Nonisothermal Crystallization Behavior of Poly(butylene adipate-*co*-terephthalate)/Clay Nano-biocomposites

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ABSTRACT: The study of the nonisothermal crystallization behavior of layered silicates micro- and nano-biocomposites based on poly(butylene adipate-*co*-terephthalate) (PBAT), a biodegradable copolyester, has been carried out with different theoretical models. They were applied and developed with the aim to describe and better understand the influence of the layered silicates dispersion on crystallization. The nucleation efficiency of the layered silicates has been demonstrated with the use of the "Modified Avrami model," thanks to the higher crystallization rate parameter, Z_c, and of the lower crystallization half-time, $t_{1/2}$, compared to the neat matrix. The crystallization activation energies, E_a, calculated from "Kissinger's model" have shown that layered silicates have a negative effect on the crystallite growth process. Thus, these analyses have shown that layered silicates have a double effect on the crystallization process. These two opposites' phenomena depend on the dispersion quality and are more pronounced for the intercalated nano-biocomposites. © 2007 Wiley Periodicals, Inc. J Polym Sci Part B: Polym Phys 45: 1503–1510, 2007

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INTRODUCTION

Using persistent polymers, which are a significant source of environmental pollution, for short term applications is not entirely adequate. That is why the replacement of conventional plastics by degradable polymers is of major interest for example, on packaging.[1] Nevertheless, these biopolymers (biodegradable polymers) have not yet found extensive applications. Thus, to be more attractive, some biopolymer properties have to be enhanced (mechanical properties, gas barrier properties, etc).

A strategy to improve polymer properties consists of the dispersion of nanofillers (nanoscale fillers) into a polymer matrix to build up new powerful materials called nanocomposites. Various nanoreinforcements are currently under investigation. The most intensive researches are focused on layered silicates as the reinforcing phase due to their availability, versatility, and respectability towards the environment.[2] One additional advantage is that relatively small amounts of layered silicates (less than 5 wt %)[3,4] are required to obtain the best properties as a result of the nanometric scale dispersion. Recently, a new nanocomposite class called "nano-biocomposite,"[5] which combines nanomaterials with an environmental approach, has been developed. They are obtained by the addition of nanofillers into a biodegradable polymer matrix.

Layered clay minerals, and especially montmorillonites, are commonly used in polymer nanocomposite preparations. If the polymer-silicate compatibility is low, clay dispersion at

nanolevel is impossible and a microcomposite is obtained. Therefore, an ion-exchange of inter-gallery inorganic cations with alkyl ammonium cations is often carried out to promote the polymer-silicate compatibility.[6] When these nano-particles are dispersed into a polymer, they can either be intercalated by macromolecules or exfoliated. Intercalated structures show regularly alternating layered silicates and polymer chains in contrast to exfoliated structures in which the clay platelets are individually delaminated and dispersed in the polymer matrix. The best performances are commonly observed with the exfoliated structure.

Depending both on the matrix and the nanofiller nature, nanofiller incorporation could lead to different crystallization trends, as an increase or a decrease in the crystallization degree.[7,8] To understand this influence, different authors have shown that the study of crystallization process is required.[9–11] Generally, these studies are limited to isothermal conditions because problems associated with cooling rates and thermal gradients within specimens are avoided. Nevertheless, in our case, because of the low crystallization degree of the polymer, the isothermal analyses failed to provide interpretable data, thus nonisothermal measurements have been performed. To understand the nonisothermal crystallization behavior of polymers, several models have been developed such as "Ozawa's model"[12] or "modified Avrami model."[13] Many studies based on these models have been carried out on different kind of nondegradable polymers-based nanocomposites such as polyamide-6,[9,14] polyethylene,[15–17] or poly(butylene terephthalate).[10]

This article completes and expands a previous publication based on the elaboration and the characterization of poly(butylene adipate-*co*-terephthalate) nano-biocomposites.[5] This work is more particularly focused on the analysis of the nonisothermal crystallization behavior of these materials to better understand the influence of layered silicates on crystallization. The effect of the layered silicates dispersion is thus investigated in the case of micro-biocomposites and intercalated nano-biocomposites. Crystallization activation energies are calculated with the use of the Kissinger's equation.[18] Finally, the validity of the conclusions obtained on the nonisothermal crystallization analyses of PBAT micro- and nano-biocomposites are validated by monitoring ΔH_c variations.
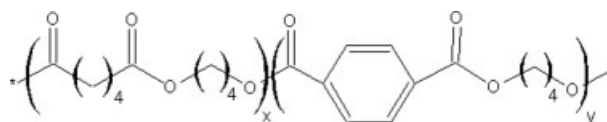
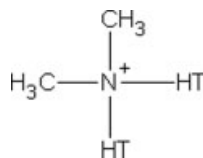## EXPERIMENTAL

Materials and Elaboration Protocol

The PBAT is a biodegradable aromatic copolyester, which has been kindly supplied by Eastman (EASTAR BIO Ultra Copolyester 14766). Figure 1 shows PBAT chemical structure. The ratio between each monomer has been determined by ^{1}H-NMR (CDCl$_3$). The integration of the peaks of the butylene adipate unit (BA) and the butylene terephthalate unit (BT) at $\delta = 2.33$ and 8.1 ppm, respectively, gives PBAT composition, 57% of BA and 43% of BT. As determined by size exclusion chromatography (SEC), average molecular weight (M_w) and polydispersity index (I) are 48,000 g/mol and 2.4, respectively. The crystallinity degree (χ) estimated from the differential scanning calorimetry (DSC) analyses is $\sim$11%.

