Available online at www.sciencedirect.com

SCIENCE DIRECT®

Polymer 46 (2005) 7346–7351

polymer

www.elsevier.com/locate/polymer

Deformation processes of ultrahigh porous multiwalled carbon nanotubes/polycarbonate composite fibers prepared by electrospinning

G.-M. Kim[a,*], G.H. Michler[a], P. Pötschke[b]

[a]Department of Materials Science, Martin-Luther University Halle-Wittenberg, D-06099 Halle/S, Germany
[b]Leibniz Institute of Polymer Research Dresden, Hohe Str. 6, D-01069 Dresden, Germany

Received 24 January 2005; received in revised form 30 May 2005; accepted 5 June 2005
Available online 1 July 2005

Abstract

Mechanical deformation processes of electrospun composite fibers based on polycarbonate with multiwalled carbon nanotubes (MWCNTs) were investigated by in situ tensile tests under transmission electron microscope (TEM) depending on morphology. Using chloroform as solvent and optimizing process conditions, uniform nanoporous composite fibers were generated by electrospinning process. TEM images indicate that the MWCNTs were embedded in the fibers as individual elements, highly aligned parallel to one another along the fiber axis, which makes the mechanical load transfer from the polymer matrix to the MWCNT more favorable. Due to the slippage of individual MWCNTs within the fibers the strain at break of composite fibers is significantly enhanced. In addition, the nanopores on the fiber surface provide the effective sites for stress concentration for the plastic deformation to form nanonecking of fibers under tensile load. Combination of these unique features makes the electrospun composite fibers extremely strong and tough. The results from present work may provide a feasible consideration of such electrospun composite fibers for use as the reinforcing elements in a polymer based composite of a new kind.

Keywords: Multiwalled carbon nanotube; Electrospinning process; Composite fibers

1. Introduction

Since their discovery by Iijima in 1991 [1], due to their small diameter, low density, high aspect ratio, mechanical strength and flexibility [2–4], the carbon nanotubes (CNTs) have gained considerable attention for use as the reinforcing elements in polymer based composite of a new kind. Due to their enormous high surface-to-volume ratio, CNTs offer chemically facile sites that can be functionalized with additives thereby resulting in a strong interfacial bond with the matrix. Furthermore, the very high aspect ratio of nanotubes implies that large interfacial area is available for stress transfer, much more favorable than in conventional fiber composites [5]. As a consequence, CNTs effectively provide for stress transfer sites under external mechanical loading at relative low contents [6,7]. Beside them, due to their novel electronic properties, CNT-polymer composites are also promising for functional applications in displays, conductive polymers [6,8], electromagnetic interference shielding [9,10], and optoelectronic devices [11].

For rational design of new composites it should be guaranteed at least two essential structural requirements; uniform dispersion of nanofillers to avoid localization of stress concentration and good interfacial bonding between them and polymer matrix to achieve effective load transfer across the filler–matrix interface [12–14]. Unfortunately, it has been extensively reported that nanofillers often are dispersed in the polymer matrix in form of agglomerate. This kind of agglomerates reduces significantly their ability to bond with matrix due to less contact area and decreases their effective aspect ratio of the reinforcement. Although CNTs hold great promise as possible reinforcing elements for producing composite materials of a new kind, there are still remained great challenges to this end. In order to overcome this general tendency we have attempted to apply the electrospinning (ES) technique [15–20]. The aim of this

---

[*] Corresponding author. Address: Department of Materials Science, Polymerwerkstoff, Geusaer, 06217 Merseburg, Sachsen-Anhalt, Germany. Tel.: +49 3461 462571; fax: +49 3461 462535.
E-mail address: gyeong-man.kim@iw.uni-halle.de (G.-M. Kim).

0032-3861/$ - see front matter © 2005 Elsevier Ltd. All rights reserved.
doi:10.1016/j.polymer.2005.06.008

work is to structurally characterize the composite nanofibers with directly embedded CNTs, with respect to the orientation and uniform dispersion of CNTs within the electrospun fibers. At the end, surface morphology of electrospun composite fibers and their deformation mechanisms will be reported.

