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Synthetic organofluoromica/poly(lactic acid) nanocomposites: Structure, rheological and thermal properties

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ABSTRACT

Organically modified fluoromica/poly(lactic acid) (PLA) nanocomposites were prepared by melt processing at different compositions in an internal mixer at the same conditions. Gel permeation chromatography (GPC) was used to measure the molar masses of PLA alone, before and after processing. The results indicated that PLA presented some degradation during melt mixing. With the addition of the organically-modified fluoromica, higher reduction in the polymer molar masses was found. The structure of the synthetic mica and of the clay polymer nanocomposites (CPN) was studied by small-angle X-ray scattering (SAXS), which revealed the presence of nanometer-sized clay mineral aggregates. Dynamical rheological measurements were carried out in the linear viscoelastic region for both PLA and CPN molten samples. A predominantly viscous behavior was obtained for the polymer samples, whereas the CPN presented a pronounced elastic behavior. Addition of mica to PLA also had a significant effect on the complex viscosity of PLA, imparting an increasing shear thinning behavior with increasing mica composition. Below T_g, dynamical mechanical analysis results showed a substantial decrease of rigidity of the CPN in relation to PLA alone, attributed to the presence of high content of organic intercalant in the synthetic fluoromica. Lower cold crystallization rate was detected for the CPN in comparison with processed PLA alone.

1. Introduction

Research on biodegradable materials has grown significantly over the last decade due to new requirements for environmental protection. It is also of high importance, considering that the oil reserves, the raw material for the manufacture of synthetic polymers, are exhaustible. In this sense, the development of materials based on biodegradable materials like poly(lactic acid) (PLA) becomes an important issue due to many factors. PLA is the front runner among alternatives to petroleum based plastics for disposable items due to its close similarity with poly(ethylene terephthalate) (PET) (Ahmed et al., 2009; Auras et al., 2004).

Over the last two decades, the addition of nano-sized layered silicates into polymeric matrices has been found to offer improvements to a great number of properties, such as thermal, rheological, mechanical, optical and physical properties over the neat polymer, with just a small quantity, typically in the range of 3–5 mass%. These clay polymer nanocomposites (CPN) have gained tremendous interest in both the academic and industrial areas due to their unique structure as well as properties (Dennis et al., 2001; Fischer et al., 1999; Fordiani et al., 2013; Messersmith and Giannelis, 1994, 1995; Ray et al., 2003). Layered clay minerals have been found to be useful in the design of nanocomposites due to their lamellar structure that have high inplane strength and stiffness and a high aspect ratio (>50).

A prerequisite to optimize the properties of CPN is the good dispersion (exfoliation or intercalation) and spatial distribution of the clay mineral layers in the matrix. So the interaction between the clay mineral and the polymer matrix is crucial for the nanocomposite morphology (Laza et al., 2007). Nevertheless, clay minerals have hydrophilic surfaces, which are incompatible with hydrophobic polymers. For this reason, to increase the interaction between clay mineral and polymer and thus improve properties, the clay minerals are treated with organic molecules (Zilg et al., 2000). Therefore, adequate selection of the organoclay/polymer pair with effective interaction to each other has become an essential criterion for obtaining high performance CPN.

In the present study, a synthetic mica organomodified with a quaternary ammonium salt containing a poly(propylene glycol) chain was used. Unlike natural micas (eg. muscovite mica), a synthetic mica is an expandable phyllosilicate with high aspect ratio and structure similar to montmorillonite. Synthetic clay minerals have as advantages over natural one typical features such as highest purity and composition that can be more easily controlled (Carrado, 2000; Jaber and Miéhé-Brendlé, 2005; Kloprogge et al., 1990a,b). Due to the high aspect ratio of individual layers, this organomodified fluoromica could generate CPN with high performance barrier properties and potential technological applications such as high gas barrier biodegradable packaging. Thus, this work reports the preparation of CPN based on Somasif MPE

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organofluoromica and poly(lactic acid) (PLA) as well as the structure, rheological behavior and thermal properties of these nanocomposites.

2. Experimental

2.1. Materials

Poly(lactic acid) (PLA) Ingeo 2002D from NatureWorks were used to prepare the CPN. Synthetic fluoromica (Somasif MPE) were obtained from CO-OP Chemical Co. The Somasif MPE is an organomodified fluoromica containing methyl-diethyl-polypropylene glycol ammonium (M2EPG) as intercalant (Fig. 1). According to the manufacturer, the Somasif mica have the general chemical composition: $(Na)_{2x}(Mg)_{3-x}(Si_4O_{10})(F_yOH_{1-y})_2 \cdot nH_2O$, where $0.15 < x < 0.5$; $0.8 < y < 1.0$.

2.2. Sample preparation

PLA can absorb a certain amount of moisture during storage, which may cause hydrolysis during melt processing, reducing its molecular weight, and thus compromising its properties. So it must be completely dried before processing in the molten state. Thus, before processing, PLA was dried for 4 h at 90 °C in a vacuum oven. Synthetic orgnomodified mica MPE, which is also capable of absorbing moisture, was dried under the same conditions.

