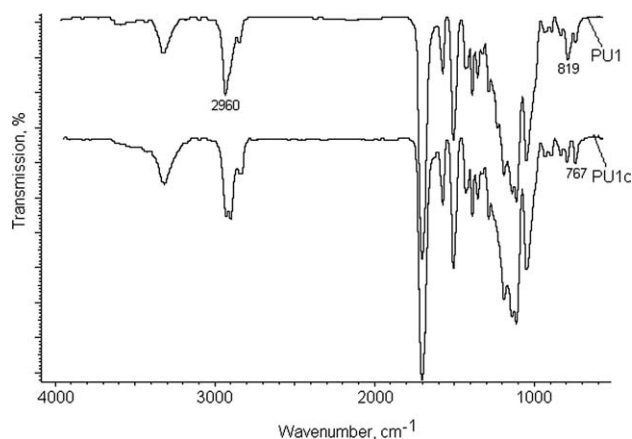


Figure 1 FTIR spectra of the polyurethane samples PU1 initially and after 30 days (c) degradation in distilled water at 37°C.

RESULTS AND DISCUSSION

The polymeric matrix of the crosslinked polyurethanes contains both physical crosslinking through hydrogen bonds as well as chemical crosslinking from the triols chain-extender. In poly(ester urethanes) the ester group is the most susceptible to hydrolysis but the crosslinked structure prevents water from easily reaching the labile ester groups, thus improving the resistance to hydrolytic degradation. The relationship between the hard segment structure and the changes in surface and mechanical properties indicates hydrolytic degradation of the crosslinked polyurethanes. Under the current working conditions, polyurethanes obtained from aromatic diisocyanates are less stable than those containing aliphatic diisocyanates.

The FTIR spectra of the polyurethane samples that have exhibited changes in mechanical properties after 30 days of degradation in water are shown in Figures 1–6.

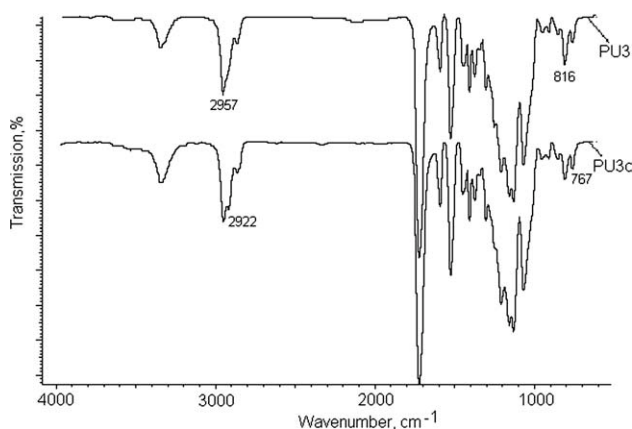


Figure 2 FTIR spectra of the polyurethane samples PU3 initially and after 30 days (c) degradation in distilled water at 37°C.

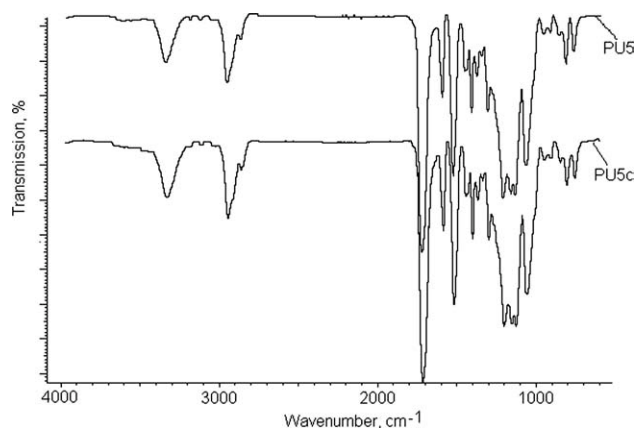


Figure 3 FTIR spectra of the polyurethane samples PU5 initially and after 30 days (c) degradation in distilled water at 37°C.

