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Polyethylene Crystallization Nucleated by Carbon Nanotubes under Shear

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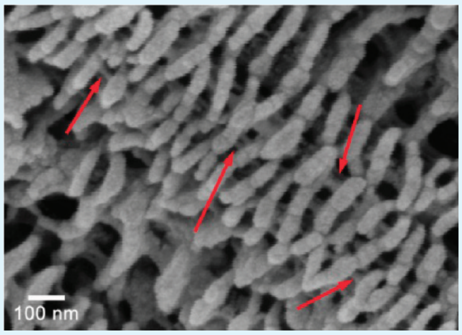
ABSTRACT: Polyethylene crystallization under shear has been studied in the presence of single-wall, few-wall, and multiwall carbon nanotubes (SWNT, FWNT, and MWNT). Polyethylene crystal *d*-spacings for (110) and (200) planes in polyethylene/carbon nanotubes (CNT) are smaller than in the control polyethylene without CNT and the polymer chain is oriented along the CNT axis. The single-wall carbon nanotube templated polyethylene crystals do not redissolve in boiling xylenes; instead, the chain morphology transforms to an amorphous conformation but remains oriented along the nanotube axis. SWNT crystal peaks were also observed in polyethylene/SWNT fibers.



KEYWORDS: *polyethylene, carbon nanotubes, crystallization, shish-kebab*

■ INTRODUCTION

Carbon nanotubes act as a nucleating agent for polymer crystallization.[1−11] This has been demonstrated in a number of polymer systems including polypropylene,[12] polyethylene,[13,14] nylon,[7,15] poly(ethylene terephthalate) (PET),[16] poly(butylene terephthalate) (PBT),[17] poly(vinyl alcohol),[18−21] poly(ε-caprolactone),[22] and poly(*m*-phenylenevinylene-co-2,5 dioctyloxy-*p*-phenylenevinylene).[23] It is being increasingly recognized that a small quantity of individually dispersed carbon nanotubes can affect polymer orientation and crystallization.[1,9,13,21,24−29] There are no other nucleating agents as long and as narrow as CNTs, and particularly SWNTs. Most polymer/CNT crystallization studies to-date have been carried out in quiescent state. The current study has been carried out under a shear flow field to promote polymer alignment in the presence of nanotubes. Moreover, in order to understand the polymer/CNT interaction, an attempt has also been made to dissolve away the crystallized polymer. Results show that crystalline polyethylene in the vicinity of CNT does not readily dissolves in boiling xylene. However, it becomes amorphous and remains oriented along the CNT axis, suggesting good polyethylene/CNT interaction.

■ EXPERIMENTAL SECTION

High-density polyethylene was obtained from Aldrich ($M_w \approx 35\,000$ g/mol; $\rho = 0.906$ g/cm^3). Carbon nanotube (CNT) used in this study were single-wall carbon nanotubes (SWNT) (batch # P-0247, average diameter about 1 nm, manufactured by Carbon Nanotechnologies Inc. using the HiPCO process.); multiwall carbon nanotube (MWNT) (obtained from Cheaptubes Inc., average diameter ~20 nm); and few-walled carbon nanotube (FWNT) (batch XO-021UA, catalytic impurity ~1.3 wt %, manufactured by Unidym, Inc.). Xylene was obtained from Sigma-Aldrich and used as-received. CNT powders were sonicated in xylenes at a concentration of ~3 mg/mL in a bath sonicator (Fisher FS30 bath sonicator, frequency 43 kHz, power 150 W) for 24 h at ~55 °C. Crystallization was carried out using the following procedure: (i) Polyethylene was dissolved in xylenes (at ~10 mg/mL) using an overhead mechanical stirrer (Caframo high shear mixer, model # BDC-1850) equipped with a cylindrical stir bar at a speed of 650 rpm and at a temperature of ~125 °C. (ii) After polymer dissolution, solution temperature was reduced to the crystallization temperatures (T_c) of ~90 °C. (iii) A glass syringe equipped with a 22-gauge blunt tip needle was used to insert 1 mL of the freshly sonicated CNT dispersion in the polymer solution under shear (see Figure 1).