2. Experimental

The nanocomposite (NC) of polycarbonate (PC) with 4 wt% multiwalled carbon nanotubes (MWCNTs) was prepared by dilution of a masterbatch of 15 wt% MWCNT in PC (Hyperion Catalysis International Inc., Cambridge, MA, USA) [21]. The MWCNTs are vapor grown and typically consist of 8–15 graphitic layers wrapped around a hollow 5 nm core. They are produced as agglomerates and exist as curved intertwined entanglements. Typical diameters range from 10 to 15 nm, while lengths are between 1 and 10 μm. The density is approximately 1.75 g/cm^3; a surface area of 250 m^2/g was determined by the BET method [22]. To achieve the solution for electrospinning, NC was dissolved in chloroform to make 4 wt% NC solution. The solution was vigorously stirred for at least 24 h at room temperature and sonicated for 30 min to ensure homogeneous solution. ES was carried out under ambient temperature in a vertical spinning configuration using a 1 mm inner diameter flat-end needle with a 5 cm working distance. The applied voltages were in the range from 3 to 20 kV, driven by a high voltage power supply (Knürr-Heizinger PNC, Germany). Morphological studies of polymer composite fibers were conducted by a TEM (JEOL 200CX) and a field emission gun-environmental scanning electron microscopy (FEG-ESEM, Philips ESEM XL 30 FEG). To study mechanical deformation processes, single electrospun fibers were in situ deformed in TEM by electron beam induced thermal stresses [5].

3. Results and discussion

Recently, the ES technique has attracted more and more attention in materials science community, because polymer fibers from the solution (or melt) prepared thereby can be achieved in the nanometer range straightforwardly and even more inexpensively. The basic mechanism involves applying a high electrostatic field between the capillary and collector. When the electrostatic force overcomes the surface tension of pendent drop at the capillary tip, a fine jet is ejected. As the solvent evaporated during flight of the jet, fibers are deposited on the collector in form of nonwoven fabric. Up to now it has been well established that through appropriate selection of solvent for a polymer to be electrospun as well as proper processing parameters different types and surface morphologies of the electrospun fibers can be obtained [23–25].

Fig. 1 shows the overview of electrospun composite fibers. As the use of solvent as chloroform with the combination of optimal process conditions in this work, the fibers are relatively uniform and exhibit little formation of beads, which are most commonly occurred in electrospinning processes (Fig. 1(a)). They are circular shape with submicron sized diameters (about 350 nm in average) and exhibit well developed nanoporous morphology on the fiber surface (Figs. 1(b), 2(a) and 3). The elliptical shaped pores with the long axis being oriented along the fiber axis are in the order of 100 nm in width and 250 nm in length, which is believed to be caused by the uniaxial extension of the jet under electric field. Formation of nanopores on the fiber surface can be explained with a rapid phase separation during electrospinning process. Over a certain value of applied voltage, the electrostatic force overcomes the surface tension of pendent drop at the capillary tip, and then the fine charged jet is ejected. Rapid evaporation of solvent as the jet is being ejected from the capillary immediately gives rise to the lowering of temperature on the ejected jet (such as a quenching effect in conventional spinning processes). Thereby, the fluid jet becomes thermodynamically unstable and phase separation takes place via spinodal decomposition, which yields polymer-rich and solvent-rich phases. The concentrated polymer-rich phase solidifies quickly after phase separation and builds up

