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Comparative assessment of miscibility and degradability on PET/PLA and PET/chitosan blends

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ABSTRACT

This work reports the synthesis and miscibility of PET/PLA and PET/chitosan blends as well as their degradation in real soil environment (6 months) and in accelerated weathering (1200 h). For this purpose, commercial polyethylene terephthalate (PET) and recycled PET (R-PET) were used as polymer matrixes and extruded with different amounts of polylactic acid (5, 10 and 15 wt-%) or chitosan (1, 2.5 and 5 wt-%) to form filaments. Different characterization techniques such as X-ray diffraction (XRD), Fourier transform infrared spectroscopy (FTIR), differential scanning calorimetry/thermogravimetric analysis (DSC/TGA) and scanning electron microscopy (SEM) were used before and after degradation process. The results indicate weak interactions between blend components suggesting secondary bonds by hydrogen bridges or by electrostatic forces. The miscibility of chitosan in both PET matrixes is lower in comparison with PLA; the saturation of PLA into polymer matrixes was reached up to an amount of 10 wt-% whereas longer amounts of 5 wt-% of chitosan become rigid and brittle. The best performance in the miscibility and degradation process was found for PET/chitosan (95/5) which is comparable with commercial bottles of BioPET under similar experimental conditions.

1. Introduction

The long-lasting petroleum polymers have been widely used provoking that the waste of this kind of polymers takes a very long time to be broken down. Nowadays, this indiscriminate use of petroleum-based polymers has caused a big pollution problem [1,2]. To reduce this problem, it has been used biodegradable polymers from renewable sources like collagen, keratin, gluten, milk proteins, soy proteins, polysaccharides like starch, cellulose derivatives, chitosan, alginate, carrageenan, pectins. These biodegradable polymers have a short-lifetime because of are ideal for short-time applications such as; disposable packages, agricultural mulches, horticultural pots, etc [3–6]. They are also naturally degradable when disposed in the environment. Despite its advantages, many of these kinds of polymers exhibit poor thermal stability, low steam and gas barrier and low mechanical properties, making them unsuitable for other applications [7,8]. Therefore, the general trend is to combine the mechanical, barrier and thermal properties of petroleum based polymers with the biodegradability properties of renewable polymers, resulting in the production of polymeric materials with controlled lifetime. The designed materials must be resistant during their use and must have short time degradation at the end of their useful life [4,9].

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The most favorable packaging material for disposable soft drink bottles is polyethylene terephthalate (PET), a kind of semicrystalline, thermoplastic polyester with high strength and transparency properties as well as excellent barrier properties. Unfortunately, most of these beverage bottles are used only once and then discarded, which inevitably generates serious environmental problems (white pollution) [10]. Therefore, recycling the discarded PET polymer along with obtaining biodegradable PET-based blends are efficient approaches to reduce the resources consumption and to protect the environment at the same time [11]. The recycling of post-consumer packaging materials into direct food contact packaging applications was not possible, because of the lack of knowledge about the contamination of packaging polymers during first use or recollection. However, for PET the situation is much favorable: due to its inert character, recycling technologies have been developed to establish a bottle-to-bottle recycling of post-consumer PET bottles [12].

On the other hand, most biodegradable polymers are thermoplastics (e.g. poly(lactic acid), poly(hydroxyalkanoate), poly(vinyl alcohol)) [9]. Among them, poly(lactic acid) (PLA) is a bio-based polymer obtained from renewable sources mainly from corn and starch [13]. PLA is an aromatic polyester and has several applications, for example, is used for films, extrusion-thermoformed containers and medical applications for tissue engineering, bone reconstruction and controlled delivery systems [14]. The use of PLA in beverage bottles is limited due to its poor oxygen barrier and low mechanical properties [15]. Another interesting biodegradable polymer is chitosan, a biopolymer derived from chitin, a natural compound from crustacean shells; chitosan has the ability to form semipermeable films and, in recent years, the efforts have been intensified to develop chitosan films and its application in food packing [16]. Biodegradable copolymers of PET and aliphatic polyesters have been synthesized, such as poly(lactic acid), poly(β-hydroxyalkanoate), poly(ε-caprolactone) and poly(butylene succinate) in order to obtain a degradable polymer with a faster degradation rate [17,18]. Additionally, physical mixtures of conventional and biodegradable phases have been studied [19]. To our best knowledge, few researches are focused in determine the effects on physicochemical, structural and morphological properties as well as degradation time of blends PET/PLA or PET/Chitosan. In this work, the issue has been investigated from different perspectives and the results are discussed in the terms of the quantities of biodegradable polymers that were added in two different matrixes commercial PET and recycled PET during extrusion process.

