Molecular Crystals and Liquid Crystals

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl20

Morphological Characteristics of Electrospun Poly(Methyl Methacrylate) Nanofibers Containing Multi-Walled Carbon Nanotubes

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Version of record first published: 22 Sep 2010

To cite this article: Dong Ouk Kim, Jae Do Nam, Dai Hoe Lee, Jun Young Lee, Jong-Jin Park & Jong Min Kim (2007): Morphological Characteristics of Electrospun Poly(Methyl Methacrylate) Nanofibers Containing Multi-Walled Carbon Nanotubes, Molecular Crystals and Liquid Crystals, 464:1, 137/[719]-144/[726]

To link to this article: http://dx.doi.org/10.1080/15421400601030761

Mol. Cryst. Liq. Cryst., Vol. 464, pp. 137/[719]–144/[726], 2007

ISSN: 1542-1406 print/1563-5287 online
DOI: 10.1080/15421400601030761

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The electrospinning process was investigated to embed multi-walled carbon nanotubes (MWNTs) in the electrospun nanofibers of poly(methyl methacrylate) (PMMA) for anisotropic alignment and effective dispersion of carbon nanotubes in the transparent polymer substrate. The morphology of MWNT-incorporated electrospun nanofibers was substantially influenced by the types of solvent and the content of carbon nanotubes exhibiting various forms of beads, undulated fibers, or uniform fibers. In the fibrous forms of electrospun PMMA, the MWNTs were mostly attached on the surface of polymer by physical interlocking. On the other hand, when the bead-shaped PMMA was produced by the electrospinning process, most of the MWNTs were embedded in the PMMA matrix without being exposed on the polymer surfaces. Using the O_2 plasma treatment for cutting-off the polymer-rich surface layer of the beads, the embedded MWNTs were exposed out of the beads and subsequently an urchin-shaped structure was obtained.

This work was supported by the Korea Research Foundation Grant (KRF-2004-005-D00063). We also appreciate technical and instrumental support from Samsung Advanced Institute of Technology (SAIT) through research project to Sungkyunkwan Advanced Institute of Nanotechnology (SAINT).

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The protruded MWNTs of the urchin-shaped beads could stabilize the polymer beads by the steric stabilization in the solution state and provide facile electronic pathway and percolation in the condensed solid state.

Keywords: alignment; carbon nanotube; dispersion; electrospinning; plasma treatment; radius of gyration

INTRODUCTION

The electrospinning process can provide polymer nanofibers with diameters ranging from a few to several hundred nanometers and is attracting much interest due to their large surface-to-volume ratios in biomedical device and electronic applications. In electrospinning process, a high voltage is applied between a negatively charged polymer solution and conductive nanofiber collector to make polymer jet on the capillary tip. By rapid solvent evaporation, polymer solutions are transferred into nanofibers and stick on the metallic collector for random orientation form. It is known that the optimum viscosity of the solutions is about $0.5 \sim 50$ poise for the electrospinning process [1]. This process has been focused on aligning the nanofibers by using various arrangements of electrode systems for the applications in microelectronics and photonics [2]. Furthermore, it is interesting to electrospin polymer solutions containing heterogeneous entities (particles, fibers, tubes, etc.) because the heterogeneous entities could be well-dispersed and anisotropically-aligned by the electrospun fibers. There is a great possibility that the heterogeneous entities tend to maintain the well-dispersed solution state because the electrospun fibers are solidified for a short period of evaporation time. At the same time, however, the high elongation strain exerted on the electrospun fibers may influence the special arrangement of heterogeneous entities in the deforming polymer fibers.

Since the discovery of carbon nanotubes (CNTs) [3], they have been the focused with intensive investigation due to their unique properties and great potential applications [4–6]. In particular, when compared with other conductive filling materials such as spherical-shaped particles, their extremely large aspect ratios of the composite systems provide high electric conductivity at a low concentration of carbon nanotubes to give a low percolation threshold [7,8]. However, the realization of application still remains as challenge in many areas of research mainly due to difficulties in obtaining alignment control and homogeneous dispersion in organic/inorganic solutions and matrices. Recently, tremendous progress has been made in control

and fabrication of carbon nanotube nanocomposites through surface treatment by functionalization [9], utilization of surfactant [10], mechanical shear mix and in-situ bulk polymerization [11] etc. We believe that the electrospinning process could also be an effective way of dispersing and aligning carbon nanotubes, where the electrospun polymeric nanofibers work as dispersing matrices that could be aligned along with nanotubes.

