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Influence of single wall carbon nanotubes and thermal treatment on the morphology of polymer thin films

Jaime J. Hernández [a],*, Mari-Cruz García-Gutiérrez [a],*, Daniel R. Rueda [a], Tiberio A. Ezquerra [a], Richard J. Davies [b]

[a] *Instituto de Estructura de la Materia, IEM-CSIC, Serrano 121, 28006 Madrid, Spain*
[b] *ESRF, B.P. 220, F-38043 Grenoble Cedex, France*

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Homogeneous and stable thin films of poly(butylene terephthalate) PBT and its nanocomposites based on single wall carbon nanotubes (SWCNTs) were prepared by spin coating. PBT thin films show crystalline structures for thicknesses above 40 nm, consisting of submicrometer size 2D-spherulites. In the case of nanocomposites, carbon nanotubes act as nucleating agents and provide a template for the crystallization of PBT. This gives rise to hybrid shish-kebab structures, even in the thinnest films (~10 nm thick). Melting and recrystallization provoke the crystallization of PBT and its nanocomposites, and can be used to control morphology. For PBT thin films, the orientation of crystalline lamellae undergoes a transformation, changing from a disposition perpendicular to the substrate ("edge-on") to a parallel arrangement ("flat-on") after recrystallization. In the case of the nanocomposites, the CNT influence on the polymer crystallization morphology in thin films is less significant than in the bulk due to the effect of the substrate interactions. Using Raman microscopy it is possible to directly observe both, the degree of dispersion and the location of carbon nanotubes in the films. The results reveal that bigger agglomerates act as more effective nucleating points than isolated bundles of SWCNTs during crystallization of the polymer matrix.

1. Introduction

Polymer thin films have attracted great attention owing to the important role in a variety of technological applications, such as adhesion, electronics, liquid crystal alignment, and coatings [1,2]. When a polymer crystallizes in thin films, the orientation of lamellae is crucial to the film properties. It has been generally observed that thin films of several hundreds of nanometers exhibit predominantly edge-on lamellae while ultrathin films exhibit flat-on lamellae. Nevertheless, there are several factors, besides thickness [3], such as the interaction with the substrate [4] or the crystallization temperature [5] that may control the crystalline lamellae orientation.

A polymer/CNT nanocomposite often exhibits properties that differ substantially from those of the pristine polymer matrix [6]. One of the most important parameters dictating those properties is the level of CNT dispersion in the polymer matrix. CNTs and single wall carbon nanotubes (SWCNTs) in particular, are usually synthesized in bundles [6]. Dispersive van der Waals forces hold the bundles together. Because of their long length and high polarizability, the amount of energy required to separate an individual tube from the bundle is relatively high. Furthermore, because of its long length, a single nanotube can have one section that resides in a bundle whilst another section remains isolated.

In addition to dispersion on the nanoscale, i.e., bundled versus isolated nanotubes, dispersion is also important over larger length scales. For example, CNTs segregated at the interface of sintered polymer particles or segregated to one phase of a two-phase co-continuous blend, can significantly change the relationship between electrical conductivity and tube weight fraction. Hence it is useful to consider two length scales of dispersion, the nanoscale (10^{-9} m) and microscale (10^{-6} m). It is also worth pointing out that the final dispersion of CNTs in a polymer is not only a function of the method(s) used to separate individual tubes, but also depends upon the method(s) used to mix the tubes with the polymer and the way in which the nanocomposite is processed into its final shape.

The level of CNT dispersion in a nanocomposite is interrelated to the level of CNT aggregation. This in turn has a direct effect on different properties of the materials. This includes their mechanical properties [7] and conductivity in both, bulk form [8] and in thin films [9]. Several previous studies have shown that CNTs act as nucleating agents and enhance the degree of polymer matrix

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* Corresponding authors. Tel.: +34 915616800; fax: +34 915645557 (M.-C. García-Gutiérrez).
E-mail address: maricruz@iem.cfmac.csic.es (M.-C. García-Gutiérrez).

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crystallinity [10,11]. The effect of CNTs in templating polymer crystallization has also been investigated [12,13]. In addition to the level of CNT aggregation, changes induced by the presence of CNTs, i.e. changes in the degree of crystallinity and morphology, will also affect the physical properties of the nanocomposite [14].

This work reports on the morphology of a series of thin and ultrathin films of spin-coated poly(butylene terephthalate) PBT and its nanocomposites based on SWCNTs. The aim of this work is to study the dispersion of CNTs in polymer nanocomposite thin films at the micro-scale. It will also attempt to correlate dispersion with morphological changes induced in thin films by CNT/substrate interactions, at both micro- and nano-length scales.

2. Experimental section

2.1. Materials and sample preparation

Nanocomposites of poly(butylene terephthalate) (PBT) ($M_w \approx 15{,}000$ g/mol, $T_m \approx 225$ °C) and oxidized single-wall carbon nanotubes (CNI Technology Co., Texas, USA, synthesized using the HiPco method) were prepared by in-situ polymerization as described previously [15]. The diameter of the SWCNTs, as characterized by Raman Spectroscopy, ranges from about 0.6 nm to 1.4 nm [16]. A SWCNT weight concentration of 0.2% was chosen because it is the highest achievable by this method.

