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Synthesis, characterization and biodegradability of poly(ethylene succinate)/poly(ε-caprolactone) block copolymers

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Abstract

In the present study, a series of poly(ethylene succinate)/poly(ε-caprolactone) block copolymers were prepared by using a two step process. In the first step, poly(ethylene succinate) (PESu) was synthesized by the melt polycondensation process while in the second, block copolymers were prepared by ring opening polymerization of ε-caprolactone (ε-CL) in the presence of stannous octoate. The copolymers were analysed with ^{1}H NMR spectroscopy and were confirmed to possess final compositions very similar to the initial feed compositions. An increase in the ε-CL content led to an increase in the molecular weights of the copolymer, while polydispersity was narrowed. In the DSC thermographs, two melting points were recorded for copolymers containing 75 and 50 mol% PESu, confirming that block copolymers were prepared. The incorporation of ε-CL content in macromolecular chains resulted in a substantial decrease of the crystallization rates of the copolymers. PESu is a brittle material due to its low molecular weight, while the copolymer containing 75 mol% ε-CL possesses sufficient tensile strength and elongation at break. Enzymatic degradation was performed using *Rhizopus delemar* lipase in a buffer solution at 37 °C. Biodegradation rates were mainly affected by the crystallinity of copolymers, rather than from their molecular weight. PESu and copolymer films were degraded into very small fragments after six months soil burial while polycaprolactone remained almost unaffected. © 2002 Published by Elsevier Science Ltd.

Keywords: Poly(ethylene succinate); Poly(ε-caprolactone); Polyesters

1. Introduction

The synthesis of aliphatic polyesters has been well established for several years [1]. Often, however, the synthesized polyesters possess low thermal stability due to their low melting point and glass transition. These properties, along with their low molecular weight and inferior mechanical properties, resulted in their limited usage in few applications, and mostly as plasticizers in PVC [2]. Their advantage of being fully biodegradable could therefore not be used. In the past few decades there has been an upsurge of interest in recyclable or fully biodegradable polymers replacing synthetic non-biodegradable polymers due to the problem of polymer disposal after use. Currently, almost all polymers used do not physically decompose due to their high chemical stability, leading to serious environmental problems. Worldwide polymer production is increasing. It is estimated that polymers can be found in municipal waste or landfills at about 8 wt% or 20 vol%. Only a very small amount of all the polymers produced (~1%) is recycled [3]. Despite the environmental problems caused by the long life of plastics, it can be considered that polymer production and processing cause less pollution than paper, glass or metal containers, as well as requiring less energy for the process [4].

In the past few years a number of biodegradable aliphatic polyesters have been commercially available, such as polycaprolactone (PCL), poly(hydroxybutyrate) (PHB) and its copolymer with hydroxyvaleric acid poly(3-hydroxybutyrate-*co*-3-hydroxyvalerate) (Biopol®) which can also be produced in vivo at very high molecular weights by microorganisms [5], poly(butylene succinate), and poly(butylene succinate-*co*-adipate) (Bionolle®). In addition, several polyesters from different lactic acid derivatives can be used as drug carriers for controlled release devices, as well as copolymers between of aliphatic acids and other biodegradable monomers. PCL is an attractive thermoplastic, fully biodegradable, non-toxic and compatible with

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other aliphatic polyesters. When it consists of a high molecular weight, it can be formed into fibres or blown films having similar mechanical properties with low-density polyethylene (LDPE). However, its low melting point and heat stability in conjunction with the fact that it is relatively expensive has restricted its use in plastic technology. On the other hand, PHB has a higher melting point than PCL (175 °C) and comparable properties with PP. Its low produced volume, however, is a negative point for extended use [6].

In order to overcome the aliphatic polyester problems of low melting point and poor mechanical properties, copolymers with monomers containing aromatic segments such as terephthalic acid [7–9], 1,4-cyclohexane dimethanol [7], and trimesic acid [10], were prepared. Aliphatic polyesters can also be melt blended with thermoplastic polymers such as polycarbonate [11] or poly(butylene terephthalate) [12]. Aromatic segments can act as physical cross-links thereby improving the mechanical properties of aliphatic polyesters. Their incorporation in macromolecular chains can also increase the melting point, glass transition and thermal stability. However, even in such copolymers or blends, microorganisms will only attack the biodegradable portion of the copolymer while non-biodegradable parts remain unaffected. Furthermore, when aromatic parts amount to more than 50 wt%, biodegradation of aliphatic polyesters can be suppressed [13]. Similar results were obtained when PCL was melt blended with other thermoplastics like polycarbonate (PC) [11]. As the PC amount was increased in the blend, biodegradation rate was decreased.

There are many factors that can influence the biodegradability of polymers. The chemical structure continues to be the main factor since polymers must contain appropriate bonds, which can be degraded via enzymatic hydrolysis by microorganisms. Molecular weight has a negative effect on biodegradability. An increase in molecular weight decreases the biodegradability up to a certain value, after which, it has been reported that it has no effect on biodegradation rate. For PCL it was found that above a molecular weight of 15 000, the biodegradation rate is negligible [14] (in non-biodegradable plastics such as LDPE, its molecular weight must be reduced at 451 from 20×10^4 to 60×10^4 in order to become biodegradable [15]). The degree of crystallinity is an additional factor affecting biodegradability, since enzymatic hydrolysis takes place at the amorphous parts of polymers. Functional end groups, such as the hydroxyl, amino and carboxylic groups that affect hydrophilicity, can also enhance the biodegradability of polyesters.

On the other hand, when PCL is copolymerized or blended with polymers that have a higher biodegradation rate, this leads to materials that can degrade faster compared to pure PCL [16]. Poly(ethylene glycol) (PEG), which is a hydrophilic, water soluble and fully biodegradable polymer, is also used in block copolymer preparation by direct polycondensation of low molecular weight PEG with ε-caprolactone (ε-CL) [17], or by anionic ring opening polymerization [18,19]. In the latter case, it was found that the prepared copolymers have a broad molecular weight distribution, which also depends on the molecular weight of PEG, temperature and time of polymerization. PEGs lack of toxicity allows its usage in many biomedical and pharmaceutical applications and with other polymers as a drug carrier [20]. Changing the segments of each copolymer can control the hydrophilicity–hydrophobicity of the copolymers. It was additionally found that the melting temperature and the crystallinity of PEG/polyester copolymer decreased on increasing the PEG content [21–23].

