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Polymer Testing

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TESTING

ROGER BROWN

Material properties

Crystallinity study of nano-biocomposites based on plasticized poly(hydroxybutyrate-co-hydroxyvalerate) with organo-modified montmorillonite



Marcia Cristina Branciforti^a, Maria Clara Silveira Corrêa^{b,c}, Eric Pollet^b,
José Augusto Marcondes Agnelli^c, Pedro Augusto de Paula Nascente^c,
Luc Avérous^{b,*}

^a Universidade de São Paulo, Escola de Engenharia de São Carlos, Departamento de Engenharia de Materiais, Av. Trabalhador São-carlense 400, CEP13566-590 São Carlos, SP, Brazil

^b BioTeam/ICPEES-ECPM, Université de Strasbourg, 25 Rue Becquerel, 67087 Strasbourg, Cedex 2, France

^c Universidade Federal de São Carlos, Departamento de Engenharia de Materiais, Via Washington Luís km 235, CEP 13565-905 São Carlos, SP, Brazil

ARTICLE INFO

Article history:

Received 21 May 2013

Accepted 5 August 2013

Keywords:

Polyhydroxyalkanoates (PHA)

Organoclay

Nanocomposites

Crystallization

Mechanical properties

Aging

ABSTRACT

The influence of nanofiller, plasticizer and hydroxyvalerate (HV) contents on the properties of poly(hydroxybutyrate-co-hydroxyvalerate) (PHBV)/clay nano-biocomposites is studied. Analyses by wide-angle X-ray diffraction and differential scanning calorimetry showed that both the organo-modified montmorillonite clay and acetyl tributyl citrate plasticizer facilitate the crystallization process of PHBV. Despite its nucleating effect, the nanoclay hampers the spherulite growth and leads to a reduction in the copolymer crystallinity, while the addition of plasticizer induces the formation of thicker spherulites.

For all studied systems, it was shown that the variation of mechanical properties of these nano-biocomposites is strongly influenced by their changes in crystallinity.

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1. Introduction

The current search for economically viable and environmentally friendly new materials has led to many studies aiming at improving the processability and properties of biodegradable and biobased polymers. Polyhydroxyalkanoates (PHAs) have been extensively studied because they are produced by bacteria, derived from renewable sources, are completely biodegradable and have properties close to those of conventional plastics. The poly(hydroxybutyrate) (PHB) and poly(hydroxybutyrate-co-hydroxyvalerate) copolymer (PHBV) are the main representatives of this family of biodegradable polyesters [1,2].

Among the different tacticities, the only one for PHB obtained by bacterial fermentation is the isotactic form. PHB obtained by biosynthesis is extremely regular, resulting in high crystallinity and the formation of large spherulites [1,2].

When PHB samples are submitted to mechanical testing at various post-processing times, a great change in mechanical behavior is observed with, for example, dramatic reduction in elongation at break. This increased fragility reflects the aging of the material with time. Some reasons that contribute to this aging are: secondary crystallization of the amorphous phase at room temperature; glass transition temperature close to room temperature; low density of nucleation, which promotes the appearance of “large” spherulites, inter-spherulitic cracks and amorphous regions confinements, with consequent deterioration of the mechanical properties [3].

* Corresponding author. Tel.: +33 3 68852784; fax: +33 3 68852716.
E-mail address: luc.averous@unistra.fr (L. Avérous).

Various studies focused on the crystal structure of PHAs [4–6]. From these studies it was concluded that PHB crystallize in an orthorhombic unit cell packing with helical shape with two-fold axis along the direction of propagation of the chain. In the case of PHBV, with the increase in the amount of HV, the crystalline structure changes from the PHB homopolymer to that of PHV. This phenomenon is known as isodimorphism [2].

The main characteristics of PHBV are, except the isodimorphism phenomenon, that it presents slow crystallization and high degree of crystallinity. Possible solutions have been studied to minimize these problems, among them are studies focused on the production of nano-biocomposites using lamellar clays as filler [2]. However, these nanoclays and their corresponding organo-modifiers can increase the thermo-mechanical degradation during molten state processing [7,8].

Recently, some of us reported a very promising study about the addition of plasticizer (acetyl tributyl citrate – ATBC) to PHBV nano-biocomposites with organo-modified montmorillonite clay (PHBV/OMMT) [9]. In the present study, differential scanning calorimetry (DSC) and wide-angle X-ray diffraction (WAXD) have been used to investigate the changes in the crystallization behavior and the crystalline structure of PHBV with the incorporation of organoclay (OMMT) and plasticizer (ATBC), as well as variations in the HV content of the copolyester.

