Contents lists available at ScienceDirect

Polymer

Interfacial crystallization of isotactic polypropylene surrounding macroscopic carbon nanotube and graphene fibers

John P. Abdou [a], Karina J. Reynolds [a], Michaela R. Pfau [a], Justin van Staden [a], Gregory A. Braggin [a], Navid Tajaddod [b], Marilyn Minus [b], Víctor Reguero [c], Juan J. Vilatela [c], Shanju Zhang [a, *]

[a] Department of Chemistry and Biochemistry, California Polytechnic State University, San Luis Obispo, CA 93407, United States
[b] Department of Mechanical and Industrial Engineering, Northeastern University, Boston, MA 02115, United States
[c] IMDEA Materials Institute, Getafe, Madrid 28906, Spain

ABSTRACT

A comparative study on interfacial crystallization of isotactic polypropylene (iPP) surrounding macroscopic carbon nanotube and graphene fibers has been carried out in single fiber polymer composites by means of in situ polarized optical microscope, scanning electron microscope and X-ray diffraction. Ordered interfacial microstructures of iPP nucleate on both nanocarbon fibers in the form of a transcrystalline interphase. Nanotube fibers tend to promote negative birefringence transcrystals whereas graphene fibers induce positive birefringence transcrystals. The microstructures of transcrystals are strongly dependent on the thermal history and the double-layered transcrystals consisting of a negative inner layer and a positive outer layer occur under certain conditions. Transcrystallization kinetics has been studied and the Lauritzen–Hoffman theory of heterogeneous nucleation used to analyze the dynamic crystallization process. While the fold surface energy of iPP transcrystals surrounding both nanocarbon fibers shows little difference, the nanotube fiber promotes shorter induction time than the graphene fiber. Thermal resistance test demonstrates that the ordered interfacial microstructures possess higher melting temperature in the nanotube fiber composites than those in the graphene fiber composites. Under appropriate conditions, the β-form transcrystals of iPP are observed. The amount of the β-form iPP surrounding the nanotube fiber is much higher than that surrounding the graphene fiber. A theoretical model is proposed to interpret the difference between the nanotube and graphene fiber composites and the mechanisms behind its influence on interfacial crystallization.

© 2016 Elsevier Ltd. All rights reserved.

1. Introduction

Nanocarbons, such as carbon nanotubes and graphene, have been considered as effective reinforcing nanofillers for the production of functional polymer nanocomposites for various emerging applications [1–5]. Nanotubes and graphene possess a unique combination of properties, including the high specific surface area, exceptional mechanical properties, high carrier mobility and outstanding thermal conductivity. A common strategy to exploit these "molecular" properties is by combining the nanocarbon with a polymer matrix, to form a composite. Polymer nanocomposites reinforced by nanotubes and graphene have

different reinforcement efficiencies [6], but both share in common the important role of the large nanocarbon/polymer interface arising from their high surface-to-volume ratio.

It is well known that the interfacial interactions between the polymer and nanofillers are determinative to the reinforcement efficiency [7–12]. In particular, the nanofillers in the semi-crystalline polymers can act as heterogeneous nucleating agents for promoting polymer crystallization at interfaces [10–12]. It has been reported that both nanotubes and graphene accelerate polymer crystallization when they have strong interactions with polymers [13–17]. The resulting interfacial crystals possess different microstructures and morphologies as compared to those in the bulk in terms of polymer chain orientation and crystal polymorphism. Importantly, the ordered interfacial microstructures significantly improve the interfacial adhesion and load transfer [18–20]. As a

result, the mechanical performance [12], thermal properties [21] and electrical conductivities [22] of the polymers have been greatly enhanced.

Recent advances in nanocarbons allow the production of continuous macroscopic fibers made of nanotubes [23—25] or graphene [26—28]. When the nanotube or graphene fibers are embedded in the polymer matrix, the polymer crystals grow perpendicular to the long axis of nanocarbon fibers, resulting in the oriented lamellar microstructures at interfaces that are termed as transcrystals [29—32]. Most recently, it has been reported that many semicrystalline polymers can grow transcrystals in the present of nanotube fibers and a soft-epitaxy model has been proposed [33]. Interestingly, the crystal polymorphism often occurs in the transcrystalline layer [29,30,34]. The single-fiber pull-out tests have demonstrated that transcrystalline microstructures markedly improve interfacial adhesion and stress transfer [31,32]. Clearly, polymer transcrystallization induced by the nanocarbon fibers is a facile approach to investigate interfacial interactions between polymers and nanocarbons.

Isotactic polypropylene (iPP) is one of the most widely studied polyolefins and there exists three possible polymorphic crystal forms: monoclinic α, hexagonal β, and orthorhombic γ [35]. The α-form of iPP is the most common crystal form, while the β- and γ-forms are unstable and only achieved under the specific conditions. Interestingly, the β- and γ-form iPPs exhibit better mechanical properties than the α-form iPP [36,37]. In this work, iPP is chosen as a model system to study polymer transcrystallization and crystal polymorphism in the presence of the nanocarbon fibers. In particular, we systematically investigate the dynamic process of iPP transcrystallization surrounding both nanotube and graphene fibers. To the best of our knowledge, these results are the first experimental comparative study showing the different reinforcement mechanisms. We put forward arguments that interpret why carbon nanotubes and graphene fibers behave differently when they are mixed with the polymer matrix.

