 DOI: 10.1002/masy.200750445

Fabrication of Ordered Porous SWNT-Polymer Nanocomposites by Emulsion Templating

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Summary: Porous polymer films were produced from water-in-oil emulsion. Aqueous droplets were dispersed in PMMA/benzene solution without any emulsifier. Simple dip-coating of the emulsion on a substrate and air-drying led to hexagonally ordered porous thin films. Porous single walled carbon nanotubes (SWNT)-polymer composite films were prepared through the similar procedures also. The electrical conductivity of porous SWNT-polymer composites increased with the content of SWNT.

Keywords: carbon nanotube; nanocomposite; PMMA; porous thin film

Introduction

Porous polymeric materials have gathered a lot of attention because they have large specific surfaces, light weight, and thermal & electrical insulating properties. Due to those advantages porous polymeric materials will be potentially utilized in diverse applications such as catalytic supports, adsorbents, chromatographic materials, filters, light-weight structural materials, and insulators.[1–4] In particular, porous carbon nanotube-polymer nanocomposite film can be used for light weight EMI shieling material and transparent electrode.[5,6]

In this study we introduce simple method for producing porous polymer films from inverse emulsion. Water droplets were dispersed in polymer solution without any emulsifier by simple sonication process. A small amount of sucrose was dissolved in dispersed phase to prevent the coalescence of water droplets. The prepared emulsion was dip-coated onto a glass substrate and air-dried to form a porous thin film. Uniformly sized pores are hexagonally ordered in the thin film. SWNTs were added to polymer solution to prepare carbon nanotube composites. Porous nanocomposite films were produced by the similar process for porous polymer films.

Experimental Part

Poly(methyl methacrylate) (PMMA), sucrose, and 1-pyrenebutyric acid were purchased from Aldrich and used without further purification. Molecular weight of PMMA was 350,000 kg/mol. Benzene, HPLC grade, was obtained from Merck and used as received. SWNT was purchased from Carbon Nanotechnologies Inc. 2 wt% PMMA solution in benzene and 3 wt% sucrose aqueous solution was prepared. PMMA solution and sucrose aqueous solution were mixed with weight ratio of 98:2. The solution was sonicated for 4 hours to prepare water in oil emulsion. A slide glass was dipped into the emulsion for 30 seconds and air-dried for 30 seconds using heat gun. The dip-coating and drying cycle was performed 1 or 3 times. Dip-coated glass was washed in deionized water to remove any remaining sucrose from pores after drying. Purified SWNTs were mixed with 6 mM 1-pyrenebutyric acid in DMF to

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increase dispersibility of SWNT in PMMA matrix. [7,8] The solution was sonicated and stirred for a sufficiently long time. The weight ratio of SWNT and 1-pyrenebutyric acid was 1:1. It was the value which was calculated for the pyrene group to cover the half of SWNT surfaces. The solution was filtered and washed to remove unadsorbed 1-pyrenebutyric acid. 1-pyrenebutyric acid absorbed SWNT was dried and added to the PMMA solution phase varying its weight ratio. The weight fraction of SWNTs in the composite was from 0.5 to 5 wt%. The solution was mixed with aqueous solution of sucrose and sonicated. The porous composite film was made by the same procedure for porous polymer film described above.

Results and Discussion

The schematic procedure for fabricating porous polymer or nanocomposite film is illustrated in Figure 1. The film was simply produced by dip-coating of inverse emulsion on a substrate and subsequent air drying.

A small amount of sucrose dissolved in aqueous droplets magnificently improved the stability of emulsion. It prevented the coalescence of water droplets by suppressing Ostwald ripening. Ostwald ripening is inter-droplet mass transfer which occurs from the Laplace pressure difference due to the size distribution of droplets. This explains the disappearance of small droplet and the increase of large droplet diameter without coalescence of collision. It is known to be hampered by addition of a third component, selectively soluble in the dispersed phase only.[9] Sucrose is selectively soluble in water, such that it can be used to delay the coalescence of aqueous droplets. Without sucrose the emulsion broke down as soon as sonication was ceased.

During dip-coating of the emulsion on glass substrate, sucrose aqueous droplets are coming closer and forming hexagonally ordered porous structure. This phenomenon that liquid droplets can't recognize and coalesce each other is driven by a thermocapillary convection, which causes convective motion in and between the two bodies of fluids.[10] When the mixture of two solutions is evaporated on the glass substrate, benzene phase is more volatile and temperature gradient is formed between sucrose aqueous droplets and continuous benzene phase.[11–13] So, the convective motion in the between the droplets in made and suppresses coalescence of the two droplets, meanwhile the temperature gradient is existed.

