Ribbon-to-Fiber Transformation in the Process of Spinning of Carbon-Nanotube Dispersion

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(Received 24 May 2006; published 3 November 2006)

We describe a phenomenon of ribbon-to-fiber transformation observed in the process of spinning of single wall carbon nanotubes dispersed in polymer solutions. In the process of spinning, a gel-like ribbon comprised of nanotube bundles bound by polymer is withdrawn from a solvent bath. We show that upon crossing the liquid-air interface, the ribbon may either retain its flat shape or fold into a compact hairlike fiber. The ribbon-to-fiber transformation is caused by the capillary action of the liquid meniscus embracing the ribbon. Only sufficiently stiff ribbons can withstand the capillary compression. The critical conditions of folding, as well as the number of folds in the contractive ribbon, depend on the ribbon width, its flexural rigidity, and the solvent surface tension. We show that the ribbon rigidity can be efficiently modulated by varying the solvent composition, allowing us to control the pore structure of carbon-nanotube fibers.

DOI: 10.1103/PhysRevLett.97.188303 PACS numbers: 82.70.–y, 62.20.Dc, 68.03.Cd, 81.07.De

Particle coagulation spinning (PCS) is one of the most promising techniques to produce fibers with a high carbon-nanotube loading [1–6]. By contrast to composite fibers, where nanotubes are embedded in a polymeric matrix, the fibers produced by PCS consist of an interwoven structure of nanotubes and polymer chains. These fibers can be freely stretched, twisted, knotted, or bent. They are porous, permeable, and conductive. The range of applications of fibers made of carbon nanotubes spans supercapacitors, artificial muscles, and microwires, as well as conduits in micro- and nanofluidics devices and supports for biomedical sensors [7].

In the PCS process [1,2] employed in this work, fibers were produced from 0.6 wt. % dispersion of single wall carbon nanotubes (SWNTs) (Nanoledge) in an aqueous solution of 1.2% of sodium dodecyl sulfate (Aldrich) prepared in a horn sonicator. The SWNT dispersion was injected through a needle (internal diameter = 1 mm) into a coagulation bath rotating at the rate of 33 rpm. The coagulation bath contained a 5% aqueous solution of polyvinyl alcohol of the average molecular weight of 67 000 Da (Fluka).

Upon injection into the polymer solution, nanotube bundles aggregate in a shearing hydrodynamic field and, bound by polymer chains, form a gel-like ribbon, which is mechanically stable [Fig. 1(a)]. Next, the ribbon is rinsed in pure water for 3 h to remove the excess of polymer and surfactant and transferred to an extraction bath with a solvent (pure water or alcohol solution). Then, the ribbon is pulled out of the extraction bath by a hook for drying. Upon crossing the air-liquid interface, the ribbon may either retain its flat shape [Figs. 1(b) and 1(d)] or fold and transform into a compact fiber [Figs. 1(c) and 1(e)].

The ribbon-to-fiber transformation represents an interesting physical phenomenon of capillarity-induced instability that is relevant to the processes of buckling, wrinkling, and draping of thin elastic sheets and filaments [8–20]. As shown in Fig. 2, as the ribbon crosses the air-liquid interface, the liquid forms a meniscus embracing the ribbon. Because of capillary contraction, the meniscus exerts compressive stress on the ribbon edges. If the ribbon is soft and does not withstand the capillary pressure, the meniscus cramps the ribbon, which folds similarly to a strip of paper squeezed in the hand [Fig. 2(a)]. As the ribbon moves upward, the meniscus transforms into a quasicylindrical collar, which compresses the folded rib-

FIG. 1. Morphological variety of fibers produced from SWNT ribbons extracted from solvents of different composition: (a) ~60 cm long gel-like ribbon in the extraction bath; (b) withdrawal of a ribbon from pure methanol: ribbon is stiff and maintains its flat shape; (c) withdrawal of a ribbon from pure water: ribbon is soft and transforms into a hairlike fiber. (d) SEM micrograph of the edge of a flat fiber extracted from 80% ethanol aqueous solution. (e) SEM micrograph of the edge of a hairlike fiber extracted from pure water. SEM images were obtained with field emission scanning electron microscope (FESEM) Hitachi S-4500.
bon further. The diameter of the collar can be much smaller than the width of the ribbon [Fig. 2(a)] or comparable with it [Fig. 2(b)]. In the course of withdrawal and the expulsion of excess liquid, the folded ribbon shrinks into a dense fiber [Fig. 1(c)], which becomes thinner upon drying [Fig. 1(e)]. If the ribbon is sufficiently stiff to withstand the capillary pressure of the meniscus, it remains predominantly flat [Figs. 1(b) and 1(d)]. The transient regime between soft and stiff ribbons is most intriguing since it involves the critical conditions of ribbon folding. The flexural rigidity of the ribbon may be insufficient to withstand the surface tension of the liquid film, which becomes thinner in the process of withdrawal. In this case, the ribbon wrinkles and eventually folds like a wet curtain. The stiffness of the ribbon can be increased by either increasing its thickness (as in Fig. 2) or increasing its elastic modulus (Fig. 1). The latter can be done by varying the solvent composition in the extraction bath.