In this work, MWNT/PMMA composite nanofibers were investigated by electrospinning the PMMA and purified MWNTs in three different types of organic solvents such as chloroform, toluene and dimethylformamide(DMF). Dispersion and alignment of MWNT-incorporated PMMA fibers exhibited different structural morphologies and different MWNT-PMMA adhesion characteristics. Treated by the O_2 plasma, an urchin-shaped MWNT hairy structure was synthesized from the electrospun MWNT/PMMA composite beads.

EXPERIMENTAL

The polymeric material used in this study was poly(methyl methacrylate) ($M_W = 350{,}000\,g/mol$, $1.15\,g/cm^3$, Sigma-Aldrich). 10 wt% of PMMA was dissolved in chloroform, toluene and dimethylformamide (Sigma-Aldrich) with physical stirring. The multi-walled CNTs were received from ILJIN Nanotech (Seoul, Korea) manufactured by a thermal CVD (Chemical vapor deposition) method. The diameter and the length measured by TEM (JEM-3011 TEM, JEOL Tokyo, Japan) were about 10 nm and $1 \sim 10\,\mu m$, respectively. The impurity content was below 5 wt% estimated by thermogravimetric analysis. Heat treatment was carried out in the oxygen-flowing environment at 663 K for 1 hr to eliminate amorphous carbon impurities. A (3:1) mixture of concentrated sulfuric (98%) and hydrochloric (100%) acids was used for a standard acid treatment of CNTs. The purified MWNTs were dispersed in three types of polymer solutions and sonicated for 1 hr in at 20 kHz. The final mixture was homogeneous and stable in a dark ink-like appearance.

Electrospinning was performed by a voltage of 15 kV (Model: HYP-303D, Han Young Co., Korea) and the solution was supplied by a syringe pump (Model: 781100, KD Scientific Co., USA) with consistent rates to spinneret. Both normal and separated electrodes were used. Separated parallel electrodes were placed on the non-conductive polymer sheets to align the electrospun fibers. The O_2 plasma was applied at 100 W for 4:25 min after electrospinning. Morphology was investigated by a scanning electron microscopy (Model S-2400, Hitachi Inc., Japan).

RESULTS AND DISCUSSION

The SEM micrographs of nanofibers electrospun from chloroform solution (0.5 wt% of MWNTs) are shown in Figure 1. As can be seen, there are tiny holes (0.1–0.4 μm in diameter) formed on the electrospun fiber surfaces and some of these holes appear to propagate to form microcracks on the fiber structures (Fig. 1(c)). The surface holes seem to be developed by a rapid evaporation of chloroform, which pressurizes vapor inside fiber structure and subsequently spouts through the electrospun fiber surfaces [13]. This finding is supported by the lowest boiling temperature of chloroform (61.2°C) among three solvent systems used in this study (110.8°C and 153°C for toluene and DMF, respectively). The diameter of electrospun fibers from the chloroform solution is 1∼3 micrometers, which is larger than the the electrospun fibers from different solvent systems. It is considered that the vaporized solvent builds up the pressure inside fibers eventually to provide the pore-containing swollen fibers. The dimensions of carbon nanotube are about 10 nm in diameter and 1∼10 μm in length, while electrospun PMMA nanofibers are 1∼3 μm in diameter in a continuous form. Therefore, carbon nanotubes cannot be observed in the images at a low magnification in Figure 1(a) or (b). At a high magnification (Fig. 1(c)), the carbon nanotubes can be seen at the fractured area protruded from the fractured surface of electrospun fibers demonstrating that the carbon nanotubes are dispersed inside electrospun fibers.

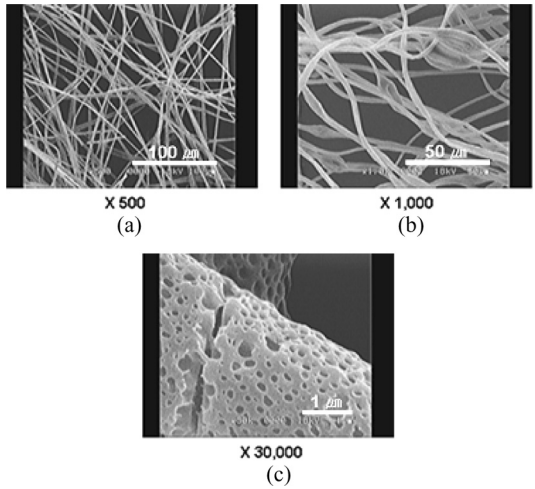

FIGURE 1 SEM micrographs of MWNT/PMMA nanofibers (0.5 wt%/10 wt%) electrospun from chloroform solution at different magnifications.

