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Material properties

Development of biopolymer/cellulose/silica nanostructured hybrid materials and their characterization by NMR relaxometry

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A B S T R A C T

The objective of this study was to investigate the preparation and properties of hybrid materials composed of poly(lactic acid) (PLA) and poly(lactic acid)/poly(lactic-co-glycolic acid) (PLA/PLGA) blends employing cellulose nanocrystals (CNCs) and/or organophilic silica (R972) as nanoparticles. The CNCs were obtained by acid hydrolysis of commercially available microcrystalline cellulose (MCC). The materials were produced in film form by solution casting. Organophilic silica was incorporated at a ratio of 3 wt.%, and CNCs were added at ratios of 3 wt.% and 5 wt.% in relation to the weight of the polymer matrix. Two series of films were obtained. The first was prepared using only PLA as the matrix, and the second was obtained using blends of PLA and PLGA. The properties of the films were evaluated by X-ray diffractometry, nuclear magnetic resonance, Fourier-transform infrared spectroscopy and measurement of mechanical properties. The results revealed that each nanoparticle, whether added individually or combined with the other type of nanoparticle, induced different final material properties. Cellulose nanocrystals can act as nucleating agents for the crystallization of PLA. There was an improvement in the mechanical performance of films with the addition of CNCs. Further, the incorporation of silica combined with CNCs resulted in the generation of films with the strongest mechanical properties. The results of this study indicate that silica decreases the surface tension between PLA-cellulose and PLA/PLGA-cellulose.

1. Introduction

In recent years, renewable polymeric materials from natural sources have been extensively researched as replacements for the non-renewable polymers commonly used in various applications [1,2]. These materials have advantages such as biodegradability, biocompatibility, low toxicity and low cost [3–6]. They can be of natural origin, such as cellulose, chitin and starch, or be synthesized from renewable raw materials. In this second class of polymers, poly(lactic acid) (PLA) is noteworthy because of some advantageous properties. PLA is a biodegradable aliphatic polyester derived from lactic acid and has similar mechanical properties to polyethylene terephthalate (PET). It differs from PET, however, because it has a significantly lower maximum continuous use temperature s [7,8].

PLA has potential for use in a large number of biomedical applications and as a conventional thermoplastic in the packaging sector [9,10]. Furthermore, products comprised of PLA can be recycled after use either by remelting and processing the material a second time or by hydrolyzing it into lactic acid [7].

The attractive properties of PLA have inspired several studies where PLA was used as a polymeric matrix with nano-sized silica, clays and other nanoparticle fillers, including some nano-sized biopolymers [11–17].

Among these biopolymers with potential for use as nanoparticles in polymeric systems, cellulose is a preferred material because it is the most abundant biopolymer in nature and is available from a wide variety of sources, such as plants and microorganisms [18–20]. In addition, cellulose nanoparticles have a large surface area and excellent mechanical properties [21]. The addition of cellulose promotes enhanced performance with regard to various properties, including barrier, thermal and mechanical properties.

However, obtaining optimal properties requires appropriate nanoparticle dispersion in the polymer matrix. The chemical compatibility between the nanoparticle and polymer are critical to the dispersion of particles in the matrix and adhesion between

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these phases.

The aim of this work was to obtain nanostructured materials composed of polymer/cellulose nanocrystal/silica systems and investigate the effect of each component on the properties of these materials.

The hybrid materials were fabricated as films by the solution casting method. Twelve films were obtained, six from a matrix of PLA while the other six utilized poly(lactic acid)/poly(lactic-co-glycolic acid) (PLA/PLGA) blends. Organophilic silica was added to improve the compatibility of other components of the system, since the use of cellulose materials with hydrophobic polymers such as PLA only promotes weak interaction, resulting in poor nanoparticle-matrix adhesion. Similarly, PLGA was used to improve nanoparticle dispersion in the polymeric systems. Using PLGA, we also verified that it was feasible to prepare films with improved flexibility without causing significant degradation of the desired material properties.

The materials obtained were evaluated using conventional techniques, namely X-ray diffraction, infrared spectroscopy and tensile testing, and an unconventional one, relaxometry, through determination of proton spin-lattice relaxation time.

The relaxation parameter allows the evaluation of the molecular dynamics of samples according to changes in the values and domain curves. In this study, we chose to evaluate this parameter through data obtained from a single exponential decay.

