

Hydrolytic degradation of PCL/PEO copolymers in alkaline media

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PCL/PEO copolymers with different compositions were obtained from ring opening polymerization of ϵ -caprolactone in the presence of ethylene oxide and characterized by various analytical techniques. Data collected from DSC and X-ray diffractometry suggested that the copolymer chains possess a blocky structure, leading to both PCL and PEO-type crystalline structures. Hydrolytic degradation of these copolymers was carried out in a pH = 10.6 carbonate buffer solution at 37 °C. Comparison was made with a PCL homopolymer and a PCL/PEG blend which had the same gross composition as one of the copolymers. The results showed that the presence of PEO sequences considerably enhanced the hydrophilicity of the copolymers as compared with PCL homopolymer. Nevertheless, the degradability of PCL chains was not enhanced due to the phase separation between the two components. These materials should be of great interest for biomedical uses such as matrices for sustained drug delivery because of the presence of both hydrophilic and hydrophobic microdomains.

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1. Introduction

During the past two decades, degradable aliphatic polyesters have been widely studied for various biomedical uses, in particular poly(lactic acid) (PLA) and poly(ϵ -caprolactone) (PCL) [1–3]. PLA is of great interest because of the chirality of lactyl repeating units which makes it possible to obtain PLA stereocopolymers with various properties [4–9]. PCL also attracted much attention due to its excellent permeability to drugs [10, 11]. Nevertheless, PCL is a highly crystalline and hydrophobic polymer with low degradability with respect to drug delivery systems, which considerably limited their potential applications in this field.

A great deal of work has been devoted to the preparation of block copolymers from lactones and ethylene oxide (EO) or polyethylene glycol (PEG) [12–20]. PEG presents outstanding physico-chemical and biological properties, including hydrophilicity, solubility in water and in most organic solvents, lack of toxicity [21], absence of antigenicity and immunogenicity [22], etc. That is why PEG has been widely utilized for biomedical and biotechnological applications [23–25].

Copolymerization of lactones with EO or PEG offers the possibility of varying hydrophilic/hydrophobic and

soft/hard segment ratios and, thus, constitutes a very attractive means to modulate the basic properties of the parent homopolymers.

Two studies have recently reported the synthesis, characterization and hydrolytic degradation of PCL/PEO multiblock copolymers with predetermined PCL and PEO block lengths [26, 27]. The copolymers were obtained under mild conditions by polycondensation of PEG bearing two carboxylic endgroups and PCL diols in the presence of dicyclohexylcarbodiimide (DCC) as coupling agent. The properties of these materials can be modulated by adjusting the chain lengths of the macromonomers. In particular, one or two crystalline structures can exist within the copolymers of various crystallinities. However, the molecular weights of the copolymers were rather low ($M_n < 35000$).

In a previous paper, Chen *et al.* reported on the synthesis of high molecular weight PCL/PEO copolymers obtained by ring opening polymerization of ϵ -caprolactone in the presence of ethylene oxide, using trimethyl aluminum as catalyst [28]. These copolymers should be interesting as matrices for controlled drug delivery because of the presence of both hydrophilic and hydrophobic microdomains. In the present work, the degradation characteristics of these PCL/PEO copolymers were investigated in an alkaline buffer medium at 37 °C. A PCL homopolymer and a PCL/PEG blend were also considered for the sake of comparison.

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2. Experimental

2.1. Materials

ϵ -caprolactone was supplied by Aldrich. Prior to use, it was dried over CaH_2 for 24 h, followed by distillation under reduced pressure. Ethylene oxide (Aldrich, > 99.7%) was used as received. Trimethyl aluminum was supplied by Aldrich in toluene solutions from which $\text{AlMe}_3\text{-nH}_2\text{O}$ catalytic systems were prepared *in situ*. PCL homopolymer was purchased from Union Carbide Corp., and PEG with number average molecular weight $M_n = 18000$ was purchased from Polysciences, Inc.

2.2. Methods

Copolymerization was carried out by introducing toluene, ϵ -caprolactone, ethylene oxide and catalyst into a dried and argon purged ampule through a syringe. The ampule was sealed and the reaction was allowed to proceed under stirring in an oil bath thermostated at $62 \pm 2^\circ\text{C}$ for 24 h. Thereafter, the resulting copolymer, namely PECL, was recovered by dissolution in chloroform and precipitation in petroleum ether. The obtained products were washed with methanol and vacuum dried at 40°C to constant weight. Two PECL copolymers were thus obtained.

