



Research paper

The effect of different clays on the structure, morphology and degradation behavior of poly(lactic acid)



Ramesh Neppalli ^{a,1}, Valerio Causin ^{a,*}, Carla Marega ^a, Michele Modesti ^b, Rameshwar Adhikari ^c, Stephanie Scholtyssek ^d, Suprakas Sinha Ray ^e, Antonio Marigo ^a

^a Dipartimento di Scienze Chimiche, Università di Padova, via Marzolo 1, 35131 Padova, Italy

^b Dipartimento di Ingegneria Industriale, Università di Padova, via Marzolo 9, 35131 Padova, Italy

^c Central Department of Chemistry, Tribhuvan University, Kathmandu, Nepal

^d Institute of Physics, Martin-Luther-Universität Halle-Wittenberg, D-06099 Halle (Saale), Germany

^e DST/CSIR Nanotechnology Innovation Centre, National Centre for Nano-Structured Materials, Council for Scientific and Industrial Research, 1-Meiring Naude Road, Brummeria, Pretoria 0001, South Africa

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ABSTRACT

In this work, polylactic acid (PLA)-based nanocomposites filled with different kinds of clay were prepared and their structure, morphology and degradation behavior were compared. A similar degree of dispersion was achieved in the case of cationic and anionic clays. However, these two types of fillers had different effects on the structure and morphology. Perkalite, an anionic clay, induced higher crystallinity, a faster crystallization rate and also a modification of the crystallization mechanism. Moreover, when perkalite was used, the lamellar framework of PLA was preserved. Cationic clays, on the other hand, were detrimental for a regular crystallization of the PLA matrix, producing very disordered lamellar stacks. The effects of anionic and cationic clays were different also on the degradation behavior, with the perkalite-containing nanocomposite degrading much faster than either the matrix or the montmorillonite-reinforced materials. This comparison shows that a rational choice of the chemical nature of the nanofiller allows to tune both the degradation rate of PLA and its structure.

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1. Introduction

Modern society produces ever-increasing quantities of waste materials, which are causing environmental concerns. Many objects produced from polymers that derive from fossil sources, once they are consumed and discarded into the environment, finally end up as undegradable wastes and therefore contribute greatly to global pollution. Increasing environmental awareness and inconsistency in petroleum pricing opened a way to develop eco-friendly materials and to replace plastics which are mainly causing environmental problems. Research mainly focused on materials from renewable resources like agricultural products and thus polymeric materials from agro-based products are not only gaining interest for environmental concerns but also for political reasons.

The development of innovative biopolymer materials has been underway for a number of years, and continues to be an area of interest for many scientists. Among the most popular and important biodegradable polymers are aliphatic polyesters, such as poly(lactic acid) (PLA).

PLA is a linear thermoplastic polyester produced by the ring opening polymerization of lactide (Ray and Ramontjia, 2009). Lactide is a cyclic dimer which is obtained from the fermentation of sugar feedstocks, corn, etc. PLA has attracted considerable attention due to its renewable sources, biodegradation, biocompatibility, superior thermal properties, and the transparency of the processed materials (Tsuji and Suzuyoshi, 2002; Urayama et al., 2002). However, there are properties such as flexural properties, gas permeability, impact strength, etc. that are to be improved for widening the end use applications of this polymer (Feijoo et al., 2005; Ray and Okamoto, 2003).

A wealth of investigations was carried out on PLA, to improve material performance, and recently the strategy for achieving this aim was focused on the preparation of clay polymer nanocomposites (CPN) (Das et al., 2010; Hasook et al., 2006; Huang et al., 2010; Jollands and Gupta, 2010; Li et al., 2009; Maiti et al., 2002b; Ogata et al., 1997; Ray et al., 2002, 2003a, 2003b; Tabatabaei and Ajii, 2011). Most of the authors observed interesting increases in tensile and functional properties as a consequence of the addition of clay, however until now CPN did not fulfill all the expectations, because the improvement in mechanical properties was not substantial in comparison to conventional microcomposites (Kontou et al., 2011).

