



Improving PLA ductility using only 0.05% of CNTs and 0.25% of an azo-dye



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ABSTRACT

The high brittleness of poly(lactic acid) (PLA) is a major drawback for many applications. In this work we develop a new highly ductile PLA composite using carbon nanotubes (CNTs) and the azo-dye disperse orange 3 (DO3). Increments up to almost an order of magnitude in strain at break and tensile toughness were achieved with the addition of only 0.05% of CNTs and 0.25% of DO3 respect to the polymer. This important improvement is explained in terms of a new spatial conformation of PLA chains due to the addition of DO3 and CNTs.

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1. Introduction

Carbon nanotubes (CNTs) have been proposed as candidates for the development of functional and structural polymer/CNTs composites, due to their exceptional mechanical and electrical properties, high aspect ratio and low density [1,2]. However, their potentiality regarding improvements of polymer mechanical properties has not yet reached its technological threshold. This is a consequence of the inherent difficulty to obtain proper CNTs dispersions at a low cost. CNTs well dispersed in a polymer matrix lead to an enhancement in the composite modulus, and depending, on the interface and the possibility of the filler to anchor cracks, strength and strain at break could both increase simultaneously [3]. Besides, the incorporation of CNTs could cause changes in the structural conformation of the polymer, leading to new mechanical properties.

Taking this into account, CNTs addition could solve one of the most important technological problems when processing thermoplastics: the achievement of high elongations at break. This is one of the critical points in the processing of poly(lactic acid) (PLA). PLA is a biodegradable thermoplastic polymer based in aliphatic polyesters, presently used in different industries such as biomedical [4] and packaging [5], as its mechanical and barrier properties are comparable to those of petroleum-based plastics

[6–8]. However, the low elongation at break that is typical of this polymer limits some of its uses. For example, extrusion casting of PLA films is relatively difficult compared to other polymers. In fact, there is no tolerance for PLA film tearing or cracking when subjected to forces during package manufacturing [6,9]. It therefore becomes important to modify these properties in such a way that PLA is able to compete with other more flexible commodity polymers such as polyethylene, polypropylene or polyvinyl chloride. Among the different efforts made to improve the properties of PLA we can find copolymerization [10], blending with other flexible polymers [11], introducing plasticizers in the material composition [12] and adding different fillers such as CNTs [5,8,13].

Covalent and non-covalent functionalizations of carbon nanotubes were proposed in order to have a good dispersion of them in a PLA matrix [5,8,13,14]. One easy and effective way to obtain this is through a non-covalent functionalization using the azo dye Disperse Orange 3 (DO3), which can interact with PLA [14].

Our group has recently developed a PLA-DO3-CNTs composite. We have already demonstrated that the incorporation of CNTs enhances some of the optical properties that DO3 confers to the polymer. It was observed that the addition of a small amount of 0.05 wt% of CNTs leads to a new phenomenon consisting of an enhancement of the optical anisotropy [14]. Moreover, diffraction gratings were recorded on the nanocomposites, and it was shown that the CNTs addition lead to increases in the maximum diffraction efficiency as well as the remanent efficiency by 20% [15].

In this work we demonstrate that, besides optical properties, the addition of only 0.05% of CNTs and 0.25% of DO3 into a PLA

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matrix can lead to a composite with an increment of strain at break up to almost an order of magnitude, keeping its stress at break value similar to that of PLA. This important improvement, vital for PLA industrial manufacturing, is explained in terms of the dye affinity for the PLA or CNTs, different crystal polymorphisms developed in PLA chains due to the incorporation of fillers, and differences in the glass transition temperatures.

2. Methods

PLA (10% D-Lactide, 90% L-Lactide) with $67,600 \text{ g mol}^{-1}$ and $49,900 \text{ g mol}^{-1}$ weight and number averaged molecular weight respectively (Shenzhen Bright China Industrial Co. Ltd), DO3 dye (Sigma-Aldrich), CNTs (Nanocyl, NC3100) and reagent grade chloroform (Biopack, Argentina) were used in order to develop the materials.

