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Thermal degradation kinetics and isoconversional analysis of biodegradable poly(3-hydroxybutyrate)/organomodified montmorillonite nanocomposites

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ABSTRACT

Poly(3-hydroxybutyrate) (PHB)/organically modified clay nanocomposites were prepared by the melt mixing method and were characterized using wide-angle X-ray diffraction. Their thermal degradation kinetics was investigated using thermogravimetric analysis at various heating rates. Further kinetic analysis was performed using isoconversional methods and the invariant kinetic parameters method was used to estimate the so-called 'true' kinetic parameters, i.e. the pre-exponential factor, A and the activation energy, E, as well as the reaction model. It was found that intercalated structures are formed and the thermal stability of the material is improved by the addition of the nano-filler. From the isoconversional analysis, it was found that the activation energy does not vary significantly with the degree of degradation denoting degradation in one step with similar values for pure PHB and for all nanocomposites. Using the invariant kinetic parameters method, it was found that the model that best describes the experimental data was that of Sestak–Berggren's with $f(a) = \alpha^n(1-\alpha)^m$, where the value of n is always larger than m and is increasing with the amount of the nano-filler. The value of the 'true' activation energy was found to be about 100 kJ mol^{-1} for all nanocomposites and the pre-exponential factor for PHB was estimated equal to 5.35×10^9 min^{-1}. Finally, the values of the kinetic rate constant k were found to decrease with the amount of the nano-filler up to 3 wt%, while for amounts larger than 3 wt% k increased reaching a value greater than that of pure PHB for the 10 wt% nanocomposites.

1. Introduction

Recently, biodegradable and biocompatible polymers have received significant attention, because they are environmental-friendly and are extensively used in the biomedical applications. Since biopolymers are obtained from renewable resources, they represent an interesting alternative route to common non-degradable polymers for short-life range applications (packaging, agriculture, etc.). Poly(3-hydroxybutyrate) (PHB) is such a fully biodegradable, thermoplastic aliphatic polyester, produced by a wide variety of bacteria from cheap renewable raw materials, which has some physical and mechanical properties comparable to those of isotactic polypropylene [1]. Because of these properties, PHB has attracted a lot of attention by the research community. However, it has some drawbacks such as stiffness, brittleness, and most of all very low thermal stability at processing temperatures slightly higher than its melting point that prevent its commercial use to a bigger extent applications. The thermal instability of PHB in the melt prevents it from substituting the non-biodegradable polymeric materials in commercial products [2]. That is why improving the thermal stability of PHB is very important. There are several approaches to overcome these drawbacks of PHB: (a) biosynthesize series of copolymers containing hydroxyalcanoate units other than 3-hydroxybutyrate units, (b) prepare miscible blends of PHB with another bio-degradable polymer with suitable properties or plasticizer, and (c) synthesize block copolymers based on PHB. As an alternative to these conventional methods, the preparation of PHB nanocomposites is investigated here.

Polymer nanocomposites are commonly defined as the combination of a polymeric matrix and fillers that have at least one dimension (i.e. length, width or thickness) in the nanoscale. Nano-biocomposites are very promising materials, since they show improved properties with preservation of the material biodegradability, without eco-toxicity. Such materials are mainly destined to biomedical applications and different short-term applications, e.g., packaging, agriculture or hygiene devices. They, thus, represent a strong and emerging answer for improved and eco-friendly materials [3]. It has been shown that, only with a few percent of nanofiller (usually from 1 to 5 wt%), the polymer nanocomposites often exhibit greatly improved thermal, mechanical and barrier properties compared to pristine polymer. Commercially, the most important type of polymer nanocomposites are those produced

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using layered clay minerals (2:1 phyllosilicates), especially montmorillonite, that are naturally abundant, environmentally friendly and economic. Montmorillonite is usually chemically modified by a cation-exchange method, by which its sodium counterions are exchanged with adequate organic, usually alkyl ammonium, cations, in order to match its compatibility with polymer matrix, which is the key to successful preparation of polymer nanocomposites.

Thermogravimetric analysis (TGA) is a common experimental method used to study the overall or macroscopic kinetics of polymer degradation. The determination of the parameters of the thermal decomposition process provides more specific information regarding internal structures of polymeric materials [4,5]. However, apart from a simple TGA scan, further computational kinetic analysis is needed to probe the degradation mechanism, as well as to predict the thermal stability of polymers. Among others, isoconversional methods have been conceived by many researchers and widely used in the thermal degradation kinetic studies [6].

Although the thermal degradation kinetics of PHB and copolymers based on PHB has been studied in the literature [7–14] only two articles have been published so far on the non-isothermal degradation of PHB nanocomposites [15,16], in combination with other two for isothermal degradation [17,18]. In the work of Erceg et al. [15,16], nanocomposites of PHB with commercial organomodified MMT under the trade names Cloisite 25A and 30B prepared by the solution-intercalation method, were employed.

