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Development of amorphous PLA-montmorillonite nanocomposites

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The large amounts of plastics that are produced mainly from fossil fuels, once they are consumed and discarded into the environment, finally end up as undegradable wastes, and therefore contribute greatly to global pollution. For this reason, there is an urgent need to produce renewable source-based environmentally benign plastic materials, specially in short term packaging and disposable applications that could allow the composting of naturally occurring degradation products.

One of the most promising candidates in this direction is poly(lactic acid) (PLA), produced from renewable resources and readily biodegradable. PLA is a linear thermoplastic polyester produced by the ring-opening polymerization of lactide. Lactide is a cyclic dimmer prepared by the controlled depolymerization of lactic acid, which is obtained from the fermentation of sugar feedstocks, corn, etc. [1, 2].

In general commercial PLA grades are copolymers of poly(L-lactic acid) and poly(D,L-lactic acid), which are produced from L-lactides and D,L-lactides respectively. The ratio of L-enantiomers to D,L-enantiomers is known to affect the properties of PLA [3], i.e. if the materials are semicrystalline or amorphous; until now all the efforts reported in order to improve the properties of PLA are focused on the semicrystalline material [3], e.g. D-content less than 6%.

There is increasing interest in using PLA for disposable degradable plastic articles; however, there are properties such as flexural properties, gas permeability, impact strength, processability, etc. that are often not good enough for some end use applications [4]. On the other hand confinement of polymer in a two-dimensional silicate gallery, so-called polymer nanocomposite, is one of the effective ways to improve material performance [5]. The most widely utilized clay is the montmorillonite (MMT) for its large cation exchange capacity [5]. Ogata *et al.* [4] first prepared blends of PLA and organically modified montmorillonite by solution casting method; several authors since then have prepared PLA/modified monmorillonite using different techniques [3].

The melt intercalation process is a very convenient approach to make polymer layered silicate nanocomposites by using a conventional polymer extrusion process widely spread in the polymer processing industry [6]. In this process, the clay is intercalated and dispersed in the polymer melt by application of shear forces during compounding.

In this work, we report about our early efforts to develop new nanocomposites comprising completely amorphous PLA and montmorillonite with the main objective of obtaining new materials.

The PLA used in this work was a commercial product (GALASTIC®, containing 12 mol% D-lactide, manufactured by GALACTIC (Belgium). The montmorillonite used was supplied by LAVIOSA MINERARIA (Livorno-Italy): DELLITE 72T and DELLITE 43B. The two different types of organically modified montmorillonite (OMM) used in this study were synthesized by replacing Na^+ ions in different silicate layers by alkyl ammonium cations by ion exchange: dimethyl-hydrogenated tallow ammonium and dimethyl-benzyl-dihydrogenated tallow ammonium used in DELLITE 72T (OMMT) and DELLIT E 43B (OMMB), respectively.

Before processing, PLA was dried at 50 °C for 4 hrs under reduced pressure and then stored in the presence of humidity absorbent. For nanocomposite preparation, OMM (DELLITE in powder form) and PLA (pellets form) were first dry-mixed by shaking them in a bag. Melt blending of PLA with clay particles was conducted on an internal mixer (Rheomix-Haake) with a rotation speed of 20 rpm for 4 min, then at 60 rpm for another 4 min, at a temperature of 150 °C. Compositions with 4wt% OMM were compounded. From these materials,

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TABLE I Interlayer d-spacing obtained fromWAXS patterns for the OMM and the PLA/4OMM nanocomposites

Nanocomposite	Nanoclay (montmorillonite)	$d(001)_{\text{nanoclay}}$ (Å)	$d(001)_{\text{nanocomposite}}$ (Å)
PLA/4OMMT	DELLITE72T(OMMT)	26	35
PLA/4OMMB	DELLITE43B(OMMB)	19	31

polymer sheets (0.8 mm thick) were obtained by compression molding at 150 °C, with a total compression time of 4 min at 1.5 MPa. Solidification was performed in air until ambient temperature was reached.

Wide-angle X-ray experiments were performed using a Siemens D5000D equipment. Radial scans of intensity versus scattering angle (2θ) were recorded at room temperature in the range of 2–28 °(2θ) (step size $= 0.03$ °(2θ), scanning rate $= 8$ s/step) with identical settings of the instrument by using filtered Cu K_α radiation ($\lambda = 1.54$ Å), an operating voltage of 40 kV, and a filament current of 30 mA; WAXS experiments were carried out on dried clay samples, and on the compression molded nanocomposite sheets.

Transmission electron microscopy (TEM) was performed using a Jeol 1010 equipped with a digital Bioscan (Gatan) image acquisition system. Thermogravimetric analysis (TGA) was carried out using a Setaram TGA92 thermogravimeter at a heating scan of 10 °C/min from room temperature to 900 °C under air flow.

