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Covalent grafting of carbon nanotubes to PLA in order to improve compatibility

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ABSTRACT

An excellent methodology for the synthesis of nanocomposite materials using a biodegradable polymer as matrix (polylactic acid, PLA) and functionalized by Fenton reaction carbon nanotubes (fMWCNTs) as reinforcement was developed. PLA was modified with benzoyl chloride and both modified materials were bounded covalently by esterification reaction. Infrared spectroscopy (FTIR) and thermogravimetry (TGA) studies were performed to verify the synthesis of the composites obtained. Films based on modified PLA reinforced with fMWCNTs (PLAmfMWCNTs) were conformed observing excellent dispersion of the filler in the PLA matrix. Finally it was shown that the addition of fMWCNTs improves Young's modulus and strength without losing deformation. Also it was observed that the good stability of the film let us to process it until 300 °C. Taking into account all these results, the new biodegradable nanocomposite material developed could be very promising to be used in packaging and biomedical industries as a replacement of the synthetic materials.

1. Introduction

The replacement of the synthetic polymers for biopolymers is one of the topics with major summit in the last times. The synthetic traditional polymers, as the polyester, polypropylene, etc., come from the oil, which price is racing day to day. While these materials have some advantages such as long life, their production presents high levels level of CO_2 and take hundreds of years to degenerate. In particular, biomedical industry has been focused in the development biodegradable materials without losing the appropriate characteristics to be use as sensors or stimulators of bone cells [1–3].

Biodegradable thermoplastic materials are macromolecules in which the repeating structural unit is obtained from natural and renewable resources. Their principal advantages over the synthetic materials are coming from renewable sources, like agriculture, because they have more stable prices, are friendly to the environment and have less cost and use less energy than synthetic traditional polymers [4]. In particular, aliphatic polyesters are biopolymers in which repeating units are bonded via ester linkages; many kinds of esters are present in nature and enzymes that degrade them, esterases, are ubiquitous in nature. Several biodegradable aliphatic polyesters are now produced on a commercial scale by a number of companies that make biodegradable plastics and poly(lactic acid) is one of the most important of them. Materials based on aliphatic polyesters have been studied for their application in packaging and, in particular, PLA, besides its application in this area [3,5] it has received attention in biomedical field in areas like sutures, implants, and tissue engineering [1,6,7]. Despite the high advantages of the PLA as a substitute for synthetic materials, by itself it cannot replace them because of its lower physical properties. For this reasons, it has been tried to implement the addition of different kind of reinforcement for the development of PLA-nano/microfiller composites. The use of multi-walled carbon nanotubes (MWCNTs) in the development of sensors as well as in biomedicine it has been taken relevance in recent years [1–3]. The excellent properties of this filler plus the fact that their electrical conductivity changes when a molecule is sorbed on the wall of the tube or trapped by some functional group generated in the wall, allow using them as sensors [1,8,9]. In addition, MWCNTs have high thermal conductivity and excellent mechanical properties [10–12], which makes that it has been tried to incorporate them in different matrices in order to obtain polyfunctional materials [13–16]. In particular, there are some precedents about their incorporation into PLA matrix [1,3,17]. From the biomedical point of view it has been shown that the immersed nanotubes in a polylactic acid matrix can simulate bones formation and also have the ability to generate a struc-

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tural reinforcement [1]. The addition of MWCNTs can modify the tenacity increasing it or diminishing it depending on the adhesion between the filler and the matrix [18,19]. Furthermore, the addition of MWCNTs affects the surface roughness and consequently the surface tension and the wear properties of the material. Since its inception, the nanotubes were questioned about their use in food industries, or for the contact with humans. However, recent studies reveal that CNT, rom the biomedical perspective, can stimulate bone formation, and at the same time, they are able to generate reinforcement [1,6] working by severely damaging *Escherichia coli*'s cell walls [20]. Furthermore, recently at Yale University it has been discovered that they might exhibit powerful antimicrobial effects [21]. In the packaging industry it is expected that their use is to secondary packaging application, not applicable directly to food.

The great use of composite materials strongly depends on the homogeneous dispersion of the filler throughout the polymer matrix and the interfacial adhesion between phases. It is known that the dispersion of the filler in the biodegradable matrix is an important problem to resolve in order to improve the nanocomposite properties. In the case of PLA, some authors propose a mixture in chloroform while others, a covalent functionalization of the polymer [3,17].

The aim of this research was to develop a biodegradable nanocomposite material with excellent bonding matrix–MWCNTs through the functionalization of the filler with modified PLA, in order to ensure good stress transfer and thus good mechanical response.

2. Experimental

MWCNTs (*Nanocyl, NC 3100*) were first subjected to a thermal treatment at 35 °C/min till 400 °C and maintained at this temperature for 30 min, in a tubular oven, to eliminate the amorphous carbon. Then, they were dried under vacuum at 120 °C for 3 h [22].

