Polyurethanes Elastomers Based on Poly(ε-caprolactone) Diol: Biodegradation Evaluation

Juliana Kloss,[*1] *Fernanda S. M. de Souza,*[2] *Edilsa R. da Silva,*[2] *Jair Alves Dionísio,*[3] *Leni Akcelrud,*[1] *Sônia Faria Zawadzki*[1]

Sumary: Plastics materials are widely used in the manufacturing of many products like bags, packings, electronic components among other applications. Most polymers are extremely durable and this durability cause serious environmental problems because of the large amount of waste discarded mainly in the urban centers. Thus, biodegradable polymers are a potencial way to minimize these problems. Polyurethanes based on poly(ε-caprolactone) (PCL) as soft segment were prepared taking into account the biodegradable charater of this last compound. The hard segment was built up by reaction between tolylene diisocyanate (TDI) and a chain extender (1,4-butanediol) or two crosslinking agents (sucrose or glucose). The biodegradation behavior of the polyurethanes was verified using solid and submerged fermentation and using natural conditions under the soil. The analysis indicated that the biodegradation was affected by the PCL segment, hard segment content, intermolecular interations manly H bonds and crosslinking.

Keywords: biodegradation; poly(ε-caprolactone); polyurethane

Introduction

Conventional materials like glasses, metals and wood are being gradually changed by plastic materials in the manufacturing of many products, considering many advantages like low cost, versatility, among others. On the other hand, the uncontrolled disposal of these polymeric materials is a great problem. Many countries all over the world have been recognizing the need to reduce the discarded plastic materials amount in the environment. The Brazil is not out of this world-wide reality regarding the environment responsability. In this context, the interest in the materials production, mainly plastics, with biodegradable characteristics has been intensified in several segments of the society.[1–8] In this work, we have studied polyurethane (PU) elastomers biodegradation through solid and submerged fermentation using *Pleurotus sajor-caju*and in the environmental degradation conditions in natural soil. The polyurethanes were based on poli(ε-caprolactone) (PCL), tolylene diisocyanate (TDI) and 1,4-butanediol (BDO) as chain extender, and either sucrose (SUC) or glucose (GLU) as crosslinking agents.

Experimental

Polyurethane Synthesis

Segmented polyurethanes were synthesized by a two-step procedure.[9–11] The hard segment content was set according to the free NCO concentration in the prepolymer step, yielding hard segment content (X) of 11% to 31%. The products were structurally, mechanically and morphologically characterized by conventional techniques

[1] Laboratório de Polímeros Sintéticos -Departamento de Química Universidade Federal do Paraná, Curitiba/PR, Brazil
E-mail: kloss@quimica.ufpr.br; zawadzki@quimica.ufpr.br
[2] Laboratório de Microbiologia -Departamento Acadêmico de Química e Biologia -UTFPR, Curitiba/PR, Brazil
[3] Departamento de Solos e Engenharia Agrícola - Universidade Federal do Paraná, Curitiba/PR, Brazil

of analysis already presented in the literature.[9–11]

Biodegradation Methods

1) Solid Fermentation Procedure

The biodegradation process was accomplished through fermentation in the solid state. For this solid fermentation it was used agar-agar (2% w/w), yeast extract (0,5% w/w) and peptone (0,5% w/w) (pH 6.0) as support for the microorganism growth (temperature = 30 °C). The PU samples (d = 20 mm and thickness = 3 mm) were precisely weighted and the PU samples were the main carbon and energy sources for the fungal development. The period of incubation was 60 days (Figure 1).

2) Submerged Fermentation Procedure

PU samples (10mmX10mm) were sterilized. They were put on the appropriated flasks with 100 mL of saline solution[12] and 10 disks of the *P. sajor-caju* fungal micelium

Figure 1.
Solid fermentation samples.

Figure 2.
Submerged fermentation flasks.

were added, which was cultivated in PDA (the activation process stayed by 7 days). The flasks were put in an incubator Shaker MA 420, to 30 °C for 60 days under rotation of 250 rpm (Figure 2).

