Promising PLA-Functionalized MWCNT Composites to Use in Nanotechnology

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Films based on polylactic acid (PLA) reinforced with multi-walled carbon nanotubes (MWCNT) were developed after using an excellent methodology to ensure an optimum dispersion of the filler in the matrix. The functionalization of MWCNT was carried out through a Fenton reaction to generate hydroxyl (OH) and carboxyl (COOH) groups on their walls. After that, COOH groups were lengthened by reacting with thionyl chloride and then with triethylene glycol to achieve a terminal OH distanced from the wall of the MWCNT. Nanocomposites based on PLA containing different concentrations of functionalized filler (fMWCNT: 0.026, 0.10, and 0.18 wt%) were prepared by casting. The influence of filler concentration was investigated using some techniques such as scanning electron microscopy (SEM), Fourier transform infrared spectroscopy (FT-IR), thermogravimetric analysis (TGA), water vapor permeability (WVP) and uniaxial tensile mechanical properties. Excellent dispersion of fMWCNT was observed suggesting that the technique of functionalization used was appropriate. All nanocomposites presented great stability, allowing them to be processed to temperatures reaching 300°C. Furthermore, an increasing trend of ultimate tensile strength (σ_u) up to 20% and a decrease of WVP around 40% with the addition of only 0.10 wt% of fMWCNT were obtained. Considering these results, the new biodegradable nanocomposites developed in this work could be very promising to replace synthetic plastics that currently are used in different areas such as nanotechnology, packaging and biomedicine. POLYM. COMPOS., 00:000–000, 2015. © 2015 Society of Plastics Engineers

INTRODUCTION

For several years, new trends related to environmental cares are concerned to replace synthetic plastics (which come from oil sources) by biodegradable polymers. Particularly, several researchers were focused in the investigation of biomaterials with the aim of applying them in fields such as the nanotechnology [1–8]. Synthetic materials cause environmental pollution and accumulation of residues. Among the important features of biopolymers, two are notoriously outstanding: they can be readily obtained from biological raw materials in nature and decompose relatively fast, disappearing in the environment as biomass and giving very low toxicity products. In addition, the materials obtained from renewable sources possess compostable characteristics [9, 10].

Many polymers were investigated in order to develop biodegradable and biocompatible materials [11–16]. Among the wide variety of biopolymers, the polylactic acid (PLA) has been an attractive alternative, especially for its low water vapor permeability (WVP), high mechanical strength and great ability to be recycled [10, 17, 18]. Even though PLA has many advantages against other biopolymers, this polysaccharide has some drawbacks compared with nonbiodegradable materials, such as low elongation at break, fragility and high permeation [19]. In order to solve these problems, several composites based on a PLA matrix with different types of nano-size fillers as reinforcement have been investigated [20–22]. A great benefit of these composites is that their mechanics, thermal and permeability properties can be improved by the addition of very small amounts of fillers [23, 24].

Multi-walled carbon nanotubes (MWCNT) consist of concentric arranged graphene sheets of molecular scale that are characterized by their exceptional mechanical properties (Young's modulus about 1.8 TPa [25, 26] and tensile strength up to 63 GPa [27, 28], from some reports), great electrical conductivity and high aspect ratio (length/diameter). Since their discovery in 1994, several researchers have focused on their properties [29] and in the possibility of using them as reinforcements of different materials, especially due their combination of high strength, flexibility and aspect ratio [30–34]. Despite doubts about the toxicity of carbon nanotubes, it has been shown that their use is not harmful and may have applications in food industries [2,

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8], for example, they can be useful to detect microorganisms, toxic proteins and food spoilage [35, 36]. It has been well established that filler size greatly influences the physicochemical properties of the composites. The high aspect ratio and large surface area per unit volume of some nanofillers result in a more effective transfer of their properties to the matrix [7, 37, 38].