The PCL/PEG blend (84/16 in weight) was prepared by extrusion of granules of both components at 70°C . The extruded strings were cut into 10 mm long cylinders. A second extrusion was performed under the same conditions to homogenize the blend.

2.3. Hydrolytic degradation

The PECL copolymers, PCL/PEG blend as well as PCL homopolymer were compression molded at 80°C using a Dake hydraulic press equipped with heating plates. The thus obtained 1.5 mm thick plates were then cut to yield $10 \times 30 \text{ mm}^2$ parallelepipeds. Each specimen was placed in a 25 ml flask filled with $\text{pH} = 10.6$ carbonate buffer solution. Hydrolysis experiments were performed at 37°C . Two specimens of each compound were withdrawn periodically from the degradation medium, washed with distilled water and vacuum dried for one week before various analyses.

2.4. Measurements

^1H nuclear magnetic resonance (NMR) spectra were recorded at room temperature with a Bruker 250 spectrometer. CDCl_3 was used as solvent at a concentration of about 3.5% w/w.

Chemical shifts were given in ppm relative to

tetramethylsilane (TMS). Gel permeation chromatography (GPC) measurements were performed on a Waters apparatus equipped with UV/RI detectors. CHCl_3 was used as mobile phase at a flow rate of 1.0 ml/min. Sample concentration of 0.5% (w/v) and injection volume of 100 μl were used. Calibration was accomplished with polystyrene standards (Polysciences, USA). Differential scanning calorimetry (DSC) thermograms were registered with a DuPont instrument DSC 912, the heating rate being $10^\circ\text{C}/\text{min}$. 10 mg of material were used for each analysis. X-ray diffractometric analyses were carried out using a Rigaku 18 kW rotating anode operated at 40 kV/50 mA and Cu $\text{K}\alpha$ radiation ($\lambda = 0.154 \text{ nm}$).

3. Results

The compositional and molecular characteristics of the various compounds selected for degradation studies are presented in Table I. The PCL/PEG blend had the same gross composition as PECL1 for the sake of comparison. The molecular weights of PCL and the two copolymers exceeded 50 000.

PECL1, PECL2, PCL and PCL/PEG were all semi-crystalline materials. In the alkaline degradation medium until 35 weeks, the opaque specimens remained apparently unchanged except for slight bending.

3.1. Weight loss

Weight loss data showed that, after the first 2 weeks, the copolymer PECL1 lost 8.7% of its initial weight (Fig. 1). Thereafter, weight loss continued to increase, but at a reduced rate. It attained 12.7% after 20 weeks. Between 20 and 35 weeks, there was an acceleration of weight loss which reached 20.8%. In contrast, PECL2 with lower EO content in its chains (7% in weight), lost only 2.3% after 20 weeks. Then, a faster increase of weight loss up to 6% was observed. The PCL/PEG blend, which had the same CL/EO ratio as PECL1, exhibited initially higher weight loss rate than PECL1. The blend lost 12.6% of its initial weight after 2 weeks (Fig. 1), probably due to dissolution of PEG. Then, weight loss continued to increase slowly to 20% at the end of 35 weeks. This indicates that the majority of initially present PEG (16%) was solubilized during the first 2 weeks, and on the other hand, weight loss partially resulted from the release of PCL degradation by-products. Insofar as PCL homopolymer is concerned, its weight loss remained slow during the whole degradation period (2.8% after 35 weeks).

TABLE I Compositional and molecular characteristics of the various compounds

Compound	PCL	PECL1	PECL2	PCL/PEG
CL/EO ^a (in mol)	100/0	66/34	84/16	66/34
CL/EO (in weight)	100/0	84/16	93/7	84/16
Molecular weight ^b ($\times 10^{-3}$)	56.6	59.9	103.2	—

^aCL/EO ratio in the PECL copolymers was determined by ^1H NMR, while CL/EO ratio in the PCL/PEG blend was determined by weighing.

^bMolecular weights were taken at the summit of GPC chromatograms.