3) Soil Degradation Study

PU samples (10 mm × 20 mm) were previously weighted and they were put in small closed screen packages (Figure 3a). They were prepared 3 samples for each composition, and for each rigid segment content (X). The materials were buried in the soil outdoors at 10–15 cm of depth (Figure 3b). The samples remained under environmental influences: temperature, rain, solar radiation, and in direct contact with the microorganisms during 60 days.

After this procedure the materials were washed and dried under vacuum (2 hours, 100 °C). They were weighted to verify the weight loss and the biodegradation processes were evaluated by scanning

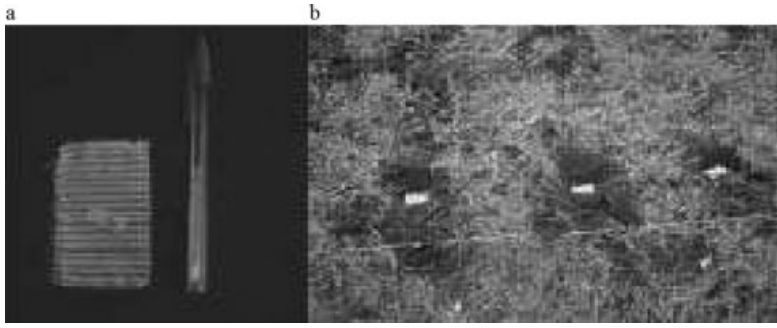

Figure 3.
Soil biodegradation.

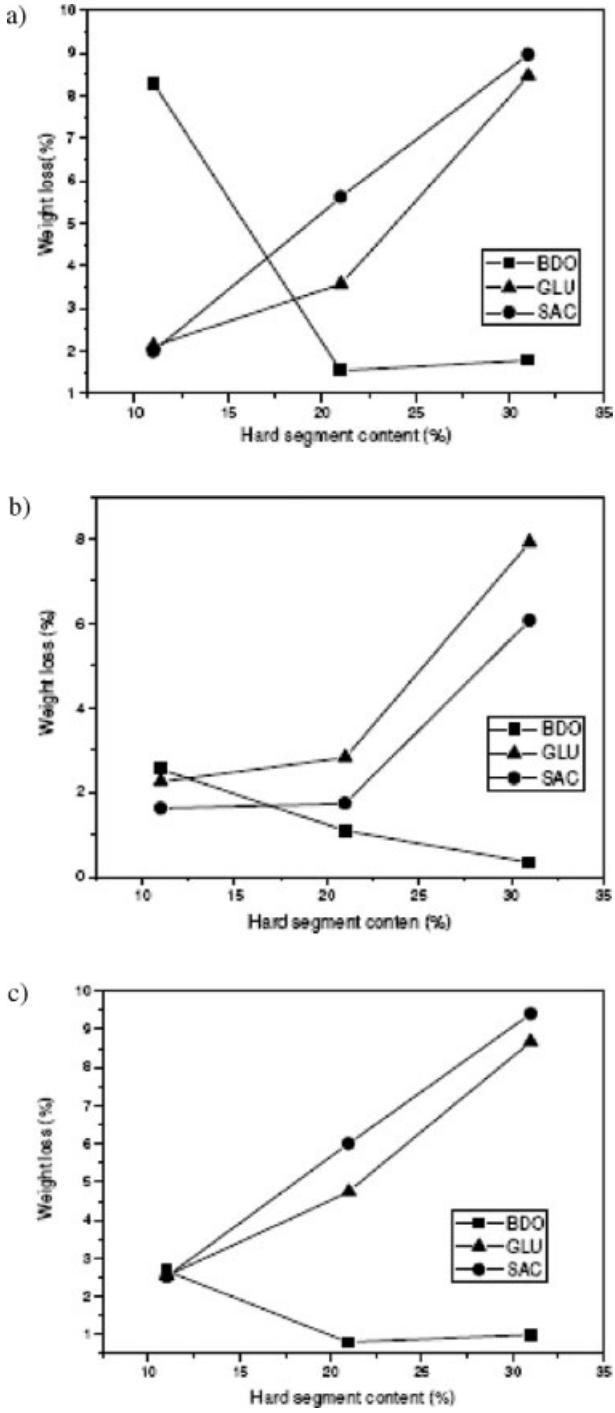

Figure 4.
Weight loss (in %, w/w) in differents biodegradation techniques. (a) solid fermentation; (b) submerged fermentation and (c) natural soil.