PLA (pellets of 90% L-LA, 10% D-LA; Mn = 49,860 determined by SEC) was manufactured by Shenzhen Bright China Industrial Co., Ltd. (Wuhan, China).

All the reagents: thionyl chloride, benzoyl chloride and solvents were obtained from commercial suppliers (Aldrich Co). They were used without further purification.

In order to incorporate the carbon nanotubes into the matrix, they were funtionalized by two reactions. The first one was the Fenton reaction to generate hydroxyl (OH) and carboxyl (COOH) groups on the MWCNT wall. Then, the carboxyl groups were lengthened by reacting with thionyl chloride to generate acid chloride groups and then with ethylene glycol leaving a terminal OH distanced from the filler wall, thereby increasing their availability because it decreases the steric hindrance. The reaction scheme is shown in Fig. 1a.

On the other hand, PLA was modified with benzoyl chloride to protect the hydroxyl group leaving only the carboxyl group to react with thinly chloride ($SOCl_2$). Thus, the COOH becomes an acid chloride which then could react to form an ester with the OH of MWCNTs. After these chemical modifications the covalent bonding between filler and modified polylactic acid (PLAm) was achieved to obtain the new material (PLAmfMWCNTs). The reactions scheme is shown in Fig. 1b.

2.1. Functionalization of MWCNTs

For the Fenton reaction were added 30 mg of MWCNTs in 20 mL of distilled water in a flask, and dispersed by ultrasonic washer for 10 min. Then, 1 mL of H_2O_2 and 1 mL of $FeSO_4$ (6.10^{-2} M) were added every 30 min, for 4 h. The reaction was carried out at 45 °C and the pH was adjusted to 3 by adding a few drops of H_2SO_4. At this pH value the reaction is autocatalytic and thus improves its effectiveness. Ammonia was used to stop the reaction. Then, it was centrifuged to separate the solid, after HCl (1 M) was added to redissolve the iron that did not react and centrifuged again to discard the residual iron. This procedure was repeated with HCl (0.1 M) to ensure complete removal of iron. Then, distilled water was added and centrifuged for 20 min, at 3000 rpm. The supernatant was discarded. This procedure was repeated 6 times until neutral pH. Finally, it was left at room temperature for 24 h and then dried in a vacuum oven until further use.

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

2.2. PLA modification

PLA (18 g) and chloroform (60 mL) were mix at 45 °C until complete dissolution of this polymer. After that, 1 mL of benzoyl chloride and 1 mL of pyridine were also added. The reaction was kept at 70 °C for 24 h.

The reaction work up was carried out with distilled water and placed on ice to induce polymer precipitation. The mixture was filtered to remove the unreacted benzoyl chloride. Then, the modified polymer (PLAm) was placed in a beaker and hot water was added to remove residual benzoyl chloride. The product obtained was left at room temperature for 24 h and then dried in a vacuum oven until further use.

2.3. Functionalization of PLAm with fMWCNTs

In order to generate acid chloride groups 9.9 g of PLAm were dissolved in a mix of CH_2Cl_2/toluene (2:1) at 70 °C. After total dissolution thionyl chloride (1 mL) was added, then 2 mL of triethylamine (TEA) was used to neutralize the generated HCl and also to catalyze the reaction. The reaction was stirring for 3 h.

To synthesize the PLA with MWCNTs (PLAmfMWCNTs), 4.5 mg of filler were added to PLAm to form an ester group. The reaction was stirring for 48 h.

It was centrifuged to remove fMWCNTs that were not functionalized with PLAm. In order to remove trimethyl ammonium chloride salts, the sample was filtered with Büchner. The solution was evaporated and the solid was washed. The polymer was redissolved in chloroform and precipitated with methanol/water (2:1).

2.4. Films performance

To develop of PLAmfMWCNTs composite films, 1 g of modified polymer was mix with 50 mL of chloroform in an orbital system at 150 rpm for 90 min. Then, the system was left in ultrasonic washer for 30 min to achieve the complete dissolution of the material. Finally, the solution was placed in petri glasses. Samples were dried first 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.

2.5. Characterization

Thermogravimetry (TGA) measurements were obtained on TGA-60 Shimadzu themogravimetric analyzer. The nitrogen flux rate was rate was 40 mL/min. Samples were heating from room temperature to 100 °C at 5 °C/min, and then were keeping at this