The FT-IR spectra of the crosslinked polyurethane elastomers indicated the presence of typical bands for polyurethanes such as —NH , (free and bonded) at $3300\text{--}3600\text{ cm}^{-1}$; the symmetrical and asymmetrical stretching of $\text{CH}_2\text{—}$ at $2850\text{--}3000\text{ cm}^{-1}$; C=O (free and bonded) at $1630\text{--}1750\text{ cm}^{-1}$; the N—H bending peak at 1530 cm^{-1} . For all the obtained polyurethanes, the band in the C=O stretching vibration Amide-I region at 1730 cm^{-1} consists of a single strong peak that suggests that chemical crosslinks hinder the formation of an increased number of hydrogen bonds. The C=C stretching of the phenyl ring can be observed at 1595 cm^{-1} for samples obtained with MDI (Figs. 1–4). The absorption bands at 1110 and 1240 cm^{-1} were attributed to the characteristic C—O—C stretching vibrations of the ester bonds. The hard segment has a strong absorption at 1385 cm^{-1} .

The intensity of the peak at 1385 cm^{-1} increases after the hydrolytic degradation of polyurethanes obtained with HDI with a high content of chemical

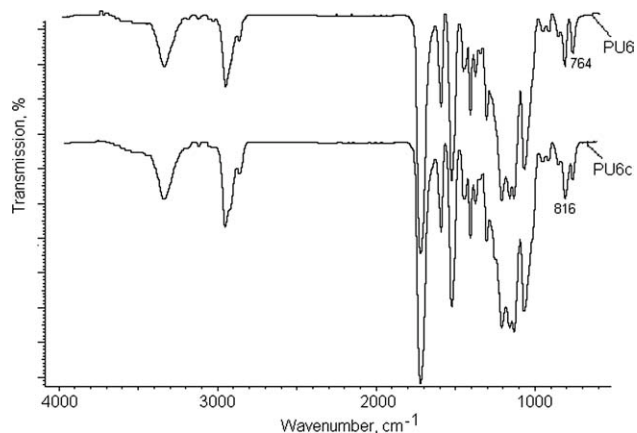


Figure 4 FTIR spectra of the polyurethane samples PU6 initially and after 30 days (c) degradation in distilled water at 37°C.

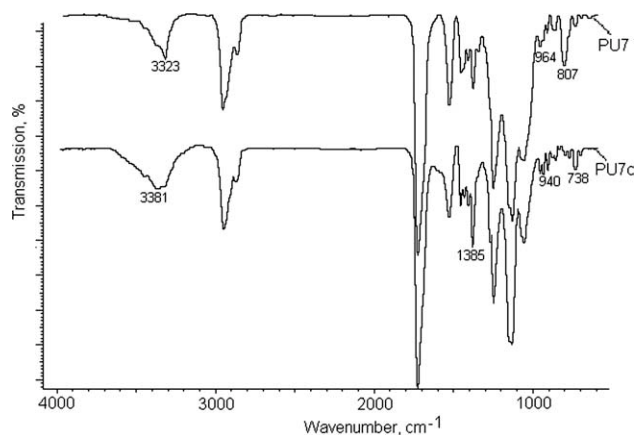


Figure 5 FTIR spectra of the polyurethane samples PU7 initially and after 30 days (c) degradation in distilled water at 37°C.

crosslinks (PU7, PU8; Figs. 5 and 6). While the polyurethane chain extended with HD (PU8) shows an increase of the peaks from 932 to 732 cm^{-1} and a decrease of the peak at 778 cm^{-1} , the polyurethane chain extended with BD (PU7) shows an increase of the peaks at 940 and 738 cm^{-1} and a decrease of the peaks at 807 cm^{-1} . Also, the NH stretching vibrations from 3381 to 3323 cm^{-1} present visible changes in the case of the polyurethane chain extended with BD (PU7). These observations obtained by the comparison of spectra could indicate some hydrolysis of the ester bond.²⁸ This can be explained by the high degree of chemical crosslinking that reduces the freedom of movement of the molecular chain, making the packaging of molecular matrix weaker and allowing the ester groups to be exposed to water degradation.