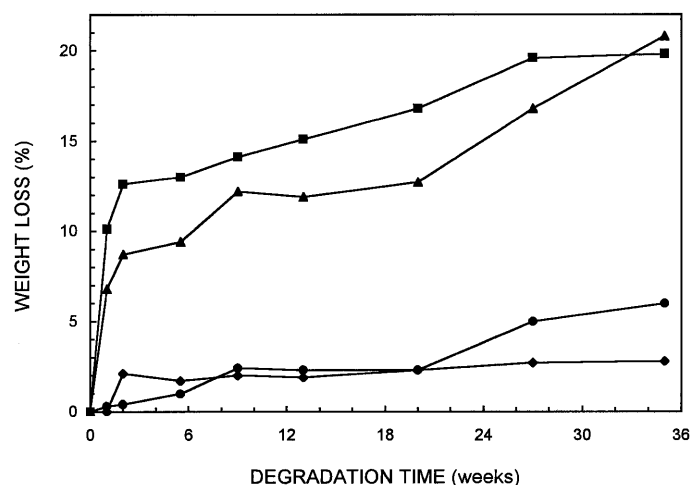


Figure 1 Weight loss of PECL1 (▲), PECL2 (●), PCL (◆) and PCL/PEG (■) with degradation.

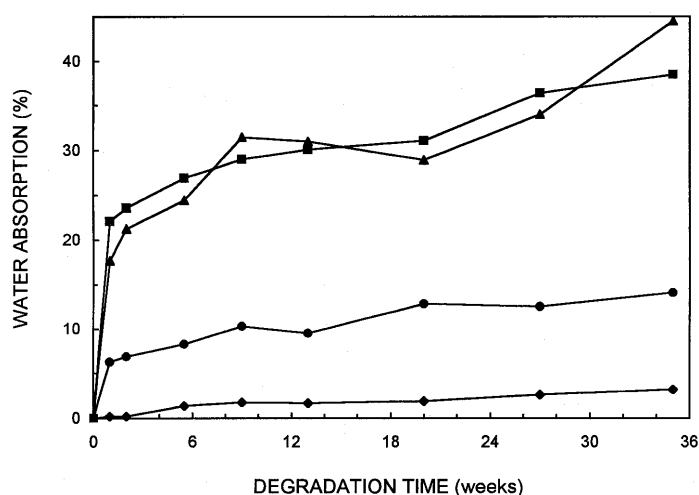


Figure 2 Water absorption of PECL1 (▲), PECL2 (●), PCL (◆) and PCL/PEG (■) with degradation.

3.2. Water absorption

PECL1 and PCL/PEG showed similar water absorption profiles. Water absorption was initially very rapid. After 1 week, PECL1 and PCL/PEG absorbed respectively 17.7% and 23.6% (Fig. 2). Then water absorption increased slowly. At the end of 35 weeks, PECL1 and PCL/PEG absorbed 44.5% and 38.5%, respectively. PECL2 appeared much less hydrophilic. Water absorption was 6.6% after one week and slowly increased to about 14.1% after 35 weeks. PCL homopolymer appeared the most hydrophobic. It absorbed only 3.2% at the end of 35 weeks. Therefore, the presence of EO units or PEG considerably enhanced the hydrophilicity of the copolymers and blend as compared with the PCL homopolymer. The higher the PEO content, the more hydrophilic the copolymer. The initial rapid increase of water absorption corresponded to the release of soluble material which created cavities inside the samples.

3.3. Molecular weight

Fig. 3 shows changes of the molecular weight taken at the summit of GPC chromatograms. The molecular weight of the two PECL copolymers, PCL as well as PCL in the blend remained almost unchanged during the first 5 weeks. Beyond, a slow decrease was observed in all

cases. At the end of 35 weeks, the molecular weight of PCL and PCL/PEG decreased from the initial 56 500 to 29 600 and 23 100, respectively, while that of PECL1 decreased from the initial 59 900 to 37 000. The molecular weight of PECL2 was initially higher than those of the three other compounds. It decreased from the initial 103 200 to 71 200 after 35 weeks. It appears that all these compounds exhibited similar profiles of molecular weight decrease. The copolymers and the blend were not more inclined to alkaline hydrolysis than the PCL homopolymer. In other words, the degradability of PCL was not enhanced by the presence of PEO component which enhanced the hydrophilicity of the material.

3.4. Chemical composition

The ^1H NMR spectrum of PECL1 is shown in Fig. 4. Several groups of signals can be distinguished. Resonances in the ranges of 4.10, 2.35, 1.67 and 1.42 ppm belong to different CH_2 in CL units, including both EO-connecting and central units, while the signal at 3.66 ppm is characteristic of methylene units within EO units. The composition of the copolymers was calculated from the integration ratio of signals at 4.10 ppm and 3.66 ppm.

