

ENHANCED THERMAL STABILITY OF BIODEGRADABLE POLY(3-HYDROXYBUTYRATE)/LAYERED SILICATE NANOCOMPOSITES

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Introduction

Polymer nanocomposites are a class of materials that has already gained a big popularity among researchers both in academia and industry due to their exceptional properties, which are superior to those of the virgin polymers and of the conventional composites [1]. These hybrid materials consist of a polymer matrix in which inorganic particles with at least one dimension in the nanometer scale are homogeneously dispersed. In the case of polymer layered silicate nanocomposites, the high aspect ratio particles interact with the polymer matrix and improve substantially many physical properties of the pristine polymer including enhanced mechanical characteristics and barrier resistance, decreased flammability and increased biodegradability in the case of biodegradable polymers.

Recently, biodegradable and biocompatible polymers have received significant attention because they are environmentally friendly and are extensively used in biomedical applications. Poly(3-hydroxybutyrate) (PHB) is rapidly gaining recognition as one of the most promising biopolymers [2]. PHB is a linear, aliphatic polyester produced by different types of microorganisms. However, the poor thermal stability at temperatures slightly higher than its melting point restricts the application field of PHB.

In the present work, various loadings of montmorillonite organically modified by octadecylamine (C₁₈MMT) were dispersed in PHB by the melt intercalation method. The aim was to produce hybrid material with improved thermal properties over the pristine PHB. Morphological characterization of the composites was conducted by x-ray diffraction analysis (XRD). The effect of clay content on the thermal properties of the material was studied by differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA).

Experimental Section

Materials

PHB was obtained from Aldrich, while sodium montmorillonite (NaMMT) (CEC=92.6 meq/100 g) was supplied by Southern Clay Products (Texas, USA). Octadecylamine (C₁₈A), chloroform (CHCl₃) and concentrated HCl were purchased from Sigma-Aldrich. All materials were used as received and without any further purification.

Preparation of the organophilic layered silicate.

Organically modified montmorillonite (C₁₈MMT) was prepared through an ion-exchange reaction[3]. An amount of C₁₈A equal to 1.5 times the cation exchange capacity (CEC) of the inorganic material and an equivalent amount of HCl were dissolved in a 1:1 solution of ethanol and water at 75 °C. The inorganic material was dispersed in water at 75 °C and then, this aqueous suspension (3 wt%) was added to the alkylamine solution. The mixture was stirred vigorously for 24 h at the

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aforementioned temperature. The precipitate was collected by filtration and washed with a hot 1:1 solution of ethanol and water until the AgNO_3 test verified the absence of chloride. Eventually, the cation-exchanged montmorillonite was dried and ground to a powder, which was kept in a desiccator for further use.

Preparation of hybrid materials

Nanocomposites were fabricated with the aid of a microextruder-compounder (Minilab, ThermoHaake) at 175 °C and 130 rpm. The compounding time was 3 min. Constant nitrogen flow during nanocomposite preparation prevented thermal decomposition of the matrix. Eventually, nanocomposites with organoclay content ranging from 1 to 10 wt% were obtained.

Characterization

The structure of the nanocomposite materials was investigated by XRD using a Rich. Seifert 3003 TT diffractometer and Ni-filtered $\text{CuK}\alpha$ radiation ($\lambda=0.154$ nm). The scanning range was varied from $2\theta=2^\circ$ to 10° .

The thermal properties of the produced hybrids were explored with the aid of a Scimadzu DSC-50 differential scanning calorimeter (DSC). Temperature scans were carried out at a heating rate of 10 °C/min under constant nitrogen flow of 20 cm^3/min . The samples were heated to 180 °C and remained at that temperature for 2 min in order to release their thermal history and, afterwards, they were quenched to -5 °C. The determination of the thermal characteristics took place during the second run.

Thermogravimetric analysis (TGA) of the hybrids was performed on a Shimadzu TGA-50 with a heating ramp of 10 °C/min up to 750 °C under both flowing nitrogen (20 cm^3/min) and static air. TGA runs in isothermal conditions were also conducted at 190 °C in air.