In polyurethane obtained with MDI that have a smaller density of chemical crosslinks (PU1 and

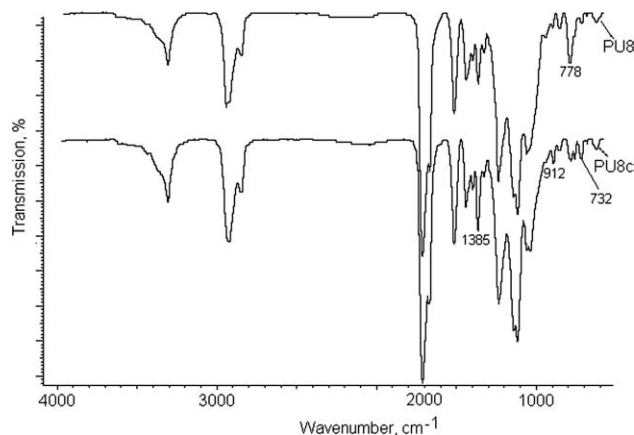


Figure 6 FTIR spectra of the polyurethane samples PU8 initially and after 30 days (c) degradation in distilled water at 37°C.

PU3), the stretching region at 2960–2920 cm^{-1} and the intensity of the peak at 816–767 cm^{-1} suffer changes after exposure to water. Polyurethane obtained with MDI that have a higher density of chemical crosslinks (PU5 and PU6) exhibit changes of the peak intensity in the range 816–767 cm^{-1} . The FTIR spectra indicated slight changes in the structure of this polyurethane—particularly changes of the ester bond—which are correlated with changes of mechanical properties after water exposure.

The immobilization of the urethane hard segment domains through physical crosslinks and chemical crosslinks determine a phase separation of the hard and soft segments which accounts for the elastomeric properties of the crosslinked polyurethanes. The presence of a triols crosslinker in the hard segments causes a steric hindrance effect that prevents the aggregation of hard segments through hydrogen bonding.

The evaluation of the differences in mechanical properties after immersion in water must take into account the number and strength of hydrogen bonds formed between hard areas and between hard and soft area, as well as the steric hindrances affecting the access of water molecules to labile ester groups. The hydrolytic degradation of polyurethane elastomers has a significant influence on tensile strength and elongation at break. Figures 7–12 show the tensile stress versus strain curves of the crosslinked polyurethane films before and after 10, 20, and 30 days in distilled water immersion.

All the crosslinked polyurethanes with MDI in their structure present a clear decrease of the stress and strain at break after hydrolytic degradation took place. After 30 days of degradation, considerable change in the stress-strain behavior is observed for

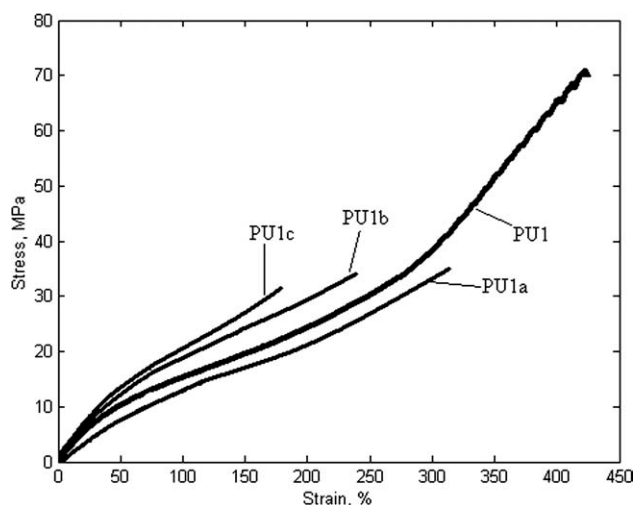


Figure 7 Stress-strain curves of polyurethane samples PU1 before and after 10 days (a), 20 days (b), and 30 days (c) of degradation in distilled water at 37°C.

