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PLA nanocomposites: Effect of filler type on non-isothermal crystallization

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ABSTRACT

Nanocomposites of poly(L-lactic acid) (PLA) with fumed silica nanoparticles (SiO_2), montmorillonite (MMT) and oxidized multi-walled carbon nanotubes (o-MWCNTs), containing 2.5 wt% nanoparticles were prepared, by solved evaporation method. SEM micrographs evidenced fine dispersion of the nanoparticles into PLA matrix. This has as result to act as efficient reinforcing agents increasing the storage modulus, as was verified from DMA analysis. The nanoparticles were found to be effective nucleaging agents in cases of silica nanoparticles and MWCNT. On cooling from the melt crystallization was accelerated by the presence of nanoparticles and the effective activation energy calculated using the isoconversional method of Friedmann decreased. The nucleation activity was calculated. Cold-crystallization was also affected by the presence of nanoparticles. However, it seems that the phenomenon begins at lower temperatures and this results in formation of imperfect crystalline structure which reduce macromolecular chain mobility of the remaining amorphous polymer, finally limiting the ultimate crystallinity.

1. Introduction

Biodegradable polyesters are materials that are hydrolysable at temperatures up to 50 °C (e.g., in composting) over a period of several months to one year [1,2]. Poly(lactic acid), (PLA), has proven to be the most attractive and useful biodegradable polymer among the numerous polyesters studied so far [3]. PLA is a biodegradable, biocompatible and compostable polyester derived from renewable resources such as corn, potato, cane molasses and beet sugar. It is a most promising environmentally friendly thermoplastic [4].

Commercially available high molecular weight PLA resins are produced via the lactide ring-opening polymerization route [5,6]. PLA has promising applications in packaging, consumer goods, fibers and in biomedicine because of its excellent mechanical properties, transparency, compostability and bio-safety [7–10].

The mechanical properties of high molecular weight PLA are comparable to other commodity thermoplastics like polystyrene and PET, and therefore it might replace these polymers for numerous applications [11,12]. But its high cost has limited its uses till recently. However, now latest technological advances have given rise to PLA resins that are commercially viable and can compete with petrochemical plastics [12–16].

Organic/inorganic nanocomposites are generally organic polymer composites with inorganic nanoparticles. The formation of hybrid organic/inorganic nanocomposite materials results in a synergetic effect of the two respective components in the nanometer scale leading to considerable improvements of various characteristics of the pristine organic material such as mechanical, thermal, and gas-barrier properties [17,18]. The small size of the fillers leads to a dramatic increase in interfacial area and this creates a significant volume fraction of interfacial polymer with properties different from the bulk polymer even at low loadings [19–22]. Typical filler amounts of less than 5 wt% result in effective enhancement of the nanocomposite [23]. There is a large variety of inorganic filler nanoparticles including nanotubes, layered silicates (e.g., montmorillonite, saponite), nanoparticles of metals (e.g., Au, Ag), metal oxides (e.g., TiO_2, Al_2O_3), semiconductors (e.g., PbS, CdS), and so forth [24].

In this work a series of PLA nanocomposites containing different types of inorganic filler nanoparticles were prepared, with constant filler content 2.5 wt% in every case, as in most cases a filler content of 2–3% leads to optimum properties [19–23]. Fillers include multi-walled carbon nanotubes, fumed silica and montmorillonite nanoparticles. The non-isothermal crystallization is studied in order to evaluate the effect of the type of filler. The study includes crystallization from the melt and from the glass (cold-crystallization). Various models are used to evaluate the nucleation efficiency of the fillers, the parameters of crystallization kinetics and the activation energy of the process.

2. Experimental

2.1. Materials

Commercially PLA reinforcement ligament for orthopedics applications under the trade name Resorbaid® was supplied from

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Cousin Biotech (France). Fumed silica (SiO_2) nanoparticles were supplied by Degussa AG (Hanau, Germany) under the trade name AEROSIL® 200, having a specific surface area of 200 m^2/g SiO_2 content >99.8% and average primary particle size 12 nm. Montmorillonite under the trade name Cloisite® 20A (org-MMT), which is modified with a dimethyl, dihydrogenated tallow quaternary ammonium chloride salt, was supplied from Southern Clay Products Inc. (Golzales, TX, USA). The particle sizes ranged between 2 and 13 nm and have modulus of elasticity 4.657 GPa, tensile strength 101 MPa and moisture content <2%. Multi-walled carbon nanotubes (MWCNTs) used in this work were synthesized by the chemical vapor deposition (CVD) process and were supplied by Nanothinx (Patras, Greece). Their diameter was between 9 and 20 nm, their length > 5 μm and were used in oxidized form (MWCNTs-COOH). For this reason, 1 g of the nanotubes were suspended in 40 ml of a mixture of concentrated nitric acid and sulfuric acid (1:3 in volume ratio) and refluxed for 15 min. After washing with deionized water until the supernatant had attained a pH around 7, the samples were dried under vacuum at 100 °C [25]. Dichloromethane anhydrous (≥99.8%) and tetrahydrofuran anhydrous (≥99.8%) were obtained from Aldrich Chemical Co.