The clay minerals studied were kindly supplied by Southern Clay Products, (Cloisite® 20A), Laviosa Chimica Mineraria S.p.A. (Dellite® LVF). Two kinds of montmorillonites (MMT) have been selected, an unmodified and an organo-modified montmorillonite that are Dellite® LVF (MMT-Na) and Cloisite® 20A (OMMT-Alk), which is organo-modified by dimethyl dihydrogenated tallow ammonium. The organo-modifier chemical structure is presented in Figure 2. Content in organics is 31 wt % for Cloisite® 20A as determined by thermogravimetric analysis (TGA).

The elaboration protocol of the micro- and nano-biocomposites, obtained with MMT-Na and OMMT-Alk, respectively, has been fully described in a previous article.[5] Before processing, PBAT and clays were dried overnight at 80 °C under reduced pressure. Then, MMT (3–9 wt %) have been added into PBAT to obtain micro- and nano-biocomposites. They were prepared with an internal batch mixer (counter-rotating mixer Rheocord 9000, Haake) by mechanical kneading at 160 °C for 15 min with a rotor speed of 50 rpm followed by mechanical kneading at 120 °C for 20 min with a rotor speed of 100 rpm. After melt processing, the molten materials were com-

Figure 1. Chemical structure of poly(butylene adipate-*co*-terephthalate).

Figure 2. Chemical structure of the OMMT-Alk organo-modifier (HT: hydrogenated tallow).

pression-molded to obtain films with a hot press at 160 °C applying 20 MPa pressure for 10 min. The molded specimens were cooled between two steel plates for 3 min to allow the specimens to be fully crystallized before testing. All along this article, the obtained samples are named PBAT/XXX $y\%$ where XXX stands for the type of (organo)clay and y the weight percentage of clay inorganics fraction.

Characterization Methods

SEC measurements were performed in THF (HPLC grade), with polystyrene standards for the calibration, on a Shimadzu LC-10AD liquid chromatograph equipped with a Shimadzu RID-10A refractive index detector and a Shimadzu SPP-M10A diode array UV detector. ^{1}H-NMR spectra were recorded in CDCl$_3$ on a Bruker 300 Ultrashield[TM] at 300 MHz.

Crystallization behavior of PBAT and its micro- and nano-biocomposites was analyzed by DSC using a DSC 2910 from TA Instrument (USA). The analyses were performed on 5–10 mg samples. The temperature selected to start the thermal treatment was 200 °C to erase all previous thermal history. For nonisothermal crystallization, samples were cooled at various cooling rates (10, 15, 20, and 25 °C/min). The crystallization temperature (T_c) is measured from the maximum of the exothermic peak. The crystallization enthalpy (ΔH_c) is measured from the area of the endothermic peak and has been corrected from a dilution effect of the nanoplatelets.
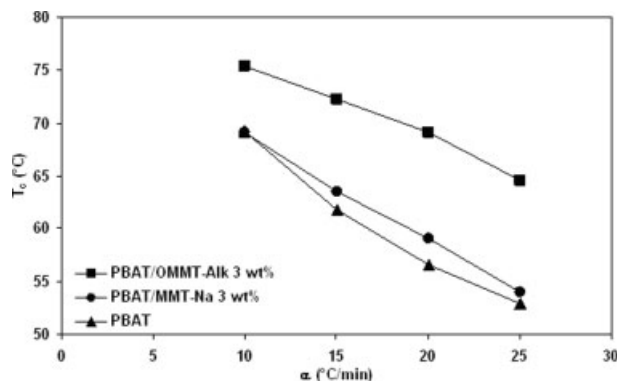
RESULTS AND DISCUSSION

Morphological Characterization of PBAT/MMT

Different characterization results of the PBAT-based micro- and nano-biocomposites, such as structural characterization (TEM and XRD),

thermal stability measurement (TGA analyses), and the mechanical properties determination (tensile tests) are given in a previous publication[5] and are not reported in this article. For the sake of clarity, the morphological analyses results will be simply summarized hereafter. On one hand, melt blending PBAT with MMT-Na led to conventional micro-biocomposites as evidenced by the constant values of interlayer spacing measured by XRD. On the other hand, the substantial increase in the OMMT-Alk interlayer spacing—from 21 nm for pristine clay to about 30 nm when dispersed in PBAT—clearly evidenced the formation of intercalated nano-biocomposite materials. Thus, different crystallization behaviors are expected for these two types of materials since intercalated nano-biocomposites are characterized by a better quality of clay dispersion compared to microcomposites.