Table 1.
Initial and maximum weight loss temperature values for pure PCL and polyurethanes before biodegradation.

Samples	$T_{initial}$ (°C)	$T_{maximum}$ (°C)
PCL pura	278	409
BDO X = 11%	316	412
BDO X = 21%	298	413
BDO X = 31%	351	409
GLU X = 11%	285	409
GLU X = 21%	296	408
GLU X = 31%	276	411
SAC X = 11%	247	410
SAC X = 21%	246	411
SAC X = 31%	236	412

electronic microscopy (SEM), wide-angle X-Ray (WAXS) and thermogravimetry (TGA) techniques.

Results and Discussion

Biodegradability studies have shown[13–16] that microstructure observation is an advantageous method to analyze the behavior of the materials. Comparing the fermentation methods applied using *P. sajor-caju*, it was verified different weight losses suggesting different degradation mechanisms: PUs submitted to submerged fermentation showed smaller weight loss than those submitted to the solid fermentation. This result can be justified by the constant stirring of the material during the essay causing a non-homogeneity between the fungal micelium and the whole PUs sample surfaces. In the solid fermentation study the micelium had a better contact with the sample. This fact caused a more efficient microorganism action. Comparing the three PUs series under the two biodegradation methods the samples containing BDO showed the smallest weight loss rate. This result was due to the linear and more packed chains of these polymers. When the crosslinking agent (SUC or GLU) was used, the sucrose-based polymers were more degraded than those containing glucose. These data can be justified by the weak glycosidic link in the SUC extender. Moreover, this crosslinking agent is bulkier making the access of the microorganisms to the PU easier. In the soil biodegradation method the results obtained were similar when the fungi fermentation procedures were used (Figure 4).

When the samples were evaluated by TGA techniques considering the weight loss maximum temperature values obtained before and after biodegradation processes (Tables 1 and 2), it was verified that the thermal stability remained practically constant when the rigid segment content increased. The determined values for the PUs weight loss were very close for the pure PCL sample weight loss value suggesting that these thermal behavior were caused by the PCL presence (Figure 5) in the PUs matrices. Moreover these results suggested that the materials presented phases' mixture (rigid with flexible segments) in according to some results already reported.[17,18]

WAXS analyses were used to verify the crystalline changes in the cristalinity samples after biodegradation essay. It

Table 2.
Initial and maximum weight loss temperature values for pure PCL and polyurethanes samples after biodegradation.

After biodegradation for Solid fermentation			After biodegradation for Submerged fermentation		
Samples	$T_{initial}$ (°C)	$T_{maximum}$ (°C)	Samples	$T_{initial}$ (°C)	$T_{maximum}$ (°C)
BDO X = 11%	286	401	BDO X = 11%	262	410
BDO X = 21%	251	408	BDO X = 21%	255	409
BDO X = 31%	250	407	BDO X = 31%	264	407
GLU X = 11%	243	407	GLU X = 11%	229	408
GLU X = 21%	23	410	GLU X = 21%	238	409
GLU X = 31%	235	409	GLU X = 11%	244	411
SAC X = 11%	257	410	SAC X = 11%	254	408
SAC X = 21%	241	409	SAC X = 21%	261	411
SAC X = 31%	237	412	SAC X = 21%	254	413