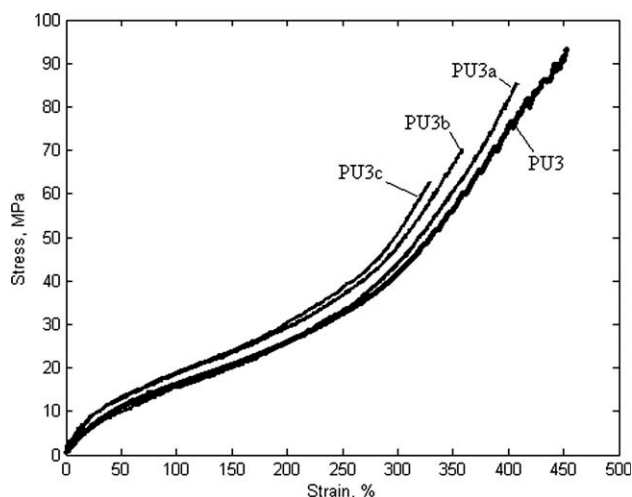


Figure 8 Stress–strain curves of polyurethane samples PU3 before and after 10 days (a), 20 days (b), and 30 days (c) of degradation in distilled water at 37°C.

those polyurethanes with a low content of hard segment and of chemical crosslinks, the stress at break dropping to 44% (PU1) and 67% (PU3) while the strain at break decreases until 38% (PU1) and 74% (PU3) compared to initial values. In polyurethane samples with a high content of chemical crosslinks (PU5, PU6), the strain decreases until 38% and stress decreases until 65–66% from the initial values. Tensile strength gradually reduced with time for the polyurethane chain extended with HD (PU3). For all other samples large decreases occur within the first 10 days, the values then remaining almost constant. Instead, the elongation at break exhibits a continuous decrease proportional with the time of exposure to water. This result may be due to a degradation of

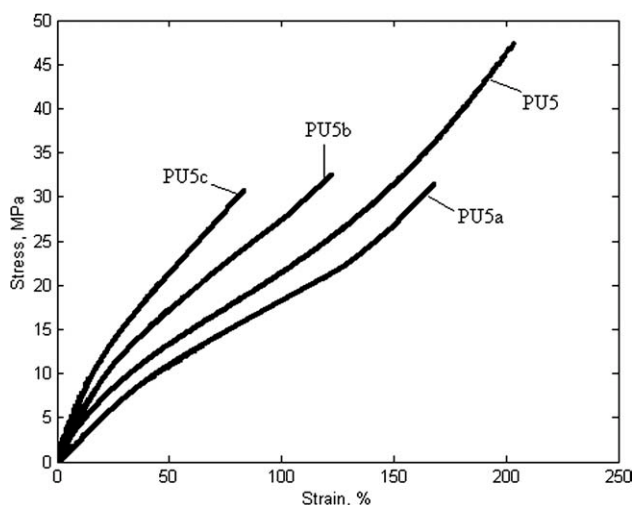


Figure 9 Stress–strain curves of polyurethane samples PU5 before and after 10 days (a), 20 days (b), and 30 days (c) of degradation in distilled water at 37°C.

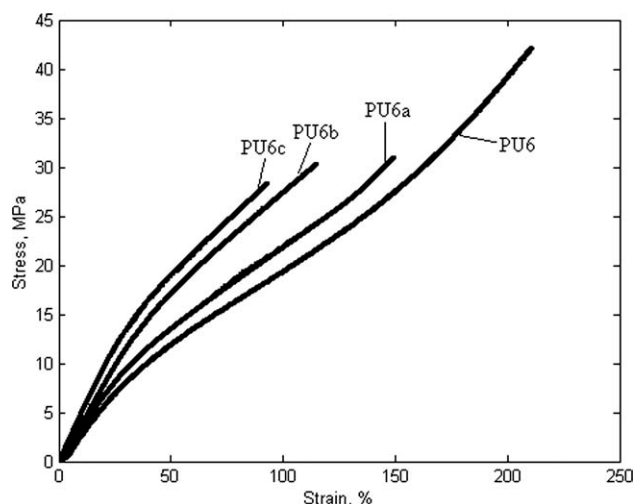


Figure 10 Stress–strain curves of polyurethane samples PU6 before and after 10 days (a), 20 days (b), and 30 days (c) of degradation in distilled water at 37°C.

the ester bonds, because the soft segment matrix influences extension and elastic recovery.

