

Biodegradable nanocomposite for food packaging application

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Abstract

Biodegradable poly(lactic) acid (PLA)/clay nanocomposites were investigated to be used as food packaging material. Several techniques were used, rheology, mechanical, gel permeation chromatography (GPC), contact and biodegradability tests, to characterize the developed materials.

The addition of organoclay improved PLA mechanical and biodegradable properties. Food contact test showed that the nanocomposites are able to be used as food packaging materials.

Keywords: Poly(lactic) acid; nanocomposites; biodegradability; packaging applications

1 INTRODUCTION

Since the industrial revolution, in particularly after World War II, the breakthrough in materials research increased fast¹. Fossil fuel based plastics have brought many benefits to human life and became to be used in different applications, including textiles, electronics, healthcare products, toys and packaging². The use of plastics have resulted in their uncontrolled disposal in landfills, with consequent production of a wide range of harmful chemicals^{3,4}. For these reasons, renewability and biodegradability have become key criteria for sustainable plastic production and utilization³.

The non-biodegradable and non-renewable nature of plastics has led scientist to research for biopolymers derived from renewable sources as potential alternatives for conventional plastic materials. Nonetheless, when compared to conventional polymers, biopolymers have some drawbacks, such as relatively poor mechanical and barrier properties, processability and thermal stability, which limit its industrial application. Recently, a new class of materials, bio-nanocomposites, has proven to be a promising option to improve the properties of biopolymers⁵. Prepared by combination of polymers coming from natural resources (biopolymers) or synthetic biofunctional polymers and fillers that have at least one dimension in the nanometric range (1 to 100nm), bio-nanocomposites combine the intrinsic properties of natural polymers, as biocompatibility and biodegradability, with the typical properties of

nanoparticles, such as mechanical properties, high thermal stability and barrier properties. Concerning food quality and shelf life, great improvements have been achieved followed by reducing of plastic waste, which stimulates the exploration of new bio-nanocomposites for packaging^{6,7}.

The present work aims to develop and characterize a bio-nanocomposite to be used in food packaging. Nanocomposites were obtained by dispersion of a modified clay mineral in poly(lactic acid) (PLA) by melt mixing in a extruder. The effects of processing condition on PLA structure were evaluated by several technics. Biodegradability was assessed in aerobic environment compost medium. Reactivity and toxicological profile of the migrating substances of the bio-nanocomposites was also tested⁸.

2 MATERIALS AND METHODS

2.1 Materials

The commercial PLA grade (2003D) was acquired to NatureWorks LLC. The modified Montmorillonite, Cloisite 30B, was supplied by Southern Clay Products. Acetic acid was purchased from Sigma Aldrich and used as received.

2.2 Preparation of nanocomposites

PLA/C30B nanocomposites were prepared in modular co-rotating twin-screw extruder, Leistritz LSM 30.34. The barrel set temperature and screw speeds were kept constant at 190 °C and 100 rpm, respectively. Feed rate (Q) was set at 3 kg/h by a Moretto Dosing

System DVM18-L for all extrusion runs. The calender roll temperature was set at 40 °C.

2.3 Characterization

2.3.1 Rheological tests

The rheological behaviour of PLA and prepared nanocomposites were determined by oscillatory rheological measurements using a PaarPhysica MCR300 rheometer at 190 °C. The gap and diameter of the plates was 1 mm and 25 mm, respectively. Nitrogen atmosphere was used to prevent thermo-oxidative degradation. A frequency sweep from 0.1 to 100 Hz under constant strain in the linear viscoelastic region was performed for each sample.

2.3.2 Gel permeation chromatography (GPC)

GPC was used to determine the molecular weight distribution of the different polymer formulations. Solutions were prepared in THF (99.9%) and prefiltered on filter plate (hydrophobic polytetrafluoroethylene, 0.45 mm pore size) before injection. A Waters Alliance GPC Model 2695, equipped with 3 PLgel MIXED-B columns (inner diameter = 7.5 mm, length = 30 mm and particle size = 10 mm) and a Waters 2410 Differential Refractometer as detector, were used for the determination. THF was used as eluent with a flow rate of 1 mL/min and the temperatures were 25 and 35 °C at the injector and detector, respectively.