Crystallization Behavior of PBAT/MMT

Figure 3 presents the variation of the crystallization temperature (T_c) at different cooling rates (α) of neat PBAT, PBAT/MMT-Na 3 wt %, and PBAT/OMMT-Alk 3 wt %. As expected, T_c shifts to lower temperatures when the cooling rate increases. Table 1 illustrates that at a given cooling rate, the T_c of PBAT/OMMT-Alk are higher than PBAT/MMT-Na ones, which are also higher than the T_c of neat PBAT. These variations imply that the addition of montmorillonite (either MMT-Na or OMMT-Alk) has an influence on the crystallization rate of PBAT and that nanofillers may act as nucleating agent.[11] Higher T_c values observed for OMMT-Alk compared to

Figure 3. Plots of T_c versus cooling rate (α) for PBAT/OMMT-Alk 3 wt %, PBAT/MMT-Na 3 wt %, and PBAT.

Table 1.   Nonisothermal Crystallization Parameters for PBAT and Related Composites

Samples	α (°C/min)	T_c (°C)	ΔH_c (J/g)	Z_c (min^{-n})	n	$t_{1/2}$ (min)
PBAT	10	69.2	14.6	0.65	4.9	1.01
	15	61.7	15.3	0.85	4.2	0.95
	20	56.5	15.7	0.95	3.9	0.92
	25	52.9	15.3	1.00	3.4	0.90
PBAT/MMT-Na 3 wt %	10	69.1	15.8	0.71	4.2	0.99
	15	63.5	16.9	0.88	4.0	0.94
	20	59.1	16.8	0.95	4.1	0.93
	25	54.0	17.5	0.98	4.1	0.92
PBAT/MMT-Na 6 wt %	10	73.0	13.3	0.73	4.2	0.99
	15	68.3	14.9	0.89	4.1	0.94
	20	64.8	15.7	0.96	4.1	0.92
	25	60.1	15.8	1.01	3.7	0.90
PBAT/MMT-Na 9 wt %	10	72.8	13.8	0.78	4.0	0.97
	15	67.9	15.1	0.91	4.1	0.94
	20	63.9	15.9	0.96	4.2	0.93
	25	59.7	16.3	1.01	3.9	0.91
PBAT/OMMT-Alk 3 wt %	10	75.4	11.9	0.89	3.8	0.94
	15	72.2	12.7	1.01	3.4	0.90
	20	69.1	13.1	1.05	3.2	0.88
	25	64.6	14.1	1.06	2.7	0.85
PBAT/OMMT-Alk 6 wt %	10	74.7	12.7	0.90	3.7	0.93
	15	71.2	12.9	1.01	3.9	0.91
	20	68.2	13.8	1.05	3.6	0.89
	25	65.0	14.3	1.07	3.4	0.88
PBAT/OMMT-Alk 9 wt %	10	73.8	11.4	0.97	3.9	0.92
	15	70.4	13.0	1.04	3.9	0.90
	20	67.4	13.6	1.07	3.8	0.89
	25	64.6	13.2	1.09	3.3	0.87

MMT-Na could be a direct consequence of the better dispersion quality of the organomodified montmorillonite. The T_c of PBAT/OMMT-Alk 6 and 9 wt % are lower than PBAT/OMMT-Alk 3 wt % one. This could be explained assuming some aggregation of the nanofillers when their concentrations rise above 3 wt % leading to lower amount of available clay platelets for the nucleation process enhancement. Such assumption is in good agreement with phenomena observed on other biopolyesters[19,20] where the highest mechanical properties and thermal stability enhancements are achieved for lower clay loadings because of the layered silicate aggregation at higher clay content.

Nonisothermal Crystallization Kinetics

Equation 1 defines the relative degree of crystallinity X_T as a function of crystallization temperature T_c, where T_0 and T_∞ are the onset and end of crystallization temperatures, respectively.

$$X_T = \frac{\int_{T_0}^{T_c}(\mathrm{d}H_c/\mathrm{d}T)\mathrm{d}T}{\int_{T_0}^{T_\infty}(\mathrm{d}H_c/\mathrm{d}T)\mathrm{d}T} \qquad (1)$$

Equation 2 allows the determination of the crystallization time t as a function of crystallization temperature T_c, where α is the cooling rate in °C/min. The transformation from temperature to time is performed using a constant cooling rate.

$$t = \frac{T_0 - T_c}{\alpha} \qquad (2)$$

Ozawa's Model of Nonisothermal Crystallization

According to Ozawa's theory,[12] the nonisothermal crystallization process is the result of an infinite addition of small isothermal crystallization steps. Equation 3 allows the determination