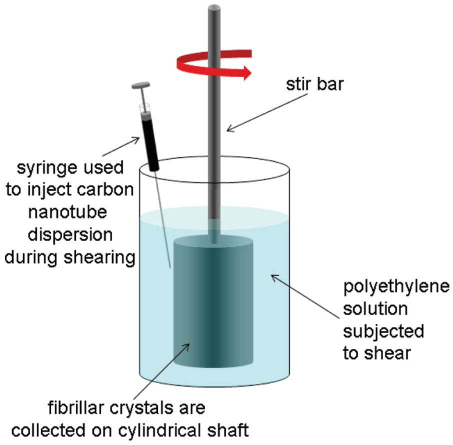


Figure 1. Schematic of the shear-crystallization setup used in this study.

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This resulted in an overall CNT concentration in the polyethylene/xylene solution of 0.06 mg/mL. (iv) Polyethylene/SWNT fibers were collected for analysis from the cylindrical stirrer bar. (v) Fibers collected from the stirrer bar were washed in hot/boiling (~130–150 °C) xylenes for periods ranging from 10 to 20 min at a time. The washing procedure was repeated 5–7 times depending on the fiber stability. Scanning electron microscopy was performed using a Zeiss Ultra60 SEM operated at 5 kV on samples sputter coated with gold. X-ray diffraction data was obtained using a Rigaku MicroMax 002 X-ray source (operating voltage 45 kV and current 0.66 mA) CuKα filtered by confocal optic system (λ = 0.15418 nm) equipped with a 2D R-Axis V^{+2} detector.

■ RESULTS AND DISCUSSION

A polyethylene/SWNT fiber collected on the cylindrical stirrer bar is shown in Figures 2a-c. Washing of the fiber in xylenes removes an outer polyethylene coating and reveals the presence of the shish-kebab morphology (Figure 2b (II & III) and 2c) commonly reported in polyethylene. In the SWNT/polyethylene fiber, shish-kebab structures show an average polyethylene lamellar thickness of about 40 nm (Figure 3). After washing in boiling xylenes for over an hour, the fibers still showed shish-kebab morphology, suggesting that the polyethylene kebabs on SWNT did not dissolve in boiling xylene (Figures 2c and 3). SEM images of the control polyethylene fiber, as well as fibers containing FWNT and MWNT also collected from the stirrer bar are shown in Figures 2d–f. The control fibers without CNTs and those containing MWNT and FWNT when treated in boiling xylenes for over an hour were completely disintegrated and could not be recovered for further analysis/observation.

