Gels of Carbon Nanotubes and A Nonionic Surfactant and High-quality Carbon Nanotube Films Prepared by Gel Coating

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ABSTRACT

This paper reports gels of carbon nanotubes (CNTs) with a nonionic surfactant, polyoxyethylene(12) tridecyl ether (POETE), and high-quality CNT films prepared by gel coating. Mixtures of multi-walled CNTs (MWCNTs) and POETE that was a fluid at room temperature became gels after mechanical grinding. The heavily entangled MWCNTs debundled during the grinding and dispersed with fewer bundles in POETE. The mechanism for the gel formation was studied by the dynamic mechanical measurements and scanning electron microscopy. The results suggest that the formation of the CNT/POETE gel is the result of the physical-crosslinking CNT networks, mediated by the van der Waals interaction between CNTs and the nonionic surfactant. The CNT/POETE gels were electrically conductive and could be processed into conductive CNT films by coating the CNT/POETE gels on a substrate by a doctor blade and subsequent heating. POETE was removed during the heating, while the heating did not degrade the CNTs. The CNT films had a good adhesion to substrate.

Keywords: carbon nanotube, gel, film, coating, surfactant

1 INTRODUCTION

CNTs have been attracting strong attention owning to their fascinating one-dimensional structure and unique mechanical, electrical and thermal properties [1-6]. CNTs are promising in various important applications. Though great progress has been made in CNTs, their application is severely impeded by their poor processibility, since they do not melt and usually have quite low solubility in solvents. Many methods have been developed to improve the dispersion capability of CNTs in solvents, including covalent sidewall modification, polymer wrapping, modification through π-π interaction with aromatic molecules, and surfactants [7-9]. However, these methods require an ultrasonication of CNTs under a high power or a chemical reaction. These methods could alter the physical properties and bring severe defects to CNTs. Moreover, they are still far away from processing of CNTs in large scale, because only in a small amount of CNTs can be dispersed by these methods. To efficiently process CNTs is still an important research topic. A simple and efficient method is strongly required. The method reported by Fukushima et al. on bucky gels of CNTs and ionic liquids opens a possibility to process CNTs in large scale [10,11]. The bucky gels were prepared by mechanical grinding, and CNTs debundled during the mechanical grinding.

Here, we report the preparation of gels of CNTs and a nonionic surfactant, POETE through mechanical grinding [12]. Conductive CNT films were prepared by coating the gels on substrates by doctor blade and removing the nonionic surfactant by subsequent heating. The CNT films have good adhesion to the substrate and can be produced in large scale.

2 EXPERIMENTAL

MWCNTs produced by chemical vapor deposition (CVD) were purchased from Chengdu Organic Chemicals Co. Ltd. run by the Chinese academy of Sciences. The specifications were: average outer diameter of 8–15 nm, average length of 50 μm, and purity higher than 95 %. POETE was purchased from Sigma-Aldrich. All the materials were used without further purification.

The CNT/POETE gels were prepared by mechanical grinding. 10 mg CNTs were mixed with 2 ml POETE in an agate mortar. The mixture turned into a sticky paste after ground for 1 hr. The paste was centrifuged with a Profuge 14D at 10,000 rpm for 30 min. The mixture separated into two phases. The top transparent liquid phase was decanted from the containers after centrifugation, and the bottom phase was collected.

The CNT/POETE gels were coated on glass substrates through a doctor blade. The gels turned into CNT films on glass substrate after heating at 250 ^{o}C for 15 min and subsequently at 475 ^{o}C for another 5 min in air.

The rheological properties of the gels were studied using a Rheometric Scientific Advanced Rheometric Expansion System. Scanning electron microscopic (SEM) images were obtained with a Hitachi S-4100 scanning electron microscope. Transmission electron microscopic (TEM) images were taken with a JOEL JEM 2010F transmission electron microscope equipped with a field emission gun. The MWCNT/POETE gel was dispersed in deionized (DI) water, and was sonicated in a Branson 1510 ultrasonic bath for 5 min. Then, the MWCNTs were put on a copper grid with carbon film, purchased from Electron Microscopy Sciences, for the TEM measurements. The conductivitives of the gels and the CNT films were measured by the four-point probe technique with a Keithley

