Polymer Degradation and Stability 98 (2013) 751–758

Contents lists available at SciVerse ScienceDirect

Polymer Degradation and Stability

journal homepage: www.elsevier.com/locate/polydegstab

Effect of bioactive glass particles on the thermal degradation behaviour of medical polyesters

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ARTICLE INFO

Article history:
Received 29 October 2012
Received in revised form
16 December 2012
Accepted 18 December 2012
Available online 24 December 2012

Keywords:
Bioglass
Polyesters
Thermal degradation
Composites

ABSTRACT

The thermal degradation behaviour of poly(ε-caprolactone) (PCL), poly(L-lactide) (PLLA) and poly(lactide/ε-caprolactone) (PLCL) and of composites of these polymers filled with bioglass particles was investigated by means of thermogravimetric analysis (TGA). According to the activation energies calculated by the Friedman approach, PCL showed the highest resistance to thermal degradation. Addition of bioglass induced a reaction between the ester groups of the polyesters and the SiO^- groups present in the surface of bioglass particles which caused a 1.3–1.9 fold decrease in activation energies of the composites with respect to their unfilled polymer counterparts. This reaction was proven by the increase in the absorbance of the carboxylate peak in the infrared spectra of the composite films maintained at 210 °C and confirmed the random chain scission of the polymer chains. This fact caused a significant decrease in the featured thermal transitions of the polymers as determined by the differential scanning calorimetry (DSC) measurements.

1. Introduction

Polylactides and polylactones are medical polymers that are attracting a great deal of attention because of their biodegradability, biocompatibility and appropriate properties for a variety of prospective applications, such as scaffolds for tissue engineering [1], long-term drug delivery systems [2], bioadhesives [3] or temporary implants [4]. Poly(L-lactide) (PLLA) and poly(ε-caprolactone) (PCL) are semicrystalline polymers presenting respectively glass transition temperatures (T_g) of ~55 °C and ~−60 °C with corresponding melting points (T_m) at ~180 °C [5] and ~60 °C [6]. While PLLA behaves at body temperatures as a glassy material, showing high strength, high modulus and low ductility, PCL is the opposite showing low strength and modulus with large elongation at break [7,8].

To complement the properties of PLLA and PCL for specific medical applications, copolymers of lactide (LA) and ε-caprolactone (ε-CL) are also being proposed. PLCL copolymers, depending on their composition and chain microstructural features, can be tailored for having different mechanical properties [9]. In addition, the high crystallinity of PCL and PLLA led to a slower *in vitro* and *in vivo* degradation rate and can cause foreign body reactions because of highly crystalline remnants. For this reason, PLCL copolymers seem to be more suitable for some tissue engineering applications due to the faster hydrolytic degradation because of the reduction in the crystallinity [10]. The PLCL studied in this work is a statistical copolymer of 70/30 (LA)/(CL) molar ratio, presents a T_g of ~23 °C and exhibits elastomer thermoplastic behaviour [11].

The lack of bioactivity of these polymers can be a disadvantage for some medical applications, yet in this case novel composites systems made of biodegradable polymers filled with bioactive particles could be a solution. In this regard, the bioactive particle filled polymer composites are increasingly being considered for use as tissue engineering scaffolds due to their improved physical, biological and mechanical properties with respect to the neat polymers. In this sense, it has been reported that the addition of inorganic bioactive particles improves the stiffness of the materials due to the incorporation of stiff particles into the soft polymer matrix and also confer bioactive behaviour to the polymer [12]. Some of the most used bioactive particles are bioactive ceramics and bioactive glasses. Bioactive glasses exhibit high bioactivity index (Class A) and excellent bond capability to both soft and hard connective tissues. Bioactive ceramics (e.g. hydroxyapatite), however, show lower bioactivity index (Class B) and bond only to hard tissues [13].

Biodegradable polyesters such as PLLA, PCL and their copolymers are prone to be conventionally manufactured by thermoplastic processing techniques such as injection moulding, blow moulding, thermoforming or extrusion [14]. Understanding of the thermal stability and degradation behaviour of the polymers is very important when using this kind of processes, especially when the

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0141-3910/$ – see front matter © 2012 Elsevier Ltd. All rights reserved.
http://dx.doi.org/10.1016/j.polymdegradstab.2012.12.015

final product is intended for use in a biomedical application. Apart from affecting dramatically some important properties of the materials (e.g. mechanical properties), any thermal degradation byproducts formed during processing may result to be toxic to the human body [15]. Hence, thermal degradation studies on PCL [16,17] and PLLA [18] have received particular attention. Persenaire et al. [16] suggested that PCL is decomposed by a two-step mechanism. The first step is produced by a polymer chain cleavage via *cis*-elimination whereas the consecutive second step consists in an unzipping depolymerization from the hydroxyl end of the polymer chain. In the case of PLLA, a multi step process was proposed by Kopinke and co-workers [19]. The dominant reaction pathway was reported to be via an intramolecular transesterification reaction that gives rise to the formation of cyclic oligomers; in addition, acrylic acid from *cis*-elimination as well as carbon oxides and acetaldehyde from fragmentation reactions were also observed.