Results and discussion

Organoclay morphology

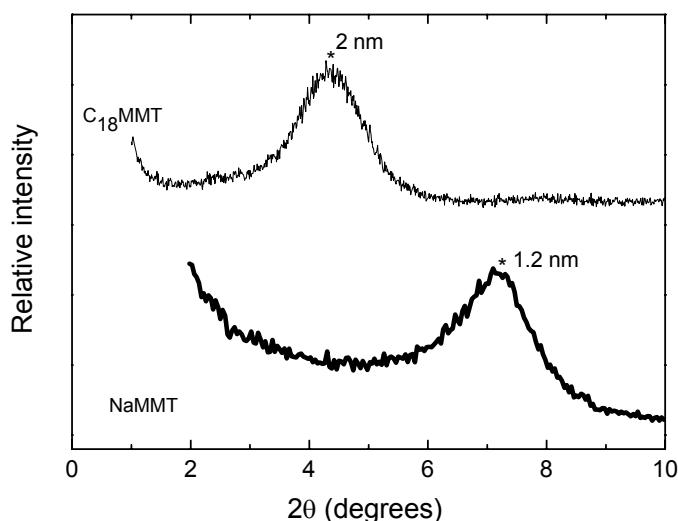


Figure 1. X-Ray diffraction (XRD) patterns of the natural and the organo-modified montmorillonite.

The basal spacing of both the natural (sodium) montmorillonite and the organically

(octadecylammonium cation) modified montmorillonite were investigated by XRD and the results are presented in Figure 1. It appears that the basal spacing of the natural mineral is 1.2 nm. Insertion of octadecylammonium ions into the interlayer spaces of the natural clay led to an increase of this spacing from 1.2 nm to 2 nm indicating a bilayer arrangement of the alkylammonium molecules [4, 5].

Structure of PHB hybrids

Figure 2 illustrates the diffraction patterns of the organoclay and the prepared nanocomposites. The characteristic peak corresponding to the basal spacing of the inorganic material is shifted towards lower 2θ values indicating that polymer chains have diffused into the clay galleries expanding the clay structure. This means, that the morphology of these composites is mainly intercalated, even though, exfoliated clay platelets may coexist. The intensity of the characteristic peak of the clay ($I_{d(001)}$) increases as the percentage of the organo-modified clay in the hybrid material becomes bigger. This is because the number density of the intercalated clay particles in the polymer matrix increases, as the clay content arises, and many more x-rays are diffracted.

Unlike PLLA nanocomposites [6] where the interlayer distance was strongly dependent on the organoclay concentration, the d-spacing of PHB nanocomposites, is not significantly affected by mineral loading.

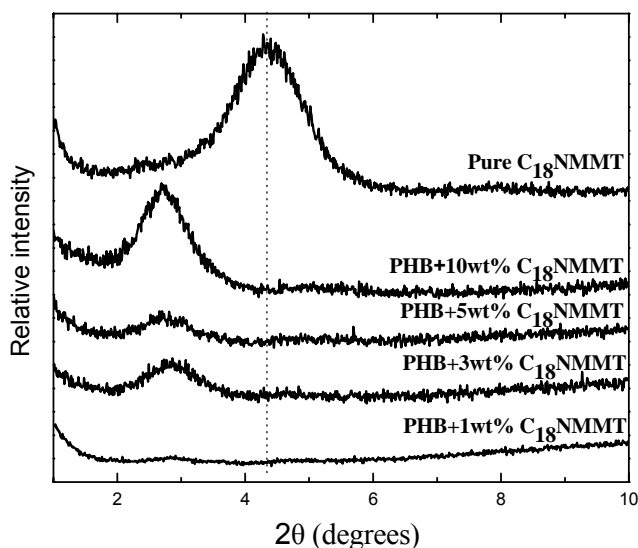


Figure 2. X-ray diffraction patterns of C₁₆MMT and PHB nanocomposites with various loadings of the organophilic clay.

Thermal behavior of PHB hybrids

Figure 3 describes the melting behavior of pure and nanocomposite PHB. It appears that the incorporation of the inorganic material affects the melting behavior of the polymer. Thus, an increase of the clay content causes a slight depression of the polymer's melting point.