The most widely used cationic clay is montmorillonite, because of its large cation exchange capacity (Das et al., 2010; Hasook et al., 2006;

* Corresponding author. Tel.: +39 049 8275215; fax: +39 049 8275161.

E-mail address: valerio.causin@unipd.it (V. Causin).

¹ Present address: Division of Polymer Science, Department of Chemistry and Polymer Science, University of Stellenbosch, Private Bag X1, Matieland, South Africa.

Huang et al., 2010; Jollands and Gupta, 2010; Li et al., 2009; Maiti et al., 2002b; Ogata et al., 1997; Ray et al., 2002, 2003a, 2003b; Tabatabaei and Ajji, 2011).

Other types of layered filler, such as layered double hydroxides are less represented in the scientific literature (Dagnon et al., 2009; Katiyar et al., 2010; Pan et al., 2008). Layered double hydroxides (LDHs), known as anionic clays, consist of a stacking of positive hydroxylated layers $[M_1^{2+} \cdot x M_2^{3+} (OH)_2]^{x+}$ separated by interlayer anionic species and water molecules $[A_n^{q-} \cdot nH_2O]$, where M^{2+} is a divalent metal ion (such as Mg^{2+} , Zn^{2+}), M^{3+} is a trivalent metal ion (such as Al^{3+} , Cr^{3+}), and A is an anion with valency q (such as CO_3^{2-} , Cl^- , NO_3^-) (Leroux and Taviot-Gueho, 2005). LDHs have high charge density and a high content of interlayer anions and water molecules, resulting in strong electrostatic interactions between the sheets and strong hydrophilic properties. As a consequence, LDH layers tend to be more tightly stacked than montmorillonite. Moreover, LDH layers tend to be more fragile than those of montmorillonite (Marega et al., 2009 and references therein), allowing to tune the physical mechanical properties of composites containing layered fillers. Because of their highly tunable properties and unique anion exchange properties, LDHs are considered an emerging class of layered materials for the preparation of polymeric nanocomposites (Kohjiya et al., 2007). Pan et al. prepared by melt mixing PLA-based nanocomposites containing dodecyl sulfate-modified LDH, and observed a good dispersion of the filler within the matrix (Pan et al., 2008). These authors mainly focused on the crystallization behavior of the polymer, which experienced a nucleating effect due to LDH (Pan et al., 2008). Dagnon and colleagues prepared CPN with a PLA matrix filled with ibuprofen-modified LDH with the aim of balancing the mechanical properties and the cell proliferation on these materials (Dagnon et al., 2009). They obtained an increase in modulus and ultimate strength, while at the same time reducing cell proliferation thanks to ibuprofen release (Dagnon et al., 2009). Katiyar and coworkers recently compared the performance of PLA-based nanocomposites containing a combination of LDH and cationic clay with analogous materials just filled with cationic clay. The presence of LDH was found to be detrimental for gas barrier properties, to modify the crystallization behavior of the matrix and to increase the tendency to filler agglomeration (Katiyar et al., 2010).

Most LDH layers disperse homogeneously in a PLA matrix in the nanometer scale yielding intercalated or exfoliated structures. Incorporation of organically modified LDH brings considerable increase in the crystallization rate of PLA, because of the heterogeneous nucleating effect. With the presence of LDH, the nucleation density increases and the spherulite size reduces. Besides, it was found that incorporation of LDH has little or no discernable effect on the crystalline structure as well as on the melting behavior of PLA. As a consequence, it is considered that LDH could possibly be promising fillers for reinforcing biodegradable polyesters to produce biocompatible CPN (Pan et al., 2008).

