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PLA-fMWCNT *Bionanofilms* With High Modulus And Great Properties To Apply In Packaging And Biomedicine

Paula González Seligra^a, Melisa Lamanna^a, Lucía Famá^{a,*}

^aLP&MC, Dep. de Física, Facultad de Ciencias Exactas y Naturales y IFIBA-CONICET, Universidad de Buenos Aires, Ciudad Universitaria Buenos Aires, C1428EHA, Argentina.

Abstract

Physicochemical properties of films based on PLA and reinforced with functionalized carbon nanotubes (fMWCNT), was investigated. The filler was functionalized in order to achieve its good dispersion in the matrix. Fenton reaction was carried out and subsequently a reaction with thionyl chloride and with triethylene glycol was performed. Excellent dispersion of the filler in the PLA matrix was observed for composites with filler concentrations till 0.10 wt%. Nanocomposites showed an important increase in the Young's modulus (almost 50 %) and cristallinity till 20 % when carbon nanotubes were added. UV-Vis spectra indicated that all the films are transparent in the UV-visible range.

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1. Introduction

Over the last decades it was an increasing interest in the development of materials based on traditional polymers to be applied in the field of nanotechnology like packaging, military and energy, pharmaceuticals, medicine, cosmetics, etc. (Auras et al., 2004). It is known that if it continues with the use of synthetic materials, their production will exceed 300 million tons in 2015 (Halden, 2010); which represents high costs and large amounts of non-degradable waste. With the objective of replace materials that are derived from raw materials such as oil, many

* Corresponding author. Tel.: +54-11-4576-3300x255; fax: +54-11-4576-3357

E-mail address: lfama@df.uba.ar

industries are adopting the use of biocomposites. Among possible aliphatic polyesters based materials that have been studied for this purpose, polylactic acid, PLA, proved to be a prime candidate because it is made from renewable agricultural sources, is readily biodegradable and biocompatible (Auras et al., 2004). In addition, this polymer is characterized by being stable when exposed to ultraviolet rays and has very interesting properties as smoothness, scratch resistance and wear resistance (Dorgan, 2010). However, PLA, by itself, has serious disadvantages compared to commonly use synthetic materials such as poor barrier properties, low toughness and ductility, and insufficient thermal stability (Balakrishnan et al., 2012).

After the incorporation of different types of nanoparticles to PLA, significant improvements were observed in the final properties of PLA-filler materials (Zou et al., 2008). In particular, in the literature there are several examples of the incorporation of carbon nanotubes in a matrix of PLA, due to its relatively high aspect ratio, outstanding mechanical properties and better electrical and thermal properties (Harrison and Atala, 2007; Singh et al., 2006).

Despite the known comments about the toxicity of carbon nanotubes, it has been shown that their use would not be harmful (Ruiz, 2009) and may have numerous applications in the food industry, from sensors on the surfaces of packagings (Avérous and Boquillon, 2004), or as a material that could act by altering the properties and characteristics of the food, including nutrition, flavor, texture, tolerance to heat and shelf life (Wu and Liao, 2007).

Biomedicine is another industry that has shown great interest in the use of these composites. For example, carbon nanotubes embedded in a polylactic acid matrix have the ability to generate a structural reinforcement and these materials can simulate bone formation (Harrison and Atala, 2007). In this class of materials, the interfacial adhesion between the filler and the matrix plays an important role in improving the properties of the final nanocomposites (Ajayan and Zhou, 2001).

In this research PLA-fMWCNT nanocomposites were developed and the effect of the addition of small concentrations of the filler in mechanical properties, crystallinity and spectroscopy ultraviolet visible were investigated.

2. Experimental procedure/Methodology

2.1. Materials

Commercial multi-walled carbon nanotubes (MWCNT) were providing by Nanocyl, NC 3100. The filler was treated at 35 °C/min till 400 °C in a tubular oven, to eliminate the amorphous carbon. Then, they were dried under vacuum at 120 °C for 3 h (De Falco et al., 2009).

PLA (pellets of 90 % L-LA, 10 % D-LA, Mn = 49860 determined by SEC) was provide by Shenzhen Bright China Industrial Co., Ltd (Wuhan, China).

Thionyl chloride, benzoyl chloride and solvents, obtained from commercial suppliers (Aldrich Co.), were used without further purification.

