Material Behaviour

Correlation between traditional techniques and TD-NMR to determine the morphology of PHB/PCL blends

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A R T I C L E I N F O

A B S T R A C T

Blends of two different biodegradable polyesters, poly(3-hydroxybutyrate) (PHB) and low molecular weight polycaprolactone (PCL), were obtained through solution casting and their miscibility and crystallinity were studied. The materials were characterized by wide angle X-ray diffraction, differential scanning calorimetry (DSC) and time-domain nuclear magnetic resonance (TD-NMR). Blends with PCL concentrations higher than 60% (w/w) were not obtained due the inability of low molecular weight PCL to form films by this method. The DSC technique revealed that the films were not miscible since there were no changes in the PHB glass transition temperature (T_g) after the PCL addition. However, the TD-NMR technique showed some partial miscibility, observed in the blend containing 10% (w/w) PCL, revealing domains around 30 nm, where the spin diffusion process was extremely close to that observed in the pure polymers. Other than that, the transversal relaxation showed that the partial miscibility of this composition occurs predominantly in the chain segments located in the interphase intercalation of the rigid regions, reducing the systems' crystallinity. These results are in accordance with the findings obtained through the WAXD analysis.

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1. Introduction

Biodegradable polymers have been intensely studied, since they have huge potential for application several medical areas, such as implants, scaffolds, orthopedic devices and stents, as well as for controlled drug release [1–4].

Poly(3-hydroxybutyrate) (PHB) is an important biodegradable polymer. It is a natural, aliphatic, linear polyester that is isotactic, semi-crystalline and stereoregular, with a configuration containing 100% R. This high regularity comes from its origin: PHB is synthetized in microorganisms as cellular grains that act as energy and carbon backup [5–7]. PHB possess properties similar to those of polypropylene, besides good gas barrier properties and humidity resistance. However, this polymer has a narrow processability window, which limits its commercial application [4,5,8].

Polycaprolactone is a biodegradable and semi-crystalline polyester, but it is obtained by a synthetic route through the opening of the ε-caprolacton ring. This polymer's molar mass and crystallinity define its physical, thermal and mechanic properties. PCL has been intensely studied regarding its uses in controlled drug release and as tissue scaffolds [9–11].

Polymeric blends are obtained through the mixture of two or more polymers, either via solution casting or through melting without creating covalent bonds [7,12,13]. These blends attract interest both in the academic field and industrial area since they exhibit versatility in their composition and have easy technological application when compared to copolymers. The use of biopolymer-based blends can be a new way to obtain polymeric products for the medical field, such as in tissue engineering [2,14].

Qiu et al. (2005) studied blends based on poly(hydroxybutyrate-co-valerate) (PHBV) and low molar mass PCL (Mw = 14.300). Through differential calorimetry scanning (DSC), the authors concluded that the blends were immiscible, even although the presence of PCL in the blends was indicated as responsible for the lower crystallization rate of the PHBV in the blends when compared to the pure polymer [15]. Lorenzo et al. (2007) prepared blends of poly(butylene terephthalate) (PBT) and PCL with different molar masses (Mw = 50,000, 10,000 and 1250 g.mol-1). They observed

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that the miscibility of the systems varied inversely with the PCL molar mass. The miscibility was explained by the fact that PCL with low molecular weight possesses a higher number of terminal hydroxyl groups, allowing a greater number of interactions with PBT [16]. Lovera and coworkers (2007) studied blends of PHB and PCL with different molar masses (Mw = 13,000, 4221 and 430 g.mol-1), finding that the PCL samples with lower molar masses were chemically modified with carboxylic groups. The authors did not observe any miscibility in the blends containing PCL with the higher molar mass, but reported reduction of the nucleation density of the PHB, explained by the possible transfer of impurities related to the fractal crystallization of the PCL. The blends containing the low molar mass PCL showed partial miscibility [17].

Hinüber e collaborators (2011) obtained blends of PHB and PCL (Mw = 120.000) using melting processing. All systems were immiscible. In spite of immiscibility the ratio PHB70/PCL30, when compared to pure PHB, presented an increase in the elongation and also better processability. The authors report that this composition showed separation of microphases, in this a narrow and homogeneous dispersion of PCL drops in the PHB matrix, indicating a good interfacial adhesion [18].

Garcia-Garcia e collaborators (2016) also studied blends formed by PHB e PCL (Mw = 50.000) using melting processing. The thermal analysis pointed for an immiscibility of the systems. Using thermal dynamical-mechanical analyses (DMTA) was possible to observe Slight changes in values in the Tg that can present interactions of PHB with PCL [19].