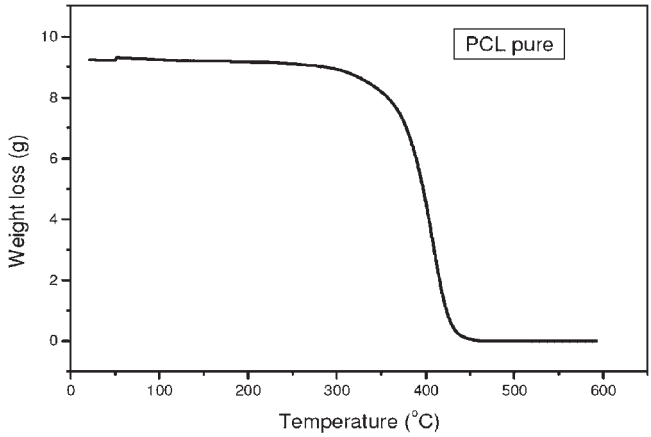

Figure 5.
Curve of TGA – PCL pure.

was observed that the crystalinity degree decreased when the chain extender (BDO) content increased. On the other hand the crystalline portion increased when the crosslinking agent (SUC or GLU) content increased indicating a preferential biodegradation of these kind of samples. The results also showed that the biodegradation ocurred in the amorphous parts of the PU samples (Figure 6).

Microscopic analysis showed that the pure samples had a homogeneous surface without phase segregation. After biodegradation essays the PUs showed an irregular texture, containing rough, small holes and clearer areas (Figure 7). These signs indicated that the microorganisms performance occurred suggesting the biodegradation. Similar results were already reported in the literature using different biodegrad-

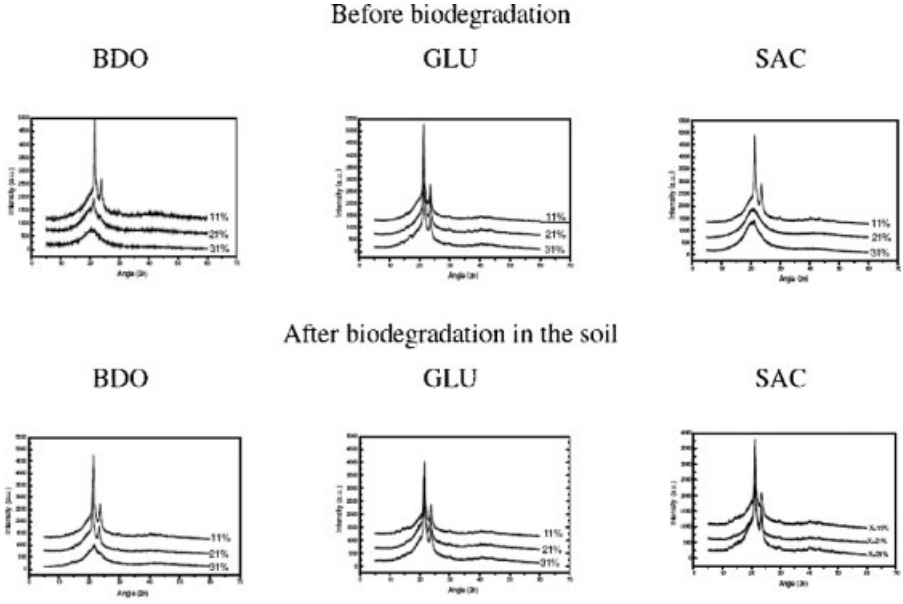

Figure 6.
Angle X-ray scattering (samples analysed after and before biodegradation in the soil).

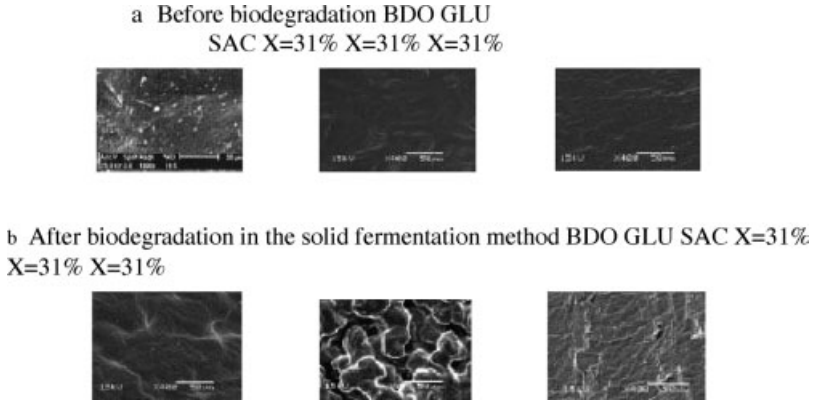

Figure 7.
Scanning electronic microscopy of the PUs.

able polymeric systems.[13–16] These signs were more visible when the crosslinking agents were used and the result was more evident for the samples with higher rigid segment content (X = 31%). The degradaded PU samples obtained using the others biodegradation techniques showed similar results when the cristalinity of the samples were analised by WAXS.

