Furanoate Polyesters/Polylactide/Reduced Graphene Oxide Nanocomposite Films: Thermomechanical and Gas Permeation Properties

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This work aims at preparing bioderived polymer films by blending poly(lactic) acid (PLA) and poly(dodecylene 2,5-furandicarboxylate) (PDoF) and containing reduced graphene oxide (rGO) as a multifunctional filler in variable weight fraction (from 0.25 to 2 phr). Although the PLA/PDoF blend results as immiscible, the addition of rGO leads to smaller (from 2.6 to 1.6 μm) and more irregularly shaped PDoF domains and to a better PLA/PDoF interfacial adhesion, which suggests that rGO may act as a blend compatibilizer. Dynamic mechanical thermal analysis (DMTA) shows that rGO shifts the glass transition of PDoF ($\approx$5°C) to higher temperatures. The addition of 10 wt% PDoF in PLA increases the strain at break (+145%), and the addition of 0.25 phr of rGO to this blend increases its tensile strength (+13%), without significantly modifying the strain at break. Finally, rGO strongly decreases the diffusivity and permeability to O_2, N_2, and CO_2 due to an increased diffusion path for gas molecules. These results highlight the positive and sometimes synergistic role of PDoF and rGO in tuning the thermomechanical and gas permeation properties of PLA.

1. Introduction

Bioplastics, that is, plastics that are biodegradable and/or bioderived, are a promising alternative to traditional petroleum-derived polymers,[1–3] as they allow a remarkable reduction in the carbon footprint over the whole product life cycle, from resources extraction to the end of life.[4] However, their full potential can be exploited only after the identification of suitable applications, in order to address their main shortcomings and optimize the properties with sustainable fillers and additives.

This concept is also applicable to one of the most diffused bioderived and biodegradable biopolyesters, that is, poly(lactic) acid (PLA).[5–7] PLA is largely employed in the packaging industry, but its use is generally limited to rigid thermoformed items. In fact, the production of flexible PLA films is limited by its poor toughness, high sensitivity to moisture, and relatively low gas barrier properties.[6] To tackle these shortcomings, one of the most efficient and inexpensive methods is blending PLA with other polymers. For example, PLA could be blended with bioderived poly(alkylene furanoate)s (PAFs), synthesized from the polycondensation between 2,5-furandicarboxylic acid (FDCA) and a diol.[8] PAFs are suitable for packaging applications, as they exhibit thermomechanical and gas-barrier properties similar or superior to those of the corresponding fossil-based poly(alkylene terephthalates) (PATs).[9–11] Their properties can be tuned by varying the length of the diol alkyl chain, as longer diols result in higher ductility and crystallization kinetics and lower glass transition and melting temperatures.[12]

This work aims to prepare and characterize polymer films by blending PLA with 10 wt% of poly(1,12-dodecylene 2,5-furandicarboxylate) (PDoF) and to add reduced graphene oxide (rGO) to simultaneously enhance blend compatibility, thermomechanical properties, and gas barrier performance.

2. Results and Discussion

Figure 1 shows the scanning electron microscopy (SEM) micrographs of the cryofracture surface of PLA-PDoF10 and