PLA-CNT nanocomposites gained significant interest over the last decades [39, 40] in various fields of science and technology intending to be used as energy, secondary packaging, pharmaceutical products, medicine, cosmetics, etc. [1–8]. One of the major problems of these materials is the difficulty of dispersing the carbon nanotubes in the PLA matrix without a proper pretreatment of the filler. The interfacial adhesion between the filler and matrix plays a crucial role in the final properties of the polymeric composites. Weak interfaces provide good energy absorption mechanisms and generate composites with low modulus and stress at break, while strong interfaces lead to materials enhancing the latter two parameters but are more fragile. Consequently, the physicochemical properties of a composite depend not only of the properties of its components but also of the bonding between the matrix and the fiber. Seligra et al. [41] developed a method of functionalization of carbon nanotubes through a Fenton reaction followed by a reaction with thionyl chloride and triethylene glycol in order to achieve greater dispersion of the nanofiller in a PLA matrix. The authors could observe important increases in the storage modulus of the composites at room temperature with the addition of very small concentrations of functionalized MWCNT.

Currently, nanocomposites for food packaging are one of the most important technological advances that are marketed in agri-food industry. Packaging formed by nano-size structures includes new technologies, for example, in permeability, improving the shelf life, durability and freshness of food or, at least, slowing the rotting process [42].

On the other hand, the use of PLA-CNT composites in biomedicine provokes great interest because they can simulate bone formation due to CNT's ability to generate a structural reinforcement [3], being very important the interfacial adhesion between the filler and the matrix [43].

The aim of this study was to investigate the effect of the incorporation of very small amounts of functionalized MWCNT on a PLA matrix on different physicochemical properties such as structure, degradation, uniaxial tensile and water the vapor permeability.

EXPERIMENTAL METHODS

Materials

Commercial MWCNT with length ~1.5 μm and diameter 20–40 nm [44] (Nanocyl, NC3100), were used as reinforcement. Before their use, the fillers were subjected to a thermal treatment in air in a tubular oven (heated at 35°C/min till 400°C and maintained at this temperature for 30 min). Then they were dried under vacuum at 120°C for 3 h [45].

PLA (pellets of 90% L-LA, 10% D-LA) was provided by Shenzhen Bright China Industrial (Wuhan, China).

All reagents and solvents were obtained from commercial suppliers (Aldrich) and were used without further purification.

Functionalization of MWCNT

In order to achieve greater dispersion of the carbon nanotubes in the PLA matrix, the fillers were functionalized before composites preparation.

The functionalization of MWCNT was carried out by different reactions. The first step was through a Fenton reaction with the objective to generate hydroxyl (OH) and carboxyl (COOH) groups on the MWCNT walls. Then, the carboxyl groups were lengthened through a reaction with thionyl chloride in order to generate acid chloride groups. Finally, a reaction with triethylene glycol was performed to leave a terminal OH distanced from the filler wall and thereby increase their availability due to the decrease in the steric hindrance.

Fenton reaction was carried out according to Seligra et al. [41]. MWCNT (30 mg) were mixed with distilled water (20 mL) and dispersed by ultrasonic for 10 min. H_2O_2 (1 mL) and $FeSO_4$ (1 mL) were added every 30 min over a period of 6 h. The process was performed at 45°C and $pH = 3$. Ammonia was used to stop the reaction. The system was then centrifuged to separate the solid. HCl (1 M) was added and centrifuged again. The process was repeated with HCl (0.1 M) to ensure complete removal of iron. Finally, distilled water was added and centrifuged for 20 min (3,000 rpm) to discard the supernatant. The resulting system was preserved at room temperature in a vacuum oven for 24 h, until use.

Carboxyl groups were lengthened by reacting with thionyl chloride to generate acid chloride groups. The process consisted on mixing 20 mg of MWCNT functionalized by Fenton with 2 mL of thionyl chloride ($SOCl_2$) under nitrogen atmosphere at 80°C for 2 h. Then, 2.3 mL of triethylene glycol was incorporated and the system was dried at 60°C for 2 h. Finally, the obtained reaction was filtered and functionalized carbon nanotubes (fMWCNT) were obtained.