Copolymers from ε-CL with other lactones can be synthesized by ring opening polymerization resulting in high molecular weight polyesters [24–26]. Such copolymers and especially those with relatively low molecular weights can be used as biodegradable drug delivery carriers. Their low molecular weight ensures good biocompatibility and ease in in vivo degradation control [27,28].

In the present study, PCL block copolymers with PESu were prepared in order to increase the mechanical properties and biodegradability of PCL. PESu is also a fully biodegradable polyester and has a melting point approximately 50 °C higher than PCL. Its repeating unit also contains hard segments that may potentially increase the mechanical properties of PCL.

2. Experimental

2.1. Materials

ε-CL monomer was purchased from Aldrich Chemical Co., dried over calcium hydride for 24 h at room temperature and purified by vacuum distillation in a nitrogen atmosphere. The fraction collected under reduced pressure (≈5 mm Hg) at 94–98 °C was used for polymerization.

Dimethyl succinate (DMSu) and ethylene glycol (EG) were also purchased from Aldrich Chemical Co. These materials were of analytical grade, and were used for poly(ethylene succinate) (PESu) polymerization without further purification.

Tetrabutyl titanate and stannous octoate [$Sn(Oct)_2$] used as catalysts were of analytical grade and purchased from Aldrich and Fluka Chemical Co., respectively.

PCL was supplied from Union Carbide Benelux N.V. with trade name Tone P787. *Rhizopus delemar* lipase was purchased from BioChemika.

Chloroform, methanol and hexane that were used as solvents were of analytical grade from Aldrich Chemical Co., dried in CaH_2 for one week and were used immediately after their distillation.

2.2. Preparation of the copolyesters

PESu was prepared using the two-stage melt polycondensation method (transesterification and polycondensation)

[29]. DMSu and EG at a molar ratio of 1:2.5 were added to a 250 ml round bottomed flask equipped with a stainless-steel stirrer. The lower part of the stirrer was curved in order to rotate parallel to the flask walls. The apparatus with the monomers were emptied and filled with nitrogen several times under stirring (200 rpm) at room temperature, in order to remove the air and avoid oxidation during the transesterification step. It was then placed in a silicon oil bath at 170 °C. The transesterification reaction was completed following distillation of the theoretical amount of methanol (about 3 h) under slow nitrogen flow. The temperature was then increased to 210 °C, nitrogen flow was stopped and the pressure was gradually reduced to 0.5 mm Hg for 0.5 h. At that time, the stirring rate was steadily increased until 500 rpm. This was necessary for the production of a thin melt film on the round bottom walls, assisting the EG evaporation produced during the polycondensation reaction. The distilled EG was collected in an ice-cooled container and the polycondensation step was completed after 2.5 h. The polymer was dissolved in chloroform, precipitated in cold methanol and dried at 40 °C under reduced pressure until a stable weight was attained.

PESu/PCL copolymers with various molar ratios, such as 25/75, 50/50 and 75/25, were prepared using the same apparatus and adding the proper amounts of PESu and ε-CL monomer. Ring opening polymerization of ε-CL took place at 200 °C under nitrogen flow and a stirring rate of 300 rpm. Stannous octoate was added as a catalyst (0.5 wt% of added materials) and the reaction was completed after 2.5 h. The prepared copolymers were purified as described before.

2.3. Measurements

2.3.1. Intrinsic viscosity

Intrinsic viscosity [η] measurements were performed by using an Ubbelohde viscometer at 30 °C in chloroform. All polymers and copolymers were dissolved at room temperature in order to prepare solutions of 1 wt%. The solution was filtered through a disposable membrane filter 0.2 μm (Teflon). Intrinsic viscosity [η] was calculated using the Solomon–Ciuta equation [30]

$$[\eta] = [2\{t/t_0 - \ln(t/t_0) - 1\}]^{1/2}/c$$

where c is the concentration of the solution; t, the flow time of solution and t_0 is the flow time of pure solvent.

2.3.2. Gel permeation chromatography

Gel permeation chromatography (GPC) analysis was performed using a Waters 150C GPC equipped with differential refractometer as detector and three ultrastyragel (10^3, 10^4, 10^5 Å) columns in series. $CHCl_3$ was used as the eluent (1 ml/min) and the measurements were performed at 35 °C. Calibration was performed using polystyrene standards with a narrow molecular weight distribution.

2.3.3. Nuclear magnetic resonance

^{1}H NMR spectra of PCL, PESu and their copolymers were obtained with a Bruker spectrometer operating at a frequency of 400 MHz for protons. Deuterated chloroform ($CDCl_3$) was used as solvent in order to prepare solutions of 5% w/v. The number of scans was 10 and the sweep width was 6 kHz.

2.3.4. Thermal analysis

Thermal analysis of the copolyesters was carried out using a Shimadzu DSC-50Q, differential scanning calorimeter equipped with a liquid nitrogen cooling accessory. The calorimeter was calibrated with indium standard. For each measurement a sample of about 8 mg was placed in an aluminium pan and heated in an inert atmosphere (flow rate 20 ml/min) to 40 °C above its melting point at a heating rate of 20 °C/min. It remained at this temperature for 5 min in order to erase any thermal history and quenched with the liquid nitrogen to -100 °C. The sample was then heated again up to the same temperature as in the first scan, using the same heating rate as before. From these scans, glass transition (T_g), cold crystallization (T_{cc}), melting temperatures (T_m) and heats of fusion (ΔH_m) were measured.

2.4. Mechanical properties

The tensile mechanical properties were studied on relatively thin films of the polymeric samples, which were prepared using an Otto Weber, Type PW 30, hydraulic press at a temperature of 100 ± 5 °C for PCL, 70 ± 5 °C for PESu, and at temperatures 20 °C above their melting points for their copolymers. A load of 6 kN was added on a ram of 110 mm and followed by a rapid cooling of the moulds. From these films, dumb-bell shaped tensile-test specimens (central portions, $\sim 5 \times 0.5$ mm thick; gauge length, 22 mm) were cut in a Wallace cutting press and conditioned at 25 °C and 55–60% relative humidity for 48 h.

