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Effect of Tungsten Disulfide (WS₂) nanotubes on structural, morphological and mechanical properties of Poly(L-lactide) (PLLA) films

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Abstract. Poly(L-lactide) (PLLA) is a semicrystalline, biocompatible and biodegradable polymer widely employed in many applications (food packaging, biomedical devices, drug delivery systems). This work deals with nanocomposites of PLLA and tungsten disulfide (WS₂) nanotubes (NTs) as a novel material to obtain thinner and stronger bioresorbable vascular scaffolds. We studied the influence of WS₂ NTs on the mechanical properties of PLLA-WS₂ films. Polarized optical microscopy reveals a high degree of orientation of the polymer molecules in stretched films that further increases with a post-stretching annealing treatment. At the same time, X-ray diffraction (XRD) and Raman spectroscopy confirm enhancement of the crystallinity induced by the WS₂ NTs.

Keywords: Polylactide; tungsten disulfide nanotubes; nanocomposites; bioresorbable vascular scaffolds.

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1. INTRODUCTION

In recent years, polylactic acid or polylactide (PLA) has generated considerable interest in different sectors of application as biodegradable material produced from completely renewable sources. In particular, since poly(L-lactide) (PLLA) degrades to non-toxic lactic acid, which is present in the human body, it has attracted the scientific community as biocompatible and bioresorbable material for different applications in the biomedical field [1].

PLLA is the first clinically approved polymeric material to manufacture Bioresorbable Vascular Scaffolds (BVSs) (2011-CE Mark, 2016-FDA) [2,3], a medical implant that aims at replacing metal stents in the treatment of Coronary Heart Disease (CHD) [4]. One of the limitations of PLLA based-BVSs is their thickness (about 150 μm), still twice as thick than metal stents, due to intrinsic brittleness of the polymer. Nevertheless, a thinner yet stronger BVS is highly desirable for an easy deployment of the device in the arteries.

We propose to use nanocomposites of PLLA and inorganic nanotubes (NTs) of tungsten disulfide (WS₂) to obtain thinner and stronger BVS. WS₂ NTs are known to enhance mechanical strength of polymer matrices due to their strength and flexibility under tensile and torsion forces [5,6]. We prepared PLLA-WS₂ nanocomposites from a relatively low concentration (0.05wt%) of WS₂ NTs. The PLLA-WS₂ films were subjected to uniaxial stretching at 500mm/min stretching rate, while kept at a temperature of 90°C and the effect of the NTs on the mechanical properties of the polymer was investigated. The films were annealed after the drawing process for different annealing times (0, 3 and 10min). Polarized optical microscopy, X-ray diffraction and Raman spectroscopy were employed to study the influence of the annealing treatment on the orientation of the polymer molecules and the crystallinity of the films.

2. EXPERIMENTAL

2.1. Materials and film preparation

Poly(L-lactic acid) (PLLA) (~98% L-isomer, <2% D-isomer, Ingeo 4032D) was purchased from NatureWorks LLC (Minnetonka, MN). Tungsten disulfide (WS₂) nanotubes were purchased from Nanomaterials Ltd (Israel) in 2011. PLLA and PLLA-WS₂ films were prepared by solvent casting and subsequently hot pressed. PLLA pellets were dissolved in chloroform at a concentration of 120mg/mL and stirred for about 3h at 40°C. The PLLA-WS₂ mixture was prepared by adding WS₂ NTs to the polymer solution (concentration of 0.05wt%), after being suspended in chloroform by sonication for 30min, and stirred for 1h. PLLA and PLLA-WS₂ mixtures were poured into petri dishes and let the solvent evaporate at room temperature for two days, then vacuum dried until the solvent was completely removed. The casted films were hot pressed by a Carver laboratory press at 180°C for 10min to obtain amorphous films of ~100μm thickness and rapidly quenched into an ice-water bath to avoid crystallization.