Nanocomposites Preparation

In order to obtain PLA-fMWCNT films with noncovalent bonding between the filler and the matrix, 1 g of the polymer was mixed with 50 mL of chloroform in an orbital agitator at 150 rpm, for 90 min. The desired concentration of fMWCNT was then incorporated to the PLA-chloroform solution and sonicated in an ultrasonic washer for 30 min at room temperature. The resultant system was first placed in petri dishes and dried at room temperature (24 h) and then in a vacuum-oven at 40°C (4 days), 50°C (150 min) and 60°C (22 h). As a result, nanocomposites with different weight fractions percent (ϕ_f) of fMWCNT ($C_1 = 0.026$ wt%, $C_2 = 0.10$ wt%, and $C_3 = 0.18$ wt%) were obtained. The thickness (e) of the films resulted ~0.26 mm.

CHARACTERIZATION

Macroscopic Observations

Photographs of commercial MWCNT and functionalized ones (fMWCNT), immersed in chloroform (after being sonicated for 1 h and rested overnight), were taken using a Kodak Easy Share C813 camera.

Fourier Transform Infrared Spectroscopy

Tests of Fourier transform infrared spectroscopy (FT-IR) were performed with Nicolet 510P equipment using KBr pellets. The infrared spectra were collected with a resolution of 2 cm^{-1}. A total of 64 scans were performed.

Scanning Electron Microscopy

Cryogenic fracture surfaces of the PLA-fMWCNT composites were observed with a field emission scanning electron microscopy (FE-SEM) Zeiss DSM982 GEMINI, using a magnification of 100 KX.

Thermogravimetric Analysis

The degradation temperature of the composites was determined by thermogravimetric analysis (TGA) using a TGA-60 Shimadzu thermogravimetric analyzer with a flux rate of air of 50 mL/min. Samples were heated from room temperature to 100°C at 5°C/min. Then, the temperature was kept at 100 for 10 min in order to remove residual water. The heating process continued at 5°C/min up to 650°C.

Uniaxial Tensile

Uniaxial tensile tests were carried out in an Instron dynamometer at 1.2 mm/min, following the ASTM D882-02 (2002) standard recommendations. Stress (σ)–strain (ε) curves were obtained. From these curves, tensile parameters such as ultimatum strength (σ_u), strain at break (ε_b), and toughness (T) were determined. The reported values were the average of at least 10 tests for each system.

Water Vapor Permeability

WVP was determined in accordance with a modified ASTM E96-00 procedure at room temperature. Circular acrylic cells containing the films were located in desiccators at relative humidity (RH) of ~56% and room temperature. Water vapor transport (WVT) was determined from the weight gain of the cells on the time. The weight was measured every 24 h for 10 days. WVP were calculated as:

$$\mathrm{WVP} = \frac{\mathrm{WVT} \times e}{P_0 \times \mathrm{RH}} \tag{1}$$

where e is the films thickness and P_0 the saturation vapor pressure of water at room temperature [46].

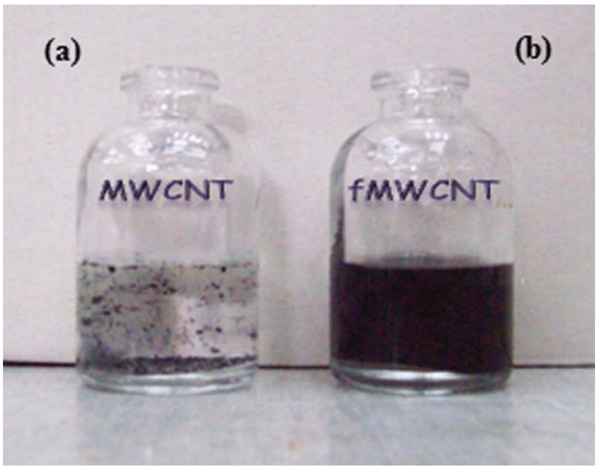

FIG. 1. Photographs of (a) pristine multi-walled carbon nanotubes (MWCNT) and (b) functionalized ones (fMWCNT), immersed in chloroform. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