2400 source/meter. The conductivities of the CNT/POETE gels were measured by placing the gel on a glass slide attached with 4 copper foils which served as the 4 probes. The conductivity of the CNT film was tested on a square CNT film on a glass substrate with the van der Pauw four-point probe technique. The thickness of the gels for the conductivity study was measured by a micrometer caliper, while the thickness of the CNT films was determined by cross-sectional scanning electron microscopy (SEM). The thermal gravimetric analyses (TGA) of POETE and MWCNTs were carried out in air with a Du Pont 2950 TGA. The samples were put at 120 ^{o}C for 10 min. Then, they were heated to decomposition at a heating rate of 10 ^{o}C min^{-1}. The Raman spectra were acquired in a back scattering configuration using a Jobin Yvon Horiba LabRam HR800 Raman system with a 514.5 nm Ar^+ laser as the excitation source. The laser power was 2 mW, and the resolution was 2.4 cm^{-1}. The accumulation time for each sample was 900 seconds.

3 RESULTS AND DISCUSSION

3.1 Gels of MWCNTs and POETE

Surfactants have been frequently used to disperse CNTs in solvents, particularly water [9]. POETE as a nonionic surfactant exhibited good wettability for MWCNTs, when they were mixed together. The mixture of MWCNTs and POETE turned to a soft, black, and sticky paste after mechanically ground for about 1 hr. Excess POETE was used to have a better dispersion of CNTs. The excess POETE was removed by the subsequent centrifugation of the paste. The paste separated into two phases in the centrifuge tube after the centrifugation. The bottom phase was a black gel, while the top was transparent POETE. Fig. 1a shows a picture of an upside-down centrifuge tube containing the two phases. The black gel remained on the bottom of the centrifuge tube and did not fall down under gravity. Since the gels of CNTs and ionic liquids are called bucky gels of ionic liquids [10], the gels of CNTs and a nonionic surfactant can be named as bucky gels of the nonionic surfactant as well. The weight percentage of MWCNTs in the MWCNT/POETE gel was determined after removing the excess POETE. It was 1.5 % by weight, that is, the maximum gelling efficiency was 66 g POETE for 1 g MWCNTs. The MWCNT/POETE gel could be extruded from a needle and did not break down under gravity. (Fig. 1b) This research work focused on the CNT/POETE gels with maximum gelling efficiency since they had the best CNT dispersion.

The MWCNT/POETE gels were stable at room temperature. They did not show any remarkable change after several weeks. The gels still kept the solid-like shape under heating up to 200 ^{o}C. They also did not shrivel even in vacuum of 10^{-4} mbar. The stability under heating or in vacuum is related to the low volatility of POETE. The gels were electrically conductive. Their conductivity was about 4×10^{-3} S cm^{-1} as determined by the four-point probe technique. The electrical conduction can be attributed to MWCNTs since the liquid component, POETE, in the gel is non-conductive.

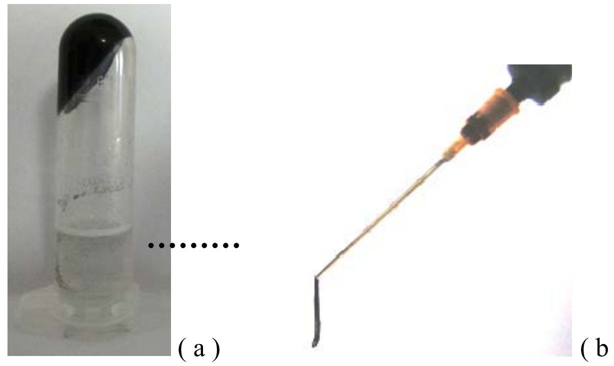

Fig. 1 Photographs of a MWCNT/POETE gel. (a) Phase-separation behavior of the gel (upper phase) and excess POETE (lower phase), observed after centrifugation of a ground mixture of MWCNTs and POETE. The dotted line indicates the surface of the liquid phase. (b) Extrusion of the gel from a needle.

Fig. 2 shows the SEM image of a MWCNT/POETE gel. The as–received MWCNTs, which were heavily entangled, and some of them bundled together, became separated and showed less bundles in the gel. This indicates that the MWCNTs debundled during the grinding, just similar to the grinding of CNTs in ionic liquid [10].