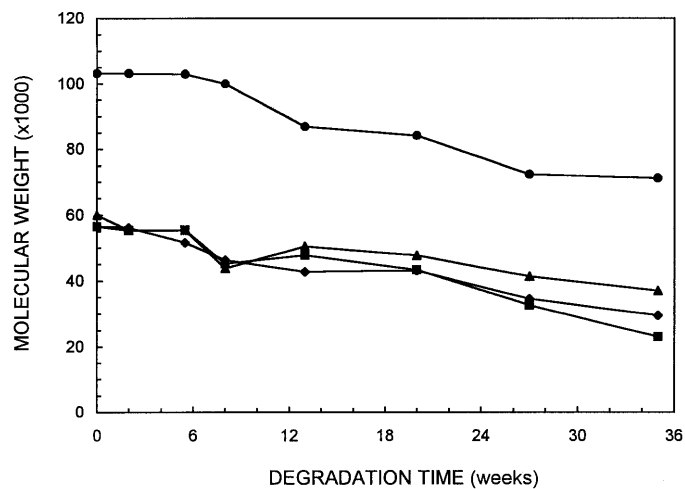


Figure 3 Molecular weight changes of PECL1 (▲), PECL2 (●), PCL (◆) and PCL/PEG (■) with degradation.

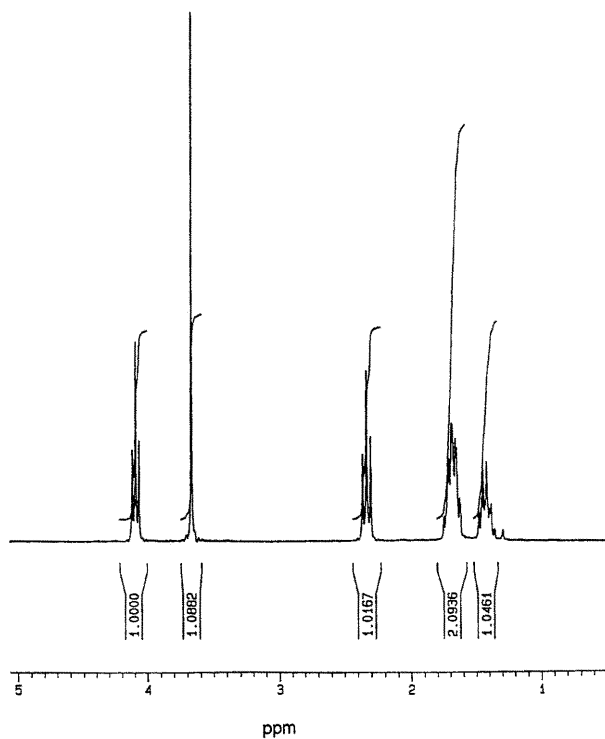


Figure 4 ¹H NMR spectrum of PECL1 in CDCl₃.

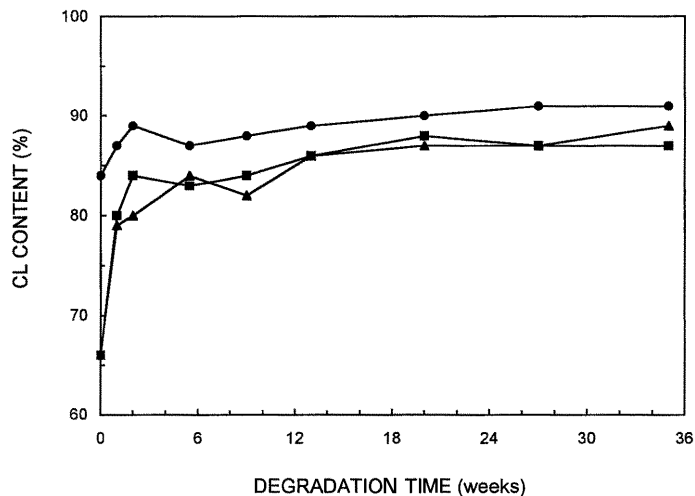


Figure 5 CL content changes of PECL1 (▲), PECL2 (●) and PCL/PEG (■) with degradation.

