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Influence of organically modified clays on the properties and disintegrability in compost of solution cast poly(3-hydroxybutyrate) films

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ABSTRACT

Polymer nanocomposites, based on a bacterial biodegradable thermoplastic polyester, poly(hydroxybutyrate) (PHB), and unmodified montmorillonite Cloisite Na^+ (CNa) and chemically modified Cloisite 15A and 93A (C15A and C93A), were prepared through a solution route. The nanostructure has been established through X-ray diffraction (XRD), while the nanocomposites were characterized by differential scanning calorimetry (DSC), contact angle measurements, and thermogravimetric (TGA) analysis. Disintegrability in composting conditions has been tested at certain times (0, 7, 14, 21, 28 and 35 days at 58 °C) and the effect of different nanoclays on the properties of biodegraded films was deeply investigated. XRD results suggest a better dispersion for C15A and C93A based nanocomposites that present also a more surface hydrophobic nature respect to PHB matrix and PHB nanocomposite loaded with unmodified Cloisite. This result is in accord with disintegrability behavior of PHB nanocomposites. Visual observation, chemical, thermal and morphological investigations proved that the disintegration in composting conditions was faster for PHB_4CNa respect to the systems loaded with modified clays suggesting the possibility to modulate the disintegrability capacity of PHB selecting a specific filler.

1. Introduction

The quantity of plastic waste is increasing every year and the precise time needed for biodegradation is unknown. Environmental awareness has driven the development of new biodegradable materials, especially for single use plastic items. Polyhydroxybutyrate (PHB) is a biodegradable thermoplastic polyester accumulated as an energy/carbon storage or reducing power material by numerous micro-organisms under unfavorable growth conditions in the presence of excess carbon source [1]. PHB is a partially crystalline polymer with a high melting temperature and a high degree of crystallinity, then it is brittle and has limited applications [2]; moreover, it is still much more expensive and lacks mechanical strength compared with conventional plastics. If the properties of the PHB can be further improved by the addition of a small quantity of an environmentally benign material, this polymer will find applications in more special or severe circumstances; in this case, it will be also necessary to know its behavior to degrade in similar to the real disposal waste. Preparation of nanocomposites represent a good alternative for reducing the final cost and an effective alternative way to acquire a new material with desired and improved properties of native biodegradable polymers such as thermal, mechanical and oxidative barrier. Montmorillonite is among the most commonly used clay because it is environmentally friendly and readily available in large quantities with relatively low cost [3,4]. Addition of nanoparticles such as nanoclays to form nanocomposites [5,6] has provided the means to improve materials performance including biodegradation. One advantage of clay nanocomposites is their capacity to improve polymer barrier properties retaining the flexibility and optical clarity of the pure matrix [7,8]. Incorporation of an organic modifier onto the clay surface, to mediate between the polarity of the hydrophilic clay surface and that of the more hydrophobic polymer, has been widely adopted for compatibilization and for easy exfoliation of the clay platelets into the polymer matrix during processing. Thus, as expected, the organoclay dispersibility within a polymer matrix has been found to depend on factors such as type and quantity of surfactant, type of clay, as well as on the processing conditions. It is reported that with only a few percent of clay,

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PHB exhibits greatly improved mechanical, thermal and barrier properties compared with the pristine polymers [9]. Recently, biodegradable aliphatic polyester nanocomposites obtained by using melt processing have been reported in the literature [10–12], while few example of solvent cast nanocomposites of PHB with organically modified montmorillonite having as surfactant organic quaternary ammonium salts have been previously reported [13]. These solution cast composites displayed intercalated morphologies and exhibited improved thermal stability, except for contents of clay in excess of 6 wt%. Since a notable characteristic of PHB is its biodegradability in the environment, many papers deal with the degradation in compost of PHAs [14–16]. Specifically, biodegradation of polyhydroxyalkanoate nanocomposites was first reported by Maiti and his colleagues in 2003 [17], in which melt extruded nanocomposites based on organically modified showed a well-ordered intercalated structure and severe degradation tendency, with increase in biodegradation rate due to the presence of acid sites which catalyze the hydrolysis of the ester linkages. The biodegradation of PHB and its nanocomposites with montmorillonite clay was also studied by Maiti et al. [18]. In this case the biodegradation rate in presence of montmorillonite was studied at room temperature and at 60 °C (under and above the glass transition of the matrix) and the results confirmed that, at the two different temperatures, silicate reinforced PHB nanocomposites showed higher degradation rate with respect of neat PHB. Nevertheless, reduced biodegradability of polymer in presence of specific nanoparticle was also reported in the literature [19]. However, few reports exist on the influence of different nanoparticles (carbon nanotubes [20], carbon nanofiber [21] and graphene [22,23]) on the degradation behavior of PHB (and copolymers) nanocomposites obtained by solvent assisted processing and also in the case of solvent cast PHB/montmorillonite nanocomposites, few papers analyzed the behavior in compost of such materials [10,24–26].