2.2. Functionalization of MWCNT

To incorporate carbon nanotubes into PLA matrix different reactions were performed, as previously reported Seligra et al. (2013). The first one was Fenton reaction to generate hydroxyl (OH) and carboxyl (COOH) groups on the walls of the MWCNT. Then, the carboxyl groups were lengthened by reacting with thionyl chloride to generate acid chloride groups, and, finally, with triethylene glycol leaving an OH terminal distanced from the filler wall, thereby increasing their availability.

To generate OH and COOH on the MWCNT (Fenton), 30 mg of MWCNT were mix with 20 mL of distilled water and dispersed by ultrasonic washer for 10 min. Then, 1 mL of H₂O₂ and 1 mL of FeSO₄ (6.10⁻² M) were added every 30 min, for 6 h. The process was at 45 °C and pH = 3. Ammonia was used to stop the reaction. The system was centrifuged and the solid was separated. Then, HCl (1 M) was added to redissolve the iron that had not reacted. Centrifugation was repeated with HCl (0.1 M) to ensure complete removal of iron. Finally, distilled water was added and centrifuged to discard the supernatant. This procedure was repeated 6 times until neutral pH. The final system was left at room temperature (24 h) and dried in a vacuum oven until use.

For the reaction with thionyl chloride and ethylene glycol, 20 mg of functionalized MWCNT (by Fenton) and 2 mL of thionyl chloride (SOCl_2) were used to produce acid chloride groups (under nitrogen atmosphere, at 80 °C, for 2 h). Then, 2.3 mL of triethylene glycol was added (at 60 °C, for 2 h). Finally, the reaction product (*fMWCNT*) was filtered.

2.3. Films performance

Three concentrations of functionalized carbon nanotubes were used to perform PLA-*fMWCNT* nanocomposites: C_1 (0.026 wt%), C_2 (0.10 wt%), and C_3 (0.18 wt%).

Nanofilms were developed mixing 1 g of PLA polymer with 50 mL of chloroform first in an orbital system at 150 rpm for 90 min. and, then, the desired concentration of *fMWCNT* was added. The final system was sonicated in ultrasonic washer for 30 min., at room temperature. Once the mixture was dissolved, it was placed in petri glasses. The plates were dried at room temperature for 24 h and, then, in a vacuum oven at 40 °C for 4 days, at 50 °C for 150 min. and at 60 °C for 22 h.

2.4. Characterizations

2.4.1. Density

Density (ρ) of the composites was determined by the principle of Archimedes at room temperature. The reported values were from 30 measurements of each system. Furthermore, the density of the samples was determined theoretically using the "Law of mixtures" (Fan et al., 1994):

$$\frac{1}{\rho_c} = \frac{\phi_m}{\rho_m} + \frac{\phi_f}{\rho_f} \quad (1)$$

where ρ is the density, ϕ the weight fraction, and subscripts c , m and f , represent the composite, the matrix and the filler, respectively.

2.4.2. Scanning electron microscopy (FE-SEM)

Cryogenic fracture surfaces were observed with a field emission scanning electron microscopy (FE-SEM) Zeiss DSM982 GEMINI, and 50kX of magnification.

2.4.3. Dynamic mechanical thermal analysis (DMTA)

Dynamic mechanical tests were carried out in a Dynamic Mechanical Thermal Analyzer (DMTA IV, Rheometric Scientific), in the rectangular tension mode at 1 Hz, at a heating rate of 2 °C/min and 0.04 % of deformation. Samples dimensions used were 15.0 mm x 5.0 mm x 0.26 mm (length, width and thickness, respectively). Tests were performed for triplicate.

2.4.4. X-Ray diffraction (DXR)

X-ray diffraction patterns were determined by means of a diffractometer Siemens D 5000 operating at $\text{CoK}\alpha$ radiation wavelength ($\lambda = 1.79 \text{ \AA}$), 40 kV, 30 mA and sampling interval of 0.02. Scattered radiation was detected in the angular range of 10–35 ° (2θ). The percentage of crystallinity of the films was reported.

2.4.5. UV-Visible spectra (UV-Vis)

UV-Vis spectra were measured by using a HP 8453 spectrometer (wavelength resolution: 1 nm). All the absorption spectra were obtained at room temperature. Three different set of samples were prepared to ensure the results were repetitive.