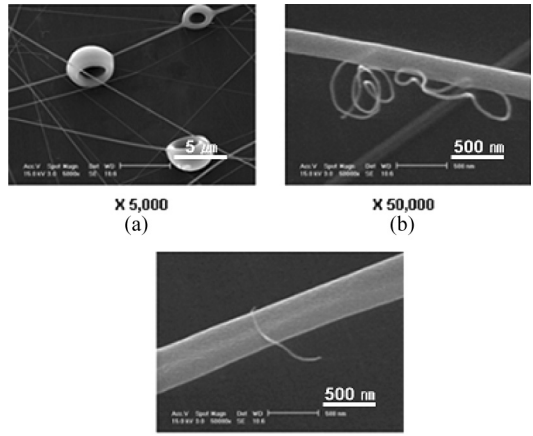

FIGURE 2 SEM micrographs of MWNT/PMMA nanofibers (0.5 wt%/10 wt%) electrospun from toluene solution at different magnifications.

The SEM micrographs of electrospun nanofibers (0.5 wt% of MWNTs) dispersed in toluene and DMF solution are shown in Figures 2 and 3. For the electrospun fibers from toluene solution in Figure 2, nanometer-sized fibers and micrometer-sized rings can be

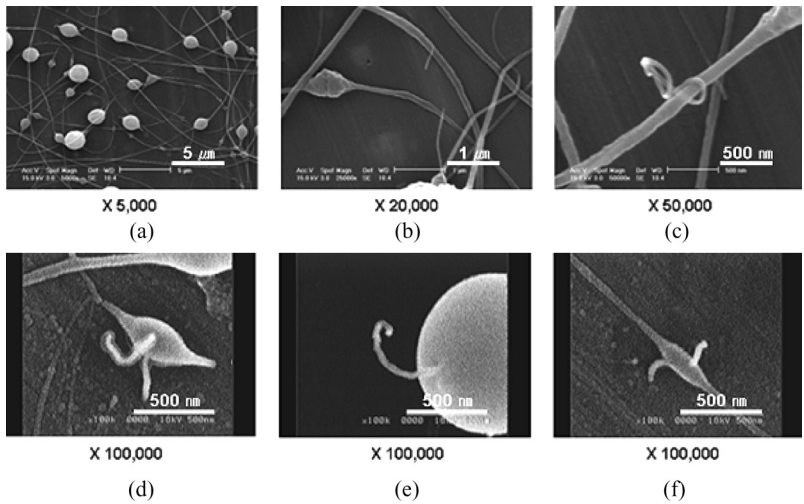

FIGURE 3 SEM micrographs of MWNT/PMMA nanofibers (0.5 wt%/10 wt%) electrospun from DMF solution at different magnifications.

seen (Fig. 2(a)). Carbon nanotubes can clearly be found on the electrospun fiber surfaces seemingly physically-interlocked without substantial chemical bondings with PMMA (Fig. 2(b) and (c)).

Figure 3 shows beads and nanofibers electrospun from DMF solutions. Comparing Figures 2 and 3 taken at high manifications, there are differences in MWNT/PMMA adhesion morphology between toluene and DMF solutions. For the MWNTs/PMMA nanofibers electrospun from toluene solutions, carbon nanotubes seemed to be physically stuck on the electrospun nanofiber surfaces (Fig. 2(b) and (c)). However, for the DMF solution system, carbon nanotubes appear to be stuck on the surface of electrospun nanofibers (Fig. 3(b),(c)) or penetrate through PMMA beads (Fig. 3(d–f)). It may demonstrate that the MWNT dispersion and the resulting MWNT/PMMA electrospun nanofibers are substantially affected by types of solvents.