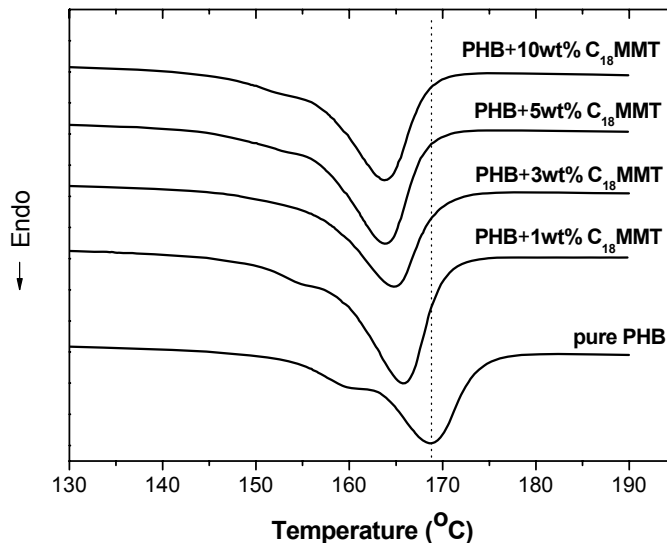
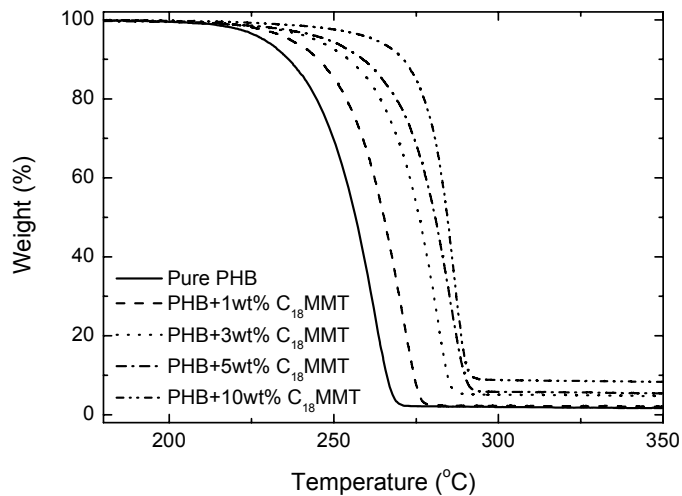


Figure 3. Melting endotherms of PHB nanocomposites with various organoclay loadings.

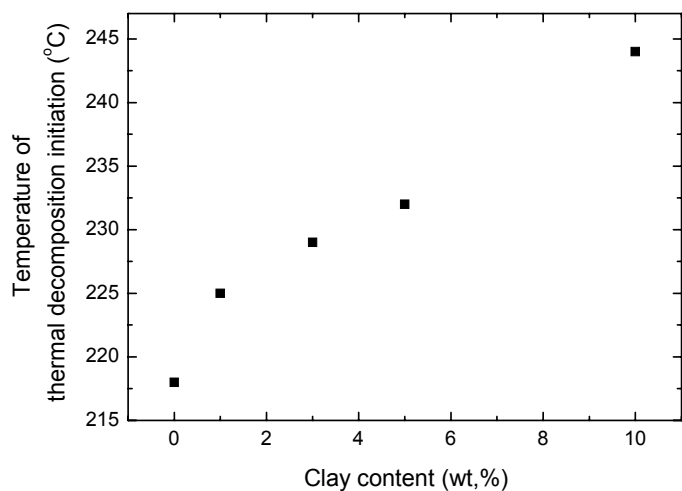
Figure 4a shows TGA data for pure PHB and its hybrids, which were taken in a N_2 atmosphere and in the temperature range of 150 °C, (where the samples are considered to be free of humidity), up to 750 °C. With a heating rate of 10 °C/min, PHB volatilizes completely in a single step beginning at about 220 °C. The introduction of organophilic inorganic material significantly improves the thermal stability of the polymer rising the temperature of decomposition initiation. This may be attributed to the labyrinth ('barrier') effect originated by the high aspect ratio clay platelets, which are dispersed in the polymer matrix delaying the escape of volatile degradation products within the nanocomposite [7].

Figure 4b presents the effect of the clay content on the temperature at which 2% of the material mass was lost, in the presence of nitrogen. It is clear that increase of the mineral loading enhances the thermal stability of the polymer. This in accordance with previous works [8].