The stress–strain data were obtained using a Zwick tensile testing machine, model 1445, and operating at an extension rate of 5 mm/min, recording rate (chart speed) 20 mm/min, and a loading tension cell 0–200 N (CTM 2511-312). The values of Young's modulus, the yield stress, and the elongation at yield, as well as the tensile strength and elongation at break, were determined according to ASTM D 1708-66. At least five specimens were tested for each sample and the average values are reported.

2.5. Biodegradation

2.5.1. Enzymatic hydrolysis

Polyesters in the form of thin films with 20 mm × 10 mm in size and about 0.15 mm thickness, prepared in a hydraulic press as described before, were placed in a small bottle containing 1 ml of phosphate buffer solution (pH 7.2) with 1 mg *R. delemar* lipase. The bottle was then incubated at 37 °C in a water bath for 15 days while the media were exchanged every 72 h. After a specified period of incubation, the film was removed from the flask, washed with fresh water and dried in a vacuum oven at 40 °C for 24 h to constant weight. The degree of biodegradation was estimated from the weight loss expressed by mg/cm^2.

Film samples were immersed in 1 ml phosphate buffer solution, without enzyme addition, in order to estimate the weight loss caused by eventual hydrolysis effects.

2.5.2. Soil burial

Polyesters in the form of thin films were placed in digested soil for up to six months. Weight loss measurements and microphotographs from scanning electron microscopy (SEM) were used in order to estimate the biodegradation rate.

2.5.3. Scanning electron microscopy

The morphology of the polymers as well as the copolymers was examined using a Jeol (JMS-840) scanning electron microscope (SEM). For this examination, the thin films received during biodegradation tests were used. The films were coated with carbon in order to avoid charging under the electron beam.

3. Results and discussion

3.1. Characterization

The prepared PESu homopolymer is light brown in colour and its physical state lies between paste and wax. This colour can be attributed to the tetrabutyl titanate that is used as a catalyst, as the final colour of polyesters depends mainly on the catalyst used, or on the formation of chromophore chemical groups due to degradation reactions. After dissolution in chloroform and precipitation in cold methanol the colour remained the same. Its molecular weight was assumed to be small based on its low intrinsic viscosity (0.35 dl/g), as shown in Table 1.

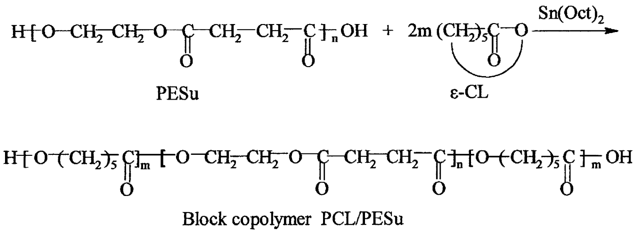
Low molecular weight is characteristic of polyesters prepared by melt polycondensation due to the competitive reactions of condensation and degradation that simultaneously take place. This problem is more significant in aliphatic polyesters, which possess lower thermal stability than linear aromatic polyesters such as poly(ethylene terephthalate). Since in the present study the polycondensation of PESu took place at 170 °C, almost 60 °C higher than its melting point, it would be expected that the degradation reactions be dominant. For this reason it was very difficult to prepare aliphatic polyesters with high molecular weight by melt polycondensation, and other techniques such as solid-state post-polycondensation or chain extension were required. However, all PESu copolymers with ε-CL possess higher viscosities which increase by increasing the ε-CL composition, and in the copolymer containing 75 mol% ε-CL, its intrinsic viscosity increased by more than twice that of the lower mol% ε-CL copolymers.

Table 1
Intrinsic viscosity and molecular weights of prepared copolymers

PCL/PESu (mol/mol)	[η] (dl/g)	$\bar{M}_n$	$\bar{M}_w$	MWD
100/0	–	120 000	185 000	1.54
75/25	0.81	45 000	85 000	1.89
50/50	0.49	25 000	52 000	2.08
25/75	0.40	15 000	32 000	2.13
0/100	0.35	11 000	29 000	2.63

According to the reaction mechanism between PESu and ε-CL it was expected that by increasing the amount of ε-CL, the macromolecular chains become more extended. The physical state of the prepared copolymers was closer to wax and their colour become whiter by increasing the amount of PCL. The copolymers that were produced were mainly of the A–B–A type, where A is the PCL segment produced during ring opening polymerization and the middle part of the macromolecular chain is the initial PESu (Scheme 1). As the amount of initial PESu decreases, the number of macromolecular chains also decreases. Consequently, less hydroxyls groups are available to act as initiators for ring opening polymerization of ε-CL monomer. It is, therefore, expected that in the prepared copolymers, the dimensions of part B remain stable in all copolymers while those of part A will increase by increasing the ε-CL content.

The mechanism of ring opening polymerization in the presence of stannous octoate and alcohols, as in our prepared copolymers, has been proposed by Kricheldorf et al. [31]. In the first stage, a complex formation between the hydroxyl groups of alcohol and stannous octoate takes place, which acts as the initiator for ring opening polymerization. Since PESu was prepared by transesterification of DMSu followed by melt polycondensation, it is expected that the macromolecular chains possess only hydroxyl end groups. However, according to Pohl's method [32], it was found that PESu contains a very small number of carboxyl end groups, 15–16 equiv./10^6 g. These carboxyl groups are an evidence for the degradation reactions that take place during polycondensation. For this reason, the production of some types of copolymers other than the above A–B–A type, as well as some random copolymers is expected to a lesser extent. These are produced during random scission of macromolecular chains that take place at



Scheme 1. Schematic preparation of ABA block copolymers of PESu and PCL.

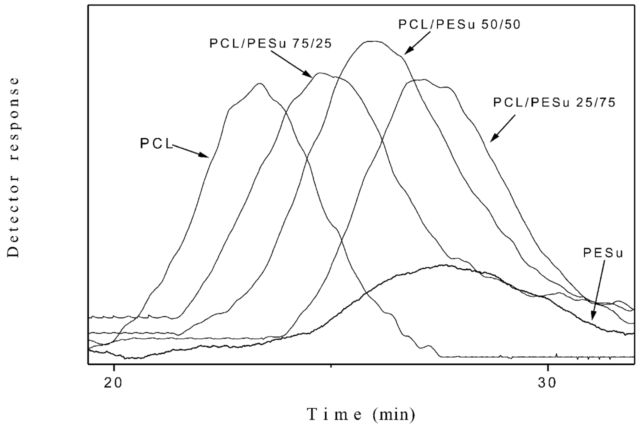


Fig. 1. GPC profiles of block copolymers and homopolymers.

