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Polycaprolactone Based Biodegradable Polyurethanes

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Summary: Two series of segmented polyurethanes were prepared with systematic variation in soft and hard segment length. The soft segment was constituted by polycaprolactone (PCL) blocks of molecular masses 530 or 2000 and the hard segment (HS) by urethane blocks, in a concentration that varied from 12% to 44% in weight of the whole polyurethane. Morphological analyses indicated that the amount of crystallinity of copolymers was strongly dependent on the PCL molar mass and hard segment content. The copolymers with longer PCL soft segments (Mn=2000) were semicrystalline, but those with shorter PCL segment (Mn=530) were unable to crystallize. The primary factor affectingthe biodegradability of copolymers as evaluated by Sturm tests was the extent of the phase separation, and that the segmental blending of the less biodegradable polyurethane (HS) blocks with PCL in the amorphous phase had a critical unfavorable consequence, which may be attributed to the size of the accessible area by microorganisms.

Keywords: biodegradable; block copolymers; morphology; polyesters; polyurethanes

Introduction

Polycaprolactone has been produced and commercialized as biodegradable materials and recent studies of its use as biodegradable segment in polyurethanes are underway to expand the possibility of its application.[1-3] Biodegradable segmented polyurethanes are of great technological interest due to the commercial availability of diisocyanates and alkanediols of diversified chemical structures, along with the wide range of physical properties attainable by relative composition variation, which allows the syntheses of elastomeric to flexible plastic urethane materials. In this work polycaprolactone (PCL) (Figure 1a) having two different molar masses was copolymerized to yield polyurethanes (Figure 1b) with systematic variation of hard

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segment (HS) content in the range from 12 to 44 % in weight. Sturm tests were performed to evaluate the biodegradability of polyurethane samples and results were analyzed in order to establish correlations among biodegradability, chemical composition, crystallinity, and phase separation.

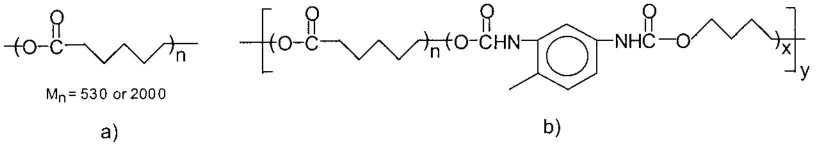

Figure 1. Chemical structures of polymers: (a) poly(ε-caprolactone) and (b) poly(ε-caprolactone – *b* - urethane)

Experimental

Synthesis of polyurethanes

The segmented polyurethanes were synthesized by a two-step procedure. The complete experimental procedure is reported elsewhere.[4] A short description of the experimental procedure is as follows: In the first step, a diisocyanate terminated prepolymer was prepared from hydroxyl terminated poly(ε-caprolactone) (PCL) and excess 1,4-tolylene diisocyanate. In the second step, the prepolymer was chain extended by an equimolar amount of 1,4-butanediol resulting in poly(ε-caprolactone-*b*-urethane). Two series of copolymers were obtained. The soft block was based on PCL of molecular masses 530 or 2000 and the hard segment molecular mass was set according to the free NCO concentration in the prepolymer step, yielding hard segment contents of 12% to 44% in weight.

Wide angle X- ray scattering (WAXS)

The WAXS spectra were performed on polymer films by using Phillips X'Pert equipment. The 1.79026 Co Kα radiation was applied on the sample in a conventional horizontal axis configuration, with a scan rate of 1°/min between 2θ = 5° and 90°.

Dynamic mechanical thermal analysis (DMTA)

A Rheometrics Scientific DMTA V was used to perform tension tests. Each sample was cut to a small rectangular film within the following range of dimensions: length of 23 to 26 mm, width of 2 to 8 mm, and thickness of 0.02 to 2 mm. A strain limit of 0.1% and a frequency of 1 Hz were applied in the temperature range from – 120 and –150 to 50 °C at a heating rate of 2 °C/min.