RESULTS AND DISCUSSION

Macroscopic Observations

In order to observe the effectivity of the functionalization technique used on the carbon nanotubes, photographs of pristine MWCNT and fMWCNT immersed on chloroform were taken (Fig. 1).

When commercial nanotubes were directly mixed with the solvent, large agglomerations were found, despite the efforts of the previous sonication (Fig. 1a). In contrast, the solubility of the filler amazingly increased after chemical modification for the sidewalls of the carbon nanotubes (Fig. 1b). Furthermore, filler aggregations were not macroscopically observed. This fact shows the need for the implementation of an appropriated methodology with the purpose of change the structure of the nanotubes to avoid aggregations. The test confirmed the efficiency of the technique used in this research to functionalize the filler. It is important to mention that having stable solutions of MWCNT gives the possibility of using them in the development of nanocomposite materials.

Fourier Transform Infrared Spectroscopy

Figure 2 shows the FT-IR spectra of the matrix and the different films containing the functionalized carbon nanotubes. In all spectra, it is observed a band at 1,750 cm^{-1} which can be attributed to C=O of the ester groups that belong to PLA. Also, in both PLA matrix and

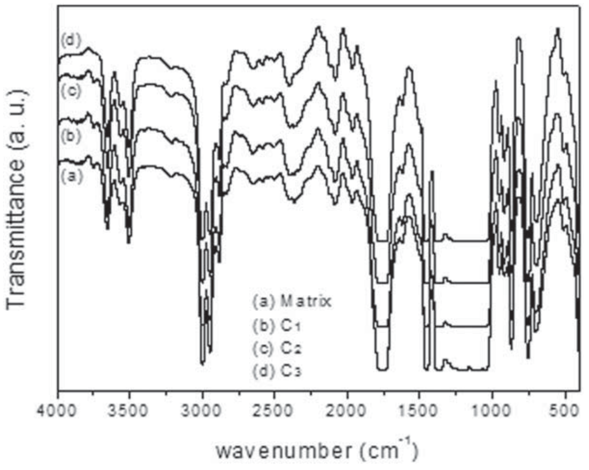

FIG. 2. FT-IR of the different nanocomposites developed.

composites, appears a small and broad signal at 3,400 cm^{-1}, corresponding to hydroxyl and carboxyl groups and also, few signals around 3,500 cm^{-1} due to the stretching of the hydroxyl group.

When the curves of FT-IR are observed throughout the whole wavelength range, the peaks of the nanocomposites donot change with respect to those of the PLA matrix. This result confirms that the preparation of these composites implied indeed a noncovalent bond between the fMWCNT and the PLA.

Scanning Electron Microscopy

The adhesion of the functionalized carbon nanotubes to the matrix was analyzed by observing the cryogenic fracture surfaces of the nanocomposites. Figure 3 shows the micrograph of a film containing the highest concentration of filler (C_3: 0.18 wt%). In the image it can be observed an isolated carbon nanotube strongly adhered to the matrix and absence of holes or fissures.