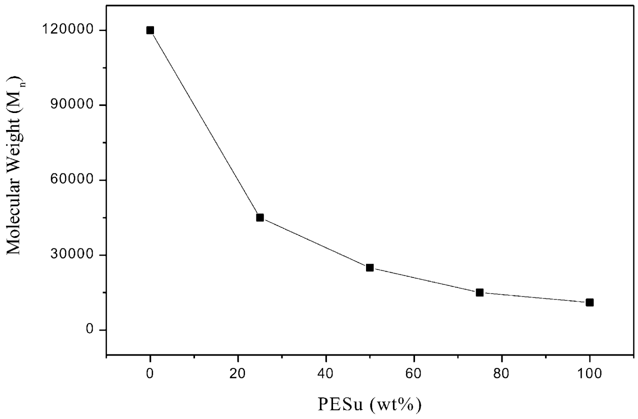


Fig. 2. Molecular weights of prepared copolymers and homopolymers.

elevated temperature and the reconstruction of macromolecular chains. In addition, the production of some copolymers of type A–B in the case that transesterification during PESu production has not been completed, and some macromolecular chains with methyl end groups, instead of –OH or –COOH are expected.

The molecular weight distribution as well as the apparent molecular weight is shown in Fig. 1, which presents the GPC chromatograms of homopolymers and their copolymers. In all cases there is a single peak, which differs in magnitude and elution time. From these chromatograms it can be concluded that the entire amount of ε-CL has reacted at the specific temperature and time during which ring opening polymerization took place, or that the unreacted ε-CL was removed during dissolution in chloroform. From a previous study of ε-CL homopolymerization at different temperatures and times, GPC showed that at low temperatures such as 100 °C, the ε-CL monomer still exists even after 20 h of homopolymerization [28]. However, when ε-CL was copolymerized with other monomers at temperatures close to 200 °C, the peak in the GPC profile attributed to the ε-CL monomer disappeared within 1 h of polymerization. For the prepared PCL/PESu copolymers, copolymerization temperature was 200 °C and the reaction time was 2.5 h so as to ensure that copolymerization was completed.

The molecular weight distribution and the polydispersity of the prepared polymers can be estimated from the GPC profiles (Table 1). As can be seen, the breadth of molecular weight distribution is almost the same for all prepared copolymers. In addition, by increasing the amount of ε-CL, the molecular weight distribution narrows down, which is characteristic for a ring opening polymerization process in the presence of stannous octoate [33]. The fact that molecular weight is controlled by ε-CL content was also shown in intrinsic viscosity measurements. For the copolymer containing 25 mol% ε-CL there is only a small increase in molecular weight of about 4000, which increases by more than twice in the copolymer, containing 50 mol% ε-CL (Fig. 2). Moreover, the molecular weight in the copolymer containing 75 mol% ε-CL is the highest of all prepared copolymers, about 45 000, but lacks in magnitude compared with that of PCL. Consequently these small molecular weights will have a negative effect on the mechanical properties of copolymers compared with those of PCL. Molecular weight might be higher in the case where a polymerization temperature lower than 200 °C were used, which would avoid the extension of degradation reactions. However, high temperatures are needed in order to complete the polymerization of ε-CL. Furthermore, such low molecular weight copolymers of A–B–A types between PEG and PCL are mentioned, in the literature which were prepared at very low temperatures such as 130 °C [23].

The ^{1}H NMR spectra of PCL, PESu and their copolymer at a 50 mol% composition are shown in Fig. 3. For PCL, the peaks at 1.25–1.4 (multiple), 1.5–1.68 (double), 2.15–2.31 (triple) and 3.9–4.08 (triple) were attributed to methylene protons c, d and f, g and e, respectively, as assigned in Fig. 3. The ^{1}H NMR spectrum of PESu is simpler, containing only two characteristic peaks at 2.55–2.67 and 4.18–4.3 attributed to methylene protons a and b, respectively. The existence of all the above peaks in the copolymer spectrum is a strong evidence that the copolymer chains consist of PESu and PCL units, whilst all the characteristic peaks are presented in Table 2. The spectra between the copolymers differ only in the magnitude of peak areas and not in their position, which remains the same.

The composition of the prepared copolymers can be calculated by taking into account the area ratios of these peaks. As can be seen, in all prepared copolymers the composition is very close to the initial PESu and ε-CL feeding. There is only a small difference for ε-CL, in which the final amount is about 2–3 mol% lower than the initial feeding in all copolymers. Since the reaction took place at normal pressure, escaped ε-CL from the reaction vessel is not a possible scenario. For this reason it can be concluded that this very small amount of ε-CL did not react with PESu reactive groups and cyclic oligomers may have been formed. These may be formed very easily at elevated temperatures and apparently, they were removed during purification of the copolymers [28]. The high conversion of

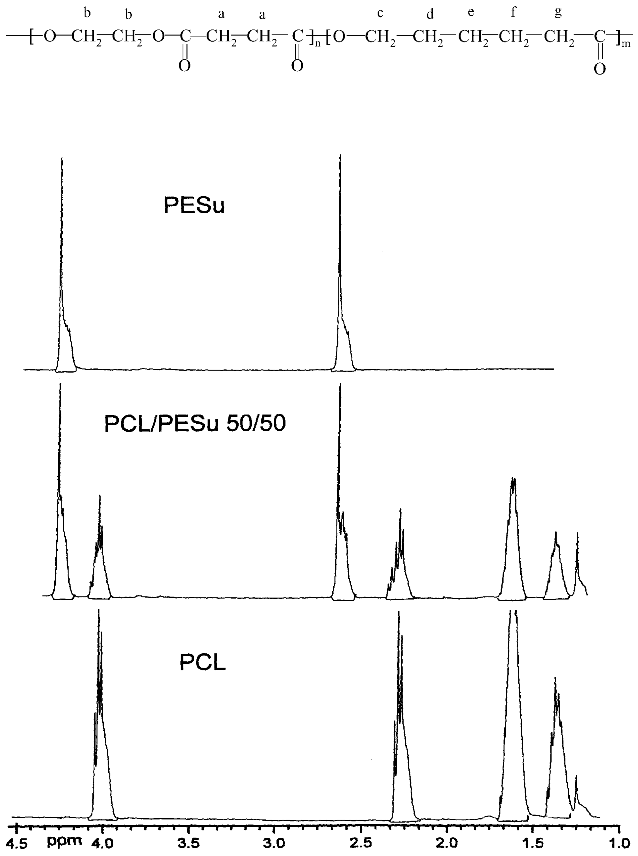


Fig. 3. ^{1}H NMR spectra of PESu, PCL and PESu/PCL block copolymer containing 50/50 mol/mol.