In this research, we report the preparation of polymer nanocomposites based on a bacterial biodegradable thermoplastic polyester, poly(hydroxybutyrate) (PHB) loaded with 4 wt% of unmodified montmorillonite Cloisite Na^+ (CNa) and chemically modified Cloisite 15A and 93A (C15A and C93A), prepared by a solution process. The nanostructure and the dispersion of the clay in polymer matrix has been established through X-ray diffraction, while the nanocomposites were characterized by differential scanning calorimetry (DSC), contact angle measurements, and thermogravimetric (TGA) analysis. Disintegrability in composting conditions of the materials has been tested at different times (0, 7, 14, 21, 28 and 35 days at 58 °C) and the effect of different nanoclays and mainly the influence of their modification on the properties of biodegraded films were analyzed by morphological, thermal and chemical investigations.

2. Experimental part

2.1. Materials

Polyhydroxybutyrate (PHB), with M_n = 250,000g/mol, was kindly supplied in pellets form by PHB Industrial S. A., Brazil. Unmodified montmorillonite (MMT) Cloisite Na^+, and two organically modified (OMMT) ones, Cloisite C15A and Cloisite C93A, were supplied by Southern Clay Products (Texas, USA). The characteristics of the clays are shown in Table 1. PHB films were obtained by casting process in chloroform and stirred at 450 rpm (15 min) at 60 °C. The obtained solution was placed on glass Petri dishes and it was allowed to evaporate at room temperature. Nanocomposites were prepared following the same procedure, but a chloroform clay solution, previously sonicated, was added to the PHB solution. All nanocomposite films, containing 4 wt% of each type of montmorillonite (named PHB_4CNa, PHB_4C15A and PHB_4C93A), were stored in a desiccator at room temperature for 30 days to allow complete crystallization of PHB [27]. The film thickness was 0.05 mm.

Table 1
Organic modifier and the interlayer distance of the clays.

	Cloisite® Na+ (CNa^+)	Cloisite® 93A (C93A)	Cloisite®15A (C15A)
Organic modifier	–	CH3 | H – N+– HT | HT	CH3 | CH3 – N+–HT | HT
d(001)	11.7 Å	23.6 Å	31.5 Å

2.2. Methods

2.2.1. X-ray diffraction analysis (XRD)

A Philips PW 1710 X-ray diffractometer system with KCuα (λ = 1.54 Å) radiation was used to perform XRD analyses. Scans were recorded in the range of $2\theta = 2–36°$ at 2°/min with an X-ray tube operated at 45 kV and 30 mA.

2.2.2. Contact angle

The sessile drop method was used to determine the static contact angle of the films. Drops of 5 μl of doubly distilled water were placed on the material surfaces. Measures were done over six drops for each sample with a Ramé Hart model 500 Advanced Contact Angle Goniometer/Tensiometer equipped with the DROP image Advanced Software.

2.2.3. Differential scanning calorimetry (DSC)

Differential scanning calorimetric (DSC) experiments were performed on a Mettler Toledo 822e, in the temperature range from −25–200 °C, at a rate of 10 °C/min and under inert nitrogen atmosphere. Melting temperature (T_m) was determined as the maximum of the endothermic signal from the heating scan.

The overall crystallinity was calculated according to the equation (1):

$$Xc(\%) = \frac{\Delta H_m \cdot (m_C/m_P)}{\Delta H_0} \cdot 100 \quad (1)$$

where ΔH_m is the melting enthalpy measured from heating experiments, ΔH_0 is the theoretical enthalpy of 100% crystalline PHB (ΔH_0 = 146 J/g) [28], m_c is the nanocomposite weight and m_p is the weight of PHB in the nanocomposite.

2.2.4. Thermogravimetric analysis (TGA)

Thermal degradation measurements were carried out using a Seiko Exstar 6300 TGA/DTA system under nitrogen atmosphere (flow rate 250 ml/min). Temperature programs were run from 20 to 600 °C at 10 °C/min heating rate. The sample weight in each run was approximately 10 mg.

2.2.5. Disintegrability in composting conditions

Disintegrability of neat PHB and PHB composite films was observed by means of a disintegration test in composting conditions according to the ISO 20200 standard. A specific quantity of compost, inoculum supplied by Gesenu S.p.a., was mixed with the synthetic biowaste, and certain amount of sawdust, rabbit food,