As shown in Fig. 5, both PECL1 and PCL/PEG exhibited a rapid increase of CL content during the first 2 weeks, from initial 66% (in mol) to 80% and 84%, respectively. This can be assigned to the release of free PEG or PEO segments attached with short PCL ones, which is in good agreement with the weight loss data. Afterwards, the composition only slightly changed, the CL content being 89% and 87% at the end of 35 weeks for PECL1 and PCL/PEG, respectively. PECL2 contained initially 84% CL units in its chains. The CL content increased to 89% after 2 weeks and then levelled off. This is also in agreement with the small weight loss of PECL2 during the whole degradation period.

3.5. Thermal properties

Thermal characteristics of the various compounds were investigated by DSC. After the first heating, the molten sample was quenched and a second run was performed so as to observe glass transition and crystallization phenomena. Melting temperature (T_m) and melting enthalpy (ΔH_m) were obtained from the first run, while glass transition temperature (T_g) and crystallization temperature (T_c) were obtained from the second run.

Both PCL and PEG are highly crystalline polymers. PCL exhibited initially a melting point at 67.6°C with $\Delta H_m = 76.1\text{ J/g}$ (Fig. 6a). At the second run, a glass transition was detected at -62.0°C , followed by a crystallization peak at -53.8°C and a melting peak. PEG showed initially a melting point at 68.5°C with $\Delta H_m = 160.4\text{ J/g}$ which is much higher than that of PCL. At the second run, a very small glass transition was

detected at -57.3°C and a very small crystallization peak at -48.1°C . In fact, it is very difficult to measure the T_g and T_c of PEG because of its very high crystallizability. Even by quenching in liquid nitrogen, one cannot obtain totally amorphous PEG. Insofar as the PCL/PEG blend is concerned, T_m , ΔH_m , T_g and T_c values were found to be 67.7°C , 84.9 J/g , -61.8°C and -53.8°C , respectively. In comparison with PCL and PEG homopolymers, it is noted that both T_g and T_c values of the blend were very close to those of PCL.

In the case of the copolymers, PECL1 exhibited an initial melting point at 65.4°C , the melting enthalpy being 77.6 J/g (Fig. 6b). At the second run, T_g was detected at -62.1°C and T_c at -53.3°C . T_m , ΔH , T_g and T_c of PECL2 were 64.6°C , 49.3 J/g , -61.9°C and -53.6°C , respectively. Therefore, the thermal characteristics of the two copolymers were very close to those of the PCL homopolymer.

During the degradation period, thermal property changes of the various compounds were rather limited (Table II). After 9 weeks, for example, T_g and T_c of PECL2 and PCL remained almost unchanged, while those of PECL1 and PCL/PEG could not be detected probably due to the increased crystallizability after degradation. T_m increased slightly in all cases, which can be assigned to the subsequent crystallization of defects and/or amorphous zones as the degradation temperature was above the T_g of the polymers. ΔH_m changes appeared more complicated. ΔH_m of PCL and PECL2 more or less increased, which could be attributed to the subsequent crystallization in agreement with T_m increase. In contrast, ΔH_m of PECL1 and PCL/PEG slightly decreased after 9 weeks. Considering the fact that