ε-CL is in agreement with the intrinsic viscosity and GPC results from which it was found that the molecular weight increases by increasing the ε-CL monomer content.

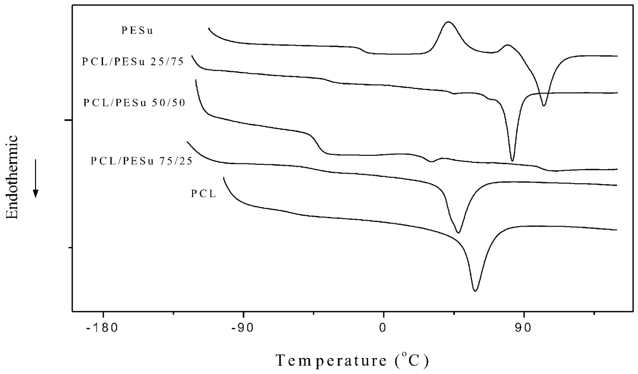


Fig. 4. DSC curves of block copolymers and homopolymers after second heating run.

3.2. Thermal analysis

Fig. 4 presents the DSC thermograms of PCL, PESu and the prepared copolymers after second heating run. From these it can be seen that PCL is a highly crystalline polymer, since, even after quenching, it crystallizes, with a heat of fusion of 70.2 J/g, melting point 59 °C, and glass transition of −58 °C. Since the heat of fusion for fully crystalline PCL, as determined by DSC, is 139.5 J/g, our sample has a degree of crystallinity of about 50% [34]. PESu as was precipitated from chloroform has a heat of fusion of 100.6 J/g and the melting point of 112 °C (first heating run), following quenching can be considered to be that of the fully amorphous form. Its glass transition can be recorded clearly at −5 °C. By increasing the temperature, PESu has a cold crystallization temperature of 56 °C characteristic for polyesters with a low crystallization rate. In this second scan, the melting point is shifted to lower temperatures (105 °C), but remains higher when compared with that of PCL. Also, the heat of fusion is lowered to 84 J/g. Because the heat of fusion for fully crystalline PESu is not known the degree of crystallinity for the prepared sample could not be reported.

Copolymers containing 75 and 50 mol% PESu have two distinct melting points but different from those of the corresponding homopolymers (Table 3). These two melting points are strong evidence that the copolymers are block copolymers, as expected. The lower melting points for the corresponding polymers may be attributed to an interaction that takes place between the PCL and PESu chain segments or to the lower crystallinity that copolymers possess when compared with the homopolymers. The different chain segments in the macromolecular chain act as an impurity by reducing the crystallite size of the homopolymer, increasing the surface free energy of crystallite and shortening the thickness of lamellae, thus producing less perfect crystals. Additionally, due to high polymerization time, some transesterification reactions could take place between PCL and PESu segments resulting in macromolecules with lower crystallinity. A similar phenomenon was mentioned in the PCL/PET block copolymers [35]. The formation of

Table 2
^{1}H NMR assignments for the prepared copolymers

PCL/PESu (mol/mol)	Chemical shift of methylene groups (ppm)						Composition in copolymer (mol/mol)
	a	b	c	d,f	e	g	
100/0	–	–	3.91–4.08	1.5–1.68	1.22–1.4	2.15–2.3	–
75/25	2.5–2.65	4.13–4.3	3.91–4.08	1.5–1.68	1.22–1.4	2.15–2.3	72.5/27.5
50/50	2.5–2.65	4.15–4.3	3.94–4.1	1.52–1.68	1.25–1.4	2.2–2.35	46.6/53.4
25/75	2.55–2.67	4.18–4.3	3.94–4.1	1.52–1.68	1.25–1.4	2.2–2.35	22.6/77.4
0/100	2.55–2.67	4.18–4.3	–	–	–	–	–

Table 3
Thermal properties of prepared copolymers after second heating run

PCL/PESu (mol/mol)	T_g (°C)	T_{m1} (°C)	T_{m2} (°C)	T_{cc} (°C)	ΔH_{m1} (J/g)	ΔH_{m2} (J/g)
100/0	−58	59	–	–	70.2	–
75/25	−44	48	–	–	48.5	–
50/50	−41	31	106	–	10.4	11.2
25/75	−28	45	89	47	3.0	42
0/100	−13	105	–	56	100.6	–

copolymers with short blocks of PCL and PESu is therefore possible, and in crystalline polymers a critical block length is necessary for components to crystallize [36].

The low degree of crystallinity of the copolymers is also indicated by the very low heat of fusion, compared with that of homopolymers and by the low and weak melting points. This is true especially in the copolymer prepared from equal amounts of ε-CL and PESu. In the copolymer containing 75 mol% PESu, the heat of fusion of the first peak is only 3 J/g, whilst that of the second is 42 J/g. Since the first peak is attributed to PCL, this signifies that the degree of crystallinity is only 8.6% based on the full polymer, while PESu (second peak) contains 56% of the crystallinity of the homopolymer. The results for the copolymer containing 50 mol% PESu are similar as the degree of crystallinity for PCL is only 15% while for PESu this is 15% of homopolymer's crystallinity.