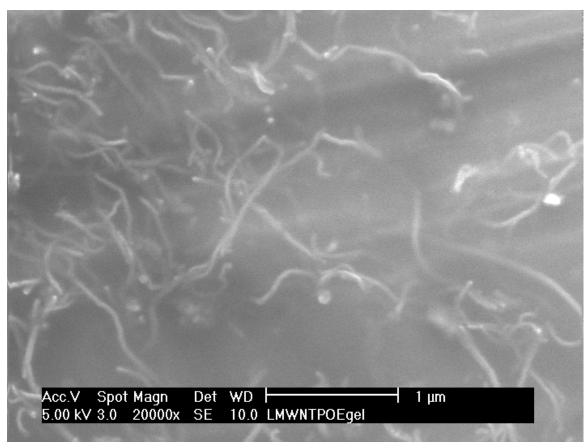

Fig. 2 SEM image of a MWCNT/POETE gel.

The rheological properties of the MWCNT/POETE gels were characterized as well (Fig. 3). The dynamic storage modulus (G') is almost flat over a wide range of the angular frequency (ω) from 0.1 to 100 rad s^{-1} at the amplitude of applied strain (γ) being 1 % or 5 %, while G" does not show any sign of relaxation. G' is always higher than G" at a certain angular frequency. This dynamic mechanical behavior is similar to that of CNT/ionic surfactant gels or CNT/surfactant suspensions obtained by ultracentrifugation of solution dispersed with surfactant and CNTs [10,11,13-

15]. These results indicate that the MWCNT/POETE gel prepared by the mechanical grinding has permanent networks and therefore behaves as a gel.

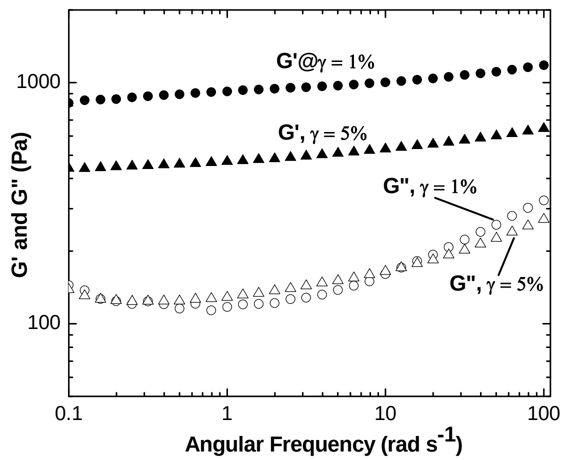

Fig. 3 Angular frequency (ω) dependencies of dynamic storage (G', solid symbols) and loss moduli (G", open symbols) of a MWCNT/POE gel at room temperature. Applied strain amplitudes (γ) were 1 % (circles) and 5 % (triangles).

The dispersion of MWCNTs in POETE is related to the van der Waals interaction between MWCNTs and POETE, since POETE is a nonionic surfactant and surfactants have been frequently used to disperse CNTs in solvents [9]. This interaction helps MWCNT debundle when ground, and it stabilizes MWCNTs in POETE. Thus, the networks in the MWCNT/POETE gel are formed by MWCNTs and mediated by the van der Waals force between MWCNTs and POETE. The conductive property of the MWCNT/POETE gel is due to the MWCNT networks in the gel.

The formation of the MWCNT/POETE gel is related to the length of the MWCNTs. Short MWCNTs, which were about 1 μm in length, were also used for the gel preparation through a similar process. The maximum gelling efficiency was down to 32.3 g POETE for 1 g short MWCNTs. The lower gelling efficiency of the short MWCNTs compared with long MWCNTs also implies that the networks in the MWCNT/POTET gels are formed by the MWCNTs. More short MWCNTs are needed to form the networks.

3.3 CNT films prepared from CNT/POETE gels

The formation of a homogeneous CNT film in a large area is important for the applications of CNTs in many aspects. The MWCNT/POETE gels could be used for the fabrication of CNT films through coating. POETE could be removed by heating. TGA results of POETE, MWCNTs and SWCNTs in air indicate that the decomposition of POETE starts at about 150 °C and finishes at 250 °C (Fig. 4). During the decomposition of POETE, the MWCNTs or SWCNTs are quite stable. Hence, the heating to remove POETE does not degrade MWCNTs and SWCNTs.