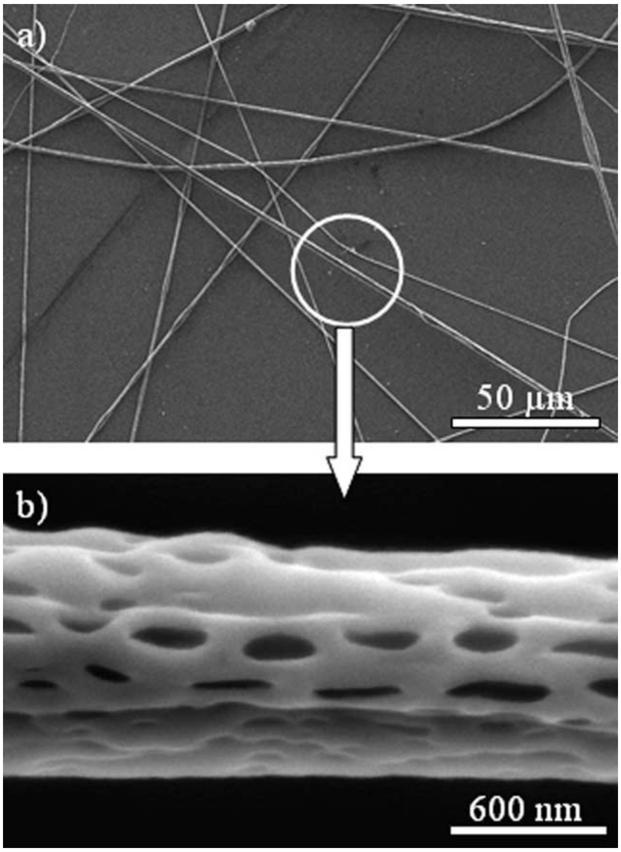

Fig. 1. (a) Overview of electrospun composite fibers, and (b) close-up micrograph of single fiber taken from FEG-ESEM.

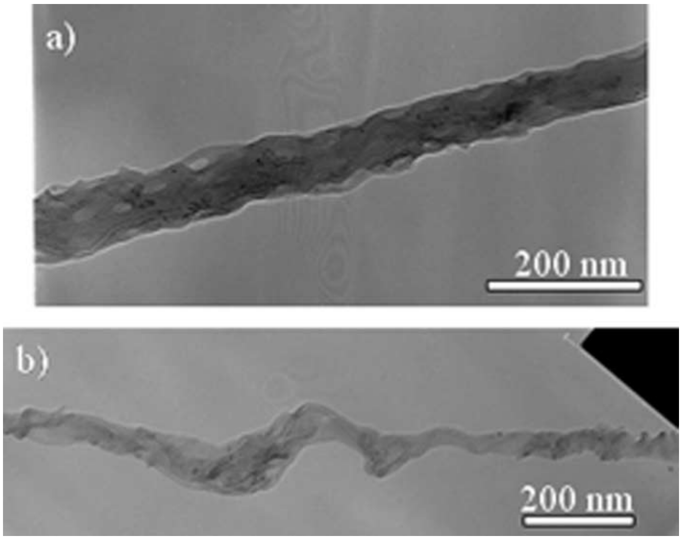

Fig. 2. TEM micrograph of nanoporous structure on the surface of electrospun composite fiber; (a) highly aligned MWCNTs within a fiber by 5 cm working distance at 8 kV, and (b) an extremely curved thin composite fiber.