The fabricated ordered porous polymer film was characterized by scanning electron microscopy (SEM). Figure 2 shows hexagonally ordered porous PMMA films. Ordered structure was formed over a relatively large area of 2 mm by 2 mm.

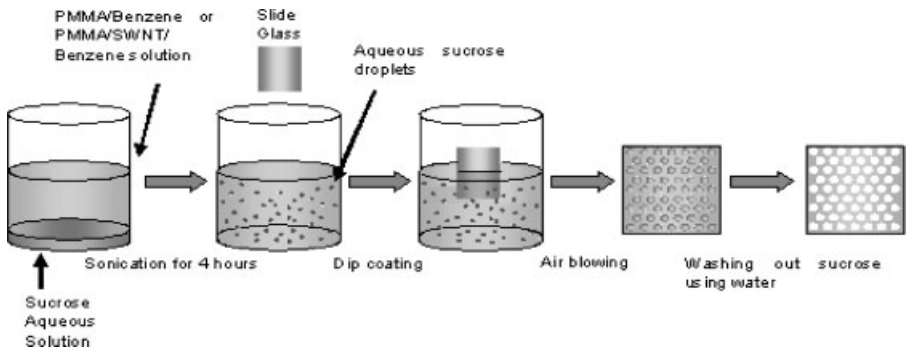

Figure 1.
Schematic procedure for porous polymer or nanocomposite film.

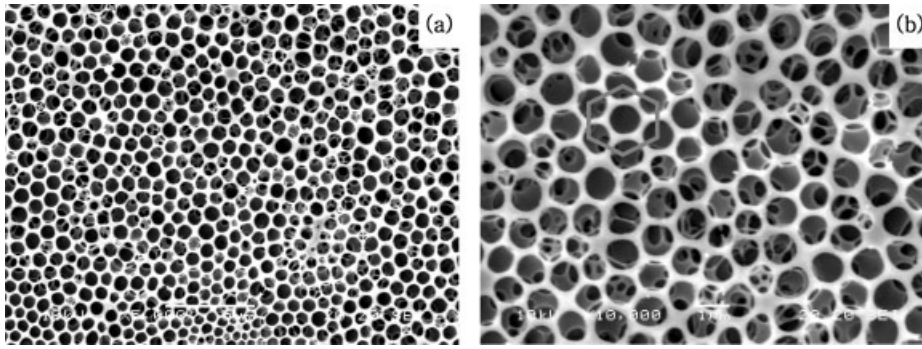

Figure 2.
SEM images of the PMMA porous films with the magnification of (a) 5000 and (b) 10000. Molecular weight of PMMA is 350,000 g mol^{-1}.

Note that the three times of successive dip-coating and drying led to three layers of pores. The average pore diameter was about 670 nm and wall thickness was 200 nm, respectively.

Figure 3 shows hexagonally ordered porous PMMA/SWNT composite films. The content of 1-pyrenebutyric acid absorbed SWNT was 2 wt%. These figures show similar ordered porous structure with homogeneous PMMA films. The average pore size in the composite was about 530 nm, which was smaller than that of pure polymeric material. SEM was used