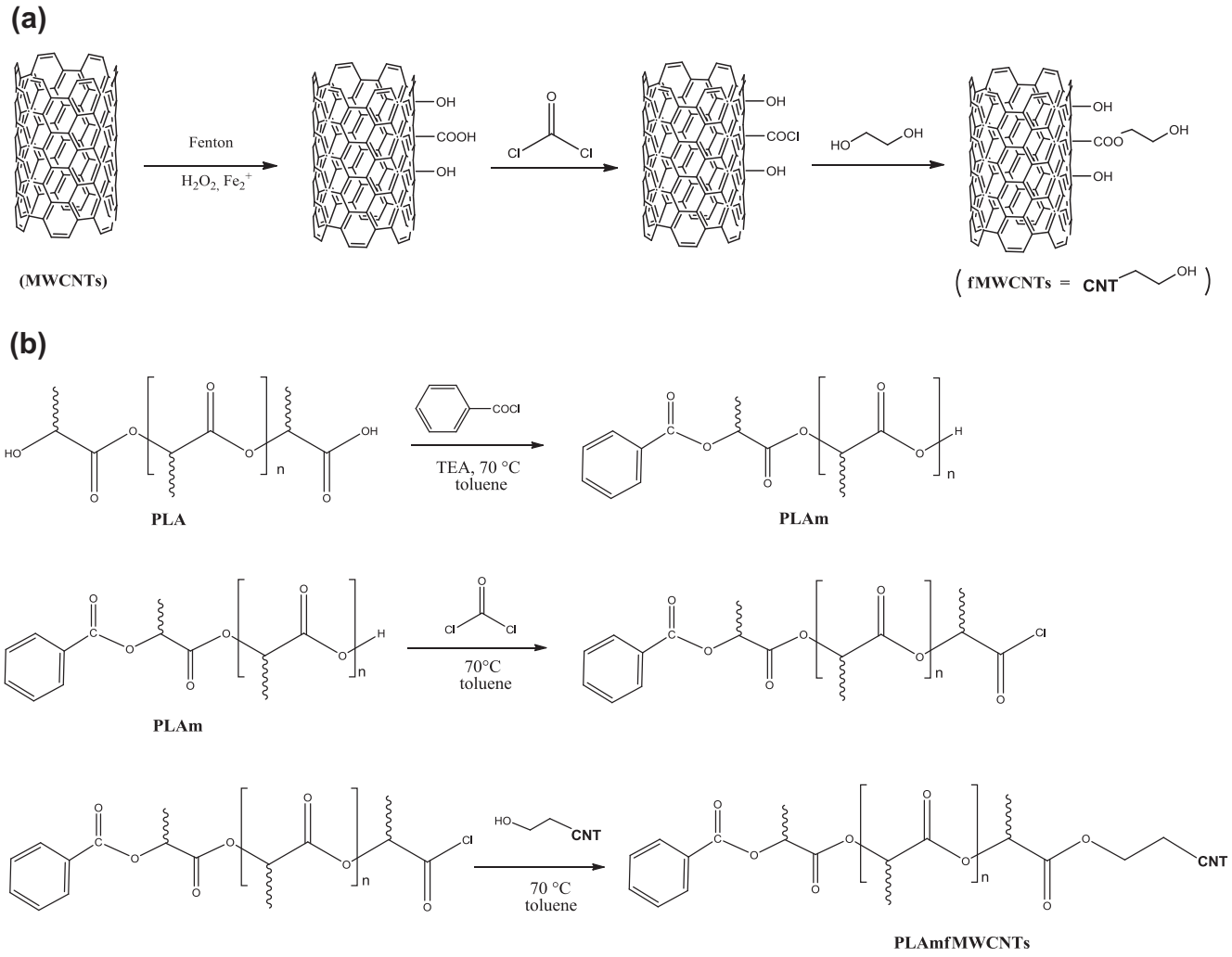

Fig. 1. Scheme of: (a) MWCNTs functionalization (fMWCNT) and (b) Synthetic modification of PLA (PLAm) and synthesis of PLAmfMWCNTs.

temperature for 10 min in order to remove residual water. After that, the heating process was continued up to 650 °C at 5 °C/min. From this analysis we could obtain the degradation temperature of the materials.

MWCNTs functionalized by Fenton reaction were analyzed in order to estimate the carboxyl groups obtained in the reaction, and also it was studied the filler modified with thionyl chloride and ethylene glycol to observe the effectiveness of them.

FTIR spectra were recorded on a Nicollet FTIR Instrument 510P in order to characterize the reaction product. FTIR was performed from 400 to 4000 cm^{-1}.

Both composite and matrix surface was studied by means of an optical microscope (Olympus BX60M), with a magnification of 20×, to determine distribution of the filler and to observe possible agglomerations.

Cryogenic fracture surfaces were observed using field emission scanning electron microscopy (FE-SEM) at a magnification of 5 KX and 50 KX.

Dynamic mechanical tests were carried out in a Dynamic Mechanical Thermal Analyzer (DMTA IV, Rheometric Scientific) in the rectangular tension mode at 1 Hz, in the range of temperature from 30 °C to 90 °C at a heating rate of 2 °C/min, and 0.04% of deformation. Samples dimensions used were 15.0 mm × 5.0 mm × 0.26 mm (length, width and thickness, respectively). Three replicates were tested for each system.

Uniaxial tensile tests were performed using an Instrong's dynamometer at 1.2 mm/min following ASTM D882-02 (2002) standard method [23]. From stress (σ) –strain (ε) curves, Young's modulus (E), tensile strength (σ_u), strain at break (ε_b) and tensile toughness values were determined. The reported values were the mean of at 10 tests for each system.