The copolymer containing 75 mol% ε-CL has a distinct glass transition at −44 °C and melting point at 48 °C, both closer to PCL temperatures, due to the fast crystallization rate of PCL. The heat of fusion is 48.5 J/g, and is attributed to a high degree of crystallinity of 93%. For this reason it is very difficult to observe the melting point of PESu in this copolymer. On the other hand, it was reported that when two polymers with different crystallization rates are mixed, the polymer with the higher rate crystallizes first and its crystal, acting as a nucleating agent, increases the crystallization rate of the second polymer [37,38]. Such a phenomenon was not possible in our copolymer, probably because of the very high crystallization rate of PCL.

From the thermograms it can also be seen that all the copolymers have a single T_g, which ranges between the glass transitions of PCL and PESu and is closer to the homopolymer in higher proportion. However, this shift of the T_gs, indicates that PCL and PESu could be miscible in the amorphous phase. If this was not the case, two distinct glass transitions corresponding to each polymer would have appeared, similar to the appearance of two melting points. Also, since the segments of PESu have less mobility than the methylene groups of PCL, it would be expected that the T_g of the copolymers increase with increasing PESu content. However, the T_g of the copolymer containing 75 mol% PESu is closer to the T_g of homopolymer PESu, whereas in the two copolymers with higher PCL content, the glass transitions are closer to that of the PCL homopolymer.

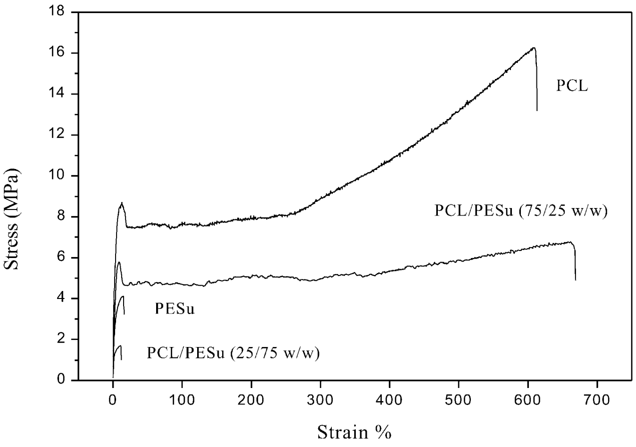


Fig. 5. Stress–strain curves of homopolymers and block copolymers.

3.3. Mechanical properties

The stress–strain curves of the synthesized polymers are presented in Fig. 5. For PCL, the highly crystalline polyester, the stress–strain curves show a distinct yield point and the characteristic stress hardening before breaking. It can be said that despite its low melting point and T_g, PCL has an interesting behaviour. Its elongation at break is similar to that of LDPE while its tensile strength is even higher. These satisfactory mechanical properties of PCL can be attributed to its high molecular weight and suggest that it can be used for blown film production. PESu, which contains more hard segments than PCL, was expected to possess a higher tensile strength and consequently lower elongation at break than PCL. On the contrary, however, the prepared sample, due to its low molecular weight, has very low tensile strength (4.11 MPa) and very low elongation at break. Therefore, the prepared PESu can be characterized as a brittle material.

The behaviour of copolymers depends on the ratio of PCL and PESu blocks. For example, the copolymer containing 75 mol% PCL has a tensile strength at break (5.45 MPa) higher that of PESu, but this is very different from that of PCL. This can be attributed to the lower molecular weight of the copolymer as well as to the weak stress hardening that occurs during extension of the sample. It can also be seen from the stress–strain curve that stress hardening, which is characteristic for high crystalline materials, is not as strong as in the PCL sample. On the other hand, this copolymer has a very high elongation at break, which is even higher than PCL (730%). The low glass transition and melting point that this copolymer possesses is responsible for this behaviour at the measured temperatures. The other two copolymers containing 50 and 25 mol% PCL have very low tensile strength, 2.02 and 1.65 MPa, respectively (Table 4), and break easily. For this reason, a

Table 4
Mechanical properties of prepared copolymers

PCL/PESu (mol/mol)	σ_b (MPa)	σ_y (MPa)	Y_m (MPa)	ε_b (%)	ε_y (%)
100/0	17.51	9.22	311	610	9.6
75/25	5.45	5.85	205	680	7.8
50/50	2.02	–	60	12	–
25/75	1.65	–	29	12	–
0/100	4.11	–	150	15	–

σ_b: tensile strength at break, σ_y: tensile strength at yield point, Y_m: Young's modulus, ε_b: elongation at break, ε_y: elongation at yield.

yield point is recorded only in the copolymer containing 75 mol% PCL.

3.4. In vitro degradation

Mechanical properties of the prepared polymers are very important as regards the practical applications of these polymers. For example, for blown films, a high elongation at break and a medium tensile strength are necessary, while injection moulded products often require high impact strength. In biodegradable polymers, biodegradation rates as well as good mechanical properties are also important. It could be said that an ideal combination between these two factors comprises the object of all research efforts in this area.

Fig. 6 presents the weight loss of neat polyesters as well as of their copolymers during enzyme hydrolysis for 15 days. PCL can be degraded when it is exposed to the environment or during soil burial but this requires some years. On the other hand, different types of lipases in a very short time can degrade it [39]. In addition, the temperature during enzymatic degradation can be kept higher than 35 °C, thus accelerating the biodegradation rate. This was the reason for which a lipase was used in this study. Other studies showed that enzymatic hydrolysis depends on several factors and especially on the enzyme origin [28]. *R. delemar* lipase was used in our study because it was found to have the strongest enzymatic activity in similar PCL copolymers. Incubation of the samples without enzyme showed no weight loss.

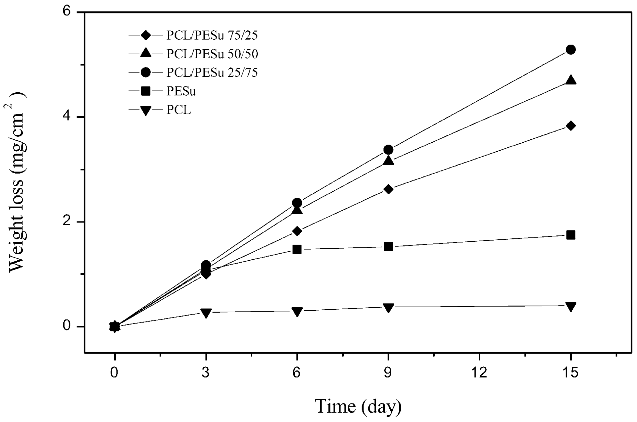


Fig. 6. Weight loss of homopolymers and block copolymers in a buffer solution containing a lipase at 37 °C for various times.