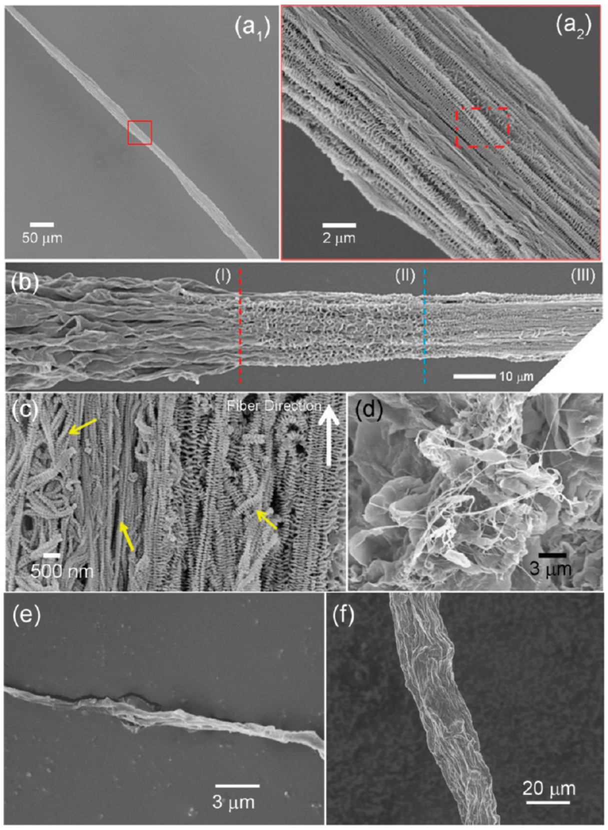


Figure 2. Scanning electron micrographs (SEM) of the washed polyethylene/SWNT fibers (a_1 and a_2). (a_2) is the higher magnification image of the boxed region in (a_1). (b) Fiber showing different stages of the washing process: (I) unwashed fiber, (II) fiber washed for 10 min, and (III) fiber washed for 20 min in boiling xylene. (c) SEM of the fiber washed repeatedly in boiling xylenes for 20 min time intervals showing the mis-alignment of the hybrid shish-kebab crystals (arrows) along the fiber direction, however the shish-kebab structure is intact. (d) Control polyethylene fibers without nanotubes grown under the same shear flow conditions. (e) Unwashed polyethylene/FWNT fiber. (f) Unwashed polyethylene/MWNT fiber.

Wide-angle X-ray diffraction (WAXD) (Figure 4) shows that the polyethylene *(200)* and *(110)* *d*-spacings in the presence of carbon nanotubes have smaller values than without carbon nanotubes suggesting an interaction between polyethylene and carbon nanotubes. Also, polyethylene *d*-spacing values reduced with decreasing carbon nanotube diameter. This suggests that the strength of polyethylene/CNT interaction increases with decreasing CNT diameter. Lower transverse *d*-spacing was also observed in the presence of carbon nanotubes in polyacrylonitrile/SWNT composite fiber.[24]

Before washing in xylene, polyethylene as well as polyethylene/SWNT fibers showed unoriented diffraction patterns (Figures 5a, b), whereas the polyethylene/SWNT fibers washed in boiling xylene showed the presence of oriented polyethylene (Figure 5c). With the xylene treatment, most of the unoriented polyethylene has been dissolved, revealing the oriented polyethylene that is strongly interacting with SWNTs. Crystal size in unwashed polyethylene/SWNT was 23 and 19 nm based on the (110) and (200) peaks, respectively, and is comparable to the values in control polyethylene without CNTs. On the other hand, polyethylene/SWNT samples washed in boiling xylene, resulted in (110) crystal size of 3.1 nm and the presence of broad amorphous type peak at 22.12° 2θ (Figure 5e).

WAXD equatorial scans for the washed polyethylene/SWNT reveal the presence of two new peaks at 2θ values of 8.7° and 13.27°, with *d*-spacings of 1.02 and 0.667 nm (Figure 5d, e). These correspond to what is expected to be the two-dimensional (10) and (11) reflections for crystalline 2D-hexagonal/trigonal SWNT arrangements. The observed d_{10}/d_{11} ratio is ~1.5. For two-dimensional hexagonal or trigonal crystalline SWNT bundles, the d_{10}/d_{11} ratio should be 1.73.[30] Deviation from the d_{10}/d_{11} = 1.73 value suggests that the lattice symmetry is more representative of a frustrated hexagonal or rectangular arrangement.[30] During the formation of the shish-kebab structure, polyethylene crystallizes around SWNT or SWNT bundles to form the shish. Polyethylene crystallizes in a rectangular orthorhombic lattice structure.[31,32] The simultaneous crystallization of polyethylene around SWNT in the shish may influence SWNT arrangement in the bundle leading to a more rectangular arrangement resulting in d_{10}/d_{11} = 1.5. Based on this arrangement, SWNT lattice parameter (a_o) was determined to be ~1.34 nm,[30] giving the nanotube diameter (d_t) of ~1.00 nm assuming an intertube distance of 0.34 nm. This 1 nm nanotube diameter is consistent with the SWNT diameter provided by the manufacturer. The fact that SWNT crystal peaks are observed in these fibers, suggests the presence of at least some SWNT bundles, and it does not rule out the presence of individual SWNTs. The SWNT crystal size obtained from WAXD using Scherrer equation[33] is ~5 nm,