In the present work, various loadings of montmorillonite organically modified by octadecylamine (C_{18}MMT) were dispersed in PHB using a micro-extruder/compounder. The aim was to produce hybrid material with improved thermal properties over the pristine PHB. Constant nitrogen flow during nanocomposite preparation prevented thermal decomposition of the matrix. The nanocomposites were characterized by X-ray diffraction (XRD). Then, the non-isothermal degradation of pure PHB and PHB/C_{18}MMT nanocomposites, as well as the influence of C_{18}MMT on the thermal stability of PHB, was investigated and a detailed kinetic analysis of the process was performed using model-based and model-free methods. In particular, isoconversional methods were employed for the determination of the variation of the activation energy with respect to the degree of degradation and the invariant kinetic parameters were estimated together with the so-called 'true' activation energy and pre-exponential factor. Finally, a kinetic model was proposed and its parameters were evaluated.

2. Experimental

2.1. Materials

Poly(3-hydroxybutyrate) (PHB) was supplied by Sigma–Aldrich Chemical Co. and used as received. Sodium montmorillonite (NaMMT) with a cation exchange capacity (CEC) = 92.6 mequiv./100 g was obtained from Southern Clay Products (Texas, USA) and was dried in a vacuum oven at 80 °C for 24 h before use. Octadecylamine and concentrated HCl were purchased from Sigma–Aldrich and used without any further purification. Organically modified montmorillonite C_{18}MMT was prepared by an ion exchange reaction between NaMMT and octadecylammonium salt [19]. The relevant quantity of octadecylamine weighed out and through the cation-exchange proceeding received the final product. It was stored in a desiccator until its use.

2.2. Preparation of specimens

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The nanocomposites were prepared by melt mixing of PHB with different amounts of C_{18}MMT in a co-rotating twin screw micro-extruder (MiniLab® by Thermo-Haake). The melt mixing was carried out at 175 °C for 3 min and 130 rpm. Constant nitrogen flow was used during nanocomposite preparation in order to prevent thermal decomposition of the polymer matrix. Nanocomposites containing 1, 3, 5 and 10 wt.% of C_{18}MMT were prepared.

2.3. Measurements

Wide angle X-ray diffraction (WAXD): XRD patterns were obtained using an X-ray diffractometer (3003 TT, Rich. Seifert) equipped with Cu Kα generator ($\lambda = 0.1540$ nm). Scans were taken in the range of the diffraction angle $2\theta = 1–10°$.

2.4. Thermogravimetric analysis (TGA)

TGA was performed on a Pyris 1 TGA (Perkin Elmer) thermal analyzer. Samples of about 10 mg were used. They were heated from ambient temperature to 400 °C under a 20 ml/min nitrogen flow. TGA measurements of each sample were performed at different heating rates of 2.5, 5, 10 and 20 °C min^{-1} and sample mass versus temperature was continuously recorded.

3. Kinetic analysis of the TGA data

The kinetics of polymer degradation is usually described by the following single-step kinetic equation [6,20]:

$$\frac{d\alpha}{dt} \equiv \beta\frac{d\alpha}{dT} = k(T)f(\alpha) = A\exp\left(\frac{-E}{RT}\right)f(\alpha) \qquad (1)$$

where α represents the extent of reaction, which can be determined from TGA runs as a fractional mass loss, β is the linear heating rate, t is time, $k(T)$ a temperature dependent rate constant usually expressed by an Arrhenius-type expression with A and E the pre-exponential factor and the activation energy, respectively and $f(\alpha)$ denotes the particular reaction model, which describes the dependence of the reaction rate on the extent of reaction.

In Eq. (1), the mutual dependence of the Arrhenius parameters A and E, which, in turn, are affected by the choice of the kinetic model function, $f(\alpha)$, recommends that at least one of the kinetic triplet $[A, E, f(\alpha)]$ elements should be computed independently from the others. In this work, in order to estimate the kinetic parameters of the non-isothermal degradation of pure PHB and its nanocomposites with different amounts of C_{18}MMT both isoconversional methods (such as the method of Friedman's, Flynn–Wall–Ozawa's and Kissinger–Akahira–Sunose's) and the invariant kinetic parameters (IKP) method were used.

3.1. Isoconversional methods

Isoconversional methods employ multiple temperature programs (e.g., different heating rates) in order to obtain data on varying rates at a constant extent of conversion. Thus, isoconversional methods allow complex (i.e. multi-step) processes to be detected via a variation of E_α with α [6].

Simple rearrangement of Eq. (1) leads to Eq. (2), which forms the foundation of the differential isoconversional method of Friedman's [21]

$$\ln\left(\frac{d\alpha}{dt}\right)_{\alpha,i} \equiv \ln\left(\beta_i\frac{d\alpha}{dT}\right)_{\alpha} = \ln[A_\alpha f(\alpha)] - \frac{E_\alpha}{RT_{\alpha,i}} \qquad (2)$$