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IN VITRO DEGRADATION AND EROSION OF DEGRADABLE LACTATE SEGMENTED POLYURETHANES

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A significant number of studies for improving the biocompatibility of polyurethanes have been concentrated on bulk and surface modifications. In this view, the knowledge of polymer degradation in body solvent-fluids (aqua), and the subsequent physical properties changes, is the first step for a better designing of polyurethanes used in biomedical applications. In this paper, the dynamics of water non-enzymatic hydrolysis of poly(lactateurethane) are analysed and the results revealed characteristics more suitable for biomedical applications, than poly(esterurethane) materials, due to the incorporation of a soft lactate segment.

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1. Introduction

Polymers are well known and widely used in many fields, in particular they are suitable for biomedical applications because of the unique combination of physical and chemical properties coupled with their biocompatibility [1].

Polymer selection for a specific biomedical application depends on: mechanical characteristics and surface properties (hydrophilicity/hydrophobicity, lubricity, smoothness, surface energy), that determine biocompatibility, durability, permeability and water sorption capacity; bulk properties (molecular weight, adhesion, solubility, thermal properties), which influence the release mechanisms, site of action, thermal stability, glass transition temperature (T_g) and melting temperature (T_m); structural properties (micro-morphology, pore size), that determine water transport into and out of the polymer [2].

Medical devices based on polymers are subjected to various mechanical, physico-chemical and thermal stresses inside the human body. In this view, the interaction control at the molecular level, between tailored polymer's components and biological media is the key to understand the rich properties of these polymers.

There are many aspects of *in vivo* polymer degradation, especially aging, by changes in chemical structure due to the enzymatic cleavage of specific chemical units, which determine the deterioration in mechanical properties, colour, and the release of hazardous chemical products.

Water is known to be one of the active factors that influence the polymers' aging [3].

Polyurethanes have relatively good biocompatibility with blood and other body fluids. Polyurethane biopolymers requirements are becoming more and more specialized to meet increasingly demand corresponding to specific environmental stresses and biomedical applications [4].

In particular, the non-enzymatic hydrolytic degradation of polyurethanes can lead to the formation of carbamic acids that are unstable and eliminate carbon dioxide to form the amino analogue of the starting isocyanate. Temperature is an important environmental factor, which influences the hydrolysis.

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In this paper, degradation and erosion of porous membranes made of the new tailored poly(lactateurethane) [5], were investigated and compared to those of the precursor poly(esterurethane).

2. Experimental

The synthesis of poly(lactateurethane) (PL) and precursor poly(esterurethane) (PU), was presented in reference [5].

From these polymers were prepared two types of membranes, dense and porous, by phase inversion method [6]. Water was the nonsolvent and DMF was the solvent, in different proportions.

After preparation, the films and membranes have been processed in different thermal conditions (Table 1).

Table 1. The phase inversion and post thermal conditions of polyurethane films and membranes.

Sample	Wet phase inversion		Dry phase inversion		Evaporation	
	$T(°C)$	$t(h)$	$T(°C)$	$t(h)$	$T(°C)$	$t(h)$
PU1 PL1	-	-	110	2	25	24
PU3 PL3	-	-	-	-	25	24
PU5 PL5	45	1 / 3	-	-	25	24
PU7 PL7	45	1 / 3	110	2	25	24

From the resulting materials have been cut samples with the size of 50×4 mm^2 and 48×23 mm^2.

In order to perform in vitro degradation experiments, the same number of each PL and PU 50×4 mm^2 eprouvettes have been introduced in a thermostat with 50 ml deionized water at 37 ^{o}C for up to 3 days, with the aim to perform in bulk pH and conductance measurements, as well as stress-strain measurements.

Degradation and erosion of PL membranes were studied and compared to precursor PU membranes.

Samples of each type of PL and PU polymers, of size 48×23 mm^2 have been introduced in 60 ml deionized water in a thermostat under the same conditions with the purpose to carry out ATR-FTIR measurements. The samples were processed by drying them *in vacuum* for 24 hours before ATR-FTIR analysis.