No significant degradation (Mw ~100K g/mol) of the polymer was detected on the hot pressed films respect to the original pellets, as verified by gel permeation chromatography.

2.2. Methods of investigation

The mechanical properties of the samples were evaluated from the stress–strain curves obtained using a dynamometric apparatus INSTRON 4301. The experiments were conducted at 90°C with 100% deformation and strain rate of 500mm/min. The elastic modulus was evaluated from the linear part of the curves at deformation 0.1%.

X-ray diffraction (XRD) patterns were recorded on the films by a Philips X'PERT MPD diffractometer equipped with a Cu sealed tube using K α radiation ($\lambda=1.54056\text{\AA}$). The stretched films were positioned with the stretching direction perpendicular to the incident x-ray beam.

Polarized light micrographs (4x magnification) of the PLLA and PLLA-WS₂ films were acquired through crossed linear polarizers on a Zeiss Universal microscope equipped with a Canon EOS DS30 camera for image acquisition. The retardance values were then evaluated for each section through the Michel-Lévi interference color chart. The films for the microscopy were cut in 70μm thick sections by a Tissue-Tek® Cryo₃ cryostat microtome after being embedded and frozen in OCT (Optimal Cutting Temperature embedding material).

Raman spectroscopy was performed through a Renishaw InVia Reflex Raman spectrometer using a laser with wavelength of 514.5nm.

3. RESULTS AND DISCUSSION

In order to study the effect of small amount of WS₂ NTs (0.05wt%) on the mechanical properties and crystallinity of PLLA, 15 films of neat polymer and 15 films of PLLA-WS₂ nanocomposite were drew up to 100% of strain by keeping the temperature inside the Instron chamber at 90°C, where the kinetics of crystallization are moderate (~50% crystallinity in ~120s [7]) (Fig. 1a). The neat polymer and the nanocomposite show similar stress-strain curves up to 100% strain, with the nanocomposites exhibiting slightly higher stress value than the neat polymer films. Moreover, the error bar length indicates a good reproducibility between the several specimens of the same type, which, in the case of the nanocomposites, reveals a good dispersion of the WS₂ NTs in the PLLA matrix. From the slope of the first linear region (elastic behavior) the elastic modulus was obtained and reported in Fig. 1b.

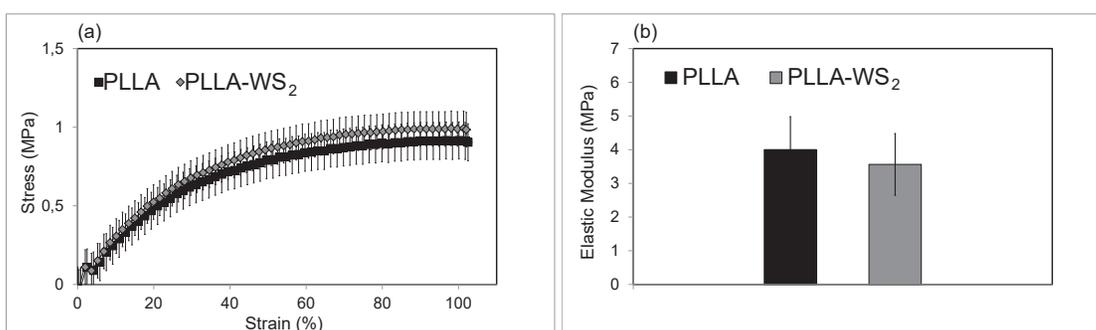


FIGURE 1. Averaged stress–strain curves at 100% strain (a) and elastic modulus (b) of 15 films of PLLA and PLLA-WS₂.

The elastic modulus has comparable magnitude (values are within the error bar) between PLLA and PLLA-WS₂. The stretching phase was followed by an annealing step. After the stretching, 5 films were immediately extracted from the Instron chamber (labelled as *0min* annealing samples), 5 films were left at the drawing temperature of 90°C for 3min (*3min* samples), and the last 5 films were annealed for 10min (*10min* samples).