As for the crosslinked polyurethane elastomers obtained with aromatic diisocyanate, they present a less ordered hard segment and the structure of the polymer matrix allows for an easier penetration of the water molecules within the hydrolytic degradable ester groups. The poorer tensile properties exhibited by aromatic diisocyanate-based polyurethane after water immersion can be explained by the presence of a rigid hard microdomain structure which inhibits domain rotation, orientation, and hydrogen bonds interconnection. Also, water penetrates the polyurethane matrix and can serve as a plasticizer in the polymer matrix resulting in a

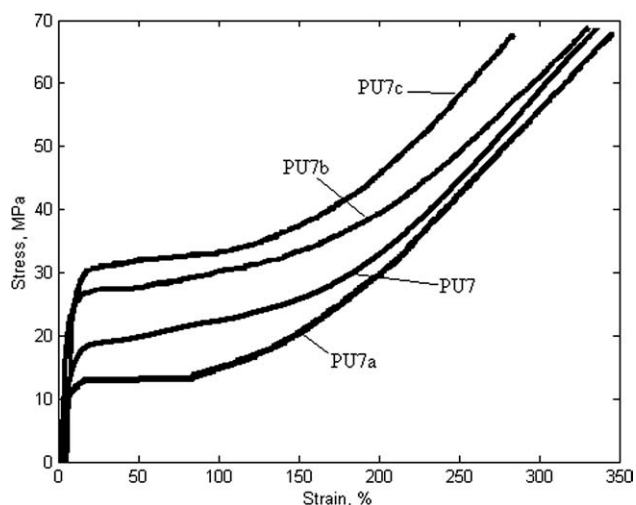


Figure 11 Stress–strain curves of polyurethane samples PU7 before and after 10 days (a), 20 days (b), and 30 days (c) of degradation in distilled water at 37°C.

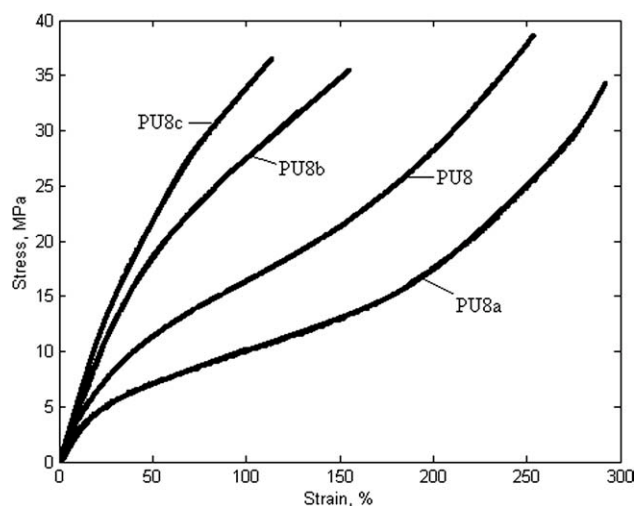


Figure 12 Stress–strain curves of polyurethane samples PU8 before and after 10 days (a), 20 days (b), and 30 days (c) of degradation in distilled water at 37°C.

decrease of the polymer matrix integrity and mechanical properties.²⁹

The crosslinked polyurethanes with aliphatic diisocyanate in the structure of the molecular chain

