



Crystallization and creep of the graphite nanosheets based poly(butylene adipate-co-terephthalate) biocomposites



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ABSTRACT

Biodegradable poly(butylene adipate-co-terephthalate) (PBAT) composites containing graphite nanosheets were prepared by melt compounding. The results reveal that the nanosheets have full distribution throughout the PBAT matrix, although they are still dispersed as the multilayered stack. Those well distributed graphite nanosheets act as the heterogeneous nucleating agent to facilitate formation of crystal nucleus and also as the physical hindrance to retard crystal growth. But the nucleation dominates overall crystallization kinetics at experimental graphite loading levels because the composites show higher crystallization rates and lower activation energies than those of the neat PBAT. The results from creep study further confirm the role of physical hindrance played by graphite nanosheets because the creep strain of system is highly restrained by the presence of nanosheets. However, this inhibiting effect is attributed to suppressed relaxation of chain coils, rather than confinement to chain segments.

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1. Introduction

Nowadays people have realized that using persistent polymers, which are one kind of main environmental pollution sources, for short term applications is a big problem. Therefore, the new materials with environmental-friendly characteristics, especially those bio-originated or biodegradable polymers, have attracted considerable attention in recent years [1]. Aliphatic polyesters constitute one of the most important families of synthetic polymers with major applications as degradable materials [2]. However, the aliphatic polyesters derived from diols and dicarboxylic acids generally presents low mechanical and thermal properties [3], and hence only one commercial product, poly(butylene succinate) (PBS), has been developed until 1998, an aliphatic-aromatic copolyester, poly(butylene adipate-co-terephthalate) (PBAT), was commercialized by BASF (Germany) with the trade name Ecoflex®. Introduction of rigid aromatic units not only gives the aliphatic-aromatic copolyesters excellent mechanical and physical properties [4], but also keeps the

biodegradability of poly(butylene adipate) (PBA) even though the amount of aromatic terephthalic acid in the copolyesters is high up to 60 mol% [5]. Therefore, PBAT overcomes the disadvantages of aliphatic materials and combines useful material properties of aromatic materials with biodegradability [6].

Like most of semicrystalline polymers, the final properties of PBAT are governed by the supermolecular morphology, which in turn is controlled by its composition ratios between butylene terephthalate (BT) units and butylene adipate (BA) ones [7–10] and the physicochemical environments during crystallization. It was found that PBAT contained small crystals with a wide size distribution after melt crystallization, and the crystalline region was mainly composed of BT units, whereas all BA units existed in an amorphous region [7]. Accordingly, the crystallization rates of PBAT decrease with reducing BT contents and, an insufficiency of crystallizable BT units makes it difficult for PBAT to form regular crystals, finally leading to decrease of crystallinity [4,7,8]. For commercial aliphatic-aromatic copolyesters, the concentration of aliphatic unit is high up to 45–65 mol% because in this case, they show optimal balance of biodegradability and physical properties [6]. Therefore, PBAT is commonly a rubbery product with low modulus because of its lower crystallization rate and/or crystallinity. One effective strategy to improve its crystallization capacity is incorporation with the nanofiller [11]. It has been reported that the presence of nanoparticles, such as nanoclay, not only serves as a

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heterogeneous nucleation site to accelerate crystallization process, but also improves the stiffness of PBAT evidently, although the degree of crystallinity is not always increased with addition of nanoclay [12–15].

Graphite nanosheets are a type of 2D carbonous material with outstanding electrical, thermal, and mechanical properties [16,17]. One of the most promising applications of graphite nanosheets, therefore, is to be used as the reinforcement or functional nanofiller in polymer nanocomposites [18]. It has been reported that like many other nanoparticles, the presence of graphite nanosheets or nanoplatelets can also promote crystallization of polymer matrix effectively [19,20]. For instance, expanded graphite or graphite nanosheets have strong nucleating effect on the crystallization of aliphatic polyesters such as polylactide (PLA) [21–23] and poly(3-hydroxybutyrate) (PHB) [24], and increase the overall rates of crystallization as a result. Since the presence of graphitic fillers has large influence on crystallization of the aliphatic polyesters, it may also affect crystallization of the aliphatic–aromatic copolyesters, such as PBAT. To our best knowledge, the relative studies have not yet been reported in literatures, however. Therefore, the crystallization behavior of the PBAT composites containing graphite nanosheets prepared by melt compounding was studied in this work. The crystallization kinetics of composite system was then explored to understand the role of nanoplatelets played in nonisothermal annealing process. Besides, the viscoelastic behavior of the composite system, such as creep, was also studied in detail, aiming at further relating the presence of graphite nanosheets with chain relaxation of the PBAT.

