

Oxidation of polycaprolactone to induce compatibility with other degradable polyesters

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Abstract

Chemical modification of poly(ϵ -caprolactone) PCL by oxidation with potassium permanganate in solution was investigated. According to the data obtained from Fourier transform infrared spectroscopy (FT-IR) and nuclear magnetic resonance ^1H NMR, after the oxidation reactions the PCL chains exhibited new functional groups (vinyl and hydroxyl) and possible intermolecular recombination, producing an oxidized-polycaprolactone (PCL-OX). Solution viscometry indicated that degradation also occurred during the oxidation reactions ($\sim 30\%$ drop in viscosity average molecular weight was detected). Differential scanning calorimetry (DSC) also indicated that PCL was chemically modified and degraded. The successive self-nucleation/annealing (SSA) treatment confirmed that a reduction (or interruption) in linear crystallizable sequences occurred. The immiscibility of blends of PCL with other degradable polyesters, such as poly(*p*-dioxanone) PPDx (PCL/PPDX 90:10 w/w), was shown by the invariability of the relevant thermal transitions as determined by DSC and FT-IR and NMR analysis. However, the blend prepared with oxidized PCL (PCL-OX/PPDX, in the same composition range) did not display signs of thermodynamic miscibility but showed an interesting thermal behaviour demonstrated by changes in the crystallization temperatures of both phases, and by the melting behaviour of the PCL-OX in the blend. These results together with spectroscopic analysis show that the oxidation of PCL induces physical interactions and/or compatibilisation among the phases of this blend.

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1. Introduction

Polycaprolactone (PCL) is a biodegradable polyester with a low melting point (around 60°C) and a glass transition temperature of about -60°C [1]. It is a Food and Drug Administration (FDA) approved material which degrades by enzymatic reactions or by hydrolysis of its ester linkages in physiological conditions (such as in the human body) and, as a result, has received a great deal of attention as an implantable biomaterial with good ultimate mechanical properties (drug delivery devices, suture, adhesion barrier) and it is being investigated as a scaffold for tissue repair [1–5]. In particular, it is a specially interesting material for long term implantable devices, due to

its degradation rate which is even slower than that of other polyesters, such as polylactide or polydioxanone, for example [2]. Despite all these characteristics, it is not easy to modify already synthesized PCL or to graft functional groups onto its backbone. Several research works have reported that they have obtained different blends of PCL with other polyesters; but in all of them, authors state that the interaction between the polymers is weak at the interface resulting between PCL/the other polyester [6–9].

Polydioxanone (PPDX) is another very interesting polyester that has been approved by the FDA for biomedical applications [1,5,7,10]. PPDX is a synthetic polymer with numerous medical applications that has been shown to have a bio-absorbable nature. This aliphatic polyester-ether degrades by hydrolytic processes, and can be metabolized or bio-absorbed by the body [5,7,10,11]. Its molecular structure confers on

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PPDX a greater flexibility as compared to other frequently used biodegradable polymers: poly(glycolic acid), poly(L-lactic acid), their copolymers and PPDX [1–5], and this polymer shows faster degradation kinetics than PCL [10,12,13].

Currently, there is an increasing interest in obtaining blends of different polyesters in order to control the degradation rate of the resulting material [4–6,10–14]. In this regard, it is necessary to try to improve the compatibility or the miscibility between their phases [6–9,12–14] and to guarantee a new material with really interesting properties for biomedical applications.

So far, researchers [12–14] have tried to blend PCL with other polyesters and have reported that, even though they have very similar chemical structures and properties, they are immiscible and not compatible, resulting in a weak material for the applications of interest.

This research paper is intended to contribute to aspects related to the chemical modification of PCL and its use as a compatibilising agent for polymer blends, by showing a simple and novel way to modify the PCL backbone (using an oxidizing agent like KMnO_4) and proving that some interactions could be induced with other polyesters, such as poly(*p*-dioxanone), to obtain a compatible blend after chemical modification.

2. Experimental

2.1. Materials

Poly(ϵ -caprolactone) (PCL) Tone-787, manufactured by Union Carbide was used [9,13]. Potassium permanganate, KMnO_4 (analytical grade supplied by Sigma), was used for the oxidation of PCL.