The chemical changes in bulk solution, by releasing the hazardous chemical products during degradation process, have been monitored by means of pH and conductance measurements with a Consort C831 Electrochemical Multimeter, and chemical changes at membrane surface, due to cleavage of specific chemical units, by ATR-FTIR spectroscopy with Jasco FTIR 410. The changes of surface morphology were investigated by scanning electronic microscopy (SEM) on a TESLA-BS-300 microscope. The stress-strain dependence of degraded membranes was obtained with Traction Trying Machine (TTM) type Mesdan - Tenso Lab 10. The proceedings of stress-strain testing of the film and membrane specimens are presented in Table 2.

Table 2. The proceedings of stress-strain testing.

Samples	Single 10 eprouvette minimum
Dimensions	L = 50 mm; l = 4 mm
Methods	Individual Constant deformation gradient
Speed of deformation	10 mm / min

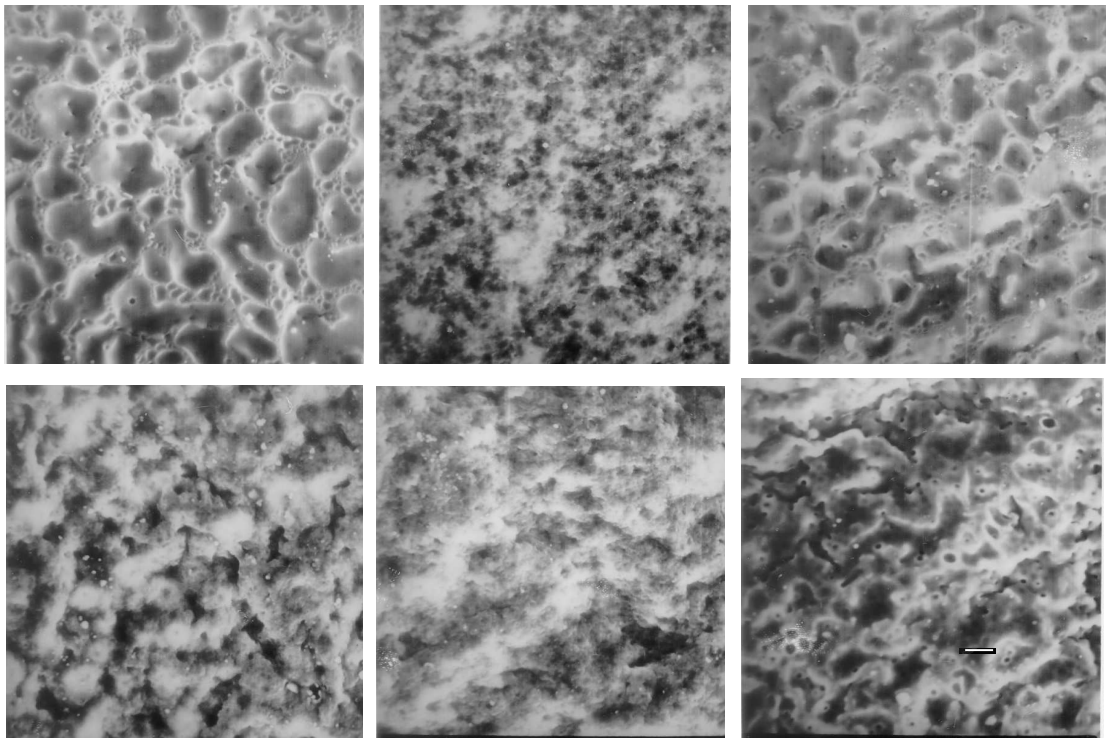
3. Results

In Fig. 1 are presented SEM photos of PL5 and PU5 samples of air facing eroded membranes, during the water degradation process.

Figs. 2 and 3 represent the changes in water bulk degradation solutions of PL and PU post treated films and membranes as mentioned in Table 1, by monitoring the pH and conductance vs. time dependences of water bulk.