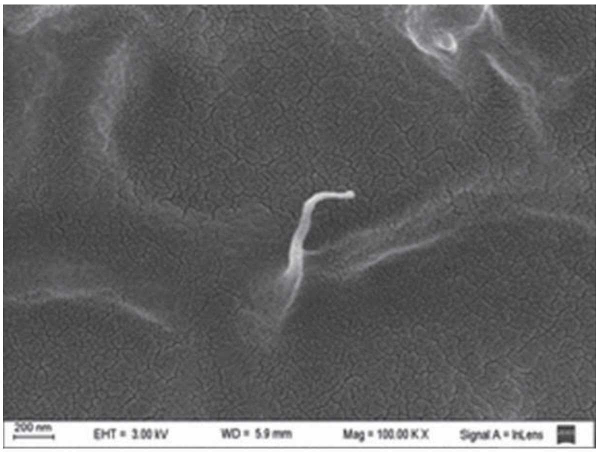

FIG. 3. FE-SEM images of cryogenic fracture surface of the nanocomposite containing 0.18 wt% of fMWCNT. Magnification: 100 KX.

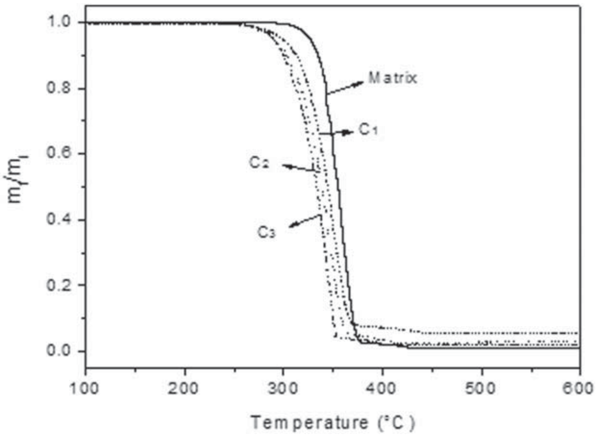

FIG. 4. TGA of the different nanocomposites developed.

Further, the micrograph reveals that the functionalization of MWCNT didnot damage the structure of the nanotube, conserving its integrity and original dimensions. This result can be due to the increased polarity of the functional groups formed on the surfaces of the fMWCNT, showing excellent interaction between the -COOH groups of the filler and the C=O groups of PLA. The great adhesion between matrix and fMWCNT is extremely important in terms of the improvements in the mechanical and barrier properties of the nanocomposites [47, 48].

Thermogravimetric Analysis

Figure 4 shows the thermogravimetric curves of the matrix and the nanocomposites with the different concentrations of filler studied. As can be observed, the TGA curves of the materials containing fMWCNT presented two different weight losses: one very small around 120°C and other of greater intensity between 340 and 350°C. The first fall corresponds to the loss of water and carbon dioxide that occurs due to the hydroxyl and carboxyl groups produced on the filler after Fenton reaction. The second weight loss process corresponds to the complete degradation of both the nanocomposites and the matrix and starts at 200–280°C [49, 50]. The values of the degradation temperature of the last weight loss were calculated from the thermogravimetric analysis curves and reported in Table 1. As can be seen, this parameter was slightly influenced by the addition of fMWCNT when the tests were performed in air. When the carbon nanotubes were incorporated the degradation temperature of the samples diminished less than 2%. By increasing the weight percent of fMWCNT the degradation of the films had a tendency to decrease but without showing significant differences between composites. Similar behavior observed Hapuarachchi and Peijs [51] in PLA-CNT composites when they tested TGA in air. The residues obtained after 400°C correspond to the char yield of PLA plus fMWCNT. It is

TABLE 1. Degradation temperature and tensile parameters: tensile strength (σ_u), strain at break (ε_b), and tensile toughness, for the different materials investigated.

Material	Degradation temperature (°C)	σ_u (MPa) [±1]	ε_b (%) [±0.3]	Toughness $\times E^{-8}$ (J/m^3)
Matrix	358 ± 2	37	4.9	1.5 ± 0.1
C_1	349 ± 3^a	40	3.8	1.2 ± 0.1
C_2	345 ± 3^a	44^b	2.5	0.75 ± 0.07
C_3	342 ± 5^a	43^b	0.9	0.23 ± 0.02

Equal letters in the same column indicates no statistically significant differences ($P \leq 0.05$).

believed that carbon nanotubes could behave in a catalyzing way in an oxidizing atmosphere [51].