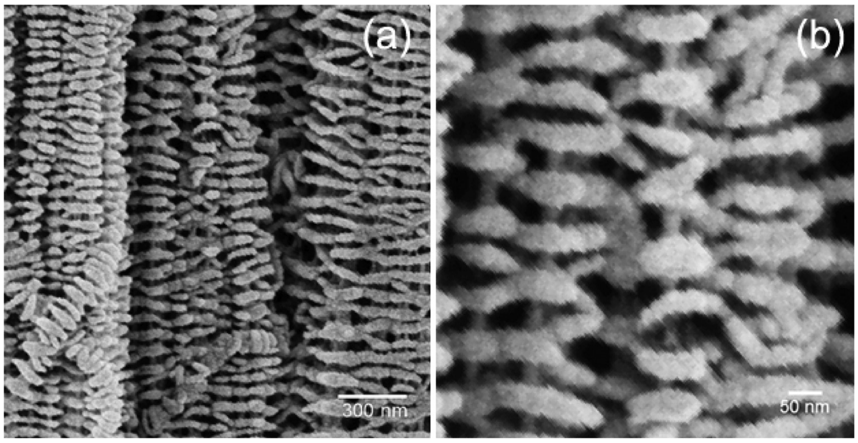


Figure 3. Scanning electron micrographs of washed SWNT/polyethylene shish-kebab structure at (a) low and (b) high magnifications.

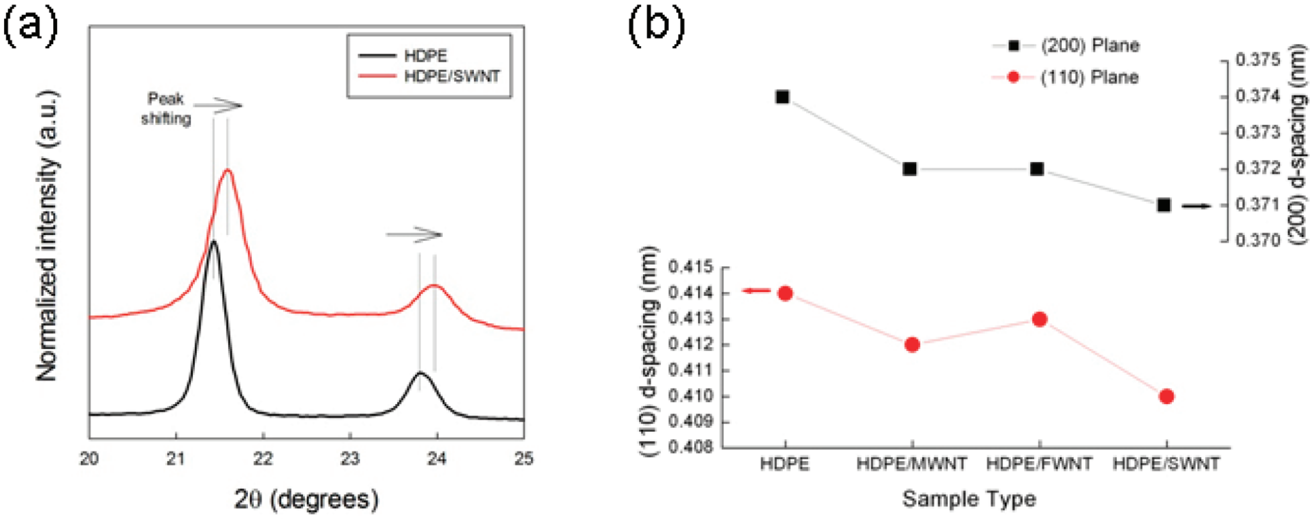


Figure 4. Wide-angle X-ray diffraction data for unwashed (a) polyethylene and polyethylene/SWNT fibers showing the shift to a smaller *d*-spacing of the polymer in the presence of the SWNT; and (b) a plot showing the trend for polyethylene (110) and (200) *d*-spacings when crystallized in the presence of various types of nanotubes.

suggesting the presence of more than 10 SWNTs in a bundle, but much less than about 500 tubes that would be present in a 30 nm diameter bundle. It is likely that SWNTs present in the bundle in a crystal registry are difficult to separate as individual tubes during sonication. Also, various SWNTs floating in the sonicated dispersion may self-select to form SWNT crystals where tubes of similar diameters come together to form small bundles/crystals. We also note that peaks corresponding to SWNT crystals were reported in PBT/SWNT composite.[17]

