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Non-isothermal cold crystallization kinetics of poly(3-hydoxybutyrate) filled with zinc oxide

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ABSTRACT

The non-isothermal cold crystallization kinetics of poly(3-hydroxybutyrate) (PHB) and PHB-ZnO composites, with ZnO content of 1%, 5% and 10% per weight, was investigated at different heating rates (5, 7.5, 10, 15, 20 and 30 °C/min) using differential scanning calorimetry. Both, Kissinger and Friedman activation energies predict correctly the slowest and fastest crystallizing composition. It was further found, that ZnO can neither be classified as a crystallization accelerator, nor as a crystallization inhibitor; its action is strongly concentration dependent. The empirical Pseudo-Avrami model has the best overall capability for fitting the experimental kinetic data. However, since the Pseudo-Avrami exponent was found to vary irregularly with heating rate and filler content, this model should not be applied for kinetic predictions of an arbitrary composition or an untested heating rate. In such cases, Mo's model should be used.

1. Introduction

Nowadays consumer products based on polymers are produced in large quantities to fulfil the needs of modern society. Concerned with continuous improvements of polymer products properties but also with the preservation of the environment, we have focused our research on biodegradable polymers, which decompose after disposal through action of microorganisms after its intended purpose. The resulting environmentally abundant products are gases (CO_2, N_2), water, biomass, and inorganic salts. Such polymers are of significant interest to a variety of fields including medicine, agriculture, and packaging [1–9].

Biodegradable polymers are available from both natural and synthetic sources; their chemical reactivity is typically governed by ester, amide, and ether functional groups. Among these polymers, we have been investigating poly(3-hydroxybutyrate) (PHB), which has been obtained from the bacterial fermentation of sugar cane. PHB is a semi-crystalline thermoplastic polymer, completely biodegradable and biocompatible; it has been used in a number of industrial applications, including packing, food containers, prosthesis, suture threads, devices for controlled drug release, containers for plant germination, blankets for pesticides release, to cite some examples [10–15].

In this work we produced PHB-ZnO composites and investigated the effect of ZnO addition on the non-isothermal cold crystallization of PHB. Zinc oxide is an inorganic and inert compound, widely used as an additive in numerous materials and products. ZnO has been known as high refractive index material; it possesses a high thermal conductivity, antibacterial action (antiseptic) and UV-protection properties. For polymer science applications, ZnO is interesting when these properties can be transferred to the final products [16–20].

From previous works dealing with nonisothermal crystallization of PHB and its compounds filled with carbon black (CB) [21] and babassu natural fiber [22], it was verified that PHB partially crystallizes from the melt during cooling and partially cold crystallizes on reheating, with the amount of polymer crystallizing during each stage depending strongly on the cooling rate and the filler content. Kinetic analyses applying Pseudo-Avrami, Ozawa, and Mo models suggest that Pseudo-Avrami model fits the experimental data well for both compounds (PHB-CB and PHB-Babassu). Ozawa model does not fit PHB-CB data well and Mo model may be considered adequate if moderately deviations are accepted. Regarding PHB/Babassu compounds, Ozawa model was found to correlate the data well, provided that two different sets of parameters were used, one set for high and another set for low cooling rates. Mo's model

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did not adequately represent the experimental data for the systems and conditions tested.

In this work, the non-isothermal cold crystallization of PHB-ZnO composites with ZnO content ranging from 1% to 10% per weight was investigated by differential scanning calorimetry (DSC), applying heating rates ranging from 5 °C/min to 30 °C/min. The activation energies (E_a) of the cold crystallization process of PHB and PHB-ZnO composites were calculated by the isoconversional method of Friedman and via Kissinger equation. Furthermore, the crystallization kinetics was analyzed using the Pseudo-Avrami and Mo model.

2. Experimental

2.1. Materials

Poly(3-hydoxybutyrate) was supplied by PHB Industrial SA (Brazil) and was used without any further treatment. The compound was prepared by microorganisms from renewable sources (mainly sugar cane). The polymer is actually a random copolymer containing approximately 4% per weight 3-hydoxyvalerate units. The manufacturer indicates a glass transition temperature of 2 °C and a melting point of 168 °C.

Zinc oxide was purchased from Acros Organics (99.5% purity). Powder characterization by scanning electron micrography shows grain sizes from 200 to 300 nm. It has a specific area of 28 m^2/g (according to Brunauer–Emmett–Teller method) and band gap of 3.2 eV. In this work, ZnO was incorporated into the PHB matrix without using any dispersion agent.