Biodegradation by Sturm test

All polyurethane samples were submitted to Sturm tests in order to evaluate the biodegradability according to IBAMA E.1.1.2-1988.[5] The carbon content and the theoretical amount of evolved CO_2 of each sample were calculated (Table 1). A known amount of organic sample, corresponding to 20 mg of carbon per liter of culture, was added to a sterile amber flask containing a nutrient solution composed of buffered inorganic basal medium, according to reference [5]. Each flask was inoculated with a standard microorganism concentrate originated from sewage water, and the final amount in the culture was calculated to reach an average concentration of 10^5 CFU/mL. In Figure 2 is shown the schematic set up for the biodegradation test. The airflow in the system was controlled and filtered to eliminate CO_2 before reaching the digesting flask. The formed CO_2 was collected at the exit of the digesting flask in barium hydroxide aqueous solution and was quantitatively determined by titration. Glucose was used as reference material to check the efficiency of the microorganism concentrate and its inhibition by the polymeric samples or its byproducts. Each poly(ester-urethane) sample was incubated with the inoculum for 28 days at ambient temperature.

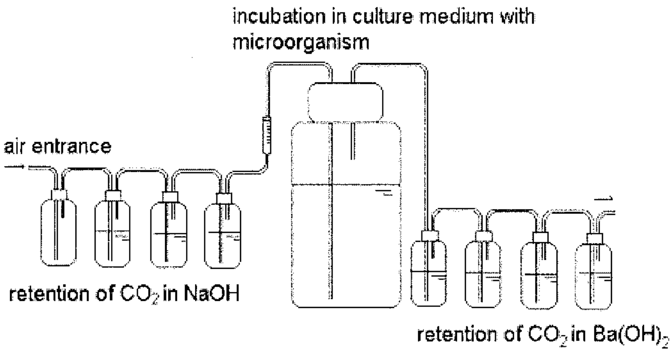

Figure 2. Experimental set up for biodegradation analysis by Sturm test

Results and Discussion

The samples evaluated in this work are presented in Table 1 with the relative segmental and elemental compositions. All polyurethane samples presented PCL as the major component by weight. The elemental compositions of the samples are quite similar.

Table 1. Composition of poly(ester-urethane)s

SAMPLE	PCL Mw	%HS	%PCL	%C	%H	%N	%O
1	530	29	71	59.44	8.08	3.08	29.40
2	530	33	67	59.42	7.97	3.50	29.11
3	530	37	63	59.40	7.86	3.93	28.82
4	530	40	60	59.38	7.77	4.24	28.60
5	530	44	56	59.36	7.66	4.67	28.31
6	2000	12	88	61.84	8.48	1.27	28.41
7	2000	17	83	61.68	8.34	1.80	28.17
8	2000	22	78	61.52	8.21	2.33	27.94
9	2000	26	74	61.40	8.10	2.76	27.75
10	2000	31	69	61.24	7.96	3.29	27.51
11	530	0	100	59.58	8.91	0	31.51
12	2000	0	100	62.21	8.81	0	28.98

The degree of crystallinity of the poly(ester-*b*-urethane)s was determined by deconvolution of their WAXD curves (Figure 3 and Table 2). The copolymers prepared from PCL 530 were completely amorphous while those from PCL 2000 were semicrystalline. The decrease of crystallinity of segmented poly(ester-urethane)s has been already reported for copolymers comprised by different segment lengths of polycaprolactone.[1,2]

The observed decrease of the crystallinity degree of the PCL phase on increasing the relative concentration of urethane can be explained in terms of the restrictions introduced by the covalent linkages, and more importantly by the presence of strong interchain interactions through hydrogen bonding.

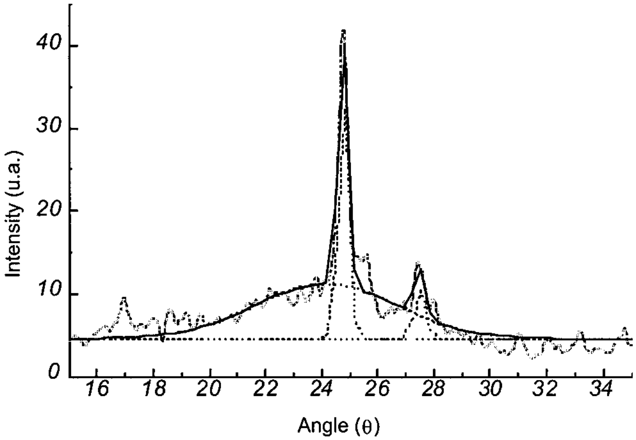

Figure 3. WAXS curve of poly(ester-urethane) **6**. Original curve: dashed line; deconvoluted curves: dot lines; and total sum of deconvoluted curves: solid line

