Polymer 55 (2014) 2077–2085

Contents lists available at ScienceDirect

Polymer

journal homepage: www.elsevier.com/locate/polymer

Melt crystallization of poly(ethylene terephthalate): Comparing addition of graphene vs. carbon nanotubes

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ARTICLE INFO

Article history:
Received 10 January 2014
Received in revised form
13 February 2014
Accepted 23 February 2014
Available online 1 March 2014

Keywords:
Poly(ethylene terephthalate)
Graphene
Carbon nanotube

ABSTRACT

Poly(ethylene terephthalate) (PET)-based nanocomposites with graphene or multi-wall carbon nanotubes (MWCNT) were prepared by melt mixing. Aspect ratio, A_f, and interparticle distance, λ, of graphene in the nanocomposites were obtained from melt rheology and transmission electron microscopy respectively. λ of PET/graphene nanocomposites was much smaller than λ in PET/MWCNT. For PET/graphene with highest A_f, λ became <1 μm at more than 0.5 wt% graphene. Non-isothermal crystallization behavior from the melt was investigated by differential scanning calorimetry. The crystallization temperatures suggest that the nucleation effect of graphene was stronger than that of MWCNT. The half crystallization time of PET/graphene became longer than PET/MWCNT with increasing graphene loading, suggesting that confinement by graphene suppressed the crystal growth rate. XRD analysis indicated that smaller crystals formed in PET/graphene than in PET/MWCNT. From Raman spectroscopy, the π–π interaction between PET and graphene was stronger than that between PET and MWCNT. This stronger interaction in PET/graphene appears to result in formation of crystals with higher perfection.

1. Introduction

Poly(ethylene terephthalate) (PET) is a thermoplastic and semi-crystalline polymer with high performance characteristics such as; high glass transition temperature (T_g), good high mechanical properties, high chemical resistance and easy forming. Due to its high performance, PET is used for many industrial applications such as fibers, films, and bottles. To produce films, PET resin is usually extruded followed by additional processing such as tentering and annealing. During these processes, high-order structures of PET such as chain orientation and crystallites are controlled and play an important role in enhancing the properties of the film. For example, gas barrier properties [1], wear resistance [2], and mechanical properties [3] are enhanced with crystallinity. Processing operations such as shear [4] and tentering [5–9] increase crystallinity and crystal orientation. However, the crystallization rate and crystallinity of PET are typically lower than those of other semi-crystalline polyesters, such as poly(butylene terephthalate) and poly(trimethylene terephthalate) [10]. This disadvantage restricts its applications, in particular by injection molding.

Adding nano-filler is one method to enhance mechanical and gas barrier properties, and improve thermal and dimensional stability. In particular, 2-D platelet nano-fillers are known to enhance these properties to a greater extent than spherical shaped fillers [11,12]. Modified clay [13–22] has been widely used as a 2-D platelet nano-filler. For example, Hasegawa et al. [13,14] reported the enhancement of modulus and strength of polyolefins by the incorporation of clay. Several studies have reported enhancement of the properties of PET/clay nanocomposites [16–20,22]. Since the crystallization behavior of PET can be altered with the incorporation of nano-fillers, many studies have focused on the crystallization behavior of PET-based nanocomposites [17–20,23]. For example, Ou et al. [19] and Gökkurt et al. [23] reported that clay accelerated melt crystallization of PET. Calcagnoa et al. [20] reported the increase of crystallization rate and crystallinity by modified clay.

Graphene has recently attracted wide interests because of its 2-D structure and outstanding electrical and mechanical properties [24–33]. As a nano-filler, graphene is capable of improving mechanical and gas barrier properties, dimensional stability, and electrical conductivity of the matrix polymer [29,31,33]. Zhang et al.

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http://dx.doi.org/10.1016/j.polymer.2014.02.055
0032-3861/

[29] melt mixed PET with graphene and showed greater increase in electrical conductivity than with graphite. Feng et al. [30] reported that PET/graphene nanocomposites prepared by *in-situ* polymerization showed a four order of magnitude increase in electrical conductivity compared to melt blending. Bandla and Hanan [31] and Li and Jeong [32] enhanced the mechanical properties by addition of graphene. However, so far there appear to have been no studies about crystallization of PET/graphene nanocomposites.

The purpose of this work is to investigate crystallization behavior of PET/graphene nanocomposites as one step for maximization of their properties (*i.e.*, mechanical properties, gas barrier performance, heat stability, and dimensional stability). In this work, two graphenes with different aspect ratios and multi-wall carbon nanotube (MWCNT) were used as nano-fillers and melt mixed into PET. The melt rheology and transmission electron microscopy (TEM) were used to estimate dispersion level for each nanocomposite. Their non-isothermal melt crystallization behavior and their structure were also investigated by differential scanning calorimetry (DSC), Raman spectroscopy and wide-angle X-ray diffraction (XRD), and compared with those of PET/MWCNT.