The degradation properties of the polymer clay nanocomposites were also investigated under oxidative atmosphere and isothermal conditions (190 °C), as shown in Figure 5a. The organoclay addition significantly delays the polymer mass loss. As illustrated in Figure 5b, the nanohybrids, prepared by the incorporation of 10 wt% of organically modified clay, require almost five times the time that the pure polymer needs for a 40% mass loss. This greatly retarded material volatilization may be attributed to the formation of a carbonaceous-silicate char structure, which is produced on the surface of the nanocomposite during burning [9]. In the presence of oxygen, the intimate contact between the clay platelets and the polymer favors this char formation [10], which acts as an excellent insulator and mass transport barrier that delays the diffusion of oxygen from air to the polymer mass and slows down the escape of the volatile products generated during decomposition. Reduction in composite volume during volatilization improves this barrier property due to reassembly of the dispersed silicate layers [7].

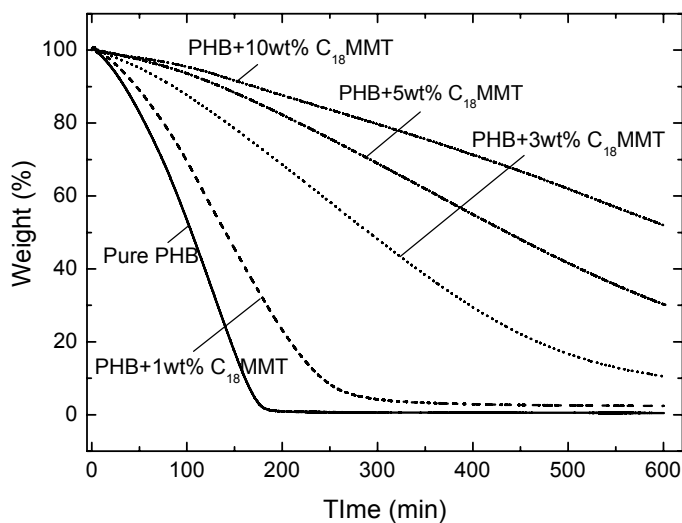


(a)

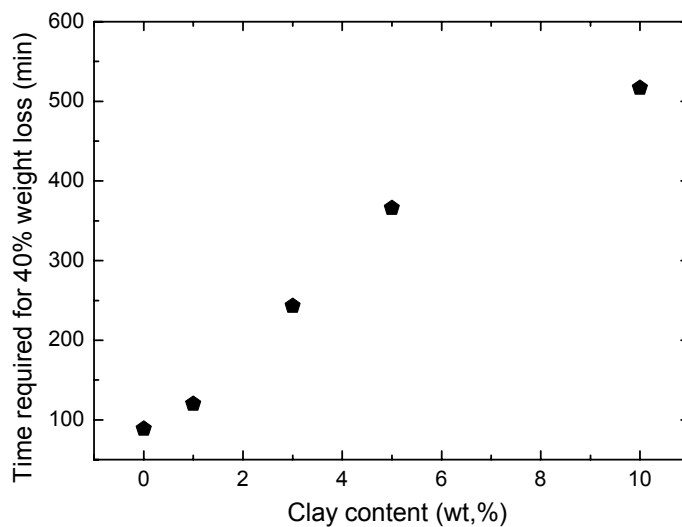


(b)

Figure 4. (a) TGA data for PHB hybrids prepared with various loadings of C₁₈MMT, in inert (N₂) atmosphere. (b) Effect of clay content on the onset decomposition temperature (estimated at 2% of polymer mass loss).



(a)



(b)

Figure 5. (a) TGA curves of PHB nanocomposites in oxidant atmosphere and isothermal conditions (190 °C). (b) Effect of clay content on the time required for 40% polymer mass loss.

Conclusions

PHB nanocomposites were successfully prepared by the incorporation of various loadings of organophilic montmorillonite using the melt intercalation method. Constant nitrogen flow during the preparation process prevented thermal decomposition of the matrix. Investigation of the composite structure revealed that the basal spacing of the inorganic material was not significantly affected by the mineral loading.

The nanocomposites displayed enhanced thermal stability compared to pure polymer. The dispersed inorganic platelets assist the formation of a protective layer on the surface of the polymer, which acts as an insulator and a mass transport barrier retarding the decomposition rate of the polymer matrix. Moreover, the organomodified clay presence led to a slight depression of the polymer melting point.

Acknowledgements

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