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Poly(lactides) co-electrospun with carbon nanotubes: thermal and cell culture properties

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ABSTRACT

Multi-walled carbon nanotubes (MWCNTs) often serve as an effective nucleating agent that facilitates the crystallization of semicrystalline polymers. Here we study the influence of MWCNTs on thermal and structural properties of electrospun fibers of Poly-lactide (PLA), a biodegradable and biocompatible thermoplastic polymer. MWCNTs were co-electrospun with either poly(L-lactide) (PLLA, with 100% L-isomer) or poly (D-lactide) (PDLA, containing 4% D-isomer) in weight ratios ranging from 1.0 to 4.0 wt.% MWCNT. Electrospun fibers had average diameters below one micron, and addition of MWCNTs reduced the average fiber diameter and narrowed the diameter distribution. Using heat capacity measurements, the crystal, mobile amorphous, and rigid amorphous fractions were evaluated in MWCNT-containing PLA fibers. More rigid amorphous fraction was observed upon increasing the MWCNT concentration to 1.0 wt.% due to the restricted polymer chain mobility induced by MWCNTs. However, at the highest concentration of 4.0 wt.% MWCNTs, the crystal and rigid amorphous fractions were both reduced due to MWCNT aggregation. Fibers were assessed for their efficacy as substrates for growth of human umbilical vein fibroblasts. Cell culture results of fibroblasts plated on oriented PLLA fibers indicated cells grew preferentially in the same direction as the fiber orientation. Cell metabolic activity was reduced, compared to a control substrate, with greatest reduction occurring in crystalline fibers, or those containing MWCNTs.

1. Introduction

Poly(lactic acid) (PLA) (–[CH(CH_3)COO]$_n$–) has been one of the most promising candidates as a biodegradable and biocompatible polymer due to its good thermal and mechanical properties, and environmentally friendly applications [1,2]. PLA is derived from sustainable and renewable resources such as corn and sugar beets, and has been selected for biomedical use [3]. PLA can be processed either from the melt or from solution, including the formation of nanoscale fibers by electrospinning [4]. The process of electrospinning (ES) is highly versatile and can produce continuous PLA polymer fibers with diameters ranging from a few micrometers to a few tens of nanometers, through the application of an external electric field imposed on a polymer solution. It has been used to make protective clothing (Polyacrylonitrile, Polybenzimidazole), drug delivery

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vehicles (PLA, Poly(ethyl vinyl acetate)), artificial blood vessels (PLLA-co-Polycaprolactone), and sensor technology (Polyethylene oxide) [5–8].

One of our particular interests in PLA is its ability to serve as a scaffold for the growth of cells. In this application, the properties of the fibers, such as mechanical stiffness and degree of orientation, become important in directing cell growth. Since PLA is a crystallizable polymer, we can tailor the properties of its electrospun fibers by varying the electrospinning variables, thermal treatments, and/or the use of appropriate additives. The additive chosen for this study is multi-walled carbon nanotubes (MWCNTs), which are co-electrospun with the PLA to form nanocomposite fibers.

Carbon nanotubes have a unique combination of mechanical, electrical, and thermal properties that make them excellent candidates as polymer reinforcements for composites instead of conventional nanofillers [9]. In this study the influence of MWCNTs on thermal and structural properties of PLA electrospun fibers was investigated. We demonstrate the successful production of PLA fibers with high alignment and surface smoothness, with the fiber quality evaluated by scanning electron microscopy (SEM). We investigate the impact of CNTs on the phase structure (crystalline fraction, mobile amorphous fraction, and rigid amorphous fraction) and crystallization behavior of electrospun PLA fibers as a function of the amount of CNTs, using temperature modulated differential scanning calorimetry (TMDSC) and real time synchrotron wide-angle X-ray scattering (WAXS). MWCNTs were co-electrospun with the poly(lactides) in weight ratios chosen as either 1.0 wt.%, 2.0 wt.%, or 4.0 wt.% MWCNT.

In semi-crystalline polymers, the rigid amorphous fraction, RAF, is characterized as a nanoscale interfacial region between the crystalline lamellae and the mobile amorphous phases, induced by tie molecules. RAF is characterized by incomplete decoupling between the crystals and the amorphous chains. It has also been observed that non-crystallizable polymers which contain additives (such as silica particles [10], or carbon nanotubes [11]) may also exhibit similar chain confinement leading to existence of RAF. In this paper, we use high precision, high accuracy heat capacity measurements to quantify the amount of RAF in PLA/MWCNT nanocomposites. We also evaluated oriented PLLA fibers for their ability to guide the growth of fibroblasts and sustain metabolic activity in these cells. Crystallization behavior is an important property of electrospun fiber substrates, affecting the cell attachment and viability for different cells [12,13]. Crystals tend to improve the fiber's elastic properties, and reduce small molecule penetration rate increasing fiber stability. The results of this work present us with more detailed thermal properties of PLA electrospun fibers and the best concentration of MWCNTs to be used in PLA electrospun fiber nanocomposites.

2. Experimental section

2.1. Materials

Poly(D-lactic acid) 2002D (containing 4% D-isomer) and poly(L-lactic acid) (with 100% L-isomer) 3051D used in this study were manufactured by NatureWorks and used, as-received, in pellet form. Systematic incorporation of D-lactyl moieties in the PLA backbone can significantly change the physical properties, morphology, and morphological development of the polymer. Properties affected by incorporation of D-lactyl units include crystallization rate, degree of crystallinity, and ability for orientation. The increase of D-content in L-PLA will result in reduced crystallization. It is reported that PLA becomes totally non-crystallizable at 15% D-content [14].

Hexafluoro-isopropanol (HFIP) from Oakwood Chemical was used as solvent to prepare the polymer solution with a concentration of 10 wt.% solids content for electrospinning. Multi-walled carbon nanotubes were purchased from MER Corporation. Before using them, MWCNTs were purified by adding them to a mixture of concentrated sulfuric acid and nitric acid (3:1 volume ratio). The solution was sonicated in a Misonix water bath sonicator for 24 h at 323 K to separate the MWCNT bundles. The resultant suspension was next diluted with deionized water and filtered through a 400 nm pore membrane (PTFE) until the water passing through the filter had a pH between 6 and 7. Finally, the dispersions were filtered to the desired concentration. The recovered MWCNTs were then added together with PLA into the solvent and stirred overnight at room temperature, resulting in uniform black solutions. The specific weight percentages of carbon nanotubes to PLA are: 1.0, 2.0, and 4.0.

2.2. Electrospinning process

Electrospinning was done at room temperature with a working distance of 10 cm between needle and collector plate. Electrospun fibers were deposited from solution, through a glass syringe of inner diameter 14.6 mm with a 16 gauge stainless steel needle, over a time span of two and a half hours at a flow rate of 0.6 ml h^{-1} controlled by a syringe pump (Sigma–Aldrich CADG5127-1EA). The high voltage power supply (Gamma High Voltage Research Inc. Model No. ES30P-5w) provided an applied voltage of 15 kV. In order to produce highly aligned fibers, a rotating drum covered by grounded copper conductive tape, was used to collect fibers using a rotation speed of 2000 rpm. A typical electrospun tape was roughly 2 cm wide and 29 cm long when removed from the rotating drum collector. The as-spun fibers were put into a vacuum oven for 24 h at room temperature to remove residual solvent. Then some of the samples were isothermally cold crystallized at either 80 °C or 120 °C for 60 min. In all the crystallization experiments for X-ray diffraction, thermal studies, and cell culture analysis, the same thermal procedure was maintained.