Table 2. Crystallinity and thermal transitions of poly(ester-urethane)s

SAMPLE	CRYSTALLINITY[a] %	T_α TRANSITION[b] °C
1	-	2
2	-	2
3	-	3
4	-	15
5	-	19
6	28	-31
7	20	-32
8	13	-25
9	11	-25
10	9	11
11	-	-
12	40	-

[a] determined by WAXS; [b] determined by DMTA

The DMTA data are also shown in Table 2. The original PCL samples were fragile and unsuitable for dynamic tension test. The DMTA E” curves showed three main transitions for poly(ester-urethane)s. A first peak at –135 °C (T_γ) was assigned to methylene sequence local relaxations, in analogy to previously reported results .[4] The second one (T_β) is located in the low temperature region (-86 °C to -90 °C) and a third one (T_α) is observed at a higher temperature (-32 °C to +19°C). T_β is related to the relaxation of the PCL segments, since this transition does not depend on copolymer composition. T_α was considered a mixing transition temperature, and would be the result of the relaxations associated to various degrees of mixing between the ester and urethane blocks. In fact, it was observed that T_α increased with the urethane content in the copolymer for both series. A sharp rise was observed for each series, at compositions around 30% of urethane blocks for the PCL2000 series and around 38% of urethane blocks for the PCL530 series.

The amount of crystallinity in copolymers from PCL2000 did not cause any restriction in the PCL amorphous phase since T_β did not suffer any significant change with copolymer composition. However, the presence of urethane linkages increased T_α of poly(ester-urethane).

All samples were prepared in conditions to yield PCL as the major component, that is, in all poly(ester-urethane)s PCL represents more than 50% in weight. The copolymers also presented similar composition with respect to their elemental constitution (Table 1). The relative biodegradability was calculated as the ratio of the CO_2 produced by the sample to the CO_2 from glucose, in parallel tests performed under the same conditions. This practice was employed in order to minimize the influence of factors such as variation in the nature of the microbial population inoculum, which is only numerically controlled, in conformity to the test method. Also in accordance with the test method the existence of an inhibiting effect of the poly(ester-urethanes) on the glucose degradation was investigated, and no negative influence was observed.

A reduction in the microbial degradation ability of PCL samples was observed, as a result of the molar mass increase (Figure 4). PCL 2000 was semicrystalline while PCL530 was amorphous, and the difference in biodegradability should be attributed to the effect of crystallinity in accordance with the results reported in literature,[6-11] where the amorphous regions are more susceptible to microbial attack than crystalline regions.

Copolymers derived from PCL530 were amorphous and presented very low biodegradability in the whole range of composition (Figure 5). The relative biodegradability of the poly(ester-urethane)s derived from PCL530 after 28 days of essay ranged from 2 to 5%, and these differences are within the experimental error.

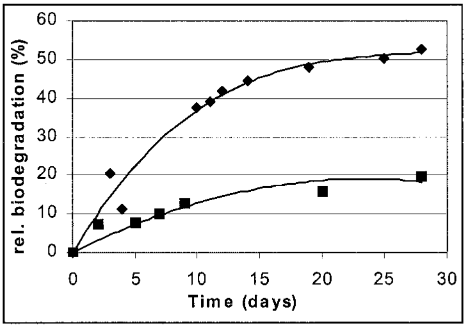

Figure 4. Relative biodegradation of PCL 530 (♦) and PCL2000(■)

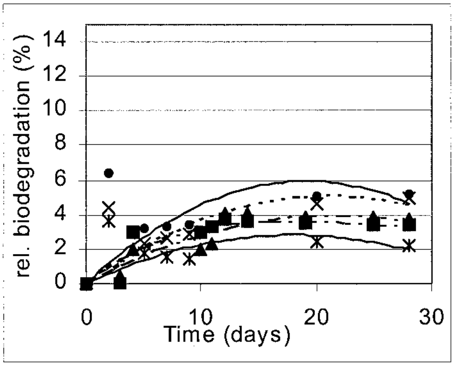

Figure 5. Relative biodegradation of poly(ester-urethanes) prepared from PCL 530: **1** (×),**2** (■), **3** (*), **4** (•), and **5** (▲)

A gradual reduction in the crystallinity ratio of the poly(ester-urethane)s derived from PCL2000 was observed with the increase of the hard segment relative concentration (Table 2 and Figure 6).