2. Experimental section

2.1. Materials

Poly(hydroxybutyrate-co-hydroxyvalerate) (PHBV) was provided by PHB Industrial S.A. (Brazil) with three different amounts of hydroxyvalerate (HV), 2, 10 and 18 mol%. The nanoclay, Cloisite 30B[®], is an organo-modified montmorillonite (OMMT) with methyl tallow bis-2-hydroxyethyl quaternary ammonium salt, supplied by Southern Clay Products (USA). The plasticizer used in this study was acetyl tributyl citrate (ATBC) provided by Scandiflex S.A. (Brazil). All these products were used without further purification except thorough drying prior to use.

2.2. Sample preparation

PHBV samples of different HV content were prepared with and without addition of plasticizer and nanoclay. The compositions of the different samples are listed in Table 1. The nomenclature for sample codes is the following: numbers before V indicate the content in HV units in the copolyester, numbers before the letter N indicate the clay loading (wt. %) in the material, and numbers before the letter A indicate the amount of ATBC plasticizer in wt. %.

Sample preparation involved first processing by melt blending in a Haake Rheomix 600 internal batch mixer equipped with Rheocord 9000 Control System, using roller rotors, at 100 rpm and 150–155 °C, for 10 min. In a second step, the final materials were produced by twin-screw extrusion, using a B&P Process Equipment and Systems model MP19 with a 19 mm diameter screw, L/D ratio of 25 and high shear screw profile. The speed was 90 rpm and the

Table 1
Nomenclature and composition of the studied samples.

Sample (Code)	HV (mol %)	ATBC (wt. %)	OMMT (wt. %)
PHB2V	2	–	–
PHB2V3N	2	–	3
PHB2V10A	2	10	–
PHB2V3N10A	2	10	3
PHB10V	10	–	–
PHB10V3N	10	–	3
PHB10V10A	10	10	–
PHB10V3N10A	10	10	3
PHB18V	18	–	–
PHB18V3N	18	–	3
PHB18V10A	18	10	–
PHB18V3N10A	18	10	3
PHB18V1N	18	–	1
PHB18V5N	18	–	5
PHB18V15A	18	15	–
PHB18V20A	18	20	–

feeding rate was kept at 1 kg h⁻¹. After granulation and drying overnight, samples were molded with a Battenfeld Plus 35 injection molding machine. For PHBV with or without nanofillers, the temperature profile was kept constant, and it was only decreased with plasticizers. The processing parameters used in the twin screw extruder and in the injection molding machine were similar to those reported in a previous work [9].

2.3. Characterization

Size exclusion chromatography (SEC) measurements were performed using a Shimadzu liquid chromatography apparatus (Japan) equipped with a refractive index detector model RID-10A and a diode array UV detector model SPD-M10A. The columns set used was composed of a 50 mm PLgel Guard 5 μm column, two 300 mm PLgel MIXED-C 5 μm columns and a 300 mm PLgel 5 μm-100Å column. Calibration was done with polystyrene standards. Chloroform was used as the mobile phase with a flow rate of 1 mL min⁻¹, and the analyses were carried out at 30 °C.

The crystalline structure of the samples was studied by wide angle X-ray diffraction (WAXD) using a Siemens D5000 diffractometer with CuK_α radiation (1.5406Å) operating at 40 kV and 40 mA, at room temperature in the 2θ range of 1.5 to 40° at 0.1° min⁻¹. Samples for WAXD analysis were thin films obtained by compression moulding at 170 °C for 5 min and 150 bar.

Differential scanning calorimetry (DSC) measurements were carried out on a DSC 2910 (TA Instruments) under nitrogen atmosphere. The analysis conditions were: first heating ramp from 20 to 180 °C or 200 °C (depending on the sample and study), isotherm for 1 min; cooling to –50 °C or –80 °C (depending on the sample), isotherm for 1 min; and finally a second heating ramp to 200 °C. All heating and cooling rates were 10 °C min⁻¹. From the DSC curves, the melting (T_m) and the crystallization temperatures (T_c), as well as the melting (ΔH_m) and the crystallization enthalpies (ΔH_c) were determined.

For PHBV with 2 mol% of HV, the value of 100% crystalline PHB, ΔH_m⁰ = 146 J g⁻¹ was used as a good approximation for the calculation of the crystallinity (X_c). For materials with HV contents equal or higher than 10 mol%,

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