Uniaxial Tensile

Figure 5 shows nominal stress–strain curves obtained under quasi static uniaxial tensile conditions for the four systems investigated. The behavior of the curves was dependent of the studied system. In all the cases it was observed a linear range at low deformations (up to ~1% on the matrix and ~0.8% on the composites) where Hooke's law is fulfilled, followed by a nonlinear behavior. In the matrix and the composite containing the highest concentration of fMWCNT (C_3), after the nonlinear behavior, the failure was observed. In the case of C_3, a precipitous drop occurred immediately after a very small nonlinear range, demonstrating that this composite was fragile. In contrast, the matrix broke after a large plastic deformation (practically 4%), showing that PLA matrix was ductile. On other hand, the stress–strain curves of C_1 and C_2 also revealed ductile characteristics but with different behaviors than the matrix. In both cases, it was observed a maximum tensile strength immediately after the transition from the linear elastic zone to the nonlinear. The peak was followed by a decrease in the strength for a period of time until the material failed. Taking into account the elapsed time until failure in both cases, it can be concluded that the material with the lowest concentration of fMWCNT (C_1) was more ductile than C_2.

Table 1 shows the tensile parameters calculated from the stress–strain curves of each system. Important improvements in ultimatum tensile strength (σ_u) were found when very small amounts of the functionalized carbon nanotubes were incorporated compared with the matrix. Furthermore, this parameter reached an increment of almost 20% on nanocomposites with only 0.10 wt% of filler.

Contrary to the increase of σ_u, the strain at break (ε_b) decreased about 20% on the composites containing the lowest concentration of filler (C_1), breaking in ~80% in case of the material with 0.18 wt% (which have fragile characteristics).

The differences in the decreased rate of ε_b compared to those of σ_u were markedly higher. Consequently, decrements of toughness values were obtained (Table 1), confirming the fragility of the composite with the highest concentration of fMWCNT used (C_3). In this case, toughness decreased approximately one order, changing from 1.5×10^8 J/m^3 (matrix) to 0.23×10^8 J/m^3.

Improvements in tensile strength, accompanied by reductions in ε_b with a concomitant decrease in tensile toughness, were also reported on composites formed by other matrices and reinforced by MWCNT [52–54]. The significant increases observed in σ_u when a very low amount of fMWCNT was used, could be due to the high modulus of the filler, as well as to their homogeneous dispersion in the PLA matrix and the great interfacial adhesion achieved [41]. The interfacial interaction between the filler and matrix is an important factor that can affect the mechanical properties of composites. If the filler is not well added to the matrix, the interfacial layer could not transfer stress. If a perfect adhesion occurs, tensile stress would be transferred to the filler and no reduction in effective surface area would be obtained [55].

The important and positive effect of the addition of these functionalized carbon nanotubes to the PLA matrix on tensile strength may be due to the stiffness of the fMWCNT which contributes to the presence of partially immobilized polymer phases [56]. Also, the functionalization of the filler helps to preserve the high aspect ratio and the great surface area of MWCNT, as well as to the effective dispersion of the nano-size filler in the matrix.

Water Vapor Permeability

One of the most important properties to be evaluated in this class of materials is WVP because of the

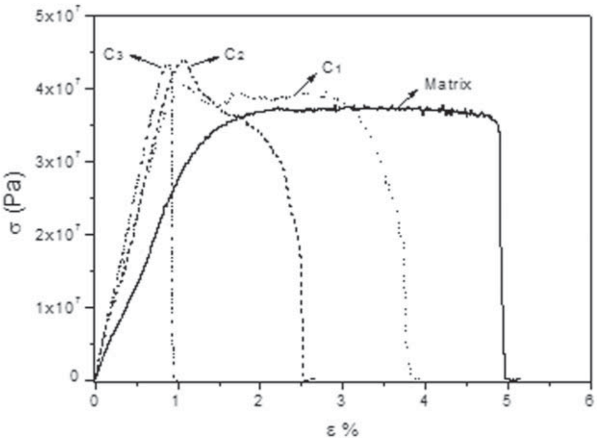

FIG. 5. Stress–strain curves obtained under quasi static uniaxial tensile.