A better understanding of the ribbon folding is not only of an academic interest. It can lead to a significant improvement of the technology of nanotube packaging. Indeed, the SWNT fibers produced by the PCS process possess a hierarchical morphology with a well-developed porosity and a high surface area [3]. The fiber pore architecture varies from core skin [3,4] to laminated and hollow structures [5,6], depending on the spinning conditions and chemical composition of employed solutions. The scanning electron microscope (SEM) images (Fig. 3) demonstrate typical pore structure morphologies of SWNT fibers produced with different solvents. Nanotube bundles in the dried ribbon form a typical nonwoven structure named “nanofelt,” with pores ranging from several to tens of nanometers [3] (Fig. 3). The next level of pore structure morphology is controlled mainly by the specifics of the ribbon folding in the process of its withdrawal from the extraction bath. Upon the evaporation of solvent, the gaps between the ribbon folds are transformed into the wide pore channels, which may be up to a micrometer size (Fig. 3). These channels determine the fiber permeability in the axial direction. Thus, by varying the number of folds in the contractive ribbon one can tailor the structural and transport properties of SWNT fibers. Soft ribbons are transformed into hairlike threads formed by multifolded nanofelt sheets [Fig. 3(a)], while stiffer ribbons give rise to laminated structures composed by few nanofelt layers [Fig. 3(b)].

To elucidate the mechanism of the ribbon-to-fiber transformation, we consider a flat ribbon being withdrawn from the bath (Fig. 2). The ribbon can be modeled as an elastic sheet compressed by the surface tension \( \gamma \) of the liquid film, which tends to gather the ribbon in a more compact form to reduce the liquid surface area. Since the ribbon is wrapped by the film from both sides, the in-plane compressive force per unit length equals \( 2\gamma \). When the compressive force exceeds a certain critical value, the ribbon undergoes the Euler-type instability [9,10,21]. The devel-

FIG. 2. Capillary contraction of SWNT ribbons in the process of withdrawal from the extraction bath with pure water: (a) \( \sim 15 \) mm wide \( (\sim 15 \) mm) and \( \sim 5 \) \( \mu \)m thin \( (\sim 5 \) \( \mu \)m) ribbon is squashed into a multifolded fiber (insets show schematics of the ribbon cross section during folding); (b) narrow \( (\sim 4 \) mm) and thick \( (\sim 20 \) \( \mu \)m) ribbon either rolls up or buckles. According to Eq. (2), the number of folds in case (b) exceeds the numbers of folds in case (c) by \( \sim 30 \) times. The images presented were obtained with a high speed/high resolution digital camera FastCam-X 1280 PCI (Photron USA Inc., San Diego, CA) mounted on an optical system.

FIG. 3 (color online). Hierarchal pore structure morphology of SWNT fibers: (a) edge of a hairlike fiber extracted from pure water: multifolded structure is composed by nanofelt layers with longitudinal transport pores; (b) edge of a flat fiber extracted from 80% ethanol-water solution: laminated structure is comprised of nanofelt layers. Note the similarity in the nanofelt structure and the difference in the shape and size of transport channels. Nanofelt consists of SWCN bundles of size \( \sim 10\text{–}30 \) nm. Transport pores range from \( \sim 0.5 \) to \( 2 \) \( \mu \)m. The cuts were done upon immersion of fibers in liquid nitrogen to avoid melting of the nanofelt structure. SEM images were obtained with FESEM Hitachi S-4500.

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development of this instability is very much similar to buckling of a carpenter ruler bent between the fingers. As follows from the Euler theory, the critical wavelength of developing perturbation in a flat sheet of thickness \( h \) stressed by the compressive force of \( 2\gamma \) is given by the following equation [21]:

\[
\lambda_c = \frac{\pi \sqrt{E h^{3/2}}}{\sqrt{6\gamma (1 - \nu^2)}} \sim \frac{E^{1/2} h^{3/2}}{\gamma^{1/2}} \sim \frac{D^{1/2}}{\gamma^{1/2}}. \quad (1)
\]