As can be seen in Fig. 6, the biodegradation rate for PCL is very slow since weight loss even after 15 days of enzymatic hydrolysis is very small. On the other hand, PESu has a higher biodegradation rate. It might be thought that their different rates could be attributed to the higher molecular weight of PCL compared with that of PESu. However, lipases are endo-type enzymes degrading the ester bonds of macromolecular chains randomly, and for this reason variations in molecular weight do not affect biodegradation rate. Therefore, the different biodegradation rates of PCL and PESu must be attributed, mainly, to their degrees of crystallinity. Since PCL has a high degree of crystallinity, water and enzyme penetration in the film matrix is very difficult. In other aliphatic polyesters, such as PHB, the rate of enzymatic hydrolysis was shown to decrease with an increase in crystallinity, but it is only slightly influenced by the size of sherulites [40]. It is remarkable that, even after quenching, PCL cannot be considered amorphous but still exhibits a degree of crystallinity of about 50%. On the other hand, PESu, as shown from its DSC thermogram after quenching, is fully amorphous. This difference in the degree of crystallinity between the two polyesters could explain their different biodegradation rates.

Copolymers with a lower degree of crystallinity degrade rapidly compared with homopolymers. There is no significant difference between the copolymers as regards the weight loss. The copolymer containing 75 mol% PESu seems to possess a higher biodegradation rate along with a lower molecular weight. On the other hand, the copolymer containing 75 mol% PCL has the lowest weight loss, due to its high degree of crystallinity. Similar accelerated biodegradation rates were also mentioned in PCL/PEG block copolymers [18] and this effect was attributed to the lower crystallinity and higher hydrophilicity of the copolymers by increasing the incorporated PEG amount in the copolymers. Water absorption affects the biodegradation rate, which decreases by increasing the crystallinity of aliphatic polyesters [41].

The higher biodegradation rates of the copolymers can also be verified from the SEM microphotographs (Figs. 7 and 8). In the case of homopolymers, only PESu presented some holes, but these were present only to a lower extent and also with small depth. Examining the surface of PCL films, there was no clear evidence that biodegradation occurs. Also, by comparing the microphotographs before and after incubation, no significant differences were found. This is in agreement with weight loss measurements where in the PCL sample weight loss is very small even after 15 days of incubation. These differences in biodegradation rate can be attributed to the lower crystallization of PESu when compared with PCL.

The films of the copolymers start to disintegrate with higher rates, as cavities were observed in all films. The

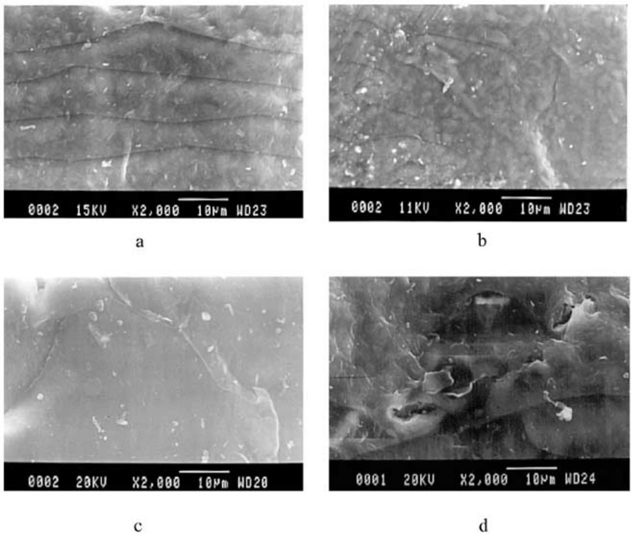


Fig. 7. SEM microphotographs of (a) PCL and (b) PESu before enzymatic degradation, (c) PCL and (d) PESu after enzymatic degradation for different times.

depth and extent of the holes depend on the copolymer composition. These holes inside the film matrix are due to easier penetration of water into amorphous parts and the hydrolysis that occurs there. In the PESu/PCL copolymer containing 75/25 mol/mol, biodegradation has created large holes that are extended to a large depth within the film mass. Additionally, large parts of the film are removed creating large cavities in the film surface. Enzymatic degradation involves hydrolysis of ester bonds and the chemical scission of macromolecular chains breaking them in small fragments or oligomers. The latter with a low molecular weight can also be soluble in water and for this reason the films start to fragmentize on the surface. The untouched parts in the film surface may be crystalline areas or PCL domains. Both of these, due to their low biodegradation rate, remain unaffected.

The differences between the above copolymer and those containing 50 and 25 mol% PCL are apparent in Fig. 8. The holes are reduced in size as the PCL amount increases in the copolymer. However, even in these copolymers, large parts of the film's surface have been removed during enzymatic hydrolysis. The weight losses of these copolymers are in agreement with this observation.