2.3.3 X-ray Diffraction

The diffraction patterns were obtained using a diffractometer (AXS Nanostar-D8 Discover, Bruker) equipped with a CuK α generator ($\lambda = 1.5404 \text{ \AA}$) at 40 kV and 40 mA, in a 2θ range from 0.08 – 10°. The clay mineral was analysed directly, whereas the nanocomposite sample was previously compression moulded into disks with a diameter of 20 mm and a thickness of 4 mm.

2.3.4 Stress-strain test

The mechanical properties of PLA and nanocomposite were characterized using stress-strain experiments in a Zwick Rowell equipment. The tensile experiments were carried out with a deformation rate of 50 mm/min at room temperature under a relative humidity of 50 %. The tests were performed on 8 x 0.6 cm rectangular samples in a longitudinal direction. At least 12 specimens of each sample were tested for each nanocomposite and the results were averaged.

2.3.5 Biodegradability test

Biodegradation of PLA and nanocomposite were assessed in compost environment at 40°C under aerobic conditions. Samples (25 x 25 x 0.125 mm) were placed in a composting medium made of soil, activated sludges from wastewater treatment, straw and animal manure. The composting medium was kept in a relative humidity of approximately 50 – 70 %. Around 20 samples of each material were vertically buried at 6 – 8 cm depth to guarantee aerobic degradation conditions at a horizontal distance of 5 – 6

cm between samples according to Fukushima⁹. At selected times (every 3 weeks), samples were collected, cleaned and dried at room temperature until constant weight was reached. Based on the sample weight before and after composting, the average percentage of residual mass for each material was calculated.

2.3.6 Contact test

Every polymeric film was acclimatized to 50% (w/w) humidity before the contact tests. Subsequently samples in the shape of cups exposed to a weak acid (pH 2.5) were placed in an electrical furnace and heated to 40 °C for 10 days. The weak acid solution was prepared using acetic acid 3% (w/v). After this process, the acid solution was recovery and its composition in aluminium, iron, magnesium and calcium determined.

3 RESULTS AND DISCUSSION

Rheological behaviour of nanocomposites depends both on the intercalation of the polymer chains and on the alignment of the silicate layers. Figure 1 shows the rheological results obtained for nanocomposite of PLA with 3 wt.% C30B. At low frequencies G' increases with the presence of clay. Such, was due to the increase in the solid-like or elastic nature of nanocomposite¹⁰. In fact, higher concentrations of clay provoke changes on G' slope at low frequencies, where G' start to becomes independent of frequency. Complex viscosity (η^*) of PLA/C30B follow the same trend as G' over the frequency range (0.01–100 Hz).

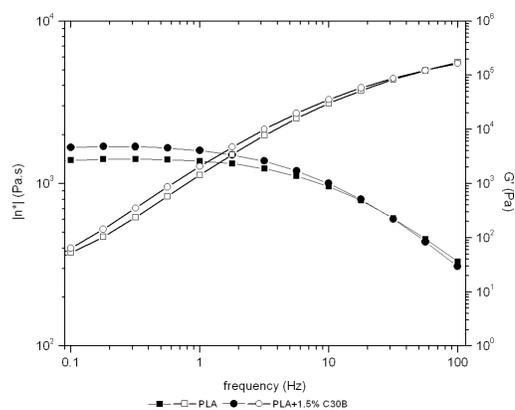


Figure 1. Rheological measurements for PLA and nanocomposite.

Figure 2 shows the mechanical properties PLA nanocomposite. Nanocomposite strain decrease compared with PLA. This might be due to the intercalation level of clay galleries within PLA matrix. XRD results (data not show) show that clay agglomerates can be present in the nanocomposites, since complete intercalation was not reached.

Agglomerates provoke microcracks at the interface of the nanocomposites, which appeared to lower strain and a subsequent premature yielding. Elongation at break is similar to the behaviour observed for such materials. Similar results were already published for our research group¹².

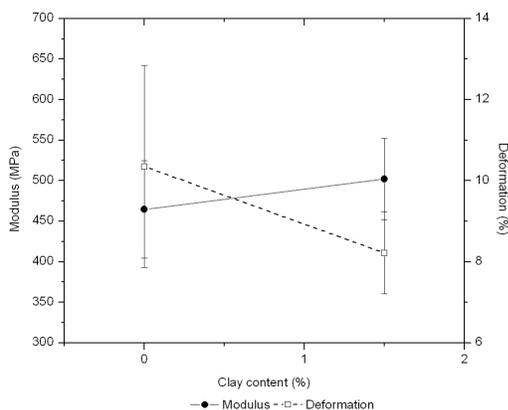


Figure 2 – Modulus (megapascals) and deformation at break (percent) for PLA and nanocomposites.