The shish diameter in the composite fibers measured from the SEM images is ∼20 nm. Considering that SWNT transverse crystal size is about 5 nm, this suggests that the shish may be composed of SWNTs covered with extended-chain polyethylene. The formation of such hybrid polyethylene/CNT shish structure is the result of the presence of shear flow field during crystallization (see Scheme 1). Differential scanning calorimetry data of polyethylene/SWNT fibers fabricated using this process show the melting peak associated with extended-chain polyethylene crystals,[34] confirming the presence of extended-chain polyethylene/SWNT hybrid shish. Previously reported, hybrid CNT/polyethylene shish-kebab structures formed by quiescent crystallization show the nucleation of folded-chain (kebab) polyethylene on the SWNT (shish).[2,3,35,36] The formation of extended-chain (shish) polyethylene crystals or fibrillar polymer crystals are known to form during shear-flow.[37,38] The extended-chain polyethylene enclosed SWNT crystals in the present study are covered with polyethylene kebabs, and the transverse dimension of kebabs is more than 100 nm. Although the kebabs washed in boiling xylene maintain their molecular orientation, the xylene washing process has rendered them mostly amorphous. However, the kebab shape survives the boiling xylene washing process. This behavior, where crystallinity is reduced or crystal registry is eliminated yet the crystal shape is retained, is not new. For example, it has been reported that during electron irradiation of polyethylene single crystals, chains transition from crystalline to amorphous arrangement (as shown by electron diffraction), while the crystal still retains its diamond shape.[39−41]