2.2. Preparation of PLA nanocomposites

PLA ligament for orthopedic surgery applications was dissolved in a mixture of dichloromethane/tetrahydrofuran 50/50 (w/w) at room temperature while at the same mixture were dispersed different nanoparticles (SiO_2, montmorillonite or oxidized MWCNTs) under sonication for 1 h. The PLA solution and nanoparticles dispersion were mixed under stirring for 1 h and sonicated for additional 1 h. The mixture was cast on a Petri dish at room temperature. The solvent was allowed to evaporate in air for 3 days and then at 50 °C for 1 day in vacuum. Thus, after complete solvent removal thin films of the nanocomposites were obtained. The prepared films were placed in a desiccator to prevent any moisture absorption. Nanocomposites containing 2.5 wt% SiO_2, 2.5 wt% montmorillonite and 2.5 wt% oxidized MWCNTs were prepared with code names PLA/SiO_2, PLA/MMT and PLA/MWCNT.

2.3. Morphological examination

Electron diffraction (ED) and transmission electron microscopy (TEM) observations were made on ultra thin film samples of the various nanocomposites prepared by an ultramicrotome. These thin films were deposited on copper grids. ED patterns and TEM micrographs were obtained using a JEOL 120 CX microscope operating at 120 kV.

2.4. Dynamic mechanical analysis (DMA)

For dynamic thermomechanical analysis Rheometric Scientific analyzer (model Mk III) was used. The bending method was used at a frequency of 1 Hz, a strain level of 0.04% in the temperature range of 0–60 °C. The heating rate was 3 °C/min. Testing was performed using rectangular bars with dimensions, approximately, 30 mm × 10 mm × 3 mm.

2.5. Wide-angle X-ray diffraction (WAXD) study

X-ray diffraction measurements of the blends were performed by an automated Philipps PW1050 powder diffractometer, using nickel filtered Cu Ka radiation, at an angle of 2θ range 5–60°, with 0.028 step and 5 s data collection time.

2.6. Differential scanning calorimetry (DSC)

A PerkinElmer Pyris Diamond DSC differential scanning calorimeter, equipped with a PerkinElmer Intracooler II and calibrated with high purity indium and zinc standards was used for DSC measurements.

For non-isothermal crystallizations from the melt, low mass samples (about 5 mg) were first melted at 220 °C for 1 min and then cooled to 25 °C at various cooling rates, namely 2.5, 5, 7.5, 10, 15 and 20 °C/min. For non-isothermal crystallizations from the glass to record cold-crystallization, the samples were first melted at 220 °C for 1 min and then cooled to 25 °C at a rate 200 °C/min. Subsequently, heating scans at rates 2.5, 5, 7.5, 10, 15 and 20 °C/min were performed in the temperature range from 25 to 220 °C.

2.7. Polarizing light microscopy (PLM)

A polarizing light microscope (Nikon, Optiphot-2) equipped with a Linkam THMS 600 heating stage, a Linkam TP 91 control unit and a Jenoptic ProgRes C10Plus camera was used for PLM observations.

3. Results and discussion

3.1. Nanocomposites preparation and characterization

For nanoparticles surface-to-volume ratio plays a crucial role. While large surface-to-volume ratio makes nanoparticles superior reinforcements of polymer matrices over conventional fillers, it also brings difficulties in dispersing them due to the strong interactions among themselves. Due to these nanoparticle interactions, it is extremely difficult to disperse nanoparticles uniformly, specially at higher particle loadings. In a previous study, in order to enhance the compatibility between PLA and SiO_2 and to achieve a fine dispersion of SiO_2 into PLA matrix, L-lactic acid oligomers reacted onto the surface of silica nanoparticles before melt blending with PLA [26] The loading of SiO_2 nanoparticles in poly(L-lactide) (PLLA) matrix greatly improves the toughness and tensile strength of this material. Wu and Liao followed a different procedure according to which SiO_2 nanoparticles were well dispersed into PLA by using acrylic acid grafted polylactide (PLA-g-AA) as compatibilizer [27]. In the present study for the uniform dispersion of nanoparticles into PLA matrix the mixture of dichloromethane/tetrahydrofuran 50/50 (w/w) was chosen since from preliminary experiments it was found that nanoparticles are well dispersed avoiding precipitation.

As can be seen from Fig. 1a the SiO_2 nanoparticles were homogeneously dispersed into PLA. Taking into account that the average diameter of the used nanoparticles is 12 nm some aggregates were also observed with sizes less than 100 nm. In the case of montmorillonite (Fig. 1b) such aggregates were not observed, as well as in PLA/MWCNTs nanocomposite. From Fig. 1c it can be seen that MWCNTs are dispersed as individual nanotubes. This fine dispersion should be attributed to the interactions between the carboxyl groups of oxidized MWCNTs with hydroxyl end groups of PLA. Furthermore, as can be seen the MMT is dispersed in intercalated form into PLA matrix.

WAXD measurements of the as prepared films showed that they were essentially amorphous, since only the amorphous halo of PLA could be seen in the respective patterns.

Dynamic mechanical analysis is a useful and very sensitive technique for the investigation of microstructure of the macromolecular chain conformations and movements during the exposure of polymers to a variety of temperatures. In Fig. 2a are presented the storage modulus of neat PLA and its nanocomposites containing 2.5 wt% of different nanoparticles, as a function of temperature.