3. Results and discussion

3.1. Thermogravimetry analysis (TGA)

In Fig. 2a could be observed the TGA analysis for pristine MWCNTs, and filler functionalized by Fenton reaction and with ethylene glycol. In the curve of pristine MWCNTs it could be observed an only one weight loss at around 560 °C assigned to the material degradation temperature, according with the literature [24,25]. Derivative TGA were analyzed to determinate all degradation temperatures.

The functionalization of MWCNTs with ethylene glycol load to a shift in the temperature of degradation to higher temperatures (>650 °C). This fact could be explain taking into account that the analysis was carried out in nitrogen atmosphere but the thermo balance has not an hermetic equipment, so that generate both degradation mechanism, thermal and oxidative. It also produces some

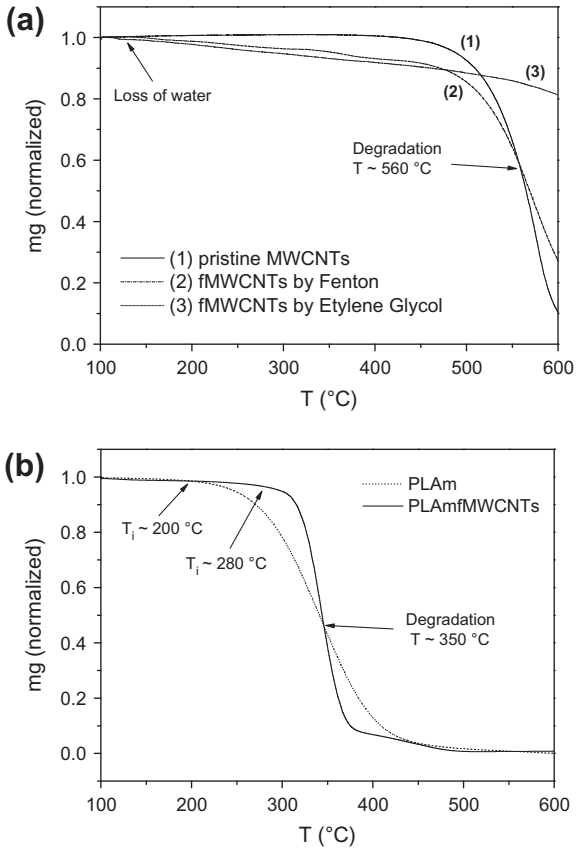

Fig. 2. TGA analysis of: (a) pristine MWCNTs (non-functionalized) (1), fMWCNTs functionalized by Fenton reaction (2), and fMWCNTs with ethylene glycol (3); (b) PLAm and PLAmfMWCNTs films.

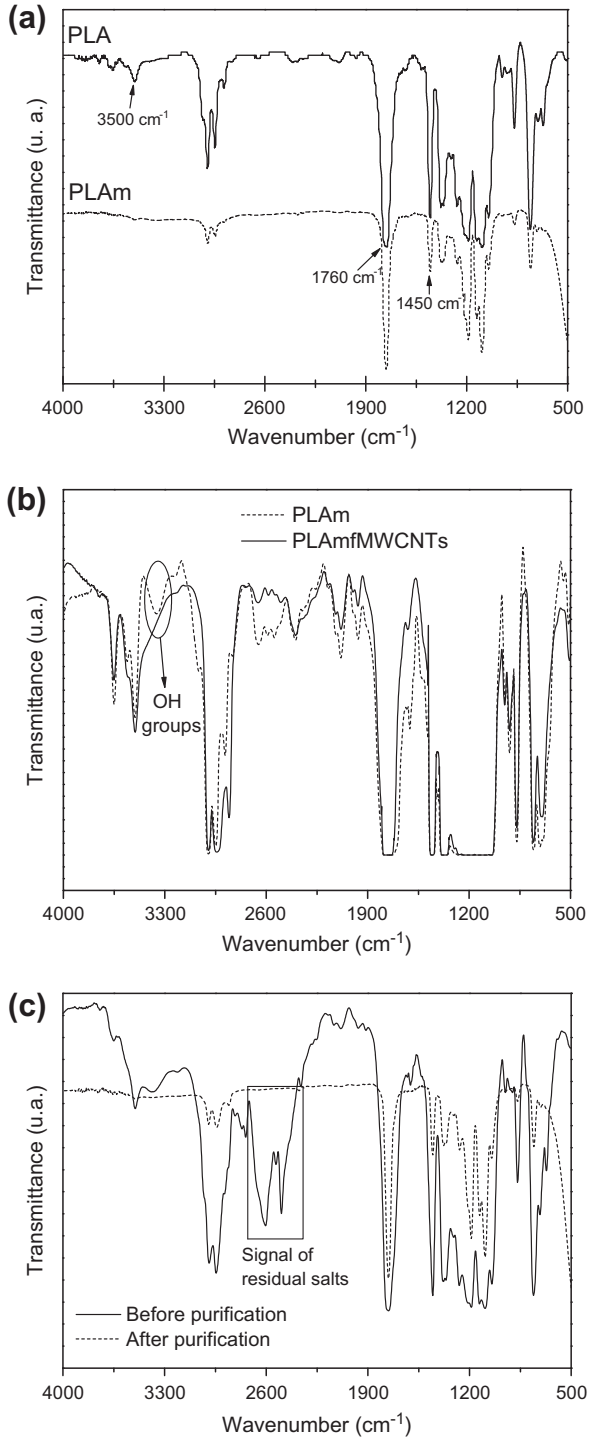

Fig. 3. FTIR spectra of: (a) neat PLA and PLAm, (b) PLAm and PLAmfMWCNTs films, and (c) before and after purification.