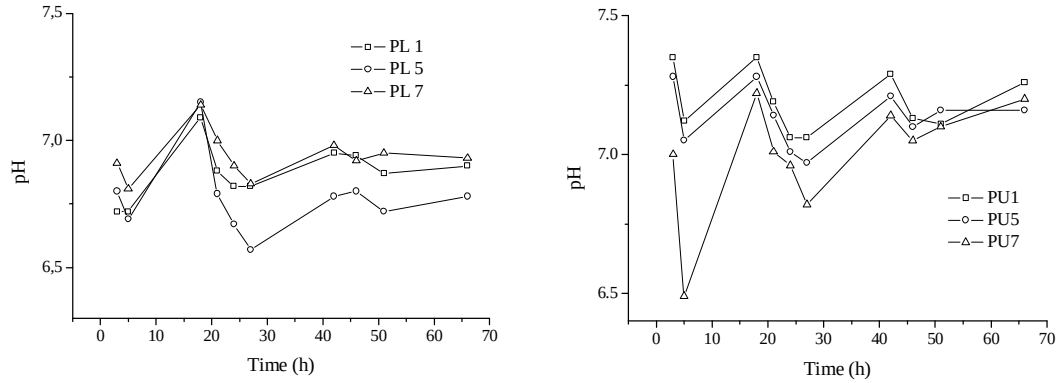
The ATR-FTIR absorbance spectra domains that show significant modifications during the degradation process, are given in Fig. 4 for porous membranes of PL5 (a) and PU5 (b), recorded at different degradation time.

Fig. 5 represent the stress-strain diagrams of PL1 (a) and PU1 (b) films at different intervals of time. The inserts represents the dependences of elastic modulus, *E*, vs. time.



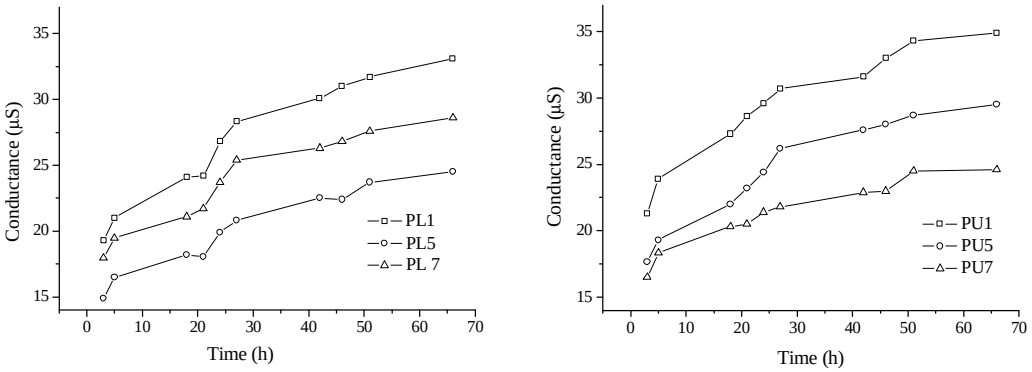
(a) (b) (c)

Fig. 1. SEM micrographs of air-facing surface of PL5 (top) and PU5 (bottom) specimen membranes for as prepared samples (a), after 3 h (b) and 21 h (c) time of degradation (white stick mark is 4 μm).



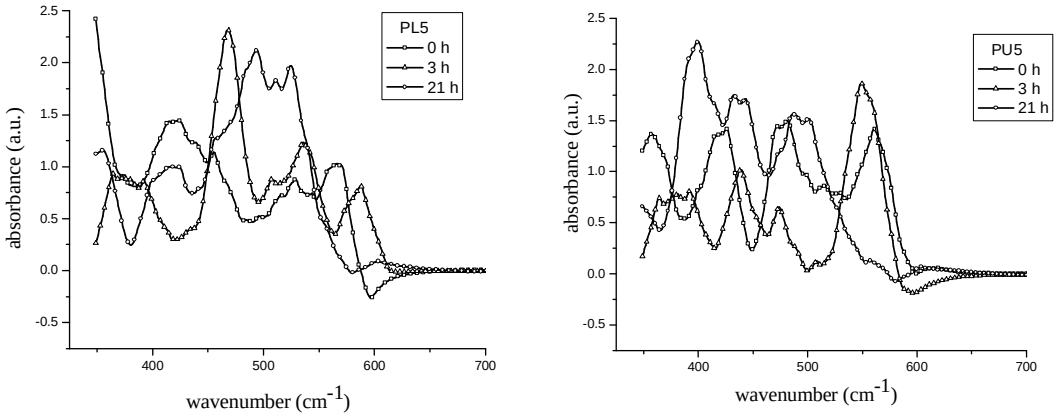
(a) (b)