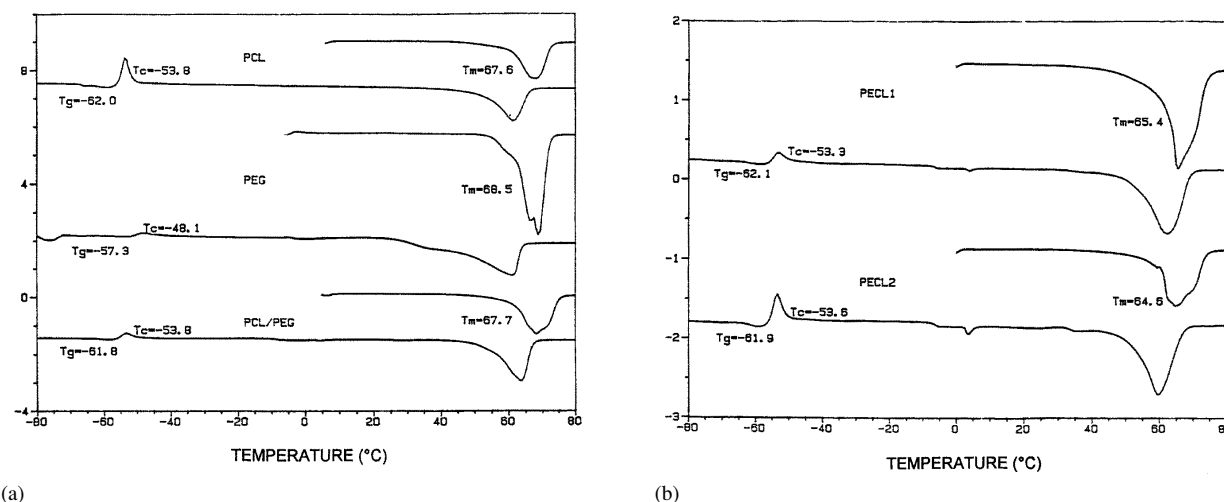


Figure 6 (a) DSC thermograms of PCL, PEG and PCL/PEG; (b) DSC thermograms of PECL1 and PECL2.

TABLE II Thermal characteristics of PCL, PECL1, PECL2 and PCL/PEG after 0 and 9 weeks degradation

Compound		PCL	PECL1	PECL2	PCL/PEG
T_g ($^\circ\text{C}$) ^a	0	-62.0	-62.1	-61.9	-61.8
	9	-61.6	n.d. ^b	-61.7	n.d.
T_c ($^\circ\text{C}$) ^a	0	-53.8	-53.3	-53.6	-53.8
	9	-53.9	n.d.	-53.8	n.d.
T_m ($^\circ\text{C}$) ^a	0	67.6	65.4	64.6	67.7
	9	70.5	70.2	71.0	71.5
ΔH_m (J/g) ^a	0	76.1	77.6	49.3	84.9
	9	76.9	74.4	62.6	82.3

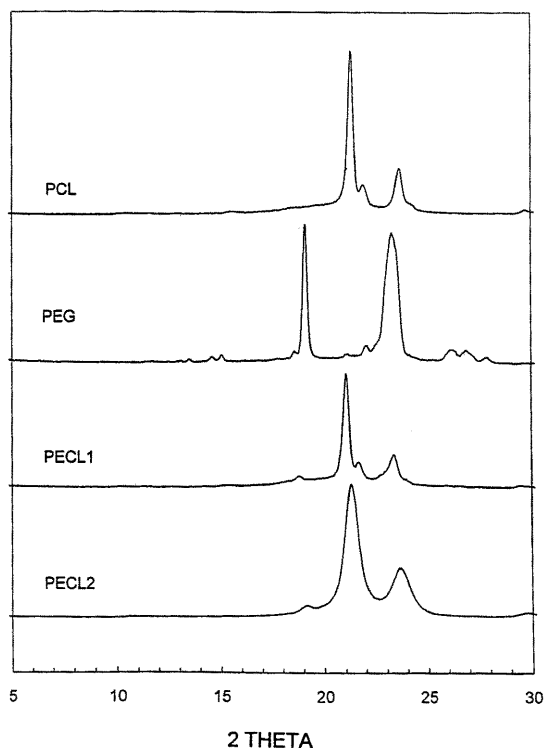


Figure 7 X-ray diffractograms of PCL, PEG, PECL1 and PECL2.

PEG has a higher ΔH_m than PCL (160.4 v 76.1 J/g), the ΔH_m decrease detected for PECL1 and PCL/PEG can be assigned to the release of PEG or PEO-rich chains, in agreement with weight loss and composition changes.

3.6. X-ray diffraction

The crystalline structure of these materials was examined by X-ray diffraction as shown in Fig. 7. The PEG diffraction pattern exhibited two intense characteristic peaks located at $2\theta = 19.2^\circ$ and 23.3° , while PCL showed two main peaks at 21.4° and 23.7° , and a smaller one at 21.8° . All these diffraction peaks were observed for the two copolymers, the peak at 23.3° of PEG being overlapped with the peak at 23.7° of PCL. In other words, the PCL and PEO components formed separate crystalline domains, thus showing a phase separation. Nevertheless, the peaks due to PEO crystallites appeared much less intense as compared with those of PCL ones. This could be explained by the low EO contents, 16% and 7% in weight (34% and 16% in mol) for PECL1 and PECL2, respectively. In the case of the blend, similar features were observed (data not shown).

During degradation, few changes were observed on the X-ray diffraction spectra. However, for the copolymers and the blend, the peaks corresponding to PEO or PEG crystallites diminished, in agreement with composition changes.