The PLA and PLA nanocomposites biodegradation was studied in composting medium. Figure 3 shows the PLA and PLA+1.5 wt.%C30B weight before and after different times in compost. The degradation of PLA in compost can, in principle, be accelerating by any factor that increases the hydrolysis tendency of PLA matrix. Experimental results show that the biodegradability of PLA and nanocomposite was similar in the first days. After 20 days in compost, the C30B catalytic effect was observed, enhancing the nanocomposite biodegradability comparatively to neat PLA. Clays have the capability to increase the polymer matrix hydrophilicity, allowing an easier permeability of water and activating the hydrolytic degradation process¹². In particular, C30B surface is modified with MT_2EtOH , introducing OH groups to improve clay dispersion, which also increase its hydrophilicity¹¹.

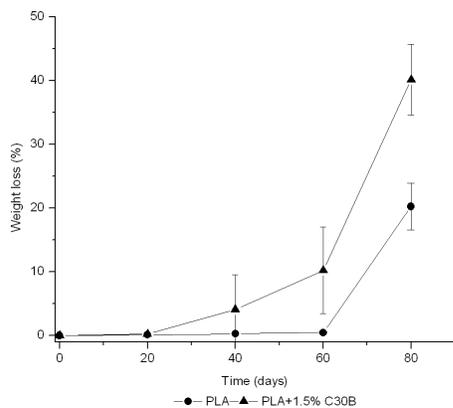


Figure 3 – PLA and nanocomposites biodegradability.

To assess the biodegradation of PLA and nanocomposite, the initial and collected samples were analysed by GPC (Figure 4). The samples molecular weight clear change after 80 days in composting medium. Chain scission was pronounced where unimodal initial distributions became bi-modals, indicating the presence of different types of molecules with lower molecular weights (higher retention time). As expected, the catalytic role of C30B on hydrolysis of the ester groups of the PLA matrix is confirmed in GPC results. The clay presence promotes a higher reduction in molecular weight.

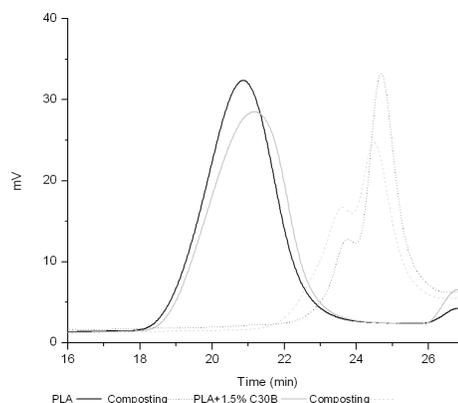


Figure 4. GPC curves of PLA and PLA+3%C30B before and after biodegradation in compost mediums.

In order to determine if synthesized PLA nanocomposite fulfil the recent regulations and European directives on food packaging, contact test using a food simulant were preformed. The overall migration limit (OML), defined 60 mg (of substances)/kg (of foodstuff or food simulant) for all substances as maximum migration. Specific migration limit (SML), specified the authorized substances and state individual limits based on toxicological evaluation. Table 1 present the migration results obtained. The contact of the PLA nanocomposites with food simulant does not produce a strong increase in Al, Ca, Fe or Mg. Thus, such results indicated that the produced biodegradable nanocomposites are safe and can be in contact with food.

To OML, 52.7 mg/kg was obtained, which satisfied the fixed limit to global migration of 60 mg/kg required for this packaging materials.

Table 1. Elements content determined in the liquid food simulant after contact with nanocomposite.

| Element | Weight (mg) |
|---------|-------------|
| Al | 0.058 |
| Ca | 1.55 |
| Fe | 0.14 |
| Mg | < QL |

4 CONCLUSIONS

Biodegradable PLA/clay nanocomposite was successfully obtained by melt mixing process in extruder. The dispersion of functionalised clay mineral results in the improvement of physical and mechanical properties.

Clay addition improved PLA biodegradability in aerobic environment compost achieving 40%. The developed nanocomposites revealed to be stable and suitable as food packaging materials according commission regulation N.10/2011.

5 ACKNOWLEDGMENT(S)

The authors acknowledge the n-STeP - Nanostructured systems for Tail, with reference NORTE-07-0124-FEDER-000039, supported by the **Programa Operacional Regional do Norte (ON.2)**.

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