Thin films were prepared by spin coating the polymer matrix and nanocomposite in trifluoroacetic acid (TFA) on silicon wafers (100). First, a polymer solution (20 g/l), referred to hereafter as (1:0), was prepared. From this, a number of less concentrated solutions were obtained by selective dilution. These were: 10 g/l (1:1), 6.7 g/l (1:2), 2.2 g/l (1:8) and 1.1 g/l (1:16). A syringe was then used to dispense 0.1 ml of each solution onto the center of the silicon substrate (20×25 mm^2 in size) whilst it was rotating at a speed of 2400 rpm. The silicon wafers were obtained from Wafer World, Inc. They had both surfaces polished and were used as supplied. The thickness of the native silicon oxide surface was determined by ellipsometry to be ≈2 nm [17] after cleaning with soap solution (commercial detergent: Procter & Gamble) and bidistilled water.

The thickness of each of the polymer-only films was determined by ellipsometry. These were found to increase with polymer concentration within the 10–150 nm range (see Fig. 1). Similar thicknesses were obtained for the nanocomposite thin films prepared from equivalent concentrations.

In order to promote crystallization of the thin films, they were thermally treated by using a Mettler FP5 chamber (Mettler Instruments AG).

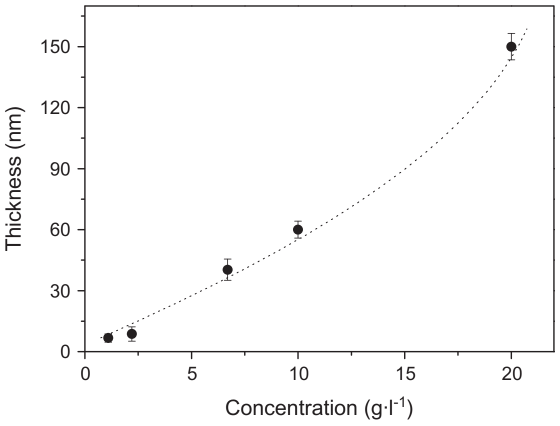

Fig. 1. Thicknesses of PBT thin films as a function of polymer concentration measured by ellipsometry. The values are equivalent for the nanocomposite thin films.

2.2. Techniques

Atomic Force Microscopy (AFM) was carried out using a NanoScope IIIA Multimode from Veeco operating in the tapping mode. This was used to investigate the surface morphology of the spin coated films at room temperature. AFM images were analyzed by means of the software NanoScope Analysis v1.10.

Raman Spectroscopy was carried out using a Renishaw InVia Raman Microscope at the ID13 beamline of the European Synchrotron Radiation Facility (ESRF). The instrument was configured with a 500 mW near-IR 785 nm diode laser, holographic Rayleigh rejection filters, a motorized sample stage and a 1200 lines/mm grating. The laser spot size was ~1 μm in diameter.

Measurements of sample thickness were done by using a spectroscopic ellipsometer [18] at angles of 60° and 70° and at wavelengths between 400 and 800 nm, in order to avoid the transparency region of Si.

3. Results and discussion

3.1. Morphology of PBT and PBT/SWCNT thin films

Fig. 2 shows AFM height images of the thin films prepared from the (1:0), (1:1), (1:2), and (1:16) solutions. These correspond to both pure PBT samples and nanocomposite samples having a 0.2 wt.% of SWCNT (left and right columns respectively). The images reveal that, in all but the thinnest films, the coatings cover the substrate homogeneously. For the thinnest films of both materials, meanwhile, a small fraction of randomly distributed holes are observed. Some authors have previously pointed out that these pores could be a consequence of the presence of air bubbles or

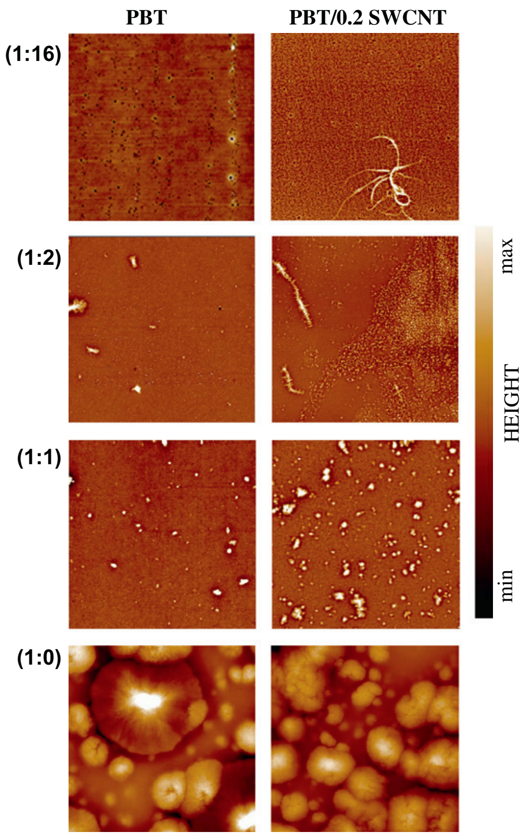

Fig. 2. AFM height images of (left) PBT and (right) PBT/0.2 wt.% of SWCNT spin coated films prepared from different dilutions. Scanned area is 10×10 μm^2.