Somasif MPE/PLA nanocomposites were prepared in a Brabender internal mixer with Roller type rotor (fill factor of 0.70) at 180 °C, 80 rpm for 5 min. Neat PLA was also processed under the same conditions for comparison purposes. CPN with Somasif MPE mica content 3, 5, 7 and 10 mass% were prepared.

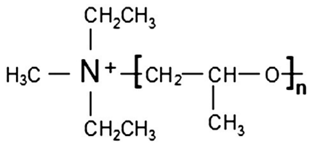
The samples for small angle X-ray scattering (SAXS) and dynamic mechanical analysis (DMA) were obtained by compression molding at 170 °C.

2.3. Gel permeation chromatography (GPC)

Molecular weights of PLA alone and in the CPN as well as non-processed PLA granules were measured by using gel permeation chromatography (GPC). For the CPN, the mica was removed from the solutions by filtration with a millipore filter. Also the molar mass of the mica's intercalant was measured after its Soxhlet extraction with THF for 72 hours. Measurements were conducted using an Agilent chromatograph with a Polymer linear column at 25 °C. Chloroform was used as the solvent and the flow rate was 1.0 mL/min with an injection volume of 20 μm. The results are expressed as “polystyrene equivalent” molar mass.

2.4. Melt rheology

Melt rheological measurements were performed on a TA Instruments Rheometer AR 2000, with a 25 mm parallel plate geometry, at 175 °C. The frequency sweep tests were performed in the range of 10^{-1}–10^{2} s^{-1} with 0.2% strain in order to maintain the response of materials in the linear viscoelastic regime.



$$H_3C-N^{+}(CH_2CH_3)_2-[CH_2-CH(CH_3)-O]_n$$

Fig. 1. Intercalant structure of Somasif MPE.

2.5. Small angle X-ray scattering (SAXS)

Small angle X-ray scattering experiments were carried out at the SAXS beam line of the Brazilian Synchrotron Light Laboratory (LNLS), Campinas (Brazil) with a fixed wavelength of 1.48 Å at room temperature. The scattering intensity $I(q)$ was plotted as a function of the scattering vector $q = 4\pi\sin\theta/\lambda$, where θ is the scattering angle. The scattering intensity was normalized by subtracting the background scattering.

The XRD and SAXS peaks were submitted to a deconvolution treatment with free peak-fitting software *fityk* [downloaded at http://www.unipress.waw.pl/fityk.].

2.6. Dynamic mechanical analysis (DMA)

Dynamic mechanical properties (storage modulus E' and tan δ) of the pure PLA and various CPN were measured with Q800 dynamic mechanical TA equipment. Experiments were carried out in the temperature range −20–120 °C at a frequency of 1 Hz with a heating rate of 3 °C/min using a tensile film clamp in strain mode at 0.01 N controlled force. The glass transition temperature, T_g, was defined as the temperature at the tan δ peak. The sample specimen dimensions were around 16.5 × 6.5 × 0.6 mm.

3. Results and discussions

3.1. Molar mass of PLA matrix

Table 1 presents average molar mass and polydispersities of PLA before and after processing as well as the molecular weights of PLA matrix in the CPN loaded with different mica content.

As expected, PLA processed in the internal mixer has lower molar mass than that of PLA granules, indicating a certain level of degradation during processing. With the addition of synthetic mica, a larger reduction in the molar mass, which is proportional to the content of synthetic mica is observed. The addition of mica in the polymer matrix has no significant effect on the polydispersity (M_w/M_n). These results suggest that, although the synthetic mica presents a high degree of purity as compared with natural clay minerals like montmorillonite, it slightly increases the degree of chain degradation, probably by some catalytic effect: both, the synthetic mica and its intercalant have hydroxyl groups in their structure which can attack the ester bond in the PLA chains, causing alcoholysis. Thus it is reasonable to think that the increase of the mica content in the CPN generates also an increase of the number of hydroxyl groups, promoting more chain break.

3.2. Nanostructural features of CPN

The nanostructure of the CPN were investigated by small-angle X-ray scattering (SAXS). Fig. 2 shows double logarithmic plots of the experimental scattering function $I(q)$ as a function of the scattering vector q for PLA, Somasif MPE mica and and the CPN.

SAXS technique is strongly sensitive to the electronic density contrast between nanodomains and the matrix in which such domains are dispersed. Therefore, even at very low volume fraction, SAXS allows the detection of domains of nanometer size dispersed in a medium of

Table 1
Molar mass (g/mol) and polydispersity of neat PLA and PLA in the Somasif MPE/PLA nanocomposites.

Sample	M_n	M_w	M_w/M_n
PLA	121,100	197,000	1.63
Processed PLA	98,300	160,800	1.64
PLA + 3% MPE	94,800	158,400	1.67
PLA + 5% MPE	89,000	143,400	1.61
PLA + 7% MPE	85,900	134,700	1.57
PLA + 10% MPE	78,300	132,000	1.68

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