Despite the relevant amount of work done on PLA-based nanocomposites, there are two aspects still underrepresented, which are the motivation of this paper. Firstly, few authors compared the performance at equal preparation conditions of anionic and cationic clays for the property improvement of PLA. Secondly, most reports focus on the investigation of the effect of clay on mechanical performance, but just a few highlight the relationship between the presence of clay, the crystallization behavior of the matrix and the degradation rate of the material.

2. Experimental

2.1. Materials

PLA, with D content of 1.1–1.7% was obtained from Unitika Co. Ltd. According to the supplier, it had a weight average molecular mass $M_w = 200$ kg/mol, density = 1.25 g/cm³ (ASTM 1238). Two different cationic clays i.e. Dellite HPS (deriving from a naturally occurring especially purified montmorillonite) and Dellite 43B (montmorillonite

modified with a quaternary ammonium salt, i.e. dimethylhydrogenated tallow ammonium) were kindly donated by Laviosa Chimica Mineraria s.p.a., Italy. Perkalite is an organically modified layered double hydroxide containing stearate, palmitate and carbonate anions (kindly donated by AkzoNobel Polymer Chemicals, Netherlands). All materials were dried at 50 °C prior to use.

All CPN were prepared with 3% of clay (W/W) in melt mixing in a camera mix (Barbender) at 190 °C. Mixing conditions were set at 80 rpm for 7 min, which were the parameters reported by Jollands and Gupta as optimal for maximum mechanical property improvement (Jollands and Gupta, 2010).

The obtained lumps were sliced into small pellets and then melt pressed in a hot press at a temperature of 190 °C in order to obtain films for further analysis. To obtain a crystalline material, all samples were annealed at 100 °C for 4 h. Only annealed samples were used for all further analysis. Filler level was kept constant in all cases, because it is reported that filler levels above 5% result in reduction of mechanical properties (Jollands and Gupta, 2010; Kontou et al., 2011).

The samples were coded according to the type of clay used for the preparation of PLA nanocomposites. For example, the CPN prepared with perkalite, was given the code PLA-PERK.

2.2. Wide angle X-ray diffraction (WAXD)

WAXD transmission patterns were recorded in the diffraction angular range 1.5–30° 2θ by a Philips X'Pert PRO diffractometer, working in the reflection geometry and equipped with a graphite monochromator on the diffracted beam (CuK_α radiation). The application of the least-squares fit procedure elaborated by Hindeleh and Johnson (1971) gave the degree of crystallinity by mass which was then transformed in degree of crystallinity by volume (ϕ_{WAXD}).

2.3. Small angle X-ray scattering (SAXS)

The SAXS patterns of the samples were recorded by an MBraun system, using a CuK_α radiation from a Philips PW 1830 X-ray generator. The data were collected by a position sensitive detector and were successively corrected for blank scattering, desmeared and Lorentz-corrected.

Finally, the Lorentz correction was applied: $I_1(s) = 4\pi s^2 I(s)$, where $I_1(s)$ is the one-dimensional scattering function and $I(s)$ the desmeared intensity function, being $s = (2/\lambda) \sin\theta$.

2.4. Differential scanning calorimetry (DSC)

All the measurements were carried out with a TA Instruments mod. 2920 calorimeter operating under N₂ atmosphere. Polymer samples weighing about 5 mg closed in aluminum pans were used throughout the experiments. Indium and tin of high purity were used for calibrating the DSC temperature and enthalpy scales. The kinetics of crystallization was studied by subjecting each sample to the following thermal cycle: after erasure of previous thermal history by keeping the polymer at 200 °C for 5 min, it was cooled at the maximum rate to the crystallization temperature (T_c). The heat evolved during the transition was monitored as a function of time during an isothermal at T_c of suitable length. The fraction X of material crystallized after the time t was estimated from the relation:

$$X = \frac{\int_0^t \left(\frac{dH}{dt}\right) dt}{\int_0^\infty \left(\frac{dH}{dt}\right) dt}$$

where the numerator is the heat generated at time t and the denominator is the total heat of crystallization. The Avrami equation (Avrami, 1941)

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