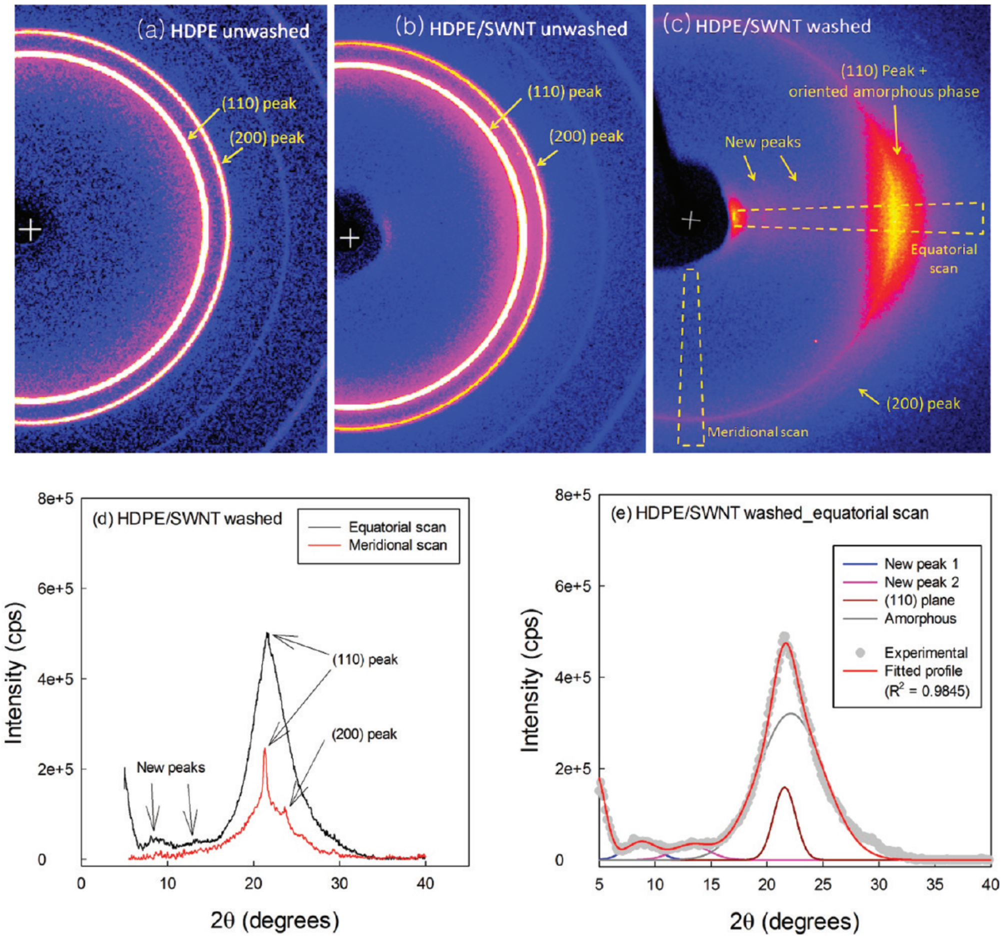
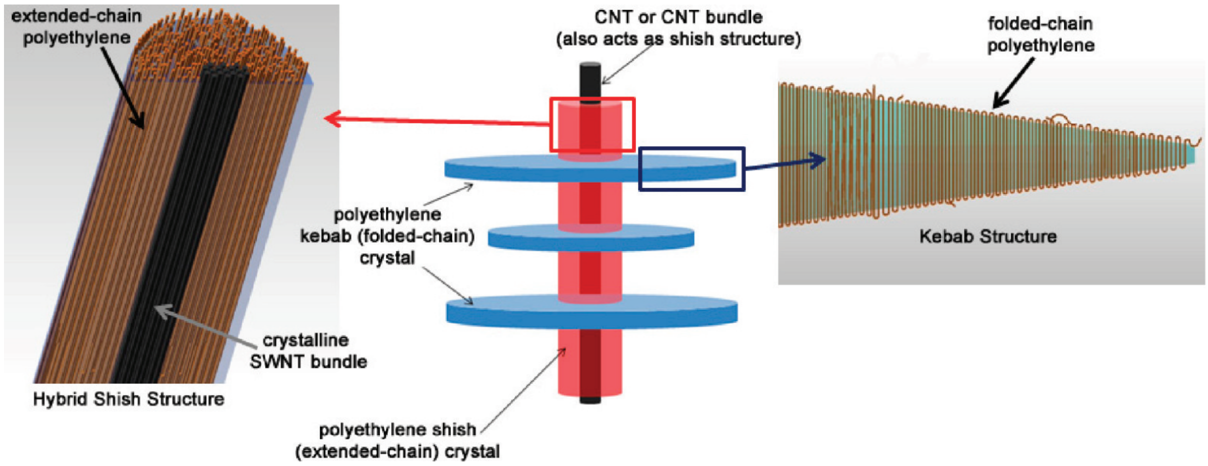


Figure 5. Wide-angle X-ray diffraction patterns for (a) the control polyethylene fibers, (b) polyethylene/SWNT fibers before being washed in xylenes, and (c) the polyethylene/SWNT fibers after washing in xylenes. (d) 2θ equatorial and meridional scans for the washed polyethylene/SWNT fibers showing the presence of both (110) and (200) peaks. (e) Integrated 2θ equatorial scan of the washed polyethylene/SWNT fiber (WAXD pattern shown in (c)) fitted with amorphous and crystalline peaks.

Scheme 1. Illustration Showing the Structure for the Hybrid Polyethylene/SWNT Shish and Polyethylene Kebab Crystal



■ CONCLUSIONS

Carbon nanotubes can template polyethylene orientation and nucleate its crystallization under shear flow field. Polyethylene crystallized in the presence of carbon nanotubes exhibited smaller crystal *d*-spacings transverse to the polymer chain direction as compared to the polyethylene crystallized under same conditions without the use of CNTs. While *d*-spacings decreased in the presence of all CNTs used in this study, most decrease occurred with the use of SWNTs. This observation coupled with the fact that polyethylene orientation was retained even after prolonged treatment in boiling xylene, suggests that there is good interaction between polyethylene and single wall carbon nanotubes. The presence of SWNT crystal peaks in polyethylene/SWNT shish-kebab structures suggests that these shish contained at least some crystalline SWNT bundles. This study is expected to provide guidance for producing polymer/carbon nanotube composites with tailored nanoscale to macro-scale morphology.

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