Fig. 2. The pH vs. time for bulk water degradation solutions of PL (a) and PU (b) membranes.



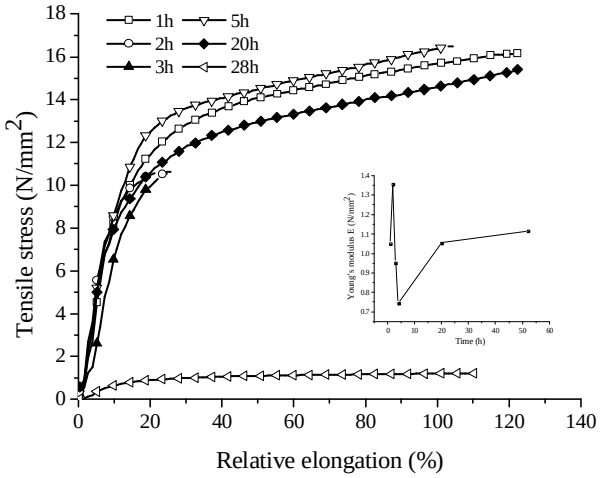
(a) (b)

Fig. 3. The conductance vs. time for bulk water degradation solutions of PL (a) and PU (b) membranes.

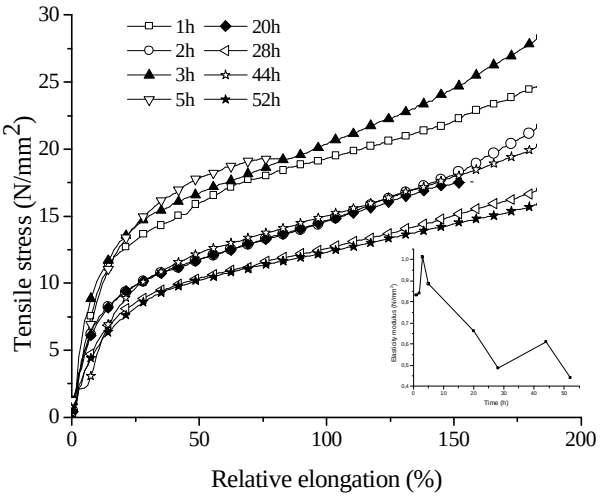


(a) (b)

Fig. 4. The ATR-FTIR spectra of PL5 (a) and PU5 (b) at different time intervals during the water degradation process.



(a)



(b)

Fig. 5. The stress-strain diagrams of PL1 (a) and PU1 (b) films degraded in water at 37 ^{o}C for various time intervals.(insert: elasticity modulus versus time).

4. Discussion

As one can see from Fig. 1, SEM analysis indicates that erosion proceeded via a surface-limited mechanism resulting in a progressive removal of material from the surface inwards with time.

The pH vs. time dependences from Fig. 2 show that PU degradation raises the pH of bulk solution to the basic pH value (Fig. 2b) while PL degradation stabilizes the pH bulk solution to biological acidity 6.8.

The bulk conductance of PL, is smaller than that of PU (Fig. 3). That suggests the possibility of a preponderant release of uncharged soft chain from PL to the bulk degradation medium. This is also confirmed by the ATR-FTIR spectra.