Four different kinds of samples were prepared, following the procedure previously reported by our group [14]: neat PLA films, PLA-DO3 films, PLA-DO3-CNTs films, and PLA-CNTs films. Basically the fillers (DO3 and/or CNTs) were dispersed in 50 mL of chloroform using a bath sonicator. After 60 min, 1 g of PLA was added to the solution and sonication continued for other 60 min. Immediately after that, the final solution was cast into flat-bottom glass Petri dishes. The solution was dried for 24 h at room temperature. Finally, the films were oven dried under vacuum at 40°C for two days and then at 60°C for 24 h. Neat PLA films were analogously prepared, with no fillers incorporation. Four different CNTs contents were studied: 0.05, 0.1, 0.3 and 0.5 wt%. In this letter we report the results obtained for the lower load, as the most important improvements were achieved. Results obtained with other contents on CNTs are reported as supplementary data in case the reader is interested. Images of the obtained films are shown in Fig. 1a. PLA-CNTs films (with no DO3 incorporation) resulted completely inhomogeneous as it is shown in Fig. 1a., and then their mechanical characterization resulted impossible.

Five different films of each kind of sample were prepared. The mean thickness of each set of five samples was $75 \mu\text{m}$ with a dispersion of $2 \mu\text{m}$.

Uniaxial tensile tests were carried out in an Instron dynamometer following the guidelines of ASTM standard method D 882-91 at a rate of 1.2 mm/s. Samples were cut into rectangular strips of $5 \times 15 \text{ mm}$ and all tests were performed at room temperature (25°C). Nominal stress–strain curves were obtained and stress (σ_b) and strain (ε_b) at break values were determined, as well as yield strength (σ_y). XRD diffractograms were obtained using a Siemens

D5000 diffractometer. Scattered radiation was detected in the angular range $10\text{--}40^\circ$, using Cu-K α radiation.

All the experiments were performed over five different films of each kind of sample in order to ensure the reproducibility of the results. The different experiments over each set of five samples did not show significant differences. In the following section the results shown are the average all measurements taken for the same type of sample.

3. Results and discussion

The obtained stress–strain curves for neat PLA, PLA-DO3 and the composite PLA-DO3-CNTs are shown in Fig. 1, and the main results obtained from the curves are summarized in Table 1. In accordance to reports in the literature, the PLA film has a small ε_b . The addition of DO3 transforms the PLA matrix increasing ε_b in almost a 100%, while inclusion of only 0.05 wt% of CNTs, together with DO3, causes increments of about an order of magnitude in this magnitude respect to neat PLA, being approximately 47.6% for the nanocomposite and 4.8% for the PLA matrix. This important increase results in a significant improvement in the tensile toughness, being approximately $17.9 \times 10^6 \text{ J/m}^3$ for the nanocomposite against $1.3 \times 10^6 \text{ J/m}^3$ for the PLA matrix.

The most important modifications in σ_y are produced by the addition of DO3, while the higher ε_b at room temperature is consequence of CNTs incorporation. Different factors can cause these differences. In particular, if changes in the structural conformation of the materials exist, it is expected for its mechanical behaviour to change.

On one hand, considering that the PLA is a semi-crystalline material, a critical point to evaluate its mechanical properties is to analyse its crystal structure. Two of the possible PLA crystal structures are the α (orthorhombic structure) and β (trigonal structure) forms [16]. X-ray diffraction pattern of PLA pellets employed in this work showed that both the α and the β crystalline structures are present. Fig. 2 shows the X-ray diffraction patterns for neat PLA, PLA-DO3 and PLA-DO3-CNTs films. The diffraction pattern for PLA films showed two very small diffraction peaks that correspond to both, the α and the β -form, analogous to what happened in the diffractogram of PLA pellets. This crystal structure is the result of the PLA pellets manufacturing procedure, as we did not perform any thermal or mechanical treatment. In contrast, the diffraction pattern for the PLA-DO3 film showed more clearly defined diffraction peaks, indicating a greater degree of crystallinity, which corresponded only to the α -form. When only 0.05 wt% CNTs