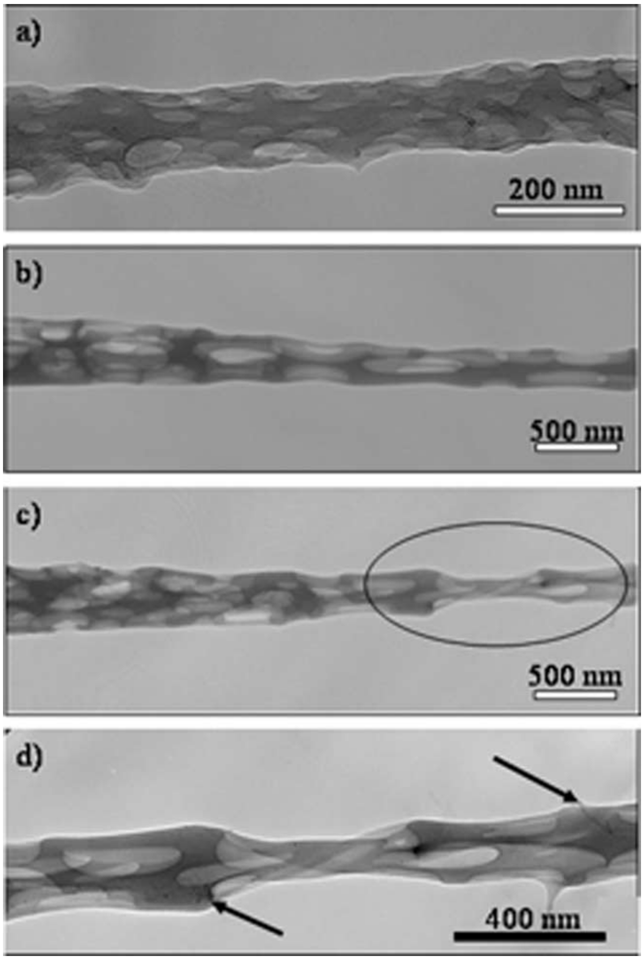

Fig. 3. In situ deformation process of single electrospun composite fiber under uniaxial tensile load in TEM; (a) an undeformed state, (b) a deformed state below a certain critical strain, (c) a state over a certain critical strain, where the necking initiates, and (d) close-up micrograph from circled area in (c).

the matrix, whereas the solvent-rich phases form the pores [19,26–28]. Through such nanopores on the electrospun nanofibers the specific surface area will be additionally increased in a large extent. These may give more feasible sites to anchor the polymer matrix chains, if used as reinforcing elements in composites, as well as to provide the ability to reversibly absorb and desorb guest molecules or nanoparticles for use specific purposes, such as drug delivery, sensors, filtration, etc.

The close inspection on electrospun composite fibers with TEM (Fig. 2) indicates that the MWCNTs are embedded in the nanofibers without any sign of agglomerates. Most MWCNTs are uniaxially well aligned along the fiber axis. Such alignment is obviously associated with the extreme high longitudinal strain rate of jet during electrospinning process, which may cause disentanglement or pulling out of curved nanotubes under high shear force. It is interesting to note that while the nanopores in a great extent are formed on the relative thick fibers (Fig. 2(a)), this tendency is considerably suppressed by reducing the fiber diameter, because there is insufficient ample room and/or time for phase separation to occur. As a consequence, the nanopores are rarely recognized in such very thin composite fibers as shown in Fig. 2(b). Polymer material in such thin fibers cannot entirely encapsulate the inherently curved MWCNTs. Therefore, the strongly curved MWCNTs are still not fully stretched by electrospinning process, which is apparently reflected on the significant curvature of electrospun composite fibers (Fig. 2(b)). This is well consistent with the fact that MWCNTs are not always in straight form, in most cases they are entangled and twisted with some curviness [29].

To study the deformation mechanism of single electrospun fibers, we have performed in situ tensile experiments on single electrospun composite fibers by electron beam induced thermal stress under TEM. The mechanism of tensile strain can be understood as follows. The bombardment of electron beam onto the fibers leads to the local thermal extension, which in turn initiates a small amount of tensile deformation within the fibers. This is similar to that in instrumented mechanical testing. Furthermore, the strain rate can be roughly controlled by the varying the electron beam flux onto the fibers [5,30–32]. Fig. 3 shows the sequence of deformation process of an electrospun composite fiber under tensile loading in TEM.

Once the tensile stress is generated by thermally induced electron beam, the fiber is stretched parallel to the fiber axis, which is connected with simultaneous stretching of nanopores. As the strain increases, the fiber elongates and the diameter of fiber reduces gradually (Fig. 3(b)). With further increase of strain the necking apparently takes place on the uniaxially stretched fiber (Fig. 3(c)). In-depth investigation on the necking area shows that the nanonecking obviously occurs at the end of a MWNT embedded into fiber (Fig. 3(d)).