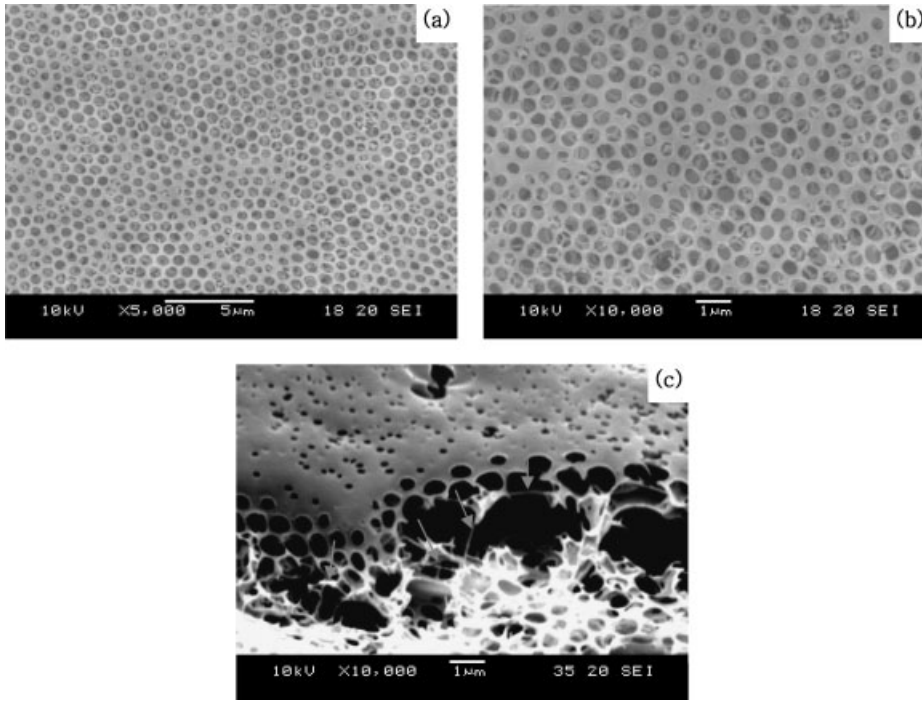

Figure 3.
SEM image of the PMMA/SWNT porous films with the magnification of (a) 5000, (b) 10000. (c) Tilted image of beam-damaged composite film containing 2 wt% SWNT. Molecular weight of PMMA was 350,000.

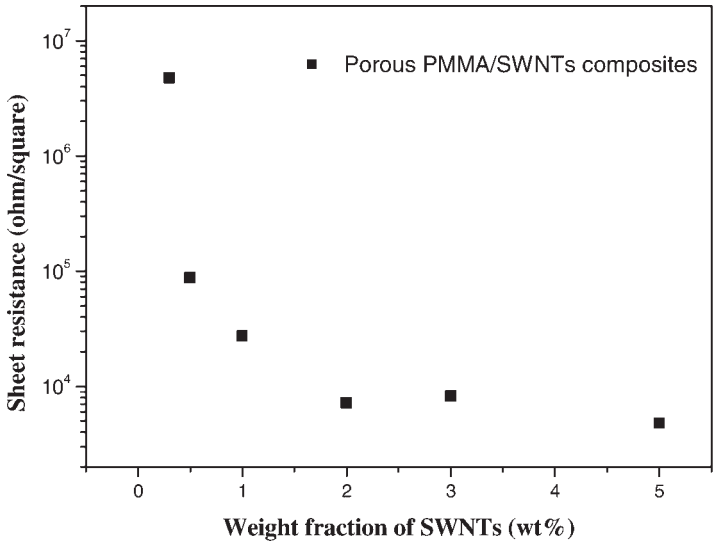

Figure 4.
Sheet resistance of porous PMMA/SWNT composite films vs. the concentration of SWNT.

with different method to examine the dispersion of SWNTs existed in this porous structure. Arrows in Figure 3. (c) indicates the region where SWNTs were exposed due to electron beam damage under SEM observation. Upon the exposure to electron beam organic PMMA matrix was seriously damaged and SWNTs were pulled out from the matrix. The well-dispersed state of SWNT in PMMA matrix was verified by SEM characterization.

To measure the electrical property of PMMA/SWNT composite, the sheet resistance of composite films including various amounts of SWNTs was examined with four point probe method. The results are plotted in Figure 4. The sheet resistance of homo PMMA was out of the range which is measurable by the instrument, higher than 10^{12} (ohm/square). Sheet resistance decreased from 4.753×10^6 to 4.775×10^3 ohm/square, when the concentrations of SWNT increased from 0.3 wt to 5 wt%. The sheet resistance decreased very rapidly below 1 wt% of SWNT. Above that, however, it decreased monotonically with the amount of SWNT.

Conclusions

We developed a new fabrication method for ordered porous polymer and polymer-carbon nanotube composite films using water in oil emulsion. In order to prepare porous polymeric films, the mixture of PMMA solution in benzene and aqueous solution of sucrose was sonicated. A small amount of sucrose in water prevented the coalescence of water droplets in polymeric solution. The resulting water in oil emulsion was dip-coated on a glass substrate and air-dried to get porous structure. Porous PMMA/SWNT composite films were obtained through a similar procedure, applying various amount of SWNT in polymer solution. The electrical conductivity of porous nanocomposite increased with the amount of 1-pyrenebutyric acid absorbed SWNT.

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