2. Experimental section

Graphene oxide (GO) was prepared in our own laboratory from natural graphite flakes via a modified Hummers' method [38]. The GO fibers were spun from a 5—10 mg/mL aqueous dispersion of GO via wet coagulation and they were subsequently reduced using an aqueous solution of 30% hydroiodic acid [30]. Carbon nanotube fibers were produced by the chemical vapor deposition (CVD) direct spinning method, using parameters leading to the formation of mutiwalled nanotubes of 3—5 layers and a winding rate of 40 m/min (corresponding roughly to a draw ratio of 12.5) as described in a previous work [39]. As comparison, a wet-coagulation method was also used to spin nanotube fibers [29].

The iPP was purchased from Aldrich and used as received (Melt index = 4.00 g/min, $\overline{M_n} = 9.70 \times 10^4$ g/mol, $\overline{M_w} = 3.43 \times 10^5$ g/mol). Single-fiber polymer composites were produced by introducing nanotube or graphene fibers into the films of iPP and hot pressed at 200 °C to get the composite structures. The specimens were heated to 200 °C for 5min to erase the previous thermal history and subsequently cooled to the desired isothermal crystallization temperature at 20 °C/min to grow transcrystals. There was no fiber pulling or shearing during melting and crystallization. The Linkam LTS420 hot-stage was programmed using the Linksys32 software to control the temperature with 0.1 °C accuracy.

The dynamic process of polymer transcrystallization was investigated using a Leica DM2500P polarized optical microscope (POM) that was connected with the Linkam LTS420 hot-stage. The Leica ICC50 HD video camera was employed to record the dynamic process. The morphologies of the fibers and transcrystallized specimens were studied on a FEI Quanta 200 scanning electron microscope (SEM) operated at an acceleration voltage of 20 kV. To reveal the lamellar morphology of transcrystals, the crystallized specimens were etched for 2—4 h with a 1.0 wt% solution of $KMnO_4$ in the mixed acids of 98% H_2SO_4 and 85% H_3PO_4 by a volume ratio of 2:1 under ultrasonication [30]. The etched samples were then sputtered with a fine gold layer for SEM imaging. Two-dimensional wide-angle X-ray diffraction (2D WAXD) patterns were collected on a Rigaka S-Max 3000 +007 HFM system ($\lambda = 1.5418$Å) in a transmission mode. The diffraction patterns were analyzed using Rigaku NANO-SolverTM and Jade MDI Jade software.

3. Results and discussion

3.1. Transcrystallization

Both nanotube and graphene fibers were used for investigation of iPP transcrystallization in the single fiber polymer composites. Fig. 1 shows typical SEM images of nanotube and graphene fibers. Both nanocarbon fibers are comparable in terms of fiber diameter. They are 30—60 μm in diameter depending on fiber spinning conditions. Interestingly, the nanocarbon fibers display a different surface morphology. The surface of the nanotube fiber is smooth (Fig. 1a) and close examination reveals groove-like nanostructures that are composed of aligned nanotube bundles (Fig. 1b). In contrary, the graphene fibers exhibit the wrinkled rGO sheets (Fig. 1c), leading to large micro-grooves and rough surfaces (Fig. 1d).

Fig. 2 displays typical optical micrographs of nanocarbon fiber/iPP composites in the presence of a retardation plate after isothermal crystallization. Clearly, the iPP displays a columnar growth of spherulites surrounding both nanotube and graphene fibers. These oriented interfacial microstructures are identified as transcrystals (TCs) [40]. The transcrystals surrounding both nanotube and graphene fibers show mixed blue and orange contrast irregularly, indicating mixed birefringence crystals [41]. Upon rotation of the sample, the blue and orange contrast of transcrystals changes accordingly. The transcrystals on the nanotube fiber are well aligned and they display dominant orange contrast in the one-three quadrant phase (in a web version), in particular in the vicinity of the nanotube fiber (Fig. 2a). On contrary, the transcrystals on the graphene fibers are less aligned and they exhibit most blue contrast in the one-three quadrant phase (Fig. 2b). In general, the positive birefringence spherulites exhibit blue in the one-three quadrant phase and orange in the two-four quadrant phase, whereas the negative birefringence spherulites display orange in the one-three quadrant phase and blue in the two-four quadrant phase [31,41]. Thus, our data demonstrates that the transcrystals surrounding CNT fibers have negative birefringence whereas those surrounding the graphene fibers have the positive birefringence.

The interfacial structure and morphology of iPP surrounding the nanocarbon fibers were found to be strongly dependent on the thermal history. Fig. 3a and b illustrate the formation of iPP transcrystals of the specimens that were crystallized at 130 °C for 30 min and then heated to 160 °C. Interestingly, the well-aligned transcrystals surrounding the nanotube fiber exhibit solely negative birefringence (Fig. 3a), whereas the poor-aligned transcrystals surrounding the graphene fiber show dominant negative birefringence (Fig. 3b). It is believed that the polymer chains undergo a reorientation process at the elevated temperature and thereafter they become mainly parallel to the long axis of nanocarbon fibers due to the strong interactions between iPP and fibers [30]. As a result, the radial lamellae are predominant in the transcrystals that demonstrate negative birefringence under the optical microscope [41]. Fig. 3c and d shows the structure and morphology of transcrystals of the specimens that were crystallized at 132 °C for 10 min