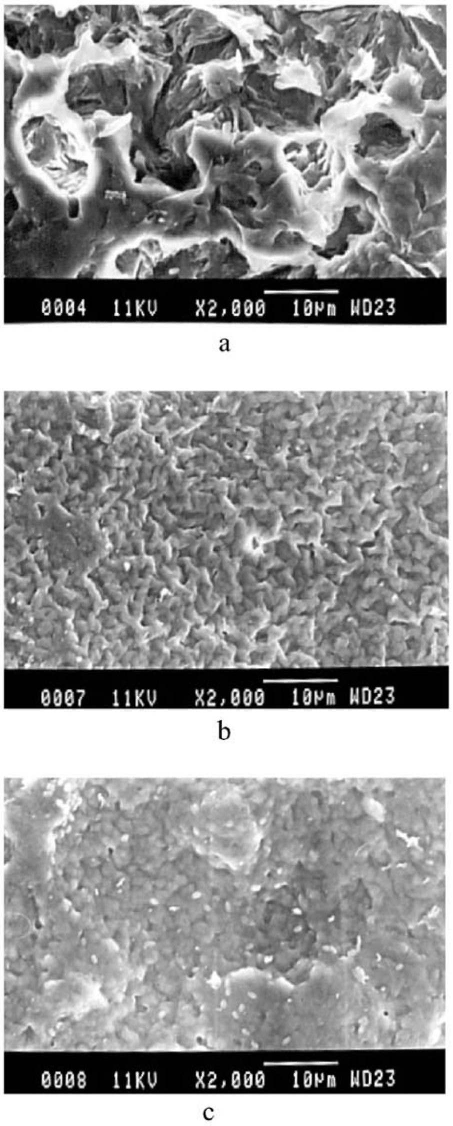
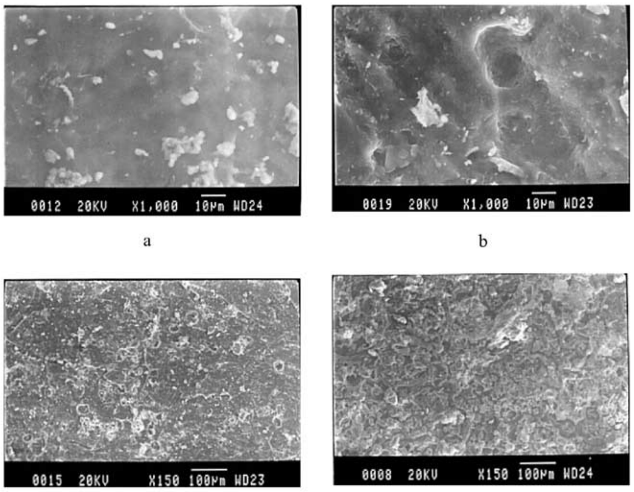


Fig. 8. SEM microphotographs of PESu/PCL copolymers containing (a) 75/25 (b) 50/50 and (c) 25/75 mol/mol after 15 days enzymatic degradation in a buffer solution at 37 °C.

3.5. Soil burial

In soil burial, observation of the biodegradation rates from weight loss constitutes a practical problem since PESu and its copolymers with PCL are waxy materials and the soil sticks on the film surface. These soil granules are very difficult to remove and therefore in all cases an increase in weight after soil burial was found. Additionally, after three months, these films broke into small fragments and after six months only a few fragments from each film remained. On the other hand, the PCL film remained stable with no visible signs of biodegradation. This can be seen also in the SEM microphotographs after two and six months of soil burial (Fig. 9).

In the PCL film after two months soil burial, the film surface appears unaffected even in high magnification. Only after six months were some holes created on the surface and the material started to disintegrate. Therefore, as in the case of enzymatic degradation, PCL is a biodegradable material with a low biodegradation rate due to its high degree of crystallinity and molecular weight. On the other hand, PESu degrades very rapidly. Large holes are created even from the second month of soil burial, which means that large parts of the material are consumed by microorganisms. This consumption leads to the fragmentation of the film after the third month, as shown in Fig. 9(c), and the homogeneity of the film surface of a small fragment is completely



a b

c d

Fig. 9. SEM microphotographs of PCL after soil burial for (a) two months (b) six months and PESu after (c) two months and (d) six months.

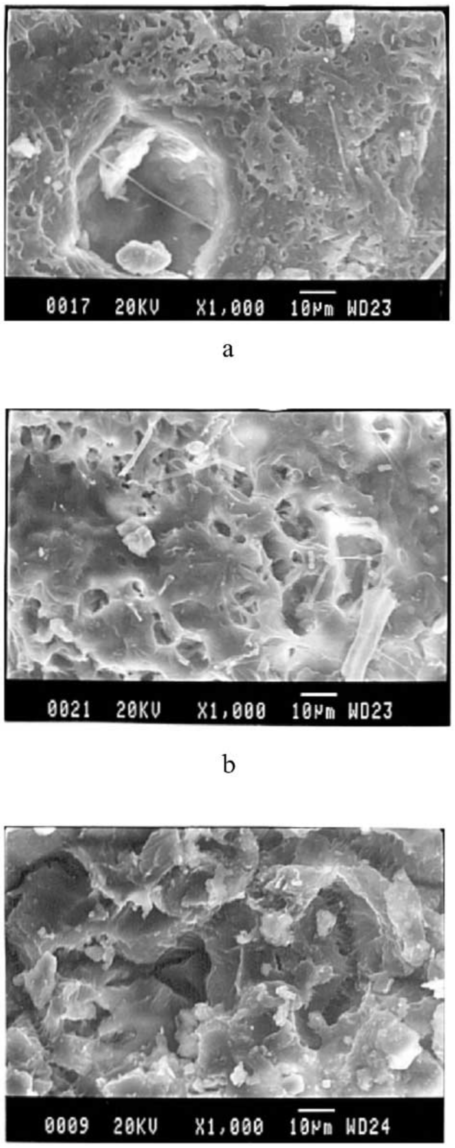
destroyed by the sixth month. Furthermore, large parts of the polyester can be very easily removed. The copolymer containing 75 mol% PESu also has the same appearance (Fig. 10), while the other copolymers show that the biodegradation rate depends on their composition.

4. Conclusions

In the present study, regular network aliphatic copolyesters were prepared from PESu and PCL. The molecular weight of the copolymers increases by increasing the amount of PCL. However, due to the initial low molecular weight of PESu, it was not possible to produce block copolymers with very high molecular weights. For this reason only the copolymer containing 75 mol% PCL possessed sufficient mechanical properties such as tensile strength and elongation at break.

The incorporation of PESu, which has higher melting point and glass transition than PCL, in macromolecular chains, affected the thermal properties of the prepared copolymers, especially the degree of crystallinity, due to its low crystallization rate. In addition, the copolymer containing 75 mol% PESu has a melting point higher than PCL.

Crystallinity is the main factor that controls the biodegradation rate of the prepared polyesters while molecular weight seems to have less effect. For this reason, copolymers containing 50 and 75 mol% PESu have a higher biodegradation rate than the homopolymers PCL or PESu. However, they have poor mechanical properties, which lead to serious limitations in their usage. On the other hand, the PCL/PESu copolymer containing 75/25 mol/mol possesses a good combination of mechanical properties and biodegradation rate. For this reason, it may be suitable for replacing commodity polymers, such as LDPE, for blown film production.



a

b

c

Fig. 10. SEM microphotographs of PESu/PCL copolymers after soil burial for six months containing (a) 75/25 (b) 50/50 and (c) 25/75 mol/mol.

Acknowledgments

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