There are many ways to investigate and characterize polymeric systems and blend miscibility, including time domain magnetic resonance [20–23]. By utilizing the transverse relaxation constants and studying the spin diffusion process, it is possible to compare the relaxation rates in blends with theoretical values and the mass fraction used in each system.

The aim of this study was to prepare blends composed of PHB and low molar mass PCL through solution casting and evaluate their miscibility and crystallinity on the basis of the mass fraction of PCL in the materials. To obtain these results, the samples were evaluated by comparing the results obtained through differential scanning calorimetry and wide angle X-ray diffraction with those obtained through time domain nuclear magnetic resonance.

2. Experimental

2.1. Materials

The polymers used in this study were poly(3-hydroxybutyrate), produced by Biocycle (PHB Industrial S/A), and polycaprolactone, supplied by Sigma-Aldrich. The molar masses of the polymers (Mw and Mn) and their polydispersity indices (PDI) were obtained through GPC analysis in a Waters model 510 gel permeation chromatograph with Styragel HT3 and HT6E columns. The data are reported in Table 1. The solvent used was PA chloroform, also provided by Sigma-Aldrich. All the materials were used without previous purification.

Table 1
M_n, M_w e PDI obtained through GPC.

Polymer	M_n (g mol^{-1})	M_w (g mol^{-1})	PDI
PHB	147.596	375.821	2.5
PCL	15.959	25.668	1.6

2.2. Experimental procedure

2.2.1. Preparing of the PHB/PCL blends

Solutions with a 5% (w/w) concentration were produced with proportions ranging from 0/100 to 100/0 (w/w) of PHB/PCL. The solutions were kept under magnetic stirring at 25 °C for 24 h. After that, they were heated in a silicon oil bath at 50 °C until complete dissolution of the PHB, and then were kept under stirring for another hour. The solutions were cooled to 25 °C and poured into Petri dishes. The films were obtained through evaporation in a chloroform saturated atmosphere for 72 h and then were kept in a vacuum oven at 40 °C for 24 h to remove the residual solvent. The films had a final weight of about 1 g.

2.3. Characterization

2.3.1. Differential scanning calorimetry

A TA Instruments Q1000 calorimeter was used with N_2 flux at a scanning rate of 50 ml/min rate in a range of −50 °C to 200 °C. The first melting rate was 10 °C/min, following by a rapid cooling at 200 °C/min, and the second and third the melting and cooling rate were 10 °C/min.

2.3.2. Wide angle X-ray diffraction

The wide angle x-ray diffraction analysis was carried out with a Rigaku Miniflex diffractometer operating at 40 kV and 30 mA, 0.05°/s and 25 °C. CuKα was used as x-ray source, with a wavelength of 0.51418 nm. The analytic range was from 2 to 60° (2θ). The crystallinity index was obtained through the Ruland-Vonk method [24] with the aid of Fityk® 0.9.8 software.

2.3.3. Time domain nuclear magnetic resonance spectroscopy

The measurements were performed in a Maran Ultra spectrometer with an electromagnetic field of 0.54 T (Larmor frequency corresponding to 23.4 MHz for the proton), internal tube diameter of 18 mm at room temperature (30 °C). The excitation pulse 90° was automatically calibrated to τp 90 = 7.5 microseconds of duration. The longitudinal (T_1) and transverse (T_{2*}) relaxation times were measured by inversion recovery (IR) and free induction decay refocused by magic sandwich echo (MSE-FID), respectively. The IR experiment was conducted exploring a list of recovery intervals of 40 values logarithmically spaced from 0.1 to 5000 milliseconds, with recycle interval of 3 s and 8 accumulations.

The data obtained through IR were adjusted exponentially according to the following equation:

$$M_z(t) = \sum_n M_n \left[1 - (1 - \cos\theta) \cdot \exp\left(\frac{-t}{T_{1_n}}\right) \right] \qquad (1)$$

where M is the initial magnetization of the n-th group of protons having n-th constant from a longitudinal relaxation T_1, and θ is the inversion angle aligned to the negative Z-axis.

The MSE-FID experiment was conducted with the acquisition of up to 4096 data points linearly spaced at intervals of 1 microsecond. After applying a 90° pulse followed by an evolution interval of τMSE (2τp90 3tφ + = 24 μs), a symmetrical pattern of eight pulses spaced at 90° tφ = 3μs was applied. With this technique, the formation of a stimulated solid echo occurs after τ MSE, which contains information concerning the crystalline and amorphous regions in each sample [25,26].

3. Results and discussion

PCL films and some of the obtained blends (specifically: PHB/PCL 30/70, 10/90) were discarded, since the low molar weight PCL does