PHB compounds containing 1%, 5% and 10% per weight ZnO were prepared in a Haake Rheomix 600 laboratory internal mixer fitted with high intensity rotors, with the chamber temperature kept at 180 °C. The nominal rotor speed was set at 60 rpm and the material was processed for 10 min. Samples of neat PHB were processed in exactly the same way for comparison purposes.

2.2. Differential scanning calorimetry

Non-isothermal cold crystallization kinetics of PHB and PHB/ZnO compounds were carried out in a TA Instruments DSC Q20 differential scanning calorimeter, under a nitrogen flow of 50 ml/min. First, samples weighting between 4 and 6 mg were heated to 190 °C and held this temperature for 3 min. Then, the melt was cooled to 20 °C and re-heated to 190 °C at predefined constant rates (5, 7.5, 10, 15, 20, and 30 °C/min). The heat flow was recorded as function of temperature and time and the exothermal (crystallization) peaks were analyzed. A typical DSC raw scan is displayed in Fig. 1; four thermal events can be identified: two endothermic melting events and the exothermic melt and cold crystallization events.

For the cold crystallization events, the start and end of departure from the underlying baseline were visually determined from the energy flow (J) versus time curve. Then the relative crystallinity x was calculated as a function of time by integration

$$x(t) = \frac{\int_{t_0}^{t} |J(t') - J_0(t')|dt'}{\int_{t_0}^{t_\infty} |J(t') - J_0(t')|dt'} \tag{1}$$

where $J(t)$ is the heat flux recorded by the DSC and $J_0(t)$ is a suitable virtual baseline; t_0 and t_∞ are the onset and end times of the crystallization event and t is an intermediate time related to a given value of x ($0 \le x \le 1$). The denominator in Eq. (1) represents the total heat for the observed crystallization process, while the numerator is a fraction of this heat, liberated during the interval t_0 to t. In this work all crystallization events were executed at a constant heating or cooling rate $\phi = dT/dt$, so an analogous equation for x as a function of temperature, $x(T)$, can be written down easily. A detailed description of the experimental procedure is given elsewhere [23,24].

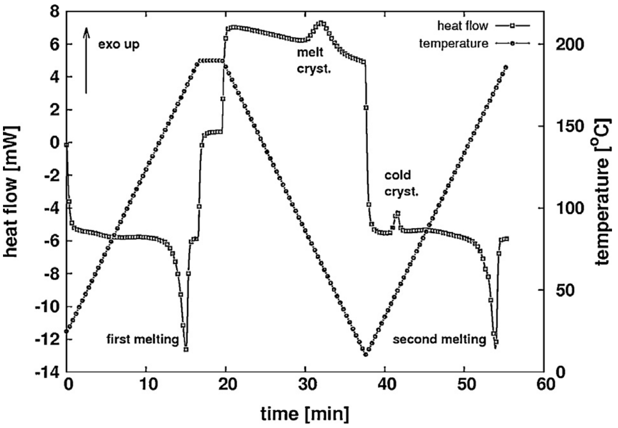

Fig. 1. DSC output of a neat PHB sample at 10 °C/min heating/cooling rate.

For kinetic analysis, it is assumed that the time dependent crystallization law can be written as

$$\frac{dx}{dt} = k(T)f(x) \tag{2}$$

where x is the extent of crystallized phase ($0 \le x \le 1$), t is time, $k(T)$ is the temperature dependent rate constant and $f(x)$ is a function related to the specific reaction model. As usual, this work considers the standard Arrhenius law as an expression for $k(T)$

$$\frac{dx}{dt} = A \exp\left(-\frac{E_a}{RT}\right) f(x) \tag{3}$$

where A is the pre-exponential factor, E_a is the activation energy and R is the gas constant. In this study only constant heating rates ϕ were considered:

$$\phi = \frac{dT}{dt}.$$

The relative crystallinity x can be easily calculated as a function of time or of temperature from the raw data according to Eq. (1). Then, dx/dT or dx/dt can be obtained via numerical differentiation.

Since the cold crystallization of any polymer might be dependent on the previous thermal history of the sample [25,26], we mention explicitly that in this study, all samples had undergone a melt crystallization event where the cooling rate was equal to the heating rate of the cold crystallization process.

2.3. Scanning electron microscopy

Scanning electron microscopy images were acquired with a TM-1000 unit, from Hitachi. The polymer samples were fractured in liquid nitrogen in order to avoid plastic deformation.

3. Results and discussion

3.1. Sample morphology

Fig. 2 shows a SEM image of a sample containing 10% per weight ZnO. The particles are quite homogeneously distributed in the polymer matrix, despite the fact that no dispersant was used during compounding. This behavior was observed for all composites produced (images not shown).