4. Discussion

In the literature, few authors reported on the hydrolytic degradation of PCL/PEO copolymers. Wang and Qiu investigated the *in vitro* degradation (pH = 6.5, 37°C) of a series of PCL/PEO triblock copolymers obtained by ring-opening polymerization of ϵ -caprolactone in the presence of PEG ($M_n = 6000$) using tetra-*n*-butyl

titanate as catalyst [20]. The authors suggested that the degradation process consists of two steps: ester bonds are first broken hydrolytically and, then free PEO segments can leach out of the bulk material. Cerrai *et al.* investigated various PCL/PEO triblock copolymers obtained by reacting ϵ -caprolactone with PEG with $M_n = 9200$, 20 000 and 35 000 in the absence of a catalyst [17]. From inherent viscosity measurements, the authors concluded that the higher the hydrophilicity of the material, the faster the degradation rate. Li *et al.* investigated the hydrolytic degradation of PCL/PEO multiblock copolymers [27]. The results showed that introduction of PEO sequences considerably increased the hydrophilicity of the copolymers as compared with PCL homopolymers. Nevertheless, the degradability of PCL sequences was not enhanced due to the phase separation between the two components.

The present work agrees well with literature data despite the fact that degradation was performed in an alkaline medium. The fact that both PCL and PEO components crystallized separately, as shown by X-ray diffractometry (Fig. 7), suggests a blocky chain structure due to the different reactivities of ϵ -caprolactone and ethylene oxide during ring opening polymerization. Water absorption data showed that the hydrophilicity of the copolymers increased with the EO content (Fig. 2). In parallel, weight loss rate increased (Fig. 1). Weight loss mainly resulted from the solubilization of EO-rich segments, in agreement with the compositional changes (Fig. 5). Nevertheless, the CL content of the copolymers tended to a limit at the end of the degradation period, suggesting a random chain cleavage along PCL blocks. In other words, no preferential cleavage occurred at ester-ether junctions. This is in contrast to the conclusion of Li *et al.* that hydrolytic cleavage of PLA/PEO triblock copolymers proceeded preferentially at ester-ether junctions [13].

GPC data showed that, after 35 weeks of degradation in pH = 10.6 carbonate buffer, the molecular weight decrease was rather limited for the copolymers as well as for the PCL homopolymer and PCL/PEG blend. In other words, the degradability of the copolymers was not enhanced by the presence of PEO sequences. This can be related to the phase separation phenomenon between PEO and PCL blocks as shown by X-ray diffraction data, as in the case of PCL/PEO multiblock copolymers [27]. The large amounts of water absorbed by the copolymers should be located in the swollen phase of PEO. Degradation of PCL blocks proceeded very slowly as in the case of PCL homopolymers.

It is well known that blends of two immiscible polymers exhibit two glass transitions regardless of the blend composition. In contrast, only one T_g is observed for blends of two miscible polymers, which varies with composition between the values characteristic of each polymer [29]. In the case of PCL/PEO copolymers and blends, it is very difficult to evaluate the miscibility of both components by T_g measurements since their T_g values are close to each other. However, the fact that only one T_g was found for the copolymers and blend suggested a certain miscibility in the amorphous state.

It is also of interest to note that the blend exhibited similar degradation characteristics as PECL1, i.e. similar

weight loss, water absorption, molecular weight decrease and thermal property changes. The CL content also tended to a limit for the blend. This was surprising since free PEG should be totally released from the blend. It can thus be assumed that part of the PEG chains was bonded to PCL ones due to transesterification reactions which occurred during extrusion of PCL and PEG components. Further studies are under way to elucidate this point.

5. Conclusion

PCL/PEO copolymers obtained from ring opening polymerization of ϵ -caprolactone and ethylene oxide exhibited a blocky structure. Both polyester and polyether blocks were phase separated, leading to PCL and PEO-type crystalline structures. The presence of PEO domains considerably enhanced the hydrophilicity of the copolymers as compared with PCL homopolymer. Compositional changes were observed during degradation due to the release of PEO and/or PEO-rich chains. Nevertheless, the degradability of PCL chains was not enhanced due to the phase separation between the two components. These materials should be of great interest for biomedical uses such as matrices for sustained drug delivery because of the presence of both hydrophilic and hydrophobic microdomains.

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