It has been also reported that the thermal degradation of polyesters may be affected in composite systems due to the presence of inorganic particles [20,21]. Moreover, the presence of impurities within particles can act as catalyst of the thermal degradation process [22], causing a reduction in thermal stability of the polymers and limiting their manufacturing by the conventional processing techniques. In the particular case of bioglass filled polymer composites, although some important properties (mechanical [23], hydrolytic degradation [24], bioactivity [25]) have been thoroughly studied, little attention has been paid to the thermal degradation behaviour. Therefore, this work investigates the effect of bioglass content on the degradation behaviour of PLLA, PCL and a PLCL statistical copolymer. Composites of these polymers filled with 5, 10 and 15 vol.% of bioglass were prepared by a solvent casting/sonication procedure. The study of their thermal degradation behaviour and its effect in the final properties of the materials was investigated by means of thermogravimetric analysis (TGA), differential scanning calorimetry (DSC), gel permeation chromatography (GPC) and infrared spectroscopy (IR).

2. Materials and methods

2.1. Materials

PLLA of a weight-average molecular weight (M_w) of 500,000 and polydispersity index (PI) of 1.56, PCL of a M_w of 120,000 and PI of 1.61 and PLCL of LA/CL molar weight ratio approximately 70/30, a M_w of 190,000 and PI of 1.67, were kindly supplied by Purac Biochem (The Netherlands).

The 45S5 Bioglass® particles were supplied by Novabone® (US). The composition of Bioglass® (in wt.%) was 45.0% SiO_2, 24.4% Na_2O, 24.5% CaO and 6.0% P_2O_5. The particles were of particle size <60 μm, a mean particle size of 9 μm and density of 2.75 g cm^{-3}. To measure the size distribution of these particles, a dispersion of the particles in ethanol was prepared and, after sonicating for 15 min, some drops were placed on a microscope glass slide. Finally, the sample was examined in a microscope and the size distribution was determined using the ImageJ software.

2.2. Preparation of samples

Neat polymers (PLLA, PCL and PLCL) and composite films of these polymers filled with 5, 10 and 15 vol.% of bioglass, were prepared by solvent casting [26] using chloroform (Panreac, Spain) as solvent. Briefly, a dissolution of polymer was prepared at a polymer weight to solvent volume ratio of 5% (w/v). Different amounts of bioglass particles were added to the polymer solution, which was then sonicated for 15 min. This process was employed to obtain an homogeneous distribution of bioglass particles in the solution and to avoid the formation of agglomerates. Finally, the mixtures were transferred to Petri dishes and dried for 24 h at room temperature and another 24 h at vacuum. In Fig. 1 the differences in the morphology between the neat polymer films and polymers filled with 15 vol.% of bioglass films can be seen. The surface of the neat polymer film (Fig. 1a) was smooth, whereas the incorporation of bioglass particles (Fig. 1b) led to an increase in the roughness of the surface. Fig. 1d and e show respectively, the fractured surface of a PCL film and a PCL film filled with 15 vol.% of bioglass. The particles are well dispersed within the polymer matrix and no agglomerates were observed. Finally, Fig. 1c and f show the detail of some bioglass particles incorporated into the polymer matrix.

2.3. Thermogravimetric analysis (TGA)

Thermal degradation behaviour of composites was studied by means of TGA into TA Instruments TGA model Q50-0545 in platinum pans, with nitrogen flux of 60 mL min^{-1} for sample. Samples of 10–15 mg were heated from room temperature to 500 °C at 1, 5 and 10 °C min^{-1} heating rates (β), recording continuously the heat flow, sample temperature, sample weight and its time derivative. In

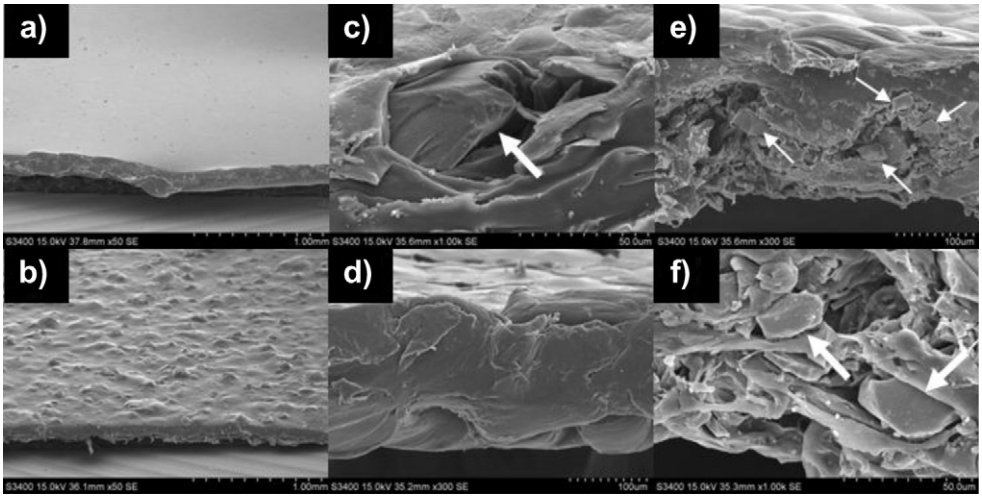

Fig. 1. SEM micrographs of a) PLLA (×50), b) PLLA filled with 15 vol.% of bioglass (×50), c) PLLA filled with 15 vol.% of bioglass (×1000), d) PCL (×300), e) PCL filled with 15 vol.% of bioglass (×300) and f) PCL filled with 15 vol.% of bioglass (×1000).