The ATR-FTIR spectra do not show any changes between degraded and non-degraded polyurethane membranes in the range 700-4000 cm^{-1}. The most important changes appear in the range 500-700 cm^{-1}, that are dependent on morphology of membranes/films obtained by a post treatement process, suggesting that the water hydrolysis process of polyurethanes consist of breaking of chemical bonds leading to reciprocal reorientation of the whole macromolecule and the phase separation process. After 3 hours of non-enzymatic hydrolysis at the surface of polyurethane membrane are removed the aliphatic ether groups, $CH_2 - O - CH_2$ (500-580 cm^{-1}), nitro groups,

R – NO_2 (475-590 cm^{-1}), and aliphatic soft segments (550-640 cm^{-1}). PL removes more easily the aliphatic soft segment and this is the reason why this band is small in PL spectrum in comparison to the PU spectrum while PU becomes depleted in nitro groups.

Also, the three monitoring parameters of degradation: pH, conductance and ATR-FTIR spectra, reveal the dynamic of erosion degradation process. This dynamics consist in combined processes of chemical cleavage, hard – soft phase separation and removal of chemical segments from membrane surfaces by erosion-diffusion mechanism due to the accumulation in bulk.

Previous studies [7] showed that the membranes prepared by dry phase inversion lead to dense and flexible materials with higher elasticity modulus. The presence of the lactate segment in the PL samples determines the minimization of the elastic modulus and the increase of the relative elongation in a good agreement with supra-molecular structure and organization [5].

The materials prepared by wet phase inversion exhibit a porous structure. In this case, the presence of the lactate segment leads to the same minimization of the elastic modulus and of the breaking effort.

The thermal annealing at the temperature of 110 ^oC leads to a slight increase of the elastic modulus and to an important increase of the breaking resistance.

From Fig. 5, in the case of PL1 and PU1, one can see that in the early stages of swelling the Young's modulus increases for both type of polyurethanes. As the aging advances, the PL1 samples rapidly deteriorate the elasticity and breaking resistance, while the PU1 membranes evoluate towards the mean value of the parameters.

5. Conclusions

The degradation process of PU and PL membranes/films depends on preparation and post treatment.

The products of PL degradation stabilize the pH of the bulk solution to the pH of the biological acidity: 6.8.

The dynamics of water non-enzymatic hydrolysis scenario consist in combined processes of chemical cleavage, hard – soft phase separation and removal of chemical segments from membrane surfaces by erosion-diffusion mechanism, that is due to the accumulation of chemical degraded products in the water bulk.

The lactate-segment enhances the susceptibility to degradation and erosion.

The mechanical characteristic parameters initially increase with swelling, and, thereafter, rapidly decrease with aging.

The presence of the lactate segment in the PL samples leads to the minimization of the elastic modulus and to the increase of the relative elongation.

These results demonstrate that the PL materials have characteristics more suitable for biomedical applications than the PU materials.

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References

[1] T. S. Burkoth, E. Beausoleil, S. Kaur, D. Tang, F. E. Cohen, R. N. Zuchermann, Chemistry & Biology, **9**(5), 647 (2002).
[2] A. Vaidya, M. K. Chaudhury, Journal of Colloid and Interface Science **249**(1), 235 (2002).
[3] O. V. Startsev, in Polymer Yearbook 11. Hardwood Academic Publishers, Glasgow, (1993), p. 91.
[4] K. Gorma, S. Gogolewski, European Cell and Materials, **1**(2), 59 (2001).
[5] V. Melnig, M. Apostu, V. Tura, C. Ciobanu, Journal of Membrane Science, Article in Press, 10 pg.; Available, 7 July 2005 in Science Direct.
[6] M. -O. Apostu, V. Melnig, C. Ciobanu, V. Tura, Timisoara Medical Journal, **53**(2), 39 (2003).
[7] V. Tura, V. Melnig, L. Obreja, A. Garlea, M. S. Neculaiasa, G. Ciobanu, L. Hristian, I-st International Conference on Biomaterials "Biomaterials & Medical Devices" BiomMedD'2004 Conference Proceeding, pp. 80, ISSN 1473-2262; Endorsed by Biomat.net; Indexed by MEDLINE, CAS and BIOSIS.