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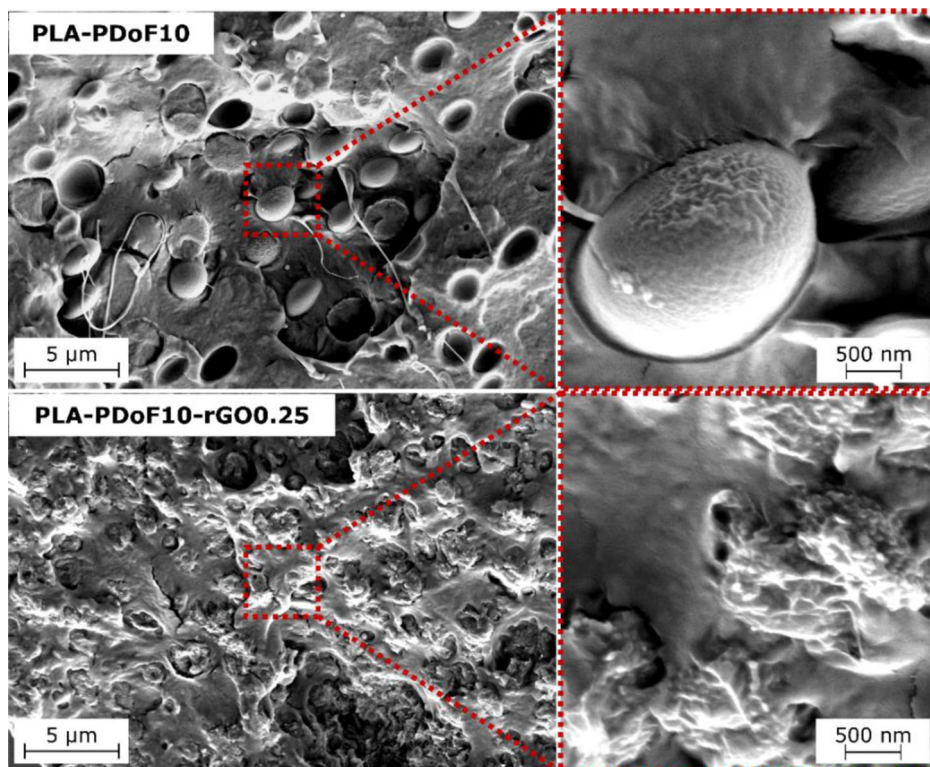
Figure 1. SEM micrographs of the cryofracture surface of PLA-PDoF10 and PLA-PDoF10-rGO0.25. PDoF, poly(dodecylene 2,5-furandicarboxylate); PLA, poly(lactic) acid; rGO, reduced graphene oxide; SEM, scanning electron microscopy.
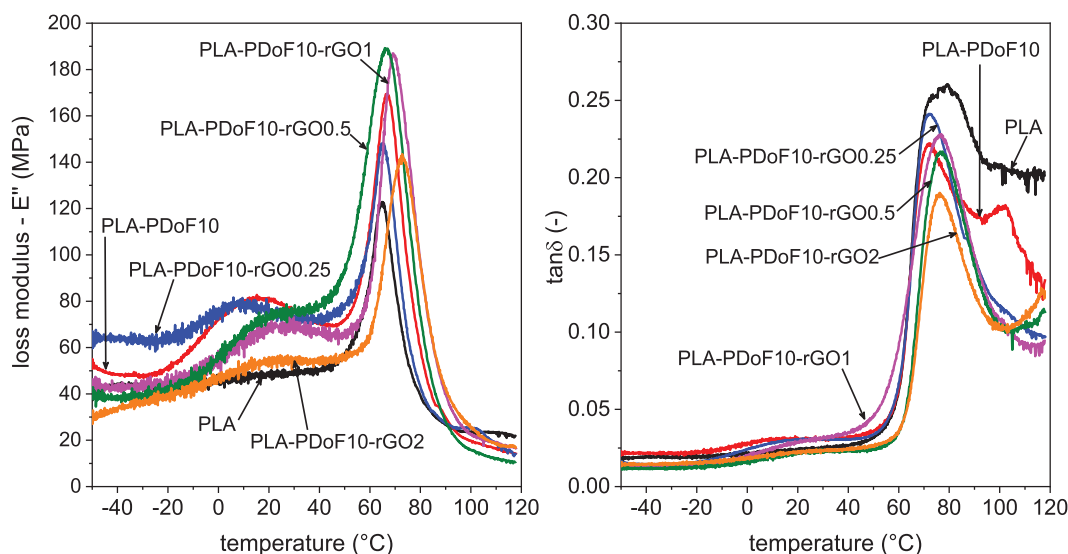

Figure 2. Dynamic mechanical thermal analysis (DMTA) thermograms of the prepared samples. Loss modulus (E'') and loss factor ($\tan\delta$) as a function of temperature.

PLA-PDoF10-rGO0.25. PDoF and PLA are immiscible and PDoF is visible as homogeneously distributed spheroidal domains with a rather smooth surface, an average diameter of 2.6 ± 0.4 µm, and a limited interfacial adhesion with PLA. The addition of 0.25 phr of rGO considerably modifies the morphology of PDoF domains, which become smaller (1.6 ± 0.3 µm) and rougher, while the interfacial interaction with PLA increases, thus suggesting an improved compatibility between the polymer phases. Similar effects are observable at higher rGO concentrations.