Here, \( E \) is the ribbon elastic modulus, \( \nu \) is the Poisson ratio, and \( D = Eh^3/12(1 - \nu^2) \) is the flexural rigidity. Thus, if the ribbon width \( l \) is smaller than \( \lambda_c \), the ribbon withstands capillary compression and remains flat upon the withdrawal. Assuming an incompressible \((\nu = 1/2)\) ribbon of thickness \( h \sim 20 \mu m \), elastic modulus \( E = 10^4 \) Pa (typical for polymeric hydrogels [22,23]), and surface tension \( \gamma = 0.03 \) N/m, we obtain that the critical wavelength for ribbons withdrawn from water is about 0.1 mm. Wider ribbons are either bent or buckled depending on the width-to-critical wavelength ratio. This ratio,

\[
n = 1/\lambda_c = \frac{\gamma^{1/2} l}{E^{1/2} h^{3/2}}, \quad (2)
\]
gives a qualitative estimate of the number of folds in the compressed ribbon and provides a practical estimate of the ribbon stability. It separates the conditions for producing flat fibers [stiff ribbons, as in Fig. 1(b)], \( n \ll 1 \), from the conditions for producing compact hairlike fibers [soft ribbons, as in Fig. 1(c)], \( n \gg 1 \). At \( n \sim 1\)–2, we may expect the ribbon to be bent into an arc as in the case of a ruler. This arc transforms into a cylindrical scroll as the liquid column contracts. Hollow fibers, which might be obtained from scroll-like ribbons, were observed in Ref. [5], where the ribbon edges are clearly seen in the micrograph. A model of buckling of a cylindrical ribbon considered in the Sec. B of gives the same estimate of the number of folds as Eq. (2). At \( n \sim 2\)–3, we may expect the ribbon to buckle into a sandwich formed by few layers. A two layer structure is shown in Fig. 3(b).

The mechanism of the instability development depends on the specifics of liquid flow along the ribbon. The wavelength of the most rapidly developing corrugation is determined by the process dynamics and is controlled by interplay of capillary, inertial, viscous, and elastic forces. The consolidation of the folding ribbon can be also affected by the flow of liquid confined in the gaps between the folds that can be addressed based on the theory of poroelasticity [24,25]. Nevertheless, Eqs. (1) and (2), which do not contain any dynamic parameters, provide a reasonable estimate for the critical width of stable ribbons and the number of folds developing in unstable ribbons, as shown by the calculations of the effects of liquid flow [26]. A similar order-of-magnitude estimate for the number of developing folds as Eq. (2) is obtained by assuming that the flexible ribbon rolls up within the meniscus into a scroll, which becomes unstable under the action of capillary forces similarly to buckling of cylindrical elastic shells under the radial compression [26–29]. It is worth noting that the authors [19] considered a relevant process of capillarity-induced instability of nanotubes confined to bubbles. Although the geometry of the nanotube-bubble system is quite different from the one of the ribbon-meniscus system, the interplay between the capillary and elastic forces brings about a criterion for buckling of the elastic rod compressed by the bubble interface that is similar to Eq. (1) derived for the elastic sheet compressed by the meniscus interface.

The specifics of ribbon-to-fiber transformation in the process of spinning give rise to the morphological variety of the pore structure of SWNT fibers shown by SEM micrographs (Fig. 3). The morphology of dry fibers reflects the process of ribbon folding. Equations (1) and (2) provide practical correlations between the size and number of nanofelt layers in the fiber and the geometrical and physical parameters of the spinning system. Our analysis shows that the pore structure of SWNT fibers can be controlled by varying the width and flexural rigidity of ribbons and the surface tension of the extraction solution. In particular, we found that the number of folds in the contractive ribbon can be altered by varying the concentration of alcohol in the extraction solution (Fig. 3). One of the factors is that the surface tension of alcohol solutions is smaller than the surface tension of pure water that reduces the effect of capillary compression. Also, alcohol appears to enhance polyvinyl alcohol adsorption to carbon nanotubes and its crystallization [30,31] by reducing the solvent quality for the polymer and by displacing adsorbed surfactant from the surface of carbon nanotubes. The opportunity of tailoring pore structure in the process of fabrication opens up new prospects for the guided design of SWNT fibers for nanofluidic conduits, biosensor supports, and other applications, in which the engineering properties of the material are determined by its porosity and permeability.

We gratefully acknowledge the NIH support through Grant No. EB002889 and fruitful discussions with Alex Lobovsky, Brigitte Vigolo, and Mikhail Kozlov.

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[26] See EPAPS Document No. E-PRLTAO-97-046645 for a quantitative analyses of two possible mechanisms of ribbon folding which confirm the estimates given by Eqs. (1) and (2) for the characteristic wavelength of folding instability and the number of folds in the contracting ribbon. For more information on EPAPS, see http://www.aip.org/pubservs/epaps.html.