A broad amorphous peak for PLLA is observed in the XRD spectra of all unstretched samples (Fig. 2). On the contrary, the stretching process induces the formation of a crystalline phase of the polymer. The most intense Bragg peak is centered at $2\theta \sim 16.5^\circ$, corresponding to the PLLA (110)/(200) reflection, superimposed to an amorphous halo (Fig. 2) which is the convolution of both the residual amorphous phase of PLLA and the glass substrate used to hold the film during the XRD data acquisition. Note that the trace of amorphous PLLA in the unstretched samples is very intense due to the larger thickness and wider dimension of the film (in this case the film covered the glass substrate, which was not exposed directly to the x-rays) respect to the thinner, stretched samples (they were about 0.5mm wide, leaving the glass underneath exposed to the x-rays).

Additionally, the lower intensity peak located at $2\theta = 18.8^\circ$ corresponds to PLLA (203) plane. The presence of WS₂ induces a higher crystallinity of the polymer. The peaks of the PLLA in the nanocomposites are indeed more intense even in the film at *0min* of annealing. As a general trend, the intensity of the PLLA (110)/(200) peak increases with the annealing time [8,9].

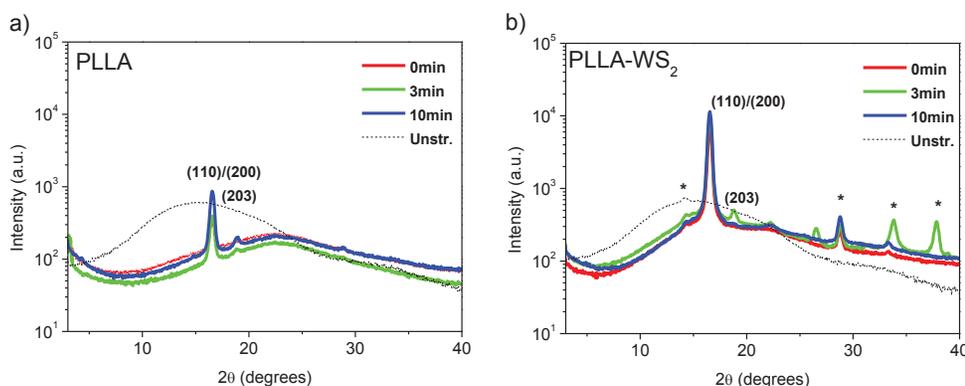


FIGURE 2. X-ray spectra of PLLA (a) and PLLA-WS₂ (b) unstretched and stretched films under different annealing times (0, 3 and 10min). The peaks labelled with * indicate the WS₂ Bragg peaks.

Polarized optical micrographs recorded on microtomed sections of the as-casted PLLA (Fig. 3a) and PLLA-WS₂ (Fig. 3b) reveal that the presence of WS₂ NTs favours the crystallization of PLLA by increasing the number of nucleation sites for PLLA, allowing the polymer chains to crystallize in a larger number of smaller spherulites. The hot press process imposes the melting of the crystalline structure of the films while the subsequent quenching keeps them into the amorphous state. Indeed, the amorphous unstretched sections appear dark in the corresponding polarized light micrographs (Fig. 3, *Unstr.*). Sections of the stretched films that were removed from the Instron immediately after the elongation, (Fig. 3, *0min*) show retardance of $\sim 200\text{nm}$ for both the neat polymer and the nanocomposite. This value of retardance dramatically increases to $\sim 800\text{nm}$ in sections that were annealed for 3min after stretching and above 900nm for sections annealed for 10min, showing that the stretching induces higher orientation of the polymer chains as the annealing time increases.