2.2. Oxidation of PCL (PCL-OX)

8.0 g of PCL pellets (0.072 mol of the repeating unit) and 3.76 g of KMnO_4 (0.024 mol) (3:1 molar ratio of the repeating unit of PCL and KMnO_4) previously ground (in a mortar using a pestle) were melted at 70 °C and mixed for 10 min using a glass rod. This blend was then dissolved in chloroform (solution concentration 2% w/v) at room temperature and stirred for 4 h. After 2 h, the solution became yellow; in the next two hours, the temperature was slowly increased to reach 35 °C and solution reached a brown-coloured appearance. After the reaction was complete, the solution was filtered to remove solid particles. The PCL-OX/chloroform solution was left at room temperature in a Petri-dish to evaporate rest of the solvent. The PCL-OX film obtained was re-dissolved in chloroform at room temperature and filtered second time to avoid possible heterogeneities in the solution and later in the modified polymer. In order to remove unreacted potassium permanganate from the oxidized PCL, and to remove some possible MnO_2 traces, the polymer solution was initially filtered and then washed with an aqueous solution containing 5% of H_2SO_4 to separate the MnO_2 . Finally, the latter sample was filtered two times more and later washed with an excess amount of distilled water.

2.3. Preparation of PCL-OX/PPDX 90:10 blends

Solution blends were prepared with the oxidized PCL and poly(*p*-dioxanone) (PPDX), and with the neat PCL and poly(*p*-dioxanone) in 90:10 compositions, respectively. The PPDX used here were monofilaments (Johnson & Johnson Co.) with a viscosity average molecular weight, M_v , of 1.6×10^5 g/mol obtained at 25 °C (in phenol/1,1,2,2 tetrachloroethane 2:3 v/v). The solvent used to prepare PCL-OX/PPDX solution blends was tetrachloroethane (Sigma), and the blends were stirred for 1 h at a mixing temperature of about 50 °C. After the mixing, the solution was placed in a Petri-dish for 72 h (at room temperature in vacuum) to allow the complete evaporation of the solvent and to obtain a thin film (at macroscopic level, no evidence of phase separation was observed).

2.4. Evidence of oxidation on PCL (PCL-OX) and characterization of blends

Chemical modification of PCL by oxidation and the possible interactions between PCL-OX and PPDX (in PCL-OX/PPDX blends) were followed using infrared spectroscopy (FT-IR) and nuclear magnetic resonance (^1H NMR). Thermal analysis was carried out by using differential scanning calorimetry (DSC) standard technique and successive self-nucleation/annealing (SSA) [15] was also applied.

2.4.1. Infrared spectroscopy (FT-IR)

FT-IR spectra (4000–400 cm^{-1} range) of solvent (chloroform) cast film from neat polymers (PCL and PPDX), oxidized PCL (PCL-OX) and blends were obtained using a Bruker (Tensor 27) FT-Infrared Spectrophotometer. A KBr beam splitter and a DTGS detector were used. Resolution was 4 cm^{-1} . Bands at 720 and 1460 cm^{-1} , corresponding to the rocking of $(-\text{CH}_2-)_n$ ($n \geq 4$), which are characteristics of PCL, were taken as a standard in order to eliminate the dependence of the carbonyl peak area on the film thickness.

2.4.2. Nuclear magnetic resonance (NMR)

^1H NMR and ^{13}C NMR liquid state spectra were obtained on a JEOL Eclipse-plus operating at a resonance frequency of 400 MHz for protons. 50 mg samples were spun on a cylindrical glass rotor; deuterated chloroform (CDCl_3) was used as the solvent at room temperature. All spectra were obtained with contact and repetition times of 2 ms and 5 s, respectively, and 256–1024 transients were accumulated. The spectral width was 31.2 kHz, and the number of data points was 4000. Chemical shifts were externally calibrated against the higher field peak of adamantane appearing at 29.5 ppm relative to TMS.

2.4.3. Thermal analysis

Thermal analysis was performed by standard differential scanning calorimetry (DSC) and by applying successive self-nucleation/annealing (SSA) technique. DSC and SSA were performed with a Perkin–Elmer DSC-7 under an ultrahigh-purity nitrogen atmosphere. The equipment was calibrated

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