Fig. 4 shows the stress concentration upon nanopores on the fiber surface. According to fracture mechanics, the nanopores effectively sever the sites for stress concentration under external load. When the uniaxial tensile stress (σ_o) is applied to a nanoporous fiber, here we assume that the pores have a hemispherical shape, the maximum stress concentration is at the equator region of a pore, perpendicular to the applied stress. Due to the number of pores on the surface of a fiber, the stress fields will intensively overlapped inside fiber (dark area inside fibers in Fig. 4). This indicates that a high uniaxial stress state will be built up inside fiber in between ligaments of matrix material between the pores [33].

Fig. 5 shows the schematic deformation processes of a single composite fiber under uniaxial tensile load. Stress will be highly concentrated at the tip of pores inside fiber, which leads to plastic deformation of composite fiber (Fig. 5(a)). At certain critical stress the MWCNTs begin to slip in tensile direction (Fig. 5(b)). At a large extent of strain the necking apparently forms at the ends of MWCNTs on the uniaxially stretched composite fiber (Fig. 5(c)) [28].

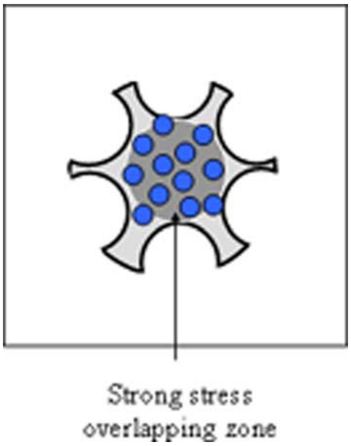

Fig. 4. Schematic illustration of stress concentration upon nanopores inside a composite fiber (cross-sectional view perpendicular to the fiber axis); white circle indicates the maximum stress concentration and the dark area within the fiber shows the strong stress overlapping zone, where the load direction is parallel to the fiber axis.

It is emphasized here that any sign of pull out of embedded nanotubes from the fiber matrix is not observed. This may be attributed to the fact that the individual MWCNTs aligned within the fibers possess some amount of absorbed layer of PC around them, indicating enhanced polymer connectivity at the nanotube surface. Through rapid evaporation of solvent during flight of the emitted jet from capillary to the collector, the MWCNTs will be highly aligned parallel to one another in the fiber direction and packed more densely due to the dimensional confinement of electrospun fibers. These compact aligned MWCNTs with strongly phase adhered interfacial layers to the polymer matrix will be significantly reinforced the composite fibers, which provides effective stress transfer mechanism [14]. So far, due to the close placing of MWCNTs in vicinity of nanopores and their high aspect ratio the aligned MWCNTs readily compensate the stress concentration upon nanpores under tensile load. As a consequence, in connection of the slippage of individual MWCNTs with their ability to damp local stress concentration the plastic deformation can be extensively activated in form of matrix shear flow to build up the formation fiber necking in ligament between the MWCNTs as well as the nanopores. This behavior might be of importance for contribution to the improvement of toughness of a composite. Slippage of individual MWCNTs embedded inside electrospun composite fibers significantly contribute to the elongation required for toughness even with enhanced strength of fibers.

4. Conclusions

We have successfully adapted the electrospinning technique to produce submicron size composite fibers based on PC/MWCNT nanocomposites. Two important structural characteristics have to be pointed out in our present work. At first, MWCNTs are uniformly embedded into fibers, highly aligned parallel to one another in the direction of fiber axis. In second, the electrospun composite fibers show an ultra-high nanoporous morphology on their surfaces. Both these features contributed to the mechanical deformation process of the single composite fibers. Under uniaxial tensile stress the nanopores effectively act as stress concentrators to build up uniaxial stress state within the fibers rather than hydrostatic state and the embedded MWCNTs slip in tensile direction. Coupling stress concentration upon nanopores with slippage of the individual MWCNTs within the electrospun fibers the strain at break responsible for toughness is significantly enhanced with simultaneous improvement of modulus of them. These

