Single-walled Carbon Nanotube Modification into a Photograft-polymerized Polymer Film via Polyion-complexation

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Shortened single-walled carbon nanotubes having anionic charges were immobilized in a cationic vinyl monomer-photografted poly(ethylene terephthalate) film. The present method is simple and useful for preparing polymer/nanotube hybrid films via the polyion-complexation of cationic photografted polymer films and anionic CNTs.

Carbon nanotubes (CNTs) discovered by Iijima[1] are nanomaterials used in many areas of science and technology due to their remarkable electrical, mechanical, and thermal properties.[2,3] By taking advantage of the CNTs' properties, a wide variety of polymer characteristics including mechanical strength, electrical conductivities, etc. are expected to be enhanced or functionalized by the addition or modification of CNTs, and for this reason, there have been a great number of papers describing the preparation and characterization of CNTs/polymer nanocomposites.[4] Methods can be classified into "solution blending," "melt blending," and "in situ polymerization." CNTs are fascinating materials[5] for preparing conducting transparent films because they are conducting nanomaterials having 1D structures. The methods of spraying the CNT dispersion on films or solvent evaporation are often used to coat polymer surfaces with CNTs. However, CNTs often cause aggregation during solvent evaporation and the interactions between the coated-CNTs and the polymer surfaces are not very strong because they are formed via a noncovalent physical modification.

In this paper, we present a new method preparing CNTs/polymer hybrid films using photograft polymerization,[6] in which we use shortened single-walled carbon nanotubes (s-SWNTs) having anionic charges and polymer films having cationic charges. Figure 1 schematically shows the immobilization of s-SWNTs in a cationic monomer-photografted poly(ethylene terephthalate) (PET) film. The method is simple, namely the photograft polymerization is followed by polyion complexation.

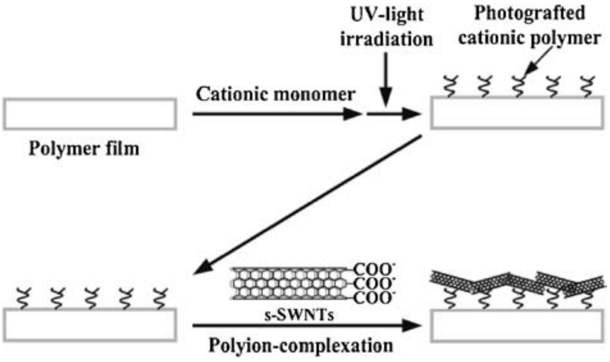

Figure 1. Schematic drawing of carbon nanotubes-modification on a polymer film via photograft polymerization and polyion complexation.

The s-SWNTs were obtained by acid treatment of SWNTs (HiPco, Carbon Nanotechnologies, Inc.) in a mixture of concentrated sulfuric acid and nitric acid (3:1 v/v) at 40 °C for 3 h,[7] followed by filtration and rinsing well with water, and then drying under vacuum. Nitrogen gas bubbling through an 1.0 M aqueous solution of [2-(acryloyloxy)ethyl]trimethylammonium chloride in a quartz cell for 30 min was conducted and then a 27 mM acetone solution of benzophenone (BP) as the initiator was added. A PET film was placed in the solution and the photograft-polymerization was carried out using a high-pressure mercury lamp (500 W) for 1 h at 70 °C in an atmosphere of nitrogen gas. After the reaction, the film was rinsed with pure water for 12 h to remove any unreacted monomer and the homopolymer generated by the photopolymerization, then dried under vacuum at 60 °C overnight. The photografting degree for the film was less than 0.2 wt %. The obtained film (photograft PET film **1**) was dipped in water-dispersed s-SWNTs overnight, followed by washing with deionized water and drying in a vacuum oven at 60 °C for 1 d to obtain a hybrid film (hybrid SWNTs/PET film **1**) of the s-SWNTs with the PET.

Figure 2 shows a photograph of (a) the hybrid SWNTs/PET film **1** and (b) the photograft PET film **1**. The photografted PET film **1** has almost no color, while the hybrid SWNTs/PET film **1** is fairly grey-colored.