2. Experimental

2.1. Materials

Poly(butylene adipate-co-terephthalate) (PBAT) was purchased from Huiying New Material Science and Technology Co. Ltd., Shandong, P. R. China, with the weight average molecular weight of 12,000 g/mol (polydispersity of 2.45), and the density of 1.26 g/cm³. The graphite nanosheets (XF021, purity >95%) with a thickness of 5–25 nm (composed by 10–20 layers) were purchased from Nanjing XFNano Material Tech Co. Ltd., P. R. China. The particles have a lateral size of about 0.5–20 μm, with a special surface area of 50 m²/g.

2.2. Preparation of PBAT/graphite composites

The PBAT/graphite nanosheets composites (PBATGs, where *s* is the weight ratio of graphite) were prepared by melt mixing graphite nanosheets with PBAT by a Haake PolyLab Rheometer (Thermo Electron Co., USA) at 150 °C and 50 rpm for 8 min. For better comparison, the neat PBAT was also processed by rheometer to keep the same thermal histories with those composites. All materials were dried at 60 °C for 24 h before using. The dog-bone shaped specimens (32 mm × 4 mm × 2 mm) were then prepared by injection molding using a Haake mini-jet for following tensile property measurements. The injection was performed at the cylinder temperature 160 °C and the mold temperature 25 °C with the injection pressure 600 bar and holding pressure 500 bar. The sheet samples with about 1 mm thickness were prepared by compression molding at 150 °C and 10 MPa for the morphological and creep measurements.

2.3. Morphology and structure characterizations

The dispersion of graphite nanosheets in PBAT matrix was investigated using a transmission electron microscope (Tecnai 12, Amsterdam, Netherlands) with 120 kV accelerating voltage. The

crystal structure was determined by a D8 ADVANCE X-ray diffractometer (XRD, BRUKER AXS, Germany) with Cu target and a rotating anode generator operated at 40 kV and 40 mA. The scanning rate was 2° min^{−1} from 0.5° to 60°.

2.4. Crystallization characterizations

The nonisothermal crystallization of the neat PBAT and its composite were recorded using a differential scanning calorimeter (DSC, NETZSCH DSC-204F1, Germany). The sample about 5 mg was first heated from room temperature to 170 °C at the rate of 10 °C/min and held for 5 min to eliminate residual thermal histories, and then were cooled to the 20 °C at various rates, during which the heat flow as a function of time were recorded. All experiments were performed under nitrogen.

2.5. Creep-recovery measurements

Firstly, linear elastic region of all samples was determined through tensile tests by an Instron Mechanical Tester (ASTM D638) at a crosshead speed of 50 mm/min. Then, creep was performed on a DMA Q800 analyzer (TA Instruments, USA) with tensile mode at various temperature and/or stress levels. The duration of measurements was determined as 10 min and 30 min for the creep and creep-recovery tests, respectively. The creep strain/recoverable strain and compliance were recorded with time. Three rectangular specimens (30 mm × 5 mm × 1 mm) were tested for each composition, and the specimen was equilibrated for 5 min before each test in order to evenly adjust for the correct temperature of the sample.

2.6. Rheological measurements

Rheological measurements were carried out on a rheometer (Haake RS600, Thermo Electron Co., USA) equipped with a parallel plate geometry using 20 mm diameter plates. The sheet samples were first molten at 150 °C for 5 min to eliminate residual thermal histories and then, experienced stepping shear flow, during which the steady stress and viscosity response to the shear rates (0.001–100 s^{−1}) were recorded.

2.7. Dynamic mechanical analysis

Dynamic mechanical analysis (DMA) was performed on a DMA 242C analyzer (NETZSCH Instruments, Germany) at bending mode over a temperature range from −60 °C to 170 °C at 5 Hz. The heating rate is 2 °C/min. Three rectangular specimens (30 mm × 5 mm × 1 mm) were tested for each composition.

3. Results and discussion

3.1. Dispersion of graphite nanosheets in the PBAT composites

The distribution and dispersion of graphite nanosheets in matrix polymer should be fully evaluated before property studies of the graphite-based polymer composites. Fig 1 gives the TEM images of PBATG1 sample. It is clear that the graphite nanosheets are fully distributed throughout the matrix after melt mixing. Some nanoplatelets present a curled-edge structure (Fig. 1(b)), indicating that they may be flexible in PBAT during melt processing. This is highly dependent on the aspect ratio of nanoplatelets and on the melt viscosity of matrix polymer. Switzer and Klingenberg [25] proposed an effective stiffness parameter (S^{eff}) as the criterion for fiber flexibility:

$$S^{eff} = \frac{E\pi d^4}{64\sigma L^4} = \frac{E\pi/64\sigma}{\lambda^4} \quad (1)$$

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