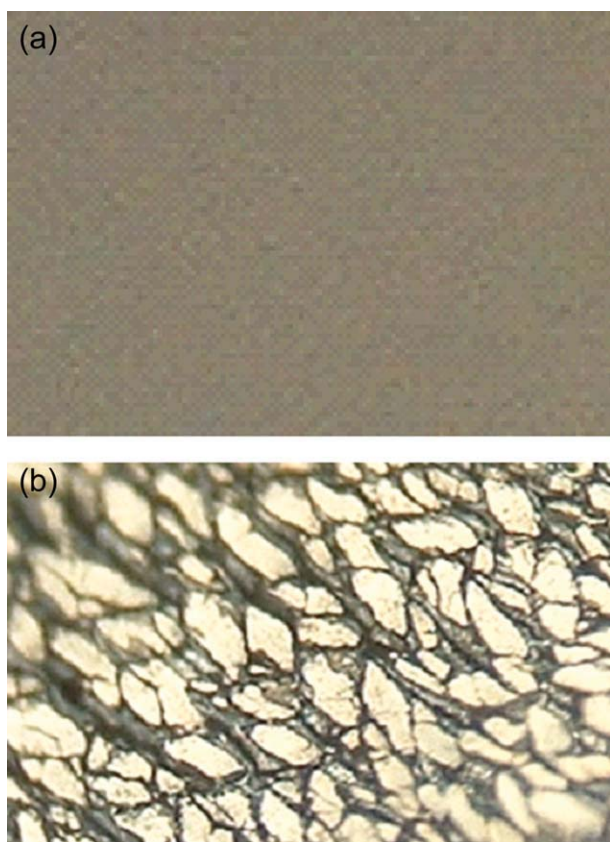


Figure 13 Surface photographs initially (a) and after 30 days (b) of hydrolytic degradation of the crosslinked polyurethane samples PU1 ($\times 40$). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

and low chemical crosslinking (PU2, PU4) maintain their mechanical properties after 30 days of hydrolytic degradation (for this reason no figures are given). The aliphatic diisocyanate-based polyurethanes with fewer chemical crosslinks allow formation of a greater number of hydrogen bonds that contribute to achievement of a long-range ordered structure and hence low-water uptake. The preservation of mechanical properties of these crosslinked polyurethanes, even after hydrolytic degradation, can be explained by the higher degree of packing of the polyurethane matrix which reinforces the polymer-chain interactions. Thus, it would be very difficult for water to penetrate the polyurethane matrix to reach labile ester groups. The aliphatic diisocyanate-based polyurethanes with the highest density of chemical crosslinks have a reduced backbone mobility which hinders the formation of a high percentage of intermolecular hydrogen bonds. Thus, PU7 and PU8 show a small decrease in strength, but a significant change in strain (decreased with about 22% for PU7 and 52% for PU8) after 30 days of immersion in distilled water.

The different degradability behavior exhibited by the studied crosslinked polyurethane elastomers rely on differences in their crosslinked network density and structure of the diisocyanate employed. Thus,

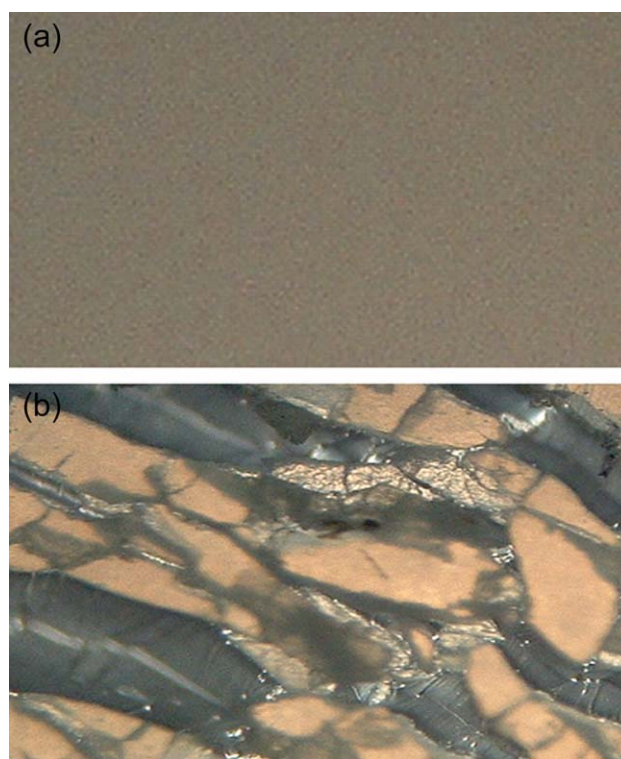


Figure 14 Surface photographs initially (a) and after 30 days (b) of hydrolytic degradation of the crosslinked polyurethane samples PU3 ($\times 40$). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