X-ray photoelectron spectroscopic measurements (PHI ESCA SYSTEM, ULVAC ELECTRONICS) were carried out on the virgin PET film, photograft PET film **1** and hybrid SWNTs/PET film **1** and it was found that the N_{1s}/C_{1s} values for these three different films were 0.0, 0.053, and 0.026, respectively. The existence of N_{1s} is due to the photograft-polymerization using the ammonium monomer. It was difficult to determine quantity the amount of the immobilized s-SWNTs because the amount is minute. We have carried out a delamination test using Scotch adhesive tape and found that no change in the absorption spectrum of the immobilized s-SWNTs was observed after the test, indicating that the adhesion between the s-SWNTs and the photografted PET surface is rather strong. The thermogravimetric curves (Shimadzu TGA-50) of the pristine-PET film,

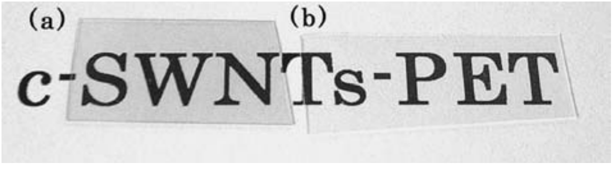

Figure 2. A photograph of (a) hybrid SWNTs/PET film **1** and (b) photograft PET film **1**.

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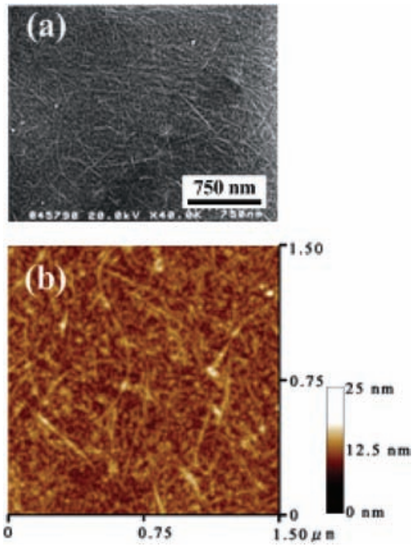

Figure 3. SEM (a) and AFM (b) images of hybrid SWNTs/PET film **1**.

photografted PET film and hybrid SWNT/PET film were virtually identical. The result means that the thermal properties of the films do not change after the photograft-polymerization and then the hybrid film formation.

The surface morphologies of the hybrid SWNTs/PET film **1** were examined using a scanning electron microscope (SEM, HITACHI S-5000) and an atomic force microscope (AFM, Digital Instruments, NanoScopeIIIa). These data are shown in Figure 3, in which we see carbon nanotubes as bundled structures in the SEM.

From the height profile of the AFM image, the average diameter of the s-SWNTs was 5–10 nm. Figure 4 shows a Raman spectrum (JASCO, NRS-3100) of the hybrid SWNTs/PET film **1**, in which the G-band at 1590 cm^{-1}, and the RBM (radial breathing mode) at 208, 230, and 266 cm^{-1} are evidently observed. The D-band that appeared at 1290 cm^{-1} is typical for the SWNTs. Based on the Raman shifts in the RBM region, we could estimate the diameters of the SWNTs using the proposed equation,[8] d (nm) $= 223.5/(\nu - 12.5)$, where d is the diameter (nm) of the SWNTs and ν is the Raman shift (cm^{-1}). The calculated values were 0.9–1.1 nm, which were similar to those of s-SWNTs.

The surface resistivity (R_s) on the obtained films were measured. Both the pristine-PET film and photograft PET film **1** were insulating (R_s values were over the measuring limit $10^8\,\Omega$/square), while that of the hybrid SWNTs/PET film **1** was ca. $3 \times 10^6\,\Omega$/square. The decrease in the surface resistivity is due to the formation of a network structure of the SWNTs on the PET film. The optimum experimental conditions would provide greater conducting PET films. Such study is in progress in our laboratory.

In conclusion, we have developed a method to prepare a PET/CNTs hybrid film via the polyion-complexation of a cationic photografted PET and anionic CNTs. The described method is simple and applicable to many polymer films because the photograft polymerization is a common method that can be used to prepare many polymer films.

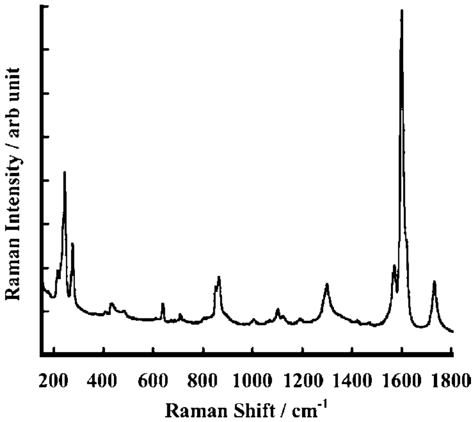

Figure 4. Raman spectrum of a hybrid SWNTs/PET film **1**.

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