modifications on degradation temperature. TGA results for MWCNTs functionalized by Fenton show two different weight losses. The first one corresponds to the loss of water and carbon dioxide due to the hydroxyl and carboxyl groups, the second weight loss process correspond to the complete degradation of the filler [26,27].

The percent of weight losses due to OH and COOH groups were determined from TGA results. For Fenton reaction the weight loss was 8.1% in. In the case of the MWCNTs functionalized with ethylene glycol the results was 9.5%, thus this increment could be due to the presence of ethylene glycol bonded to the filler. This fact evidence the effectiveness achieved in the reaction.

Fig. 2b shows thermogravimetric results for PLAm and PLAmfMWCNTs. From derivative TGA analysis it could be observed that degradation temperature was the same for both materials (around 350 °C), so the modification proposed to develop a new material did not affect the temperature in which the highest mass loss is produced, usually named as degradation temperature. Furthermore, the degradation started at Ti – 200 °C in the case of PLAm while in PLAmfMWCNTs it started at Ti – 280 °C indicating that an improvement was achieved due to the presence of MWCNTs as reinforcement.

3.2. Fourier transforms infrared spectroscopy (FTIR)

In Fig. 3a it could be observed FTIR spectra for neat PLA and modified polylactic acid. The PLAm spectrum showed a remarkable increase in the peak observed at ~1760 cm^{-1} due to the presence of carbonyl group, relative to the signal observed at ~1450 cm^{-1} which is not modified by the reaction. This increment corresponds to the ester groups that were formed in the reaction but not to the benzoyl chloride that did not react [28]. If benzoyl chloride was not covalent bounded to PLA the wavenumber of the carbonyl group would be shifted. It has to be noted that the wavenumber observed is the same for each studied case. This is evidence that reaction actually occurred. Also it can be observed a decrease in the intensity of hydroxyl group (~3500 cm^{-1}) compared with the signal at ~1450 cm^{-1}. This decrease is due to the terminal OH group of PLA which was blocked by the reaction of benzoyl chloride and does not disappear because the yield of reaction was not 100%.

In Fig. 3b are shown FTIR spectra of PLAm and PLAmfMWCNTs. As can be observed the peak corresponding to the OH groups ($\sim$3350 cm^{-1}) disappear in PLAmfMWCNTs composite due to the addition of the filler.

The FTIR spectrum of a polymer in the fingerprint region ($v \leqslant 1500\ cm^{-1}$) is used to identify and characterize the material, since the observed peaks can be assigned to different vibration modes of chemical groups by comparison with cataloged FTIR spectra. In the case of PLA, it could be identify the C—O—C stretching asymmetric mode which appears at 1089 cm^{-1}. At 871 and 754 cm^{-1} there are two bands that can be attributed to the amorphous and crystalline phases of PLA, respectively [29]. When all the spectra collected are analyzed we can observed that in all the cases the relationship between them is maintains constant which means that the amorphous and crystalline phases of PLA were not significantly modify by these reactions (Fig. 3a and b). However, in Fig. 3c it could be observed and strong bands at 690 and 754 cm^{-1} which can be attributed to the bending out of the plane of a monosubstituted aromatic ring. In our case, these signals belong to the excess of thionyl chloride that had not reacted or to the benzoic acid salts. It has to be noted that these bands disappeared when the PLAm was purified.

To verify the elimination of trielthylammonium chloride salts, FTIR were performed before and after purification (Fig. 3c). The characteristic band of this salt ($\sim$2500 cm^{-1}) was observed in the spectrum of the sample before filtration and did not appear in the spectrum of the sample after purification. This allowed us to verify the elimination of residual salts.