The copolymers were much less biodegradable than PCL2000 under the conditions of the Sturm test, with the exception of the poly(ester-urethane) **6**. This copolymer presented a higher degradability compared to its parent polyester, and this behavior is in accordance with the results observed for the majority of poly(ester-urethane), where an increase of biodegradability is reported to be associated to a decrease of the crystalline phase content. The others copolymers prepared from PCL2000 presented a low biodegradability under the Sturm test conditions. After 28 days of test, the relative biodegradability of poly(ester-urethane) **6** was 25% compared to 5 to 10% of the other three copolymers of this series. The poly(ester-urethane)s **7** and **9**, whose final relative biodegradabilities were 8 and 10%, respectively, were slightly more biodegradable compared to **10**, which yielded 5% biodegradation. The biodegradability behavior of poly(ester-urethane) **10** was similar to those observed for the poly(ester-urethane)s PCL530 series and its hard segment content (HS) (31%) was within the range of that series.

The PCL2000 series was comparatively more biodegradable than the PCL530 series, in contrast to the results observed for the parent polyester (Figures 4-6).

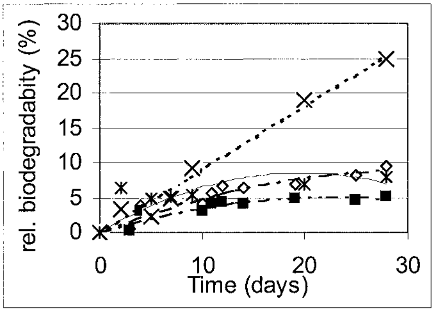

Figure 6. Relative biodegradation of poly(ester-urethanes) prepared from PCL 2000. **6** (×), **7** (*), **9** (◊), and **10** (■)

Although the poly(ester-urethane)s presented polycaprolactone as the major component, the results indicated a biodegradation process associated to the specificity of the contact between the biodegradation agent and the polymeric surface. The preferential attack of the amorphous phase of semicrystalline polymers has been widely demonstrated, however the segmented poly(ester-urethane)s here described are formed by two polymer blocks with very distinct biodegradability (PCL segments are much more biodegradable than urethane segments), and in these systems the effect of the morphology in the biodegradability was not restricted to the presence of crystallinity, but also the extent of the phase separation in the amorphous region may play a critical role in the accessibility of biodegradable region. In multiblock copolymers the phase separation is restricted by chain mobility of segments linked by covalent bonds, even when the chemical structure of the segments are dissimilar.

The correlation of DMTA and WAXS results allowed the identification of a significant reduction of chain mobility after increased incorporation of urethane linkages by copolymerization. The organization of the crystalline phase structure was gradually diminished and a decrease of the degree of crystallinity was observed as a result of the introduction of urethane linkages. Also the mixed amorphous phase presented a T_{α} correspondent to polymeric systems containing extensive hydrogen bonding. The presence of strong segmental interactions by hydrogen bonds should contribute to lowering the chain mobility in these systems and preventing further phase separation, as well as the crystallite growth.

Similar results in biodegradation of phase separated polymer blends containing polycaprolactone were reported by Iwamoto and Tokiwa [12], and in those systems a decrease of enzymatic biodegradation was observed with the miscibility improvement.

Conclusions

The biodegradability of segmented multiblock poly(caprolactone-β-urethane)s evaluated by Sturm test revealed that the the level of the phase separation presented by the polymeric systems is the prevailing factor responsible for biodegradation. In segmented copolymers, the presence of a second less biodegradable segment in the PCL matrix can alter the crystallization behavior and the extent of the amorphous phase separation. Although the crystallinity has a negative effect in biodegradation, the domain size of biodegradable amorphous phase is critical for microbial attack.

Acknowledgement

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