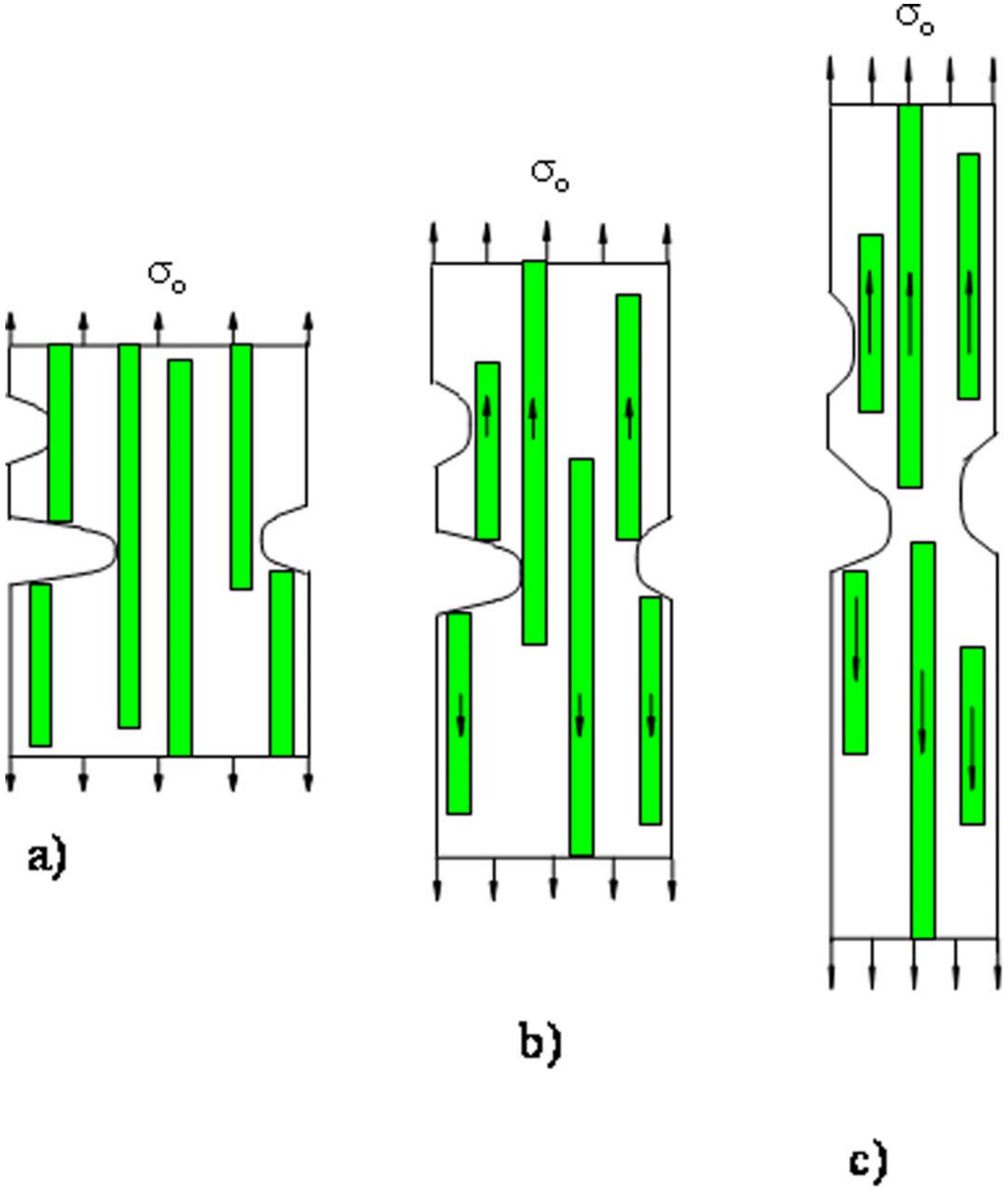

Fig. 5. Schematic illustration of mechanical deformation processes under tensile load; (a) stress concentration at the tips of nanopores, (b) the embedded MWCNTs begin to slip parallel to tensile direction at a certain critical stress, and (c) formation of nanonecking at the ends of MWCNTs followed by progress of slippage of them.

unique features provide a great potential for reinforcing elements to produce a new kind of composite.