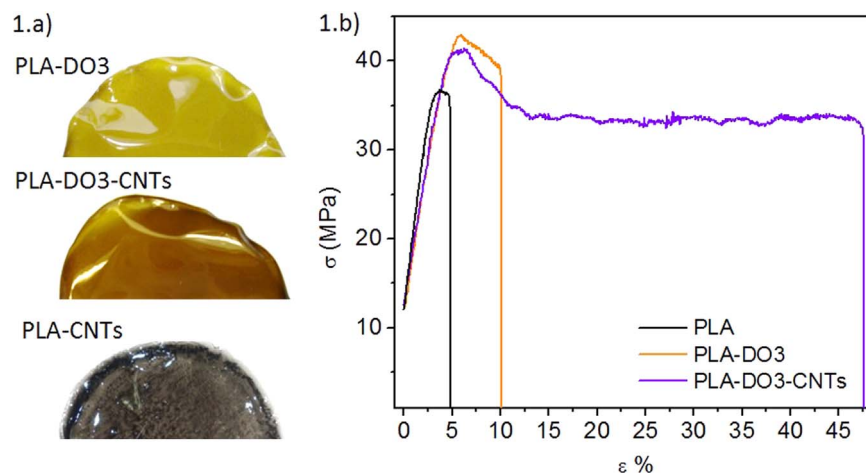


Fig. 1. (a) Images of obtained films; (b) stress–strain curve for neat PLA, PLA-DO3 and PLA-DO3-CNTs.

Table 1
Results obtained from the stress-strain curves.

	ϵ_b	σ_b	σ_y	Tensile toughness
PLA	$(4.8 \pm 0.5)\%$	(36 ± 1) MPa	(37 ± 1) MPa	$(1.3 \pm 0.1) \times 10^6$ J/m ³
PLA-DO3	$(10 \pm 1)\%$	(39 ± 1) MPa	(43 ± 1) MPa	$(3.5 \pm 0.3) \times 10^6$ J/m ³
PLA-DO3-CNTs	$(48 \pm 5)\%$	(34 ± 2) MPa	(41 ± 2) MPa	$(18 \pm 2) \times 10^6$ J/m ³

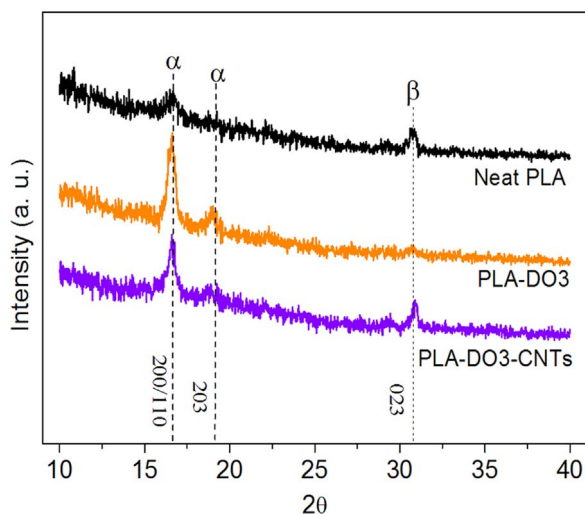


Fig. 2. XRD patterns of neat PLA, PLA-DO3 and PLA-DO3-CNT. The Miller indexes are indicated in the diffractogram.

content was added together with DO3, the β -form is again observed ($2\theta=30.9^\circ$), and the pattern shows a strong increase of crystallinity compared to neat PLA, but less crystallinity than PLA-DO3 samples.