Conclusion

The results obtained for the biodegradation analysis for solid fermentation, submerged and soil methods showed that all the samples prepared with PCL as soft segment were partially degraded. The PUs showed weight losses, significant changes in the surface and in the crystallinity. PUs with BDO presented a smaller weight loss when compared to the crosslinked samples. It was observed that the linear PUs biodegradation was smaller when rigid segment content was higher. PUs based on sucrose was more biodegradable. The presence of the SUC on the PUs samples makes the microorganisms access easier. In this case, the PU chains are more separated because of the free volume of the used crosslinking agent.

Acknowledgements: LABPOL; DQUI-UFPR; DSEA-UFPR; UTFPR; LACTEC; CNPq.

[1] D. S. Rosa, R. Pantano Filho, M. R. Calil, C. G. F. Guedes, *Europ. Polym. J.* **2003**, *39*, 233.
[2] H. Yeganeh, M. M. Lakouraj, S. Jamshidi, *Europ. Polym. J.* **2005**, *41*, 2370.
[3] D. M. Abou-Zeid, R. J. Müller, W. D. Deckwer, *J. of Biotech.* **2001**, *86*, 113.
[4] A. Marcos-Fernández, G. A. Abraham, J. L. Valentin, J. San Román, *Polym.* **2006**, *47*, 785.
[5] E. Marten, R. J. Müller & W. D. Deckwer. *Polym Degrad. and Stab.* **2005**, *88*, 371.
[6] G. L. Y. Woo, M. W. Mittelman, J. P. Santere, *Biom.* **2000**, *21*, 1235.
[7] K. Gorna, S. Gogolewski, *Polyme. Degrad. and Statbility.* **2003**, *79*, 465.
[8] M. Mehrdad, N. Sharifi-Sanjani, *Polym. Degrad. and Statb.* **2003**, *80*, 199.
[9] J. Kloss, M. Muraro, G. P. Souza, J. V. Gulmine, S. H. Wang, S. Zawadzki, L. Akcelrud, *Poym.Sci.J.* **2002**, *40*, 4117.
[10] J. Kloss, C. Bugay, S. H. Wang, L. Akcelrud, S. F. Zawadzki, *Polím.:Ciên. e Tecn.* **2005**, *14*, 1.
[11] S. H. Wang, L. F. Silva, J. Kloss, M. Muraro, G. P. Souza, S. Zawadzki and L. Akcelrud. *Macromol. Symp.* **2003**, *197*, 255.
[12] N. Durant, E. Espósito, *Microb. Amb., Embrapa*, **1997**.
[13] Y. D. Kim, S. C. Kim, *Polym. Degrad. and Stab.* **1998**, *62*, 343.
[14] M. Kim, A. Lee, J. Yoon, I. Chin, *Europ. Polym. J.* **2000**, *36*, 1677.
[15] B. Bogdanov, V. Toncheva, E. Schacht, L. Finelli, B. Sarti, M. Scandola, *Polym.* **1999**, *40*, 3171.
[16] S. R. Barratt, A. R. Ennos, M. Greenhalgh, G. D. Robson, P. S. Handley, *Appl. Microb. J.* **2003**, *95*, 78.
[17] B. Bogdanov, E. Schacht, *Therm. Analy. and Calorim. J.* **1999**, *56*, 1115.
[18] Y. Zhuohong, H. Jinlian, L. Yeqiu, Y. Lapyan, *Mat. Chem. and Phys.* **2006**, *98*, 368.