Dynamic mechanical thermal analysis (DMTA) was performed in tensile mode at 3°C min^{-1}, at 1 Hz and with a strain amplitude of 0.05% and the results are shown in **Figure 2**. The glass
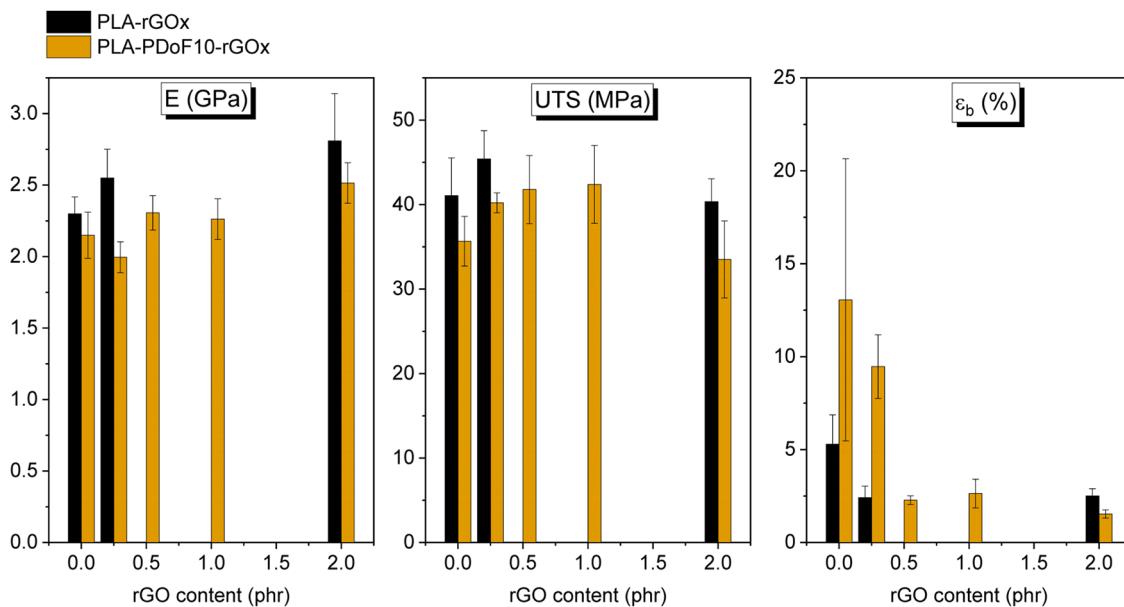
Figure 3. Main results of tensile tests on the prepared samples. Elastic modulus (E), ultimate tensile strength (UTS), and strain at break (ϵ_b) as a function of the reduced graphene oxide (rGO) content. Data from ref.[15]
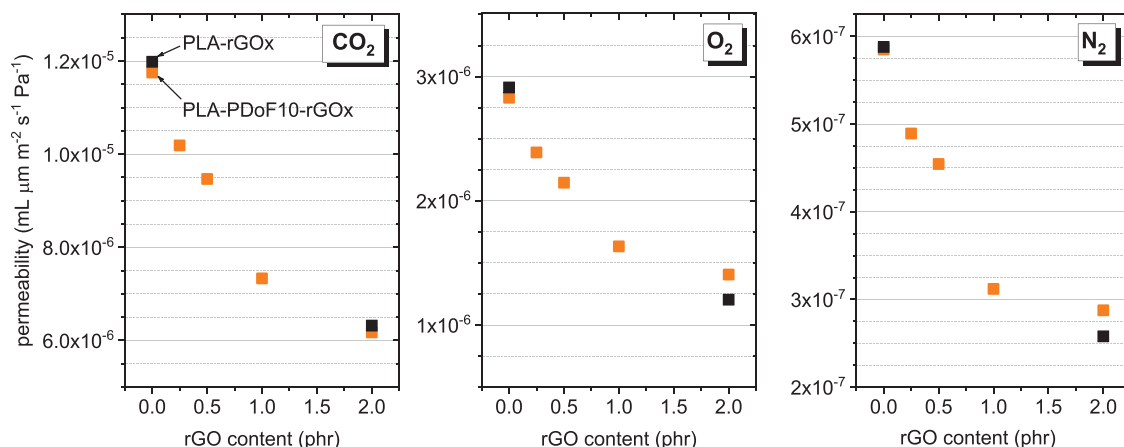

Figure 4. Permeability to CO_2, O_2, and N_2 as a function of the rGO content for the samples PLA-rGOx and PLA-PDoF-rGOx. Experimental indeterminations are inside the size of the symbols. Data from ref.[15] PDoF, poly(dodecylene 2,5-furandicarboxylate); PLA, poly(lactic) acid; rGO, reduced graphene oxide.

transition of PLA is observable at 60–70°C and that of PDoF at 0–10°C, which are both shifted to higher temperatures upon rGO addition. The sample PLA-PDoF10 also shows the melting transition of PDoF at 102°C in the tanδ signal, which is no longer visible after rGO addition, which could be due to the immobilization of PDoF chains performed by rGO.