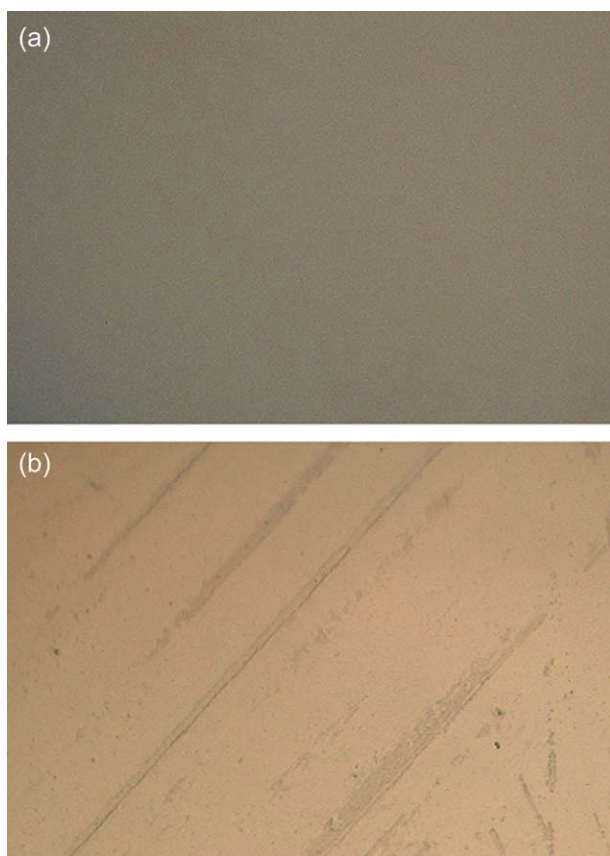


Figure 15 Surface photographs initially (a) and after 30 days (b) of hydrolytic degradation of the crosslinked polyurethane samples PU8 ($\times 40$). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

the crosslinked polyurethane with an aliphatic diisocyanate (HDI) is more resistant to degradation in distilled water and darkness conditions, while the crosslinked polyurethane with aromatic diisocyanate is very prone to degradation. This suggests that the hard segment structure has a great importance in determining microphase separation and the morphology of the polymer matrix constitutes factors that control the rate of hydrolytic degradation.

From the optical micrograph images, it can be observed that the MDI-based polyurethanes are the least resistant to hydrolytic degradation, as the surfaces exhibit fragmented landscape and aggressive pitting due to degradation. Figures 13 and 14 show the initial and degraded MDI-based polyurethane films surfaces.

If the surface of the films is initially free of surface defects, after 30 days of water immersion numerous pits are formed. The degraded surface appears like a regular distribution of humps (white zones) on continuous hollows (black zones). This degradation rate could be attributed to the hard segment composition which makes the bulk of the polymer accessible for hydrolysis.

The surface of crosslinked poly(ester-urethane) films obtained with aliphatic diisocyanate remains the least affected after hydrolytic degradation (Fig. 15).

CONCLUSIONS

The hydrolytic stability (without influence of UV or microorganisms) of HDI- or MDI-based crosslinked polyurethanes at 37°C, after 30 days of immersion, can be correlated with their hard segment chemical composition. The differences observed in hydrolytic degradation behavior can be attributed to the modified capacity of hydrogen bonding due to steric hindrance caused by chemical crosslinks, the structure of MDI, and the hydrolysis of ester groups. Aliphatic diisocyanate and lower crosslinks density in the hard segment structure enhances hydrogen bonding capacity and the ordering of the polymer matrix, which prevent water from penetrating to ester groups. It demonstrates that chemical structure of the hard area (like the diisocyanates, chain extenders, crosslinks content, or ratio of components) have a significant impact on the intensity of the hydrolytic degradation.

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