2. Experimental

2.1. Materials

The materials used in this study were supplied as follows:

- Nature Works™ 2002D PLA in pellet form from Nature Works;
- PLGA 430471, 85:15 (lactide:glycolide), in pellet form from Sigma–Aldrich;
- Microcrystalline cellulose (MCC) ph102 in powder form from Viafarma; and
- R972, an organophilic silica treated with dimethyldichlorosilane based on hydrophilic silica, with a specific surface area of 130 m^2/g, from Evonik Industries.

2.2. Isolation of cellulose nanocrystals

The MCC/H_2O suspension was prepared at a ratio of 150 g/L, put in a temperature-controlled bath at 0 °C, and stirred while concentrated sulfuric acid was added dropwise until 64% acid concentration was reached. After acid addition, the suspension was heated at 40 °C, stirred for 2 h and then the resulting suspension with cellulose nanocrystals was washed with deionized water using repeated centrifugation cycles of 10 min at 12,000 rpm. The centrifugation step was followed by resuspension of the solids of the reaction mixture in new deionized water and then the process was repeated until the supernatant became turbid. The last washing step was conducted using dialysis against deionized water until pH of 5–6 was reached. After the dialysis procedure, the suspension was freeze-dried for 48 h to obtain powdered cellulose nanocrystals.

2.3. Preparation of nanostructured materials

All nanostructured materials were prepared by solution casting using $CHCl_3$ as the solvent. Separate dispersions of PLA, PLA/PLGA and each nanoparticle type in their respective concentrations were prepared. After stirring each solution for 24 h, the dispersions of polymers and nanoparticles were mixed together for an additional 24 h, after which they were cast into sheets and placed in an oven to eliminate the solvent. Twelve films with different formulations composed of PLA or PLA/PLGA were prepared (see Table 1).

2.4. Characterization

2.4.1. X-ray diffraction

X-ray diffraction (XRD) was performed using a Rigaku diffractometer with CuKα radiation ($\lambda = 0.154$ nm, 40 Kv, 120 mA) at room temperature, scanning over the 2θ range from 2° to 40° in 0.05° steps at a rate of 1°/min.

2.4.2. Nuclear magnetic resonance

The relaxation time was analyzed in a Maran Ultra low-field nuclear magnetic resonance (NMR) spectrometer (Oxford Instruments) using an 18 mm NMR tube operating at 23 MHz for the hydrogen nucleus. The pulse sequence used to obtain data on spin lattice relaxation time was inversion-recovery (recycle delay $-$ 180° $- \tau -$ 90° -acquisition data), and the 90° pulse of 4.7 μs was calibrated automatically by the instrument's software. The amplitude of the free induction decay (FID) was sampled for 40 τ data points, ranging from 0.01 to 5000 ms, using four scans for each point. The samples were analyzed at 27 °C. The relaxation values and relative intensities were obtained by fitting the exponential data with the aid of WINFIT software. Distributed exponential fits, created by plotting the relaxation amplitude versus relaxation time, were performed using the WINDXP software. Both programs are included with the low-field NMR spectrometer.

2.4.3. Fourier-transform infrared spectroscopy

The infrared spectra were recorded with a Varian Excalibur 3100 Fourier-transform infrared (FTIR) spectrometer using the horizontal attenuated total reflectance (HATR) accessory from Pike Technologies (Miracle model), with 100 scans and resolution of 4 cm^{-1}. The samples were fabricated in the form of a film, cut and deposited onto a suitable support. However, organophilic silica and cellulose samples were mixed with potassium bromide (KBr) to form a very fine powder. These powders were compressed into thin pellets and then analyzed.

2.4.4. Mechanical property measurements

Tensile testing was done using an Instron universal testing machine, model 4204. Modulus and tensile strength of the films were determined. The tests were performed according to ASTM D882 at 22 °C. Five specimens of each film type were assessed.

Table 1
Formulations of PLA and PLA/PLGA films with and without nanoparticles.

Polymer matrix(wt.)	Nanoparticle (%)	Film
2 g PLA	–	PLA film
	3%CNC	PLA/3CNC
	5%CNC	PLA/5CNC
	3% R972	PLA/R972
	3%CNC + 3% R972	PLA/3CNC/R972
	5%CNC + 3% R972	PLA/5CNC/R972
2 g PLA/PLGA 4:1 ratio	–	PLA/PLGA film
	3%CNC	PLA/PLGA/3CNC
	5%CNC	PLA/PLGA/5CNC
	3% R972	PLA/PLGA/R972
	3%CNC + 3% R972	PLA/PLGA/3CNC/R972
	5%CNC + 3% R972	PLA/PLGA/5CNC/R972