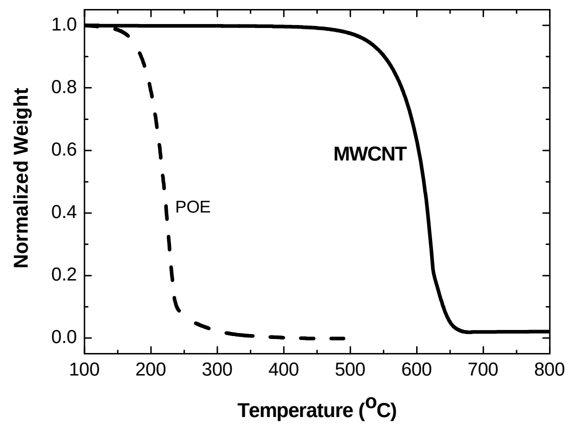

Fig. 4 TGA results of POETE (dashed line) and MWCNTs (solid line).

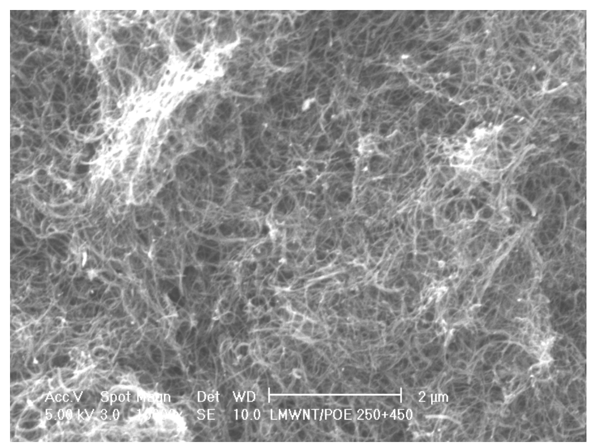

Fig. 5 SEM image of a MWCNT film. The MWCNT film was prepared from a MWCNT/POETE gel.

MWCNT films were prepared by coating the MWCNT/POETE gel on a glass substrate by a doctor blade. Then, POETE was removed by heating. A two-stage heating process in air was needed to obtain a homogeneous CNT film: at 250 °C for 15 min, subsequently at 475 °C for another 5 min. The first heating at 250 °C is important for homogeneity of the CNT film, while the following heating at 475 °C can completely decomposite POETE in a short time. The MWCNT film had a conductivity of about 13 S cm^{-1} and good adhesion to the substrate. It did not detach from the substrate under strong gas flow or when immersed into water. Fig. 5 shows the SEM image of a MWCNT film on glass. The SEM image of the MWCNT film indicates that MWCNTs entangle with each other.

The fabrication of CNT film using CNT/POETE gels is an efficient way thanks to the simple dispersion process, dispersion of high amount of CNTs in POETE, simple coating, and easy removal of POETE. This method which does not require solvent and an ultracentrifugation of solution is different from that reported by Dan et al [16]. Dan et al. demonstrated fabrication of CNT films in large scale by rod-coating suspensions of CNTs and surfactants obtained through the ultracentrifugation of aqueous solution dispersed with surfactants and CNTs. Moreover, the CNT films prepared by our method have good adhesion to the substrate, since they are fabricated through coating and the surfactant is removed by heating. This is different from the methods of preparing the CNT film through filtration of solution dispersed with CNTs or a solid-state drawing process [2,4]. The CNT films obtained by these methods have to be transferred to the desirable substrate, so that they may have a problem of adhesion to the substrate.

Finally, it is worth to point out that our method to disperse CNTs in POETE by mechanical grinding is different from the conventional methods to disperse CNTs in solution of surfactants, in which an ultrasonication process is needed [9,16-18]. No solvent is used in our method, and our method can disperse CNTs in a much higher concentration than the conventional ways.

4 CONCLUSIONS

Bucky gels were formed by mechanically grinding mixtures of MWCNTs and POETE which was a nonionic surfactant and a fluid at room temperature. The MWCNTs debundle during the grinding and form networks through the physical crosslinking in the MWCNT/POETE gels. The gels have good stability up to 200 ^{o}C or in vacuum. Homogeneous CNT films could be fabricated from the MWCNT/POETE gels through coating, and POETE could be removed by heating. The MWCNT films fabricated through this method had a conductivity of about 13 S cm^{-1} and good adhesion to the substrate. This opens a new avenue to efficiently fabricate CNT films in large scale.

ACKNOWLEDGEMENT

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