The chain interlocking of PMMA around MWNT may be evaluated by comparing the dimensions of these two materials in a molecular level. The average radius of gyration of PMMA chains in the solution may be expressed as [14]

$$\langle S^2 \rangle = a(M_w)^b \tag{1}$$

Where, $\langle S^2 \rangle$ is the mean-squared radius of gyration with a unit of $Å^2$. M_w is molecular weight of PMMA, the constant a and b are 0.0713 and 1.0098, respectively, for PMMA [15]. According to Eq. (1), the average diameter of random PMMA chains is $2\langle S^2 \rangle^{1/2}$. For the PMMA system with $M_w = 350{,}000\,g/mol$ used in this work, the average diameter of random PMMA chains can be estimated as 34 nm. Consequently, the average diameter of PMMA is only 3.4 times larger than that of carbon nanotubes (ca. 10 nm). Therefore, it may be reasonable to mention that the PMMA chain is too short to wrap up the carbon nanotubes completely. As seen in Figures 2 and 3, the incorporation of MWNTs in polymer is substantially influenced some parameters such as chemical or physical attractions, and the polarity or structural effects of solvents, etc [11,12].

The different morphologies of nanofibers electrospun from toluene and DMF may be caused by the differences in the dispersion efficiency of solvents. DMF is known as good solvent for carbon nanotubes dispersion [12]. In this work, DMF showed relatively better efficiency than the other two solvents in terms of colloidal stability. Even when the sediment time is increased up to 2000 hours in this study, there was no apparent precipitation of carbon nanotubes in the DMF solution. We believe that the well-dispersed CNT mixture in DMF gives embedded CNTs in electrospun PMMA fibers.

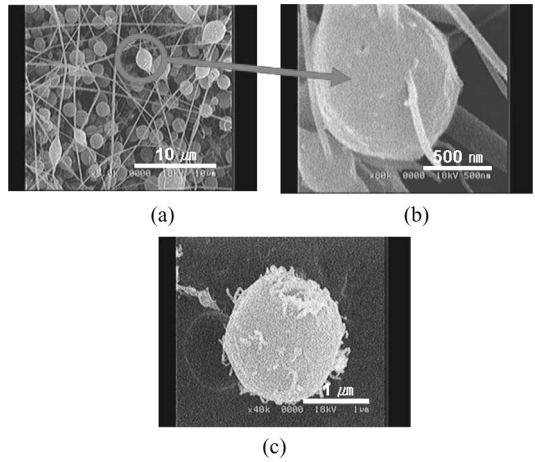

FIGURE 4 SEM micrographs of MWNT-embedded electrospun PMMA (MWNT:PMMA = 3.0 wt%: 10 wt%) nanofibers and beads from DMF solution: (a) Electrospun nanofibers with beads, (b) PMMA beads containing carbon nanotube bundles, (c) After O_2 plasma treatment, urchin-like structure with carbon nanotubes exposed on the bead surfaces.

Figure 4 shows SEM micrographs of electrospun PMMA beads and nanofibers containing 3.0 wt% of MWNT in DMF solution. Comparing Figure 3 and Figure 4, as the MWNT content in the solution is increased from 0.5 to 3.0 wt%, the numbers of beads are increased seemingly due to the increased viscosity of the solution and the coagulation of MWNTs during electrospinning [14]. Due to the high elongational stress and deformation in electrospinning, there is a great possibility that the MWNTs are concentrated inside the beads in Figure 4(b). Subsequently, treated by oxygen plasma, the MWNT/PMMA beads are shown in Figure 4(c). The carbon nanotubes embedded inside the beads are protruded by cutting-off the PMMA-rich surface layer of the beads. The resulting feature of the oxygen-treated beads exhibits an urchin-shaped structure with exposed MWNTs on the bead surface. The protruded MWNTs of the urchin-shaped beads could stabilize the polymer beads by the steric stailbization in the solution state and provide facile electronic pathway and percolation in the condensed solid state. We believe that the synthesized MWNT/PMMA urchin-shaped structure a great potential impact in various areas of microelectronics, optoelectronics, energy, display, bioengineering, etc. due to its unique characteristics combining 0-D (sphere) and 1-D (nanorod) structures.

CONCLUSIONS

The morphology of MWNTs/PMMA electrospun nanofibers was substantially affected by the types of solvents and the composition of carbon nanotubes providing various shapes of nanofibers and beads. The embedded carbon nanotubes inside the beads could be exposed by oxygen plasma treatment and an urchin-shaped structure was synthesized. Combining 0-D and 1-D structural characteristics, the urchin-shaped could be used in various microelectronic applications and device due to its unique features for providing facile electronic pathway and percolation.

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