2. Experimental

2.1. Materials

PET pellets provided from Toray Plastics America (North Kingstown, RI) were ground into powder (30 mesh particle size) by Polyvision (Manchester, PA). Intrinsic viscosity of PET powder after grinding was 0.61 dl/g (in ortho-chlorophenol). Two few-layered graphenes and one MWCNT were used as nano-fillers. Graphene 1 (G1) (XG Science, xGnP-C750, multilayer, diameter < 2 μm) and graphene 2 (G2) (Angstron Materials, N002-PDR, <3 layer thickness, diameter <10 μm) were provided and used as received. G2 has a larger diameter and is thinner and thus has a higher aspect ratio than G1. MWCNT (T1) (Nano Lab, PD15L5-20-COOH, Purity >95%, diameter 15 ± 5 nm, length 5–20 μm) was also used as received. PET powder, graphene, and MWCNT were dried in a vacuum oven at 120 °C for more than 12 h before melt blending.

2.2. Preparation of nanocomposites

The PET/graphene and PET/MWCNT nanocomposites were prepared by melt blending. PET/nano-filler mixtures of 5.5 g with different loading (from 0 to 12 wt% for G1, and from 0 to 2 wt% for G2 and T1) were fed into a recirculating twin screw extruder (Microcompounder, DACA Instruments) at 280 °C with N_2 purge. The components were mixed at 360 rpm for 8 min then extruded into an ice/water bath for cooling. The obtained nanocomposites were dried in a vacuum oven at 120 °C for more than 12 h. Thin samples for TEM, DSC and Raman spectroscopy were pressed to 120–180 μm thickness between fiber reinforced Teflon sheets at 270 °C at 1–1.5 MPa for 2 min then quenched in ice water to minimize crystallization.

2.3. Melt rheology

Rheological measurements were carried out with a strain controlled rotational rheometer (ARES, TA Instruments) at 270 °C under N_2 atmosphere. 0.6–0.7 g of nanocomposites samples were dried at 120 °C for at least 12 h then loaded between 25 mm parallel plates. They were squeezed into disks ~1 mm thick by slowly lowering the upper plate. Using a dynamic strain sweep at 1 rad/s, the critical strain, γ_{crit}, where storage modulus, G′, drops to 90% of its limiting low strain value was recorded. Then the dynamic moduli were measured at $\gamma < \gamma_{crit}$ from 100 rad/s to 0.1 rad/s.

2.4. TEM measurement and estimation of interparticle distance

TEM images of nanocomposites were obtained on a FEI Tecnai T12 microscope using an accelerating voltage of 120 kV. 70 nm thin sections of sheets were obtained by microtoming (Leica Ultracut) at room temperature with a diamond knife and then transferred onto 400-mesh Ni grids.

Interparticle distance, λ, of graphene in PET/graphene was analyzed by Basu's method [34]. On the assumption that platelet nano-fillers have a discotic shape, the mean value of λ can be calculated by equation (1)

$$\lambda = 4(1 - V_V)/(S_V)_{P-C} \quad (1)$$

where V_V is the volume fraction of platelet nano-fillers estimated from their weight fraction. For the weight to volume fraction conversion, the density of graphene was assumed to be equal to that of graphite (2.28 g/cm^3) [27,28]. The density of amorphous PET (1.335 g/cm^3) [35] was used because all samples here have less than 5% crystallinity (amorphous state) (See Fig. S1 in Supporting Information). $(S_V)_{P-C}$ is the polymer–platelet interfacial area per unit volume of sample and defined by following equation.

$$(S_V)_{P-C} = 4L_A/\pi \quad (2)$$

where L_A is the total length of perimeter of particles per unit area from TEM images. An example of the procedure for analysis of λ is shown in Fig. S2 in Supporting Information. Image analyses were conducted using ImageJ software. Graphenes in TEM image were blacked out in software then black-and-white images were extracted. Subsequently, L_A and V_V were obtained from the extracted image.

By assuming disk shaped platelets the λ values from extracted TEM image can be used to estimate graphene thickness. The surface area, S_0, and the volume, V_0, of a disk are defined by

$$S_0 = 1/2\,\pi D^2 + \pi D\,h \quad (3)$$

$$V_0 = 1/4\,\pi D^2\,h \quad (4)$$

where h and D are the thickness and the diameter of the disk, respectively. D is the product of h and the aspect ratio, A_f, of platelets ($D = A_f\,h$). $(S_V)_{P-C}$ is calculated by equation (5).

$$(S_V)_{P-C} = N_p S_0 = V_v S_0/V_0 \quad (5)$$

where N_p is number of platelets in a unit cell. Substituting equations (2)–(4) into equation (1) and rearranging gives

$$h = \lambda V_v(A_f + 2)/[2(1 - V_v)A_f] \quad (6)$$

A_f was obtained from melt rheology (See equation (10)).

2.5. DSC measurement and preparation of non-isothermal melt crystallized nanocomposites

Melt crystallization was measured using a TA Instruments Q1000 differential scanning calorimeter under a N_2 atmosphere. Samples were heated first to 280 °C at 10 °C/min and held at 280 °C for 1 min (the first heating scan), then cooled at 10 °C/min to 20 °C and held at 20 °C for 1 min (the first cooling scan) and then reheated at 10 °C/min to 280 °C (the second heating scan). The crystallized samples for XRD were removed from the DSC pan after the first cooling scan. Two crystallization parameters, melt crystallization temperature, T_c, and onset temperature, T_{on}, were obtained from the exothermic peak of crystallization from the first