3. Results and discussion

3.1. Density

Density values (ρ) of all studied systems are shown in Table 1. As can be observed, ρ of C_1 and C_2 resulted slightly higher than that of the matrix. This was expected taking into account that the density of PLA is $\sim 1.23 \text{ g/cm}^3$ (Henton et al., 2005) and ρ of MWCNT $1.2 - 2 \text{ g/cm}^3$ (Nanocyl, 2009). Non-significant differences between the materials conformed whit the smaller and middle concentration of filler (C_1 and C_2) were observed.

Density of C_3 differed from the rest by its high dispersion, which was observed in the results obtained after performing 30 tests. Their dispersion was one order of magnitude higher than the rest. This makes that ρ of that composite does not differ significantly from those obtained for the other systems.

Table 1. Density (experimental, ρ_E y theorist, ρ_T), storage modulus (E') at 30 °C, glass transition (T_g) and cristallinity

Material	ρ_E (g/cm ³)	ρ_T (g/cm ³)	$E'_{30^\circ\text{C}}$ (MPa)	T_g (°C)	Cristallinity (%)
PLA	1.232 ± 0.005^a	1.232 ± 0.001	1.8 ± 0.1	50.0 ± 0.5	< 1
C_1	1.244 ± 0.004^b	1.236 ± 0.001	2.8 ± 0.1^a	54.9 ± 0.5^a	10 ± 1^a
C_2	1.247 ± 0.002^b	1.247 ± 0.001	3.0 ± 0.1^{ab}	54.2 ± 0.5^a	11 ± 1^a
C_3	1.24 ± 0.03^{ab}	1.259 ± 0.001	3.3 ± 0.3^b	53.4 ± 1.5^a	20 ± 2

Equal letter in the same column indicates no statistically significant differences ($p \leq 0.05$)

3.2. Scanning electron microscopy (FE-SEM)

Fig. 1 shows the cryogenic fracture surface of the composite C_2 with functionalized carbon nanotubes isolated and well adhered to PLA matrix, preserving the neat filler length ($\sim 1 \mu\text{m}$). No fissures and any apparent aggregation were observed. This results may to demonstrate that the functionalization of the carbon nanotubes do not seem to produce breakage of the filler, probably resulting from the increased polarity by the functional groups formed on the surfaces of the fMWCNT as well as good interactions of the $-\text{COOH}$ groups with the $\text{C}=\text{O}$ ester groups from the PLA matrix. What is more, the adhesion of the fMWCNT to the PLA seems to be great. The interfacial adhesion between the filler and the matrix will be very important in terms of the improvement of the mechanical properties of the nanocomposites (Ajayan and Zhou, 2001; Suhr et al., 2006).

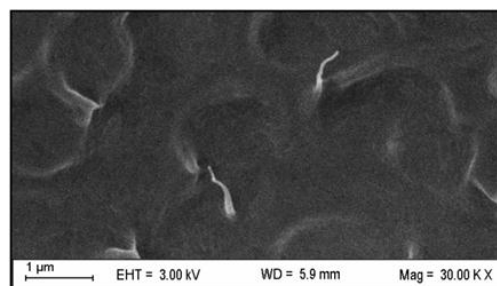


Fig. 1. Cryogenic fracture surface image of a nanocomposite with 0.10 wt % of fMWCNT. Magnification: 50 KX.