On the other, the mechanical response of the materials at room temperature depends on how close this temperature is to their T_g . In a previous work [14], we reported the thermal characterization of these materials, and important differences in the T_g were found. For PLA, the T_g was 54°C , for PLA-DO3 it was 59°C while for PLA-DO3-CNTs it was 40°C . It is well known that the presence of crystalline domains in the amorphous phase can increase the T_g by preventing the polymer chains mobility [17]. As we have already demonstrated the PLA-DO3 material has a greater degree of crystallinity than pure PLA. At the same time, low contents of additives that interact with polymer chains can have an anti-plasticizing effect in the matrix [18,19]. We have already demonstrated [14] that in our case the ester group of the PLA interacts with the amino terminal group of DO3 molecules. The important increase in the T_g of PLA-DO3 is a consequence of these two effects occurring simultaneously. It is interesting that the addition of only 0.25% of DO3 leads to a new material with overcoming properties compared to PLA. This new material results ductile, with an increment in ϵ_b of almost a 100%. The strength at break, meanwhile, showed an increase of about an 8%; and the yield of about a 16%; leading to an important increase in the tensile toughness of about a 170%.

When CNTs are added, they are non-covalently functionalized with the DO3 molecules, letting lower amount of DO3 available to interact with the PLA chains and therefore avoiding the anti-plasticizing effect. Besides, the presence of nanotubes could reduce entanglements and interactions among PLA chains, enhancing the motion of the polymer chains [20]. These two effects are probably the cause of the decrease in the T_g mentioned above.

Taking this into account, the huge elongation achieved by the PLA-DO3-CNTs film can be a consequence of its T_g value nearer

room temperature, what increases the PLA chains mobility at the tensile tests conditions. Moreover, very marked dull areas appear in the films during the stress-strain tests, implying strain-induced crystallization. Crystal drawing is usually associated to high elongations in semicrystalline polymers and it could be enhanced in the composite case by the improved chains mobility mentioned above. Simultaneously, the diffractogram shows more marked peaks in this case than in the case of neat PLA, denoting a more crystalline profile. This higher crystallinity added to the CNTs reinforcement effect could explain the fact that neither the modulus nor the stress at break decreased with the decrease in the T_g .

4. Conclusions

Ductility of PLA was strongly improved, with no detriment of its tensile strength. With the addition of such a small content as 0.05 wt% of CNTs together with 0.25 wt% of DO3, ϵ_b of the material increased from 4.7% for neat PLA to 47.5% for PLA-DO3-CNTs composite. Consequently, tensile toughness increased more than a 100%, expanding the possible applications of PLA, which were limited due to its brittleness. It is important to note that this was achieved without the need of covalent functionalization, thanks to the π - π staking between DO3 and CNTs.

Based on the obtained results, it is possible to develop novel nanocomposites from a biodegradable and renewable main raw material, reinforced with very small quantities of CNTs and DO3, with improved tensile properties.

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Appendix A. Supplementary material

Supplementary data associated with this article can be found in the online version at <http://dx.doi.org/10.1016/j.matlet.2016.06.090>.