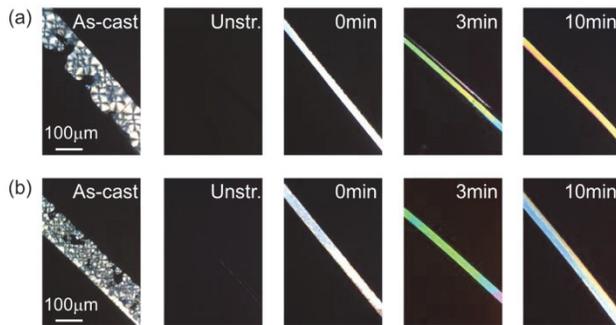


FIGURE 3. Polarized optical micrographs of neat PLLA (a) and PLLA-WS₂ (b): solution cast films (As-cast), hot pressed films before stretching (*Unstr.*), and stretched films under different annealing times (0, 3 and 10min).

The structural properties of PLLA were investigated by Raman spectroscopy. PLLA and PLLA-WS₂ Raman spectra are reported in the range 750-990cm⁻¹ (Fig. 4). In the spectra of PLLA-WS₂ the two principal bands of WS₂ were observed at 354 and 421cm⁻¹ [10], out of the reported range. All samples show an intense band located at about 870cm⁻¹, assigned to C-COO *stretching* [11]. A second band centered at 924cm⁻¹ (assigned to CH₃ *rocking* and C-C *bending* [11]) is visible in PLLA (3 and 10min samples) and in PLLA-WS₂ (0, 3 and 10min samples). Such band is present only in the crystalline phases of PLLA and reflects the presence of 10₃ helix [11], that is the typical chain conformation of α crystalline phase. This band is visible in the PLLA-WS₂ films already after the drawn process, while in the stretched PLLA films it appears only after the annealing, indicating that WS₂ NTs act as nucleation centers and promote the PLLA crystallization, in agreement with the XRD results.

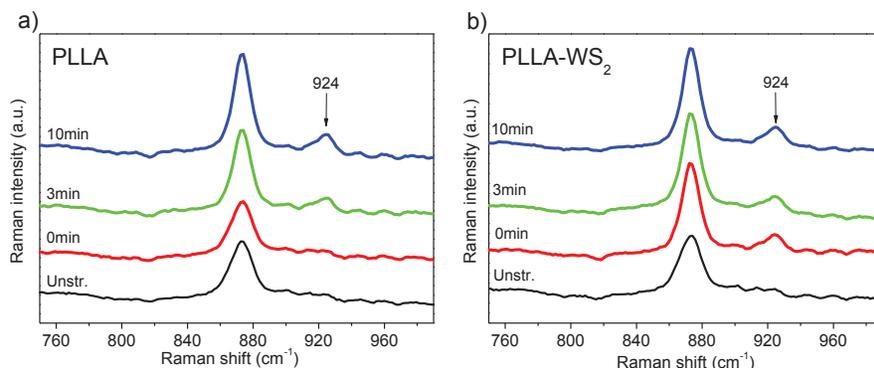


FIGURE 4. Raman spectra of PLLA (a) and PLLA-WS₂ (b) before the stretching (Unstr.) and stretched films prepared with different annealing times (0, 3 and 10min).

4. CONCLUSIONS

We studied nanocomposites of PLLA and WS₂ nanotubes as a new material for new generation bioresorbable vascular scaffolds. PLLA and PLLA-WS₂ (0.05wt% of WS₂) films were prepared by solvent casting and hot press, and their mechanical properties measured at 90°C. The neat polymer and the nanocomposite show similar stress-strain profiles up to 100% strain with comparable values of the elastic modulus. All samples were subjected to a post-stretching annealing treatment for different interval of time (0, 3 and 10min). Polarized optical microscopy micrographs reveal a high degree of orientation of the polymeric chains in all stretched films that increases with the annealing time. X-ray diffraction and Raman spectroscopy confirm the enhancement of the crystallinity induced by the presence of WS₂ nanotubes that behave as nucleation centers and depends on thermal curing time.

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