Tensile tests (10 mm min^{-1}, gauge length 50 mm) show that the addition of rGO to PLA (**Figure 3**, black bars) increases the elastic modulus and decreases the strain at break. The ultimate tensile strength (UTS) increases with an rGO content of 0.25 phr, and then it decreases for an rGO content of 2 phr due to excessive nanofiller agglomeration, similarly to what is reported in the literature.[13] The addition of 10 wt% of PDoF (orange bars) leads to a slight decrease in the elastic modulus and UTS and to a

noticeable increase in the strain at break (+145%). Although the standard deviation is quite high, these results are in good agreement with our previous work on PLA/PAF blends, which also showed a strong increase in ductility with the addition of a small fraction of long-alkyl-chain PAFs.[14] The addition of 0.25 phr to this PLA/PDoF blend increases the UTS (+13%) and does not significantly modify the strain at break. Further additions of rGO increase the UTS, which is maximum for PLA-PDoF10-rGO1 (42.4 MPa). On the other hand, the UTS decreases to 33.5 MPa with an rGO content of 2 phr, which could be again due to excessive agglomeration of rGO.

Figure 4 reports the data of permeability to CO_2, O_2, and N_2 obtained with the experimental apparatus described in previous work.[15] For all gases, the permeability decreases by increasing

the rGO concentration, and this decrease is always accompanied by a similar decrease in diffusivity (not reported). This suggests that the improved gas barrier performance is due to reduced gas mobility rather than to a decreased solubility. Moreover, the reduction in permeability is of the same order of magnitude for all gases. Given the impermeable character of the nanoplatelets, the improvement of the gas barrier properties can be ascribed to longer diffusion paths for gas molecules.

3. Conclusions

In this work, PLA/PDoF/rGO nanocomposite films were prepared by solution casting and their properties were investigated as a function of the presence of PDoF (10 wt%) and the rGO content (0.25–2 phr). The results highlight the positive and sometimes synergistic function of rGO and PDoF in balancing the properties of PLA, thus obtaining polymer films promising for packaging applications. rGO proved to be an interesting multifunctional nanofiller for this blend, able to decrease gas permeability and enhance PLA/PDoF interfacial interaction, thereby increasing the thermomechanical properties. The results also evidenced that a further improvement in thermomechanical and functional properties could be achieved by decreasing the weight fraction of both PDoF and rGO to reach a finer and more homogeneous dispersion of the dispersed phases.

4. Experimental Section

The PLA Ingeo Biopolymer 4032D was provided by NatureWorks LLC (Minnetonka, MN, USA). PDoF has been synthesized via a two-step polycondensation from 2,5-dimethylfuran-dicarboxylate and 1,12-dodecamethylene glycol, and as reported in previous work.[16] A water suspension of graphene oxide (GO) (Graphenea, Spain) (4 mg ml^{-1}) was used to synthesize rGO. Twenty-milliliter GO suspension was added to a round bottom flask with 180 ml deionized water (DI). Then, a mass of hydrazine hydrate (HH) (Sigma–Aldrich) equal to that of rGO was added. The suspension was stirred at 100°C for 24 h, then filtered, washed with DI, and dried. PLA and PDoF were dissolved in a mixture of chloroform and hexafluoroisopropanol (HFIP) 9:1 v/v (1 g polymer in 25 ml solvent), and magnetically stirred for 2 h. Then, sonicated rGO-chloroform suspension was added and the mixtures were further stirred for 3 h, mildly ultrasonicated, cast in Petri dishes, and left drying at room temperature for 24 h and in a ventilated oven at 50°C for 5 h. The prepared 50-μm thick film samples were labeled as PLA-rGOx and PLA-PDoF10-rGOx, where PDoF10 indicates a 10-wt% content of PDoF and x represents the weight fraction of rGO in phr (x = 0.25, 0.5, 1, 2).

Acknowledgements

Conflict of Interest

The authors declare no conflict of interest.

Data Availability Statement

The data that support the findings of this study are available on request from the corresponding author.

Keywords

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