References

- [1] H. Luo, Y. Ma, W. Li, G. Yi, X. Cheng, W. Ji, X. Zu, S. Yuan, J. Li, Shape memory-enhanced water sensing of conductive polymer composites, *Mater. Lett.* 161 (2015) 189–192.
- [2] C.B. Ustundag, Fabrication of porous hydroxyapatite-carbon nanotubes composite, *Mater. Lett.* 167 (2016) 89–92.
- [3] L.M. Famá, V. Pettarin, S.N. Goyanes, C.R. Bernal, Starch/multi-walled carbon nanotubes composites with improved mechanical properties, *Carbohydr. Polym.* 83 (2011) 1226–1231.
- [4] L. Ribba, M. Parisi, N.B. D'Accorso, S. Goyanes, Electrospun nanofibrous mats: from vascular repair to osteointegration, *J. Biomed. Nanotechnol.* 10 (2014) 3508–3535.
- [5] P. Seligra, M. Lamanna, L. Famá, PLA-fMWCNT bionanofilms with high modulus and great properties to apply in packaging and biomedicine, *Procedia Mater. Sci.* 8 (2015) 383–390.
- [6] R. Auras, L. Lim, S.E.M. Selke, T. Tsuji, *Poly (lactic acid) Synthesis, Structures, Properties, Processing, and Applications*, John Wiley & Sons, Inc., New Jersey, 2010.
- [7] B. Nam, K. Min, Y. Son, Investigation of the nanostructure, thermal stability, and mechanical properties of polylactic acid/cellulose acetate butyrate/clay nanocomposites, *Mater. Lett.* 150 (2015) 118–121.
- [8] P. Seligra, M. Lamanna, L. Famá, Promising PLA-functionalized MWCNT composites to use in nanotechnology, *Polym. Compos.* (2015).
- [9] N. Ljungberg, B. Wesslen, The effects of plasticizers on the dynamic mechanical and thermal properties of poly(lactic acid), *J. Appl. Polym. Sci.* 86 (2002) 1227–1234.

- [10] W. Chumeka, P. Pasetto, J.F. Pilard, V. Tanrattanakul, Bio-based triblock copolymers from natural rubber and poly(lactic acid): synthesis and application in polymer blending, *Polymer* 55 (2014) 4478–4487.
- [11] K. Hamad, M. Kaseem, F. Deri, Y.G. Ko, Mechanical properties and compatibility of polylactic acid/polystyrene polymer blend, *Mater. Lett.* 164 (2016) 409–412.
- [12] M.P. Arrieta, M.D. Samper, J. López, A. Jiménez, Combined effect of poly(hydroxybutyrate) and plasticizers on polylactic acid properties for film intended for food packaging, *J. Polym. Environ.* 22 (2014) 460–470.
- [13] M. Brzeziński, T. Biela, Polylactide nanocomposites with functionalized carbon nanotubes and their stereocomplexes: a focused review, *Mater. Lett.* 121 (2014) 244–250.
- [14] G. Díaz Costanzo, L. Ribba, S. Goyanes, S. Ledesma, Enhancement of the optical response in a biodegradable polymer/azo-dye film by the addition of carbon nanotubes, *J. Phys. D: Appl. Phys.* 47 (2014) 135103.
- [15] J. Cambiasso, S. Goyanes, S. Ledesma, Holographic gratings recorded in poly(lactic acid)/azo-dye films, *Opt. Mater.* 47 (2015) 72–77.
- [16] D. Sawai, T. Yokoyama, Crystal transformation and development of tensile properties upon drawing of poly(L-lactic acid) by solid-state coextrusion: effects of molecular weight, *Macromol. Symp.* 242 (2006) 93–103.
- [17] D. Fish, D.W. Xia, J. Smid, Solid complexes of lithium perchlorate with cross-linked polymers of α -methacryloyl- ω -methoxypoly(oxyethylene)s. Conductivities and morphology, *Makromol. Chem. Rapid Commun.* 6 (1985) 761–765.
- [18] J.A. Ramos, M. Larrañaga, I. Mondragon, W. Salgueiro, A. Somoza, S. Goyanes, G.H. Rubiolo, Correlation between nanohole volume and mechanical properties of amine-cured epoxy resin blended with poly(ethylene oxide), *Polym. Adv. Technol.* 20 (2009) 35–38.
- [19] R.J. Elwell, R.A. Pethrick, Positron annihilation studies of poly(methyl methacrylate) plasticized with dicyclohexyl phthalate, *Eur. Polym. J.* 26 (1990) 853–856.
- [20] S. Bhuvana, M. Prabakaran, Synthesis and characterisation of polyamide/halloysite nanocomposites prepared by solution intercalation method, *J. Nanosci. Nanotechnol.* 4 (2014) 44–51.