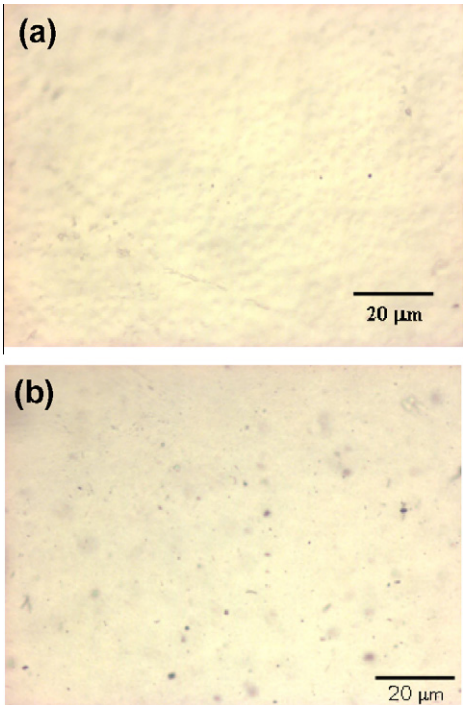

Fig. 5. Optical macroscopic images of the conformed films: (a) PLAm and (b) PLAmfMWCNT. At 20× of magnification.

3.3. Optical observations

Fig. 4 shows the photographs of different films conformed: matrix (a), nanocomposite with fMWCNTs (b) and nanocomposite with pristine MWCNTs (c).

Also, it can be observed that the addition of carbon nanotubes as reinforcement leads to a material with a dark tone respect to the matrix (Fig. 4a–b); however, the composite remind transparent and shows non-agglomerates, at least in macroscopic observations. This demonstrates that, a priori, fMWCNTs would be well dispersed in PLAm matrix. These observations showed that the funcionalization of the filler and the modification of the polymer were effective and necessary to achieve a good dispersion.

An evident difference it can be observed in the dispersion of the filler when it is functionalizated, noticing a high accumulation of the filler (badly distributed) in that composite (Fig. 4c).

To analyze the dispersion of the MWCNTs in the PLA matrix with more detail, optical microscopy was performed. Fig. 5 shows the images of the films of PLAm (a) and PLAmfMWCNTs composite (b). In the composite film can be seen dark spots corresponding to the incorporation of the MWCNTs which dispersion was seemed to be homogeneous, without the presence of agglomerates. Also, it can be noticed the absence of holes or fissures. These observations would be agreed with the results shown in density.

3.4. Scanning electron microscopy (FE-SEM)

Fig. 6 shows the cryogenic fracture surface of the different films developed: pure PLA (a), PLAm (b) and PLAmfMWCNT (c–d).

As can be observed in all samples, the structure of the materials is presented by a boss of veins, typical of the polylactic acid materials. Pure PLA surface seems to be flat and relatively smooth compared to the other materials. As was explained above, the PLA chains were chemically modified in order to achieve the formation of an ester bond between the new polymer and fMWCNTs. The chemical modification of PLA involves a protection reaction in which an aromatic moiety was incorporated, thus the forces between the polymer chains increased due to presence of pi–pi stacking interactions. This difference affects the polymer structure comparing with the one obtained with neat PLA: the modification of the PLA shows a slight decrease in the density of veins and a minor relief (Fig. 6b). A uniformly dispersed bright dots and lines that represent the ends of the fMWCNTs are shown. Almost, it can be seen that a fine dispersion of fMWCNTs is achieved throughout the PLAm matrix without any apparent aggregation. Zhao and

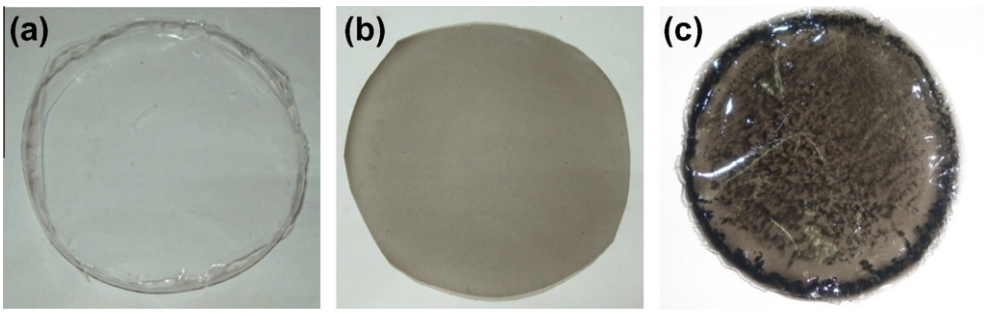

Fig. 4. Photographs of the conformed films: (a) matrix, (b) nanocomposite with fMWCNTs, and (c) nanocomposite with pristine MWCNTs.