3.3. X-Ray diffraction (DXR)

Fig. 2 shows the X-ray diffraction patterns of the different films studied. PLA pattern seems to be similar to one of an amorphous material. As it is known, polylactic acid is isotactic and can crystallize into α , β and γ -forms (De Santis and Kovacs, 1968; Hughes et al., 2012). Its crystallinity depends on its composition (L-lactic acid or D-lactic acid), and preparation process. According to the literature, pure PLA exhibits a very strong diffraction at about $2\theta = 16^\circ$, 18.4° and 21.8° , assigned to the (110) and / or (200), (203) and (006) diffraction peak planes in PLA α -crystal (Quan et al., 2012). However, these peaks were not observed in our PLA films; leading that the crystallinity of matrix was less than 1% (Table 1), showing that this material is practically amorphous (Shieh et al., 2010; Yasuniwa et al., 2008). With the addition of functionalized carbon nanotubes appreciable peaks at about $2\theta = 16.5^\circ$, 19° (α -crystal) and 29.5° (β -crystal) appear, leading to an increase in the degree of crystallinity of the composites. This effect occurs because the nanoparticles act as nucleating agents settling inside the material that allows to the crystallization of PLA, transforming these material composites in semi-crystalline. In polymer matrices, usually nanoparticles play a double role: on the one hand, when they are below the percolation concentration act as nucleating agents to enhance the crystallization; on the other hand, when this concentration exceeds, they act as a barrier to retard the crystallization (Xu et al., 2010). According to the literature, carbon nanotubes have a peak at 24° (Yurdakul et al., 2013); however, this peak was not observed in our work. This could be due to the low concentration of filler used.

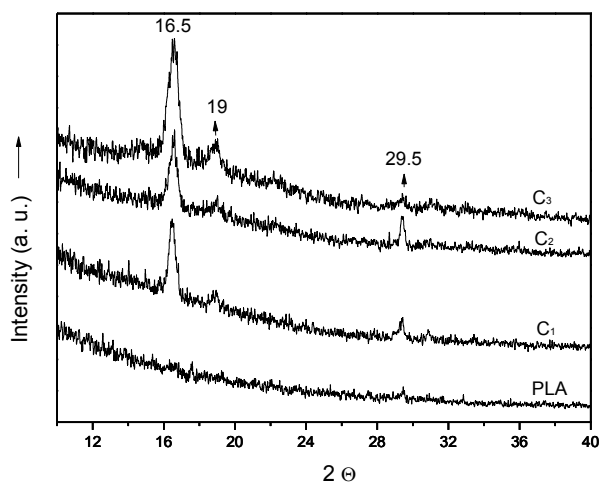


Fig. 2. X-ray diffraction patterns of the different nanocomposites developed.

3.4. Dynamic mechanical thermal analysis (DMTA)

Fig. 3 shows the dependence of loss tangent ($Tan \delta$) and storage modulus (E') with the temperature for all the composites developed. In $Tan \delta$ curve (Fig. 3 a), all the materials reveal one important thermal transitions corresponding to the predominant material, PLA, in the range $50^\circ\text{C} - 55^\circ\text{C}$ (Table 1). Matrix presented its transitions at 50°C . When the filler was added, the temperature transition peak was slightly shifted to higher temperatures. Those results can be attributed to the higher surface area promoted by the incorporation of the nanotubes and the very good adhesion between the matrix and the functionalized filler (Famá et al., 2012; Ma et al., 2008a; Ma et al., 2008b; Rao and Pochan, 2007).

The relaxation observed in the curves of loss tangent corresponds to the sharp drop in storage modulus (Fig. 3 b).