References

[1] Iijima S. Nature 1991;354:56–8.
[2] Yakobson BI, Smalley RE. Am Scientist 1997;85:324–37.
[3] Treacy MMJ, Gibson JM. Nature 1996;381:678–80.
[4] Wong EW, Sheehan PE, Lieber CM. Science 1997;277:1971–4.
[5] Qian D, Dickey EC, Andrews R, Rantell T. Appl Phys Lett 2000;76:2868–70.
[6] Sandler J, Shaffer MSP, Prasse T, Bauhofer W, Shulter K, Windle AH. Polymer 1999;40:5967–71.
[7] Pötschke P, Fornes TD, Paul DR. Polymer 2002;43:3247–55.
[8] Coleman JN, Curran S, Dalton AB, Davey AP, McCarthy B, Blau W, et al. Phys Rev B 1998;58:7492–5.
[9] Grimes CA, Mungle C, Kouzoudis D, Fang S, Eklund PC. Chem Phys Lett 2000;319:460–4.
[10] Kim HM, Kim CY, Lee CY, Joo J, Cho SJ, Yoon HS, et al. Appl Phys Lett 2004;84:589–91.
[11] Curran SA, Ajayan PM, Blau WJ, Carroll DL, Coleman JN, Dalton AB, et al. Adv Mater 1998;10:1091–3.
[12] Thostenson ET, Zhifeng R, Chou-Tsu W. Compos Sci Technol 2001;61(13):1899–912.
[13] Andrews R, Jacques D, Minot M, Rantell T. Macromol Mater Eng 2002;287(6):395–403.
[14] Gojny FH, Nastalczyk J, Roslaniec Z, Schulte K. Chem Phys Lett 2003;370:820–4.
[15] Reneker DH, Chun I. Nanotechnology 1996;7:216–23.
[16] Xia Y, Li D. Adv Mater 2004;16:1151–70.

[17] Ko F, Gogotsi Y, Ali A, Naguib N, Ye H, Yang G, et al. Adv Mater 2003;15:1161–5.
[18] Fridrikh S, Yu JH, Brenner MP, Rutledge GC. Phys Rev Lett 2003;90: 114502–4.
[19] Bognitzki M, Czado W, Frese T, Schaper A, Hellwig M, Steinhart M, et al. Adv Mater 2001;13:70–2.
[20] Dror Y, Salalha W, Khalfin RL, Cohen Y, Yarin AL, Zussman E. Langmuir 2003;19:7012–20.
[21] Frrguson DW, Bryant EWS, Fowler HC. ANTEC'98; 1998. p. 1219–22.
[22] Shenoy AV. Rheology of filled polymer systems. Dordrecht: Kluwer Academic Publishers; 1999.
[23] Koombhongse S, Liu W, Reneker DH. J Polym Sci, Part B: Polym Phys 2001;39:2598–606.
[24] Huang L, McMillan RA, Apkarin RP, Pourdeyhimi B, Conticello VP, Chaikof EL. Macromolecules 2000;33:2989–97.
[25] Lee KH, Kim HY, Bang HJ, Jung YH, Lee SG. Polymer 2003;44: 4029–34.
[26] Megelski S, Stephens JS, Chase DB, Rabolt JF. Macromolecules 2002;35:8456–66.
[27] Casper CL, Stepens JS, Tassi NG, Chase DB, Rabolt JF. Macromolecules 2004;37:573–8.
[28] Kim GM, Lach R, Michler GH, Chang YW. Macromol Rapid Commun 2005;26:728–33.
[29] Pötschke P, Bhattacharyya AR, Janke A. Eur Polym J 2004;40: 137–48.
[30] Lourie O, Wagner HD. Appl Phys Lett 1998;73:3527–9.
[31] Lourie O, Cox DM, Wagner HD. Phys Rev Lett 1998;81:1638–41.
[32] Ye H, Lam HL, Titchenal N, Gogotsi Y, Ko F. Appl Phys Lett 2004; 85:1755–77.
[33] Kim GM, Michler GH. Polymer 1998;39(23):5689–97.