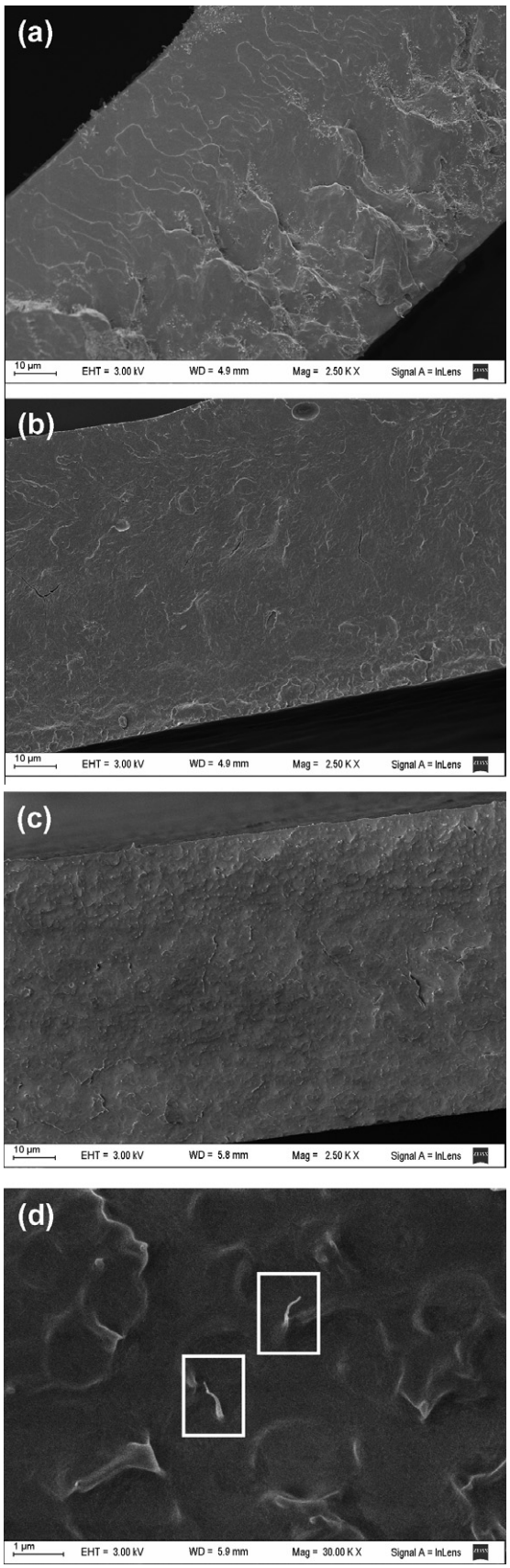

Fig. 6. FE-SEM micrographs of the cryogenic fracture surface of the different films developed: (a) pure PLA, (b) PLAm, and (c,d) PLAmfMWCNT.

coworkers [30] reported the same behavior for PLA-functionalized MWNTs with 0.5 w% of filler, but slight aggregation they sow with further increasing the MWNTs content.

In Fig. 6c it can be observed the presence of MWCNTs isolated and well adhered to PLAm matrix, preserving the length of the filler near to 1m (it is to say, the functionalization of the filler and the modification of PLA 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 fMWCNTs as well as good interactions of the —COOH groups with the C=O groups of the PLA matrix. Meng and coworkers [31] reported that acid-treated MWCNT was effectively dispersed in polyamide 6 (PA6) matrices because the functional groups on the surface of modified filler probably have reacted with PA6 in melt-mixing process, resulting in better dispersion state and stronger interfacial adhesion. In other hand, Kim et al. [32] showed the same behavior in MWCNTs/PEN matrix after filler functionalization.

This interfacial adhesion between the filler and matrix will be crucial for improving the mechanical properties of the nanocomposites [18,19,33,34]. Furthermore, in SEM imagine does not be seen any holes or fissures, confirming that the functionalization procedures were efficient to conform the promising composites.

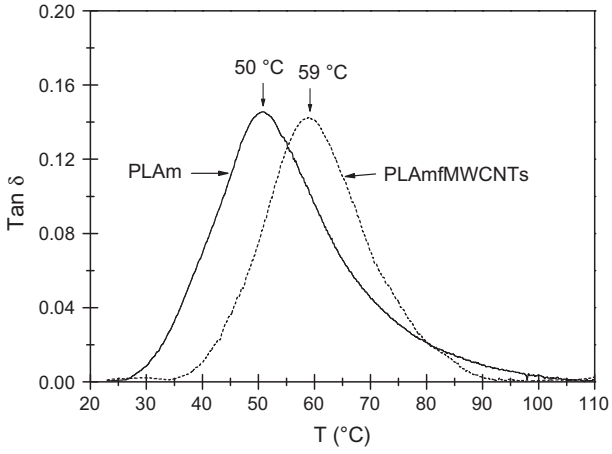

Fig. 7. Loss tangent, $tan\delta$, as a function of temperature for PLAm and PLAmfMWCNT.

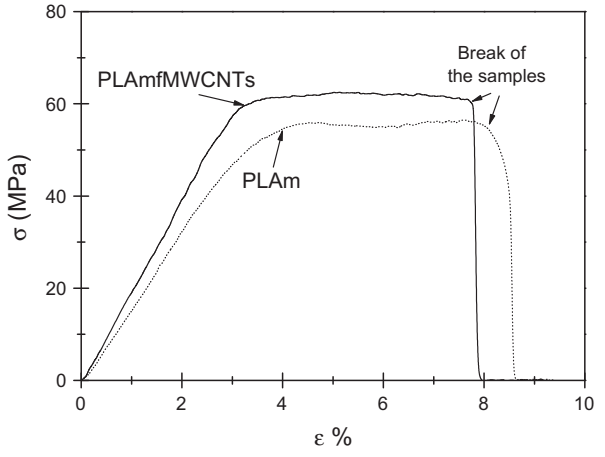

Fig. 8. Stress–strain curves for PLAm and PLAmfMWCNT.

