Journal of Radiation Industry 1 (2) : 97~100 (2007)

Synthesis of Poly (styrene-*co*-maleic anhydride)-grafted MWNT by Radiation Induced Graft Polymerization

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Abstract − Single-step in situ synthesis of poly (styrene-*co*-maleic anhydride)-grafted multi-walled carbon nanotubes (MWNT-*g*-P (St-*co*-MAH)) under ^{60}Co γ-ray irradiation is described. Raman spectra, and thermal gravimetric analysis (TGA) results showed that poly (styrene-*co*-maleic anhydride) was successfully grafted onto the surface of multi-walled carbon nanotubes (MWNTs). The polymer content in MWNT-*g*-P (St-*co*-MAH) can be up to ~36 wt%, as determined by TGA. The TEM images showed that the MWNT-*g*-P (St-*co*-MAH) was dispersed individually, and the external diameter of resultant MWNTs was increased. The functionalized MWNTs were dispersed well in organic solvent such as tetrahydrofuran.

Key words : Carbon nanotube, Grafting, Irradiation

INTRODUCTION

Carbon nanotubes (CNTs) can be viewed as rolled up graphite sheets held together by van der Waal's bonds. CNTs were discovered by Iijima when they were produced from a cathode by a carbon-are discharge method similar to that used for preparing fullerenes (Iijima *et al*. 1991). CNTs exist in two forms, single-walled carbon nanotube (SWNT), in which the tube is formed from a single layer of carbon atoms, and multi-walled carbon nanotubes (MWNTs), in which the tube consists of several layers of coaxial carbon tubes (Dresselhaus *et al*. 2001). These CNTs have diameters in the range between fractions of nanometers and tens of nanometers and lengths up to several centimeters with both their ends normally capped by fullerene-like structures. CNTs have aroused increasing interest from many researches due to their remarkable tensile strength, high chemical stability, resistant to high current density, high thermal conductivity, flexibility and other physicochemical properties (Hu *et al*. 2005; Khabashesku *et al*. 2005). The functionalized CNTs are believed to be very promising in fields such as preparation of functional and composite materials and biological technologies (Chen *et al*. 2005).

In this work, we report on single-step in-situ preparation of CNTs composites by covalently grafting styrene and maleic anhydride to the surface of MWNTs under ^{60}Co γ-ray irradiation.

EXPERIMENTAL

1. Materials

Multi-walled carbon nanotubes were obtained from Iljin Co. HNO_3 was supplied by Supelco Company. Methanol was used as solvent and was supplied by Merck. Styrene and maleic anhydride were used as monomer throughout this study and were supplied by Aldrich Chemical Com-

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pany, USA.

2. Sample preparation

The impurities were eliminated by refluxing the MWNTs in 2.5 M HNO_3 for 12 h and washed several times with deionized water and dried. Typically, 0.1 g of purified MWNTs, 29.4 g of styrene, 7.35 g of maleic anhydride and 36.75 g of methanol were mixed together in a glass tube. The mixture was sonicated for 30 min and purged with N_2 gas to remove the air for 20 min before irradiation and then subjected to γ irradiation of ^{60}Co source to a total dose of 10, 20 and 30 kGy (dose rate: 10 kGy hr^{-1}). After irradiation, the mixture was filtered through 0.2 μm microporous poly (ether sulfone) membrane 10 times. To ensure that no possible homopolymer and free reagents exist in the product, at each time, the filter mass was dispersed in tetrahydrofuran (THF), then filtered, and washed with THF. The poly (styrene-*co*-MA) grafted MWNTs (MWNT-*g*-P (St-*co*-MAH)) were obtained by filtration and drying overnight under vacuum.

3. Characterization

The Raman measurement was performed on a LabRam HR and a 0.5 mW argon-ion laser (514 nm) was used. TGA measurement was carried out under a flowing nitrogen atmosphere at a scan rate of 10°C min^{-1} from 50 to 600°C. Transmission electron microscopy (TEM) observations were performed with a JEOL microscope at an accelerating voltage of 200 kV. The samples for TEM observation were prepared by depositing a drop of the nanotubes aqueous suspension on carbon-coated copper grids and then allowing them to dry in a desiccator.

RESULTS AND DISCUSSION

Fig. 1 shows the Raman spectroscopy of pristine and polymer grafted MWNTs. Raman spectroscopy studies of carbon nanotubes exhibited two strong bands at approximately 1,280 and 1,580 cm^{-1} that corroborated to D-band and G-band. The peak at 1,283 cm^{-1} (D-band) of pristine MWNTs suggests the existence of amorphous carbonaceous material adhered to the defective pentagon and heptagon structures in the graphitized walls. However, grafting