2. Experimental

2.1. Materials and processing

During the first set of experiments, it was used a commercial PET (CLEARTUF®-MAX2, lot no. 1008-03219) provided as pellets by M&G Polymers Company whereas in the second step recycled PET (R-PET) was obtained from discarded bottles after they were washed, dried and cut into flakes. The polylactic acid pellets, PLA-2002D (containing 4.4 wt-% in average of isomer D), (batch: YA0828b131) and chitosan (low molecular weight, with a deacetylation degree ⩾75%) were purchased from NatureWorks LLC, USA and Sigma Aldrich, respectively. Before processing, the raw materials were dried at 60 °C during 24 h in an oven (Thermolyne). Different amounts of PLA (5, 10 and 15 wt-%) or chitosan (1, 2.5 and 5 wt-%) and commercial PET or R-PET were hand mixed previous to extrusion process. It is important to mention that, initially, we tried to add into the polymer matrix the same quantities of chitosan or PLA (5, 10 and 15 wt-%), unfortunately, we observed that synthesized samples with chitosan become rigid and brittle, regarding the chitosan polymer is a brittleness material, however, this characteristic depend if the material is derived of fungal biomass, crustacean shell and insect cuticles [20,21]. Thus, after several experiments we found that an optimal percentage to evaluate chitosan is less than 5 wt-%. Blends with a filaments shape (1 mm in diam. × 200 cm length) were obtained in a single-screw extruder (C.W. Brabender) with L/D ratio of 25:1 and four heating zones: feeding (225 °C), compression (237.5 °C), distribution (260 °C), and finally, the extrusion die (225 °C).

2.2. Characterization

Structural characterization of the polymer blends was carried out using a Bruker D8 Advance diffractometer from $2\theta = 5–60°$ (Cu Kα, $\lambda = 0.154$ nm) and a rate of 1.5 °/min.

The Fourier Transform Infrared Spectroscopy (FT-IR) spectra were recorded with a Nicolet FT-IR spectrometer (Magna System 550) equipped with an attenuated total reflectance (ATR) accessory between 2000 and 650 cm^{-1} at an optical resolution of 4 cm^{-1} (40 scans).

Simultaneous thermal analysis was carried out in a Labsys Evo, Setaram instrument, which was used in the DSC/TGA configuration with the sample and reference crucibles made of α-Al_2O_3. Sample amount in the crucible was about 10 mg. The samples were firstly heated at 40 °C and hold for 2 min and subsequently, the measurements were carried out in the range of 40–300 °C to evaluate thermal degradation under argon atmosphere with a heating rate of 10 °C/min. Then, the samples were hold at 300 °C for 2 min followed by a cooling with the same rate. It is well known that peak temperature is influenced by the scan rate; however, in this case such displacement was considered neglected. It is also important to mention that DSC heating was intentionally evaluated from 40 °C to 300 °C in order to observe the total degradation of these samples. After accelerating weathering tests, DSC/TGA analysis were also conducted on the samples with similar procedure and heating rate but using a temperature range from 40 °C to 500 °C.

In order to dissolve the biopolymer phase and to evaluate the dispersion in the different matrixes (PET and R-PET) as well as evaluate the morphology of the as-prepared samples, the polymer blends were solubilized in chloroform and acetic acid for PLA and chitosan, respectively. The dissolved samples were observed by SEM to analyze the cross section of the blends; before characterization,