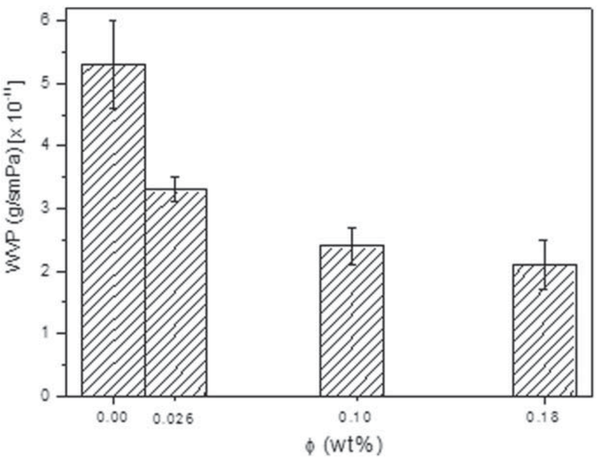

FIG. 6. WVP of the different nanocomposites developed.

significant role that water plays in degradation and microbial growth. In packaging industries and food coatings, for example, one relevant factor is preserve fresh and natural products as much as possible, avoiding any type of oxidation and/or microbial attack. The results of WVP of the matrix and nanocomposites are shown in Fig. 6. The value of WVP of matrix resulted around 5.3×10^{-11} g/ms Pa, which agrees with the literature [57]. This parameter decreased when functionalized carbon nanotubes were incorporated. Furthermore, as the amount of fMWCNT increased, WVP decreased, achieving values almost 60% lower than that of the matrix for example, in the composite with only 0.18 wt% of filler (C_3).

The high efficiency of the functionalized filler to reduce WVP can be explained in terms of the "tortuous path" [58]. Taking into account that water resistance of composites resulted better than that of matrix the addition of fMWCNT probably introduced a tortuous path for the pass of water molecules through the film [59]. Jamshidian et al. [60] reported that water vapor transition rate of PLA films decreases monotonously as crystallinity increases (when the crystallinity is between 0 and 20%). In a previous work of Seligra et al. [41], a slight increase in the crystallinity of the materials was observed when small concentrations of fMWCNT were incorporated. This result would contribute to the understanding of the decrement of WVP showed in this research.

CONCLUSION

The key to perform these improvements was the amazing functionalization process of MWCNT through Fenton reaction and a reaction with thionyl chloride and triethylene, leading to a strong interfacial adhesion between the nanofillers and the PLA. These modifications allowed achieving a great dispersion, absence of holes and very high adhesion between the filler and the PLA. An important result was that the maximum tensile strength increased 20% with only 0.10 wt% of functionalized MWCNT. Furthermore, the incorporation of fMWCNT provoked a significant decrease on WVP, reaching reductions up to 60% in the case of the samples with 0.18 wt% of filler. The decrease in the degradation temperature of the materials containing the functionalized nanofillers was less than 2%. With increasing concentration of fMWCNT, this parameter showed no significant differences, leading to the conclusion that the addition of the filler after being functionalized did not contribute to the deterioration of the material. Considering the results obtained in this research, it can be concluded that the nanocomposites developed from a biodegradable and renewable source as PLA and reinforced with very small concentration of functionalized MWCNT have suitable properties to be used in different industries such as packaging, coatings, medicine, textile and engineering. Furthermore, these films could be an alternative for manufacturers and businessmen to replace the current synthetic plastics by biodegradables in order to contribute to environmental conservations.

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