The structure of the nanocomposites in the nanometer range has been established using WAXS patterns and TEM observations [7]. WAXS is useful for the measurement of d-spacing in intercalated systems. Fig. 1 represents the WAXS patterns of pure PLA, OMM (OMMB and OMMT), and PLA/4OMM nanocomposites in the range of $(2\theta) = 2$–18 °. PLA pattern was characterized by a broad intensity maximum appearing approximately at $2\theta = 17$ °, indicating an amorphous structure for this sample. The mean interlayer spacing of the (001) plane for the OMM is 2.6 nm for OMMT and 1.9 nm for OMMB. Taking in to account that the d-spacing reported for Na^+-montmorillonite is 1.19 nm, it is clear that the WAXS data shift to smaller angles for the modified clays. Organic modification results in a substantial increase in the interlayer distance for montmorillonite, being higher for the OMMT, almost 1.5 nm.

In the case of PLA/OMM nanocomposites, two sharp peaks are obtained at $2\theta = 2.8$ ° (3.5 nm) for PLA/4OMMT and $2\theta = 3.16$ ° (3.1 nm) for PLA/4OMMB respectively, both corresponding to the (001) plane of the stacked and intercalated silicate layers dispersed in the PLA matrix. In this case the higher shift corresponds to the PLA/OMMB, ca. 1.2 nm, implying a higher interaction of the PLA with the OMMB inside the gallery, as a consequence of a lower steric repulsion of the one alkyl tail in comparison with two present in the OMMT nanoclay. However, the largest net shift (see Table 1) in the interlayer distance corresponds to the PLA/4OMMT system, dominated by the steric effect of the two long alkyl chains of the ammonium salt present in the OMMT nanoclay. TEM offers a qualitative understanding of the internal structure through direct visualization. Fig. 2a and b is TEM bright field image of the nanocomposites PLA/4OMMB and PLA/4OMMT; they show the typical result of a TEM bright field image in which dark entities are the cross section of stacked intercalated OMMB and OMMT layers and bright areas are the matrix [7]. In the TEM image, in addition to the observed stacked intercalated silicate layers with large anisotropy, it is possible to

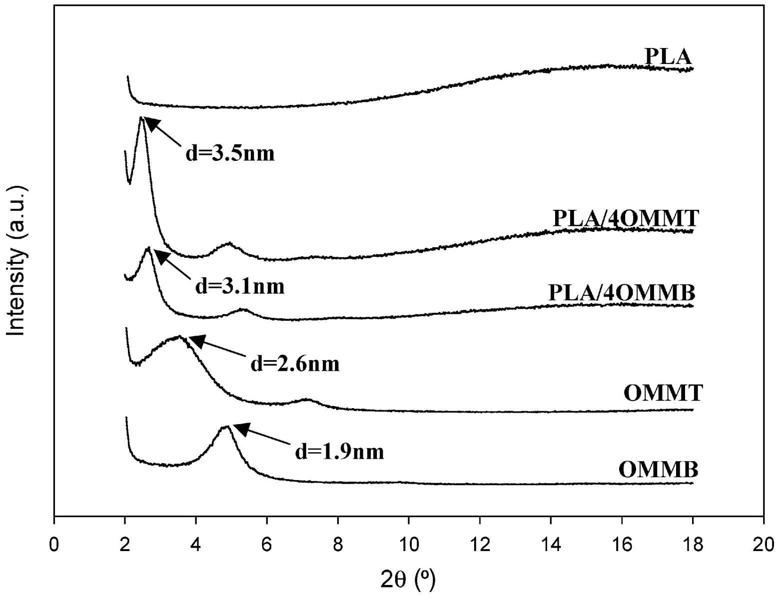

Figure 1 WAXD patterns curves for OMM nanoclays, PLA/4OMM nanocomposites and PLA.