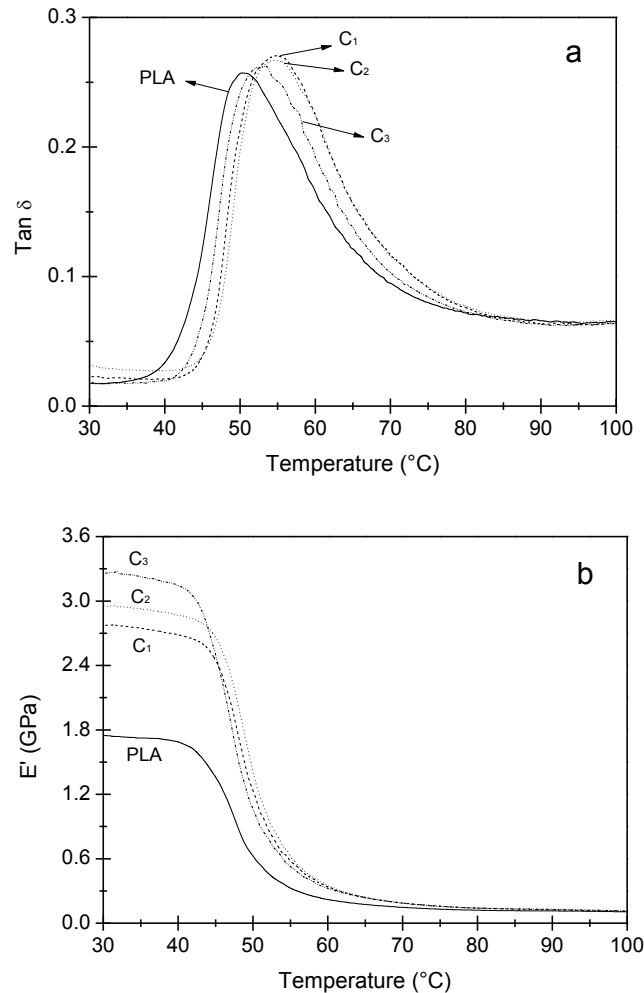


Fig. 3. Curves of (a) loss tangent ($Tan \delta$) and (b) storage modulus (E'), with the temperature, for all the composites studied.

3.5. UV-Visible spectra (UV-Vis)

UV-Visible absorbance spectra's of the four materials developed are shown in Figure 4.

All the systems studied present only one important absorption band at around 230 nm, that corresponding to the PLA absorption. With the addition of different concentrations of functionalized carbon nanotubes no new peak was generated. Moreover, the conformed materials seem to conserve the spectra of PLA. As it is known, carbon nanotubes have an absorption band around 4.5 eV (~ 274 nm) associated to MWCNT π -Plasmon electronic transition (Murakami et al., 2005). In this work, this band was not observed, may be to the small concentration of carbon nanotubes used. Another important result was observed in the range between 290 and 400, where both PLA film and nanocomposites have negligible absorbance. This demonstrates that, despite the addition of carbon nanotubes, the developed materials are transparent in the UV visible range.

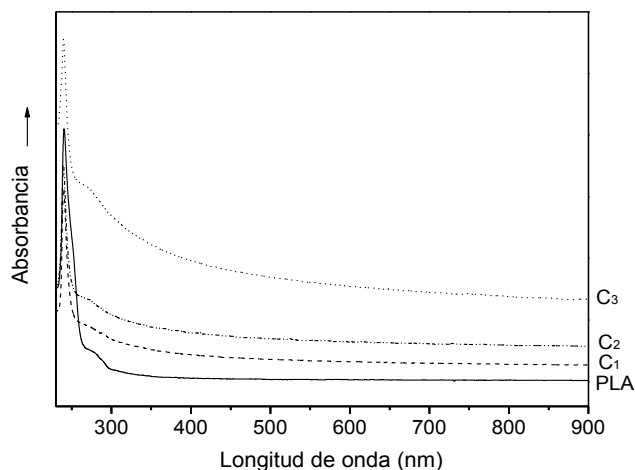


Fig. 4. UV-Vis absorption spectra of the different nanocomposites developed.

4. Conclusions

Nanocomposites based on PLA and reinforced with functionalized carbon nanotubes were developed. Filler functionalization consisted in a Fenton reaction and subsequently in a reaction with thionyl chloride and with triethylene glycol.

Structure, mechanical properties, density and cristallinity were investigated. The results of these studies showed significant improvements in the properties tested with the addition of very small concentrations of the functionalized filler.

SEM observations showed excellent adhesion of the carbon nanotubes to the PLA matrix till 0.10 wt%, with the absence of holes or cracks. These images also showed no damage on the functionalized nanotubes, preserving their dimensions.

The density of the nanocomposites has an increasing trend with the addition of fMWCNT. Samples with 0.18 wt% of filler presented a high degree of dispersion in density value, suggesting the idea that the dispersion of the functionalized carbon nanotubes in that material was not optimal.

The results of the addition of very small amounts of fMWCNT to PLA matrix showed an important increase in the Young's modulus (almost 50 %) and a slightly shift of T_g to higher temperatures.

X-ray patterns revealed that the cristallinity of the PLA films was less than 1 %, and with the addition of functionalized carbon nanotubes it increases around 10 % for the composites with 0.10 wt% and 20 % for the composites with the highest concentration of filler studied.

UV-Vis spectra indicated that all the films are transparent materials in the UV-visible range, independent of the concentration of carbon nanotubes added in this research.

It can be concluded that the nanocomposites developed from biodegradable and renewable source and reinforced with very small concentration of functionalized carbon nanotubes have suitable properties to be used in some industries as a replacement of synthetic materials and, thus, to contribute to the environmental preservation.

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