Table 1
Tensile parameters for the different materials investigated. Young's modulus (E), tensile strength at break (σ_b), strain at break (ε_b) and tensile toughness.

Material	E (GPa) [±0.02]	σ_b (MPa) [±1]	ε_b (%) [±0.3]	*Toughness* (MJ/m^3) [±0.02]
PLAm	1.65	56	8.5	3.71
PLAmfMWCNTs	1.98	61	7.9	4.85

3.5. Mechanical testing

Fig. 7 shows the dependence of loss tangent values ($tan\,\delta$) with temperature for PLAm (a) and PLAmfMWCNT (b) films. $Tan\,\delta$ curves reveal one important thermal transitions corresponding to the PLA. In matrix modified material the transition (T_g) was observed at ~60 °C. This value is slightly higher than those reported in the literature for pure PLA [35,36]. When the filler is addition, the temperature transition peak was shifted to higher temperatures and diminished in intensity. This behavior is typical to composite materials with good adhesion of the filler in the matrix. This observed results can be attributed to the higher surface area promoted by the incorporation of the nanotubes and the very good adhesion between the modified matrix and the functionalizated filler [37–39]. In particular, Wu and Liao [3] showed a shift in the T_g of PLA/MWNTs hybrids almost 4 °C to higher temperatures.

During the glass transition temperature, the long-range polymer chain acquires mobility and therefore dissipates a great amount of energy through viscous movement. This is shown by the loss tangent peak in a dynamic-mechanical test. Hence, a depression in loss tangent values indicates the reduction of the number of mobile chains during the glass transition [40–43]. In this case, intermolecular interactions between PLAm and fMWCNTs, reduce the molecular mobility of the PLAm in contact with the carbon nanotubes surface and therefore, decreased $tan\,\delta$ values and increased relaxation peak temperature values were observed.

The addition of carbon nanotubes also modified storage modulus and tensile parameters. Fig. 8 shows the stress (σ) and–strain (ε) curves, obtained under quasistatic uniaxial tensile loading conditions, corresponding to PLAm (a) and PLAmfMWCNT (b) films. As can be observed, the behavior of the curves presents a lineal zone at about 2.5% (representing the lineal elastic behavior), following by a nonlineal zone, until break of the samples (around 8%).

The parameters of uniaxial tension: storage modulus (E'), tensile strength (σ_b), stress at break (ε_b) and toughness are reported in Table 1. As can be seen, when fMWCNTs are added to PLAm, both E' and σ_b increase about 20% and 10% respectively, without losing deformation. Some researchers report the same effect in storage modulus and strength at break when filler is incorporate to polymer matrix, but they always observe a decrease in the deformation at break in composites [27,43,44]. In particular, Chen and coworkers [44] showed in PLA-MWCNTs functionalized by Ring-Opening polymerization, increases around 20% in the modulus and strength, but a decrease almost 50% in the elongation at break. In our case, it is important to note that the influence of fMWCNT did not affect the deformation of the samples and toughness.

4. Conclusions

A new methodology to link covalently MWCNTs with a biodegradable polymer (PLA) was developed, achieving the filler remain dispersed in the matrix.

By thermogravimetric characterization it was showed that the amount of hydroxyl and carboxyl groups produced in the Fenton reaction was 8.1% m/m$_i$, while the numbers of groups extended with ethylene glycol, 9.5% m/m$_i$. As the percentage difference was greater than 1.0 ± 0.3%, it was verify the generation of OH groups in the wall of the nanotubes and the extension of these with ethylene glycol.

Through infrared spectroscopy analysis it was observed an increase in the beak associated with the stretching of carbonyl groups (~1760 cm^{-1}) and a decrease in the intensity of the beak associated with the stretching of hydroxyl group (~3500 cm^{-1}). These facts let us to verify the funcionalization of the PLA with benzoyl chloride.

An efficient methodology was achieved to purify the material, by removing the salts of trimethyl ammonium chloride, verifying their removal by FTIR spectroscopy.

A procedure for the formation of biodegradable composite films of PLA matrix, reinforced with MWCNTs was developed, loading to obtain an excellent dispersion of the filler in the polymer matrix.

Mechanical properties result in a shifts in glass transition temperature with the addition of carbon nanotubes in PLA modified matrix, reveling a very good adhesion between the modified matrix and the functionalizated filler, attributed to the higher surface area promoted by the incorporation of the nanotubes. Storage modulus and strength at break were improved with the addition of fMWCNT without losing deformation properties. E' increases more than 20% and σ_b around 10%, without affecting the strain and toughness of the samples.

Finally, it is possible to conclude that the novel biodegradable composite material developed in this work, has promising characteristics to be used in biomedicine and in packing industry.

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