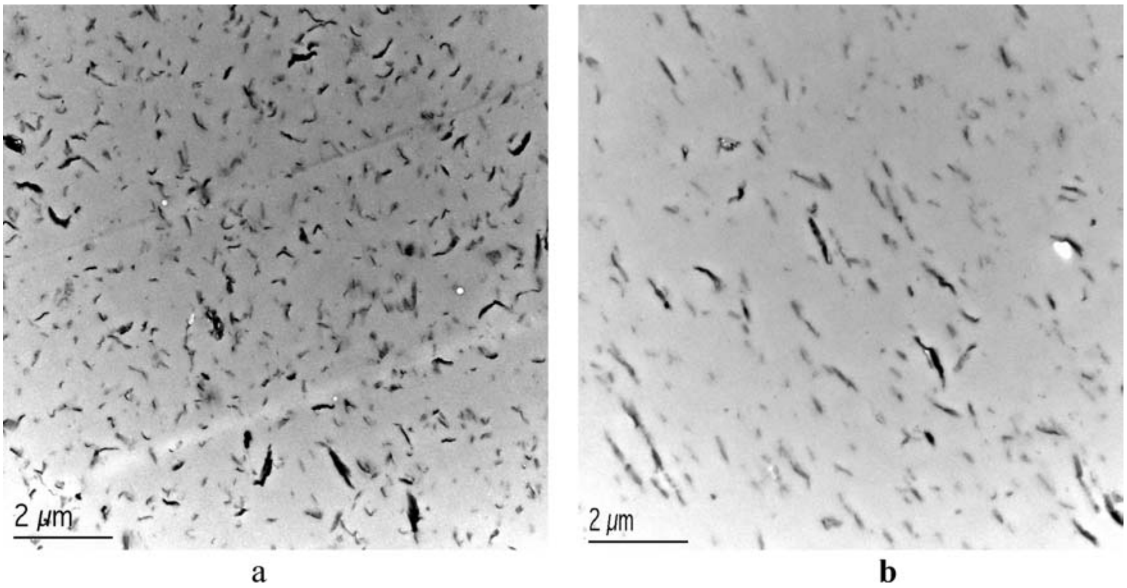

Figure 2 Bright field TEM images of PLA/OMM nanocomposites: (a) PLA/4OMMB and (b) PLA/4OMMT.

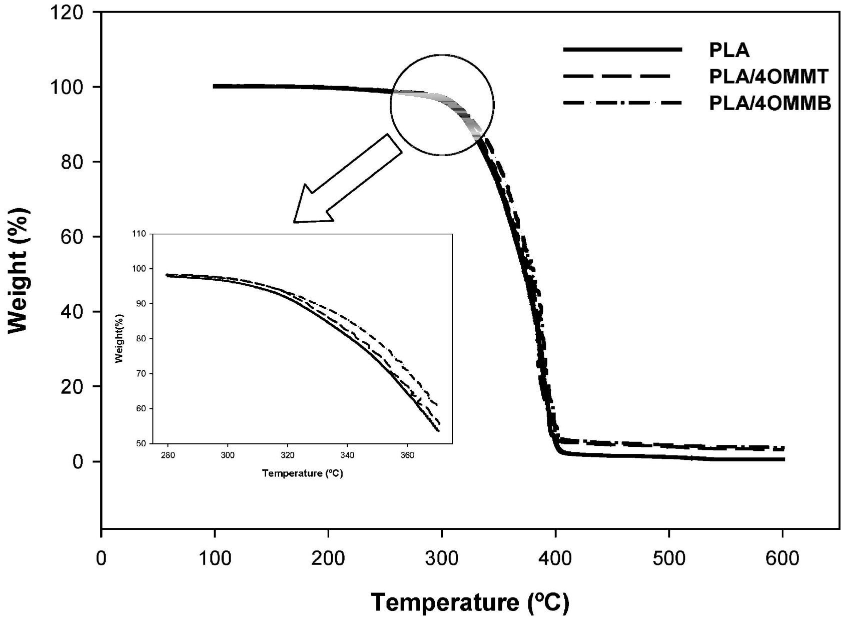

Figure 3 TGA curves for pure PLA and PLA/4OMM nanocomposites.

observe partially exfoliated layers which are randomly distributed in the PLA matrix. It can be concluded from Fig. 2 that PLA/4OMMB nanocomposites exhibit a higher dispersion than PLA/4OMMT, as a consequence of the higher interaction of PLA with OMMB nanoclay.

Based on the fact that inorganic silicates have good thermal stabilities, it is generally believed that the introduction of inorganic into polymers can improve their thermal stabilities. This increase in the thermal properties has been attributed to the higher thermal properties of clay and to the interaction between the clay particles and the polymer matrix [8]. Fig. 3 depicts TGA mass loss curves for the nanocomposites as well as for the neat PLA. The thermal stability of the PLA/OMM systems is not greatly affected by the presence of the modified montmorillonite, only a moderate increase in the onset of initial decomposition of PLA/OMMB system in comparison with the pure PLA and the PLA/4OMMT samples, as can be seen in detail in Fig. 3; this moderate increase in thermal stability for the OMMB in comparison with the OMMT can be attributed to the higher interaction and better dispersion of this nanoclay with the PLA matrix, as has been mentioned before. In contrast to the above-mentioned results, other studies of PLA (semicrystalline)/modified montmorillonite have reported either an increase in thermal stability [3] or a decrease in these properties [9]. These results point to a better understanding of the mechanism of the interaction between the clay particles and polymer matrix, including the effect of the organically modified clay in the crystallization behavior of semicrystalline PLA and how this could affect the thermal behavior of the PLA in addition to the effect of the nanoclay.

The mixing of amorphous PLA with 4% organically modified montmorillonite OMMT and OMMB can lead to nanocomposites with stacked intercalated and partially exfoliated layers' morphologies shown by WAXS and TEM analysis, in a simple melt blending step. The OMMB presents the higher interaction with PLA, reflected in the better dispersion of the organoclay in the PLA matrix. PLA/4OMMB nanocomposites exhibit a slightly higher thermal stability in comparison with neat PLA and PLA/4OMMT nanocomposites. From the above results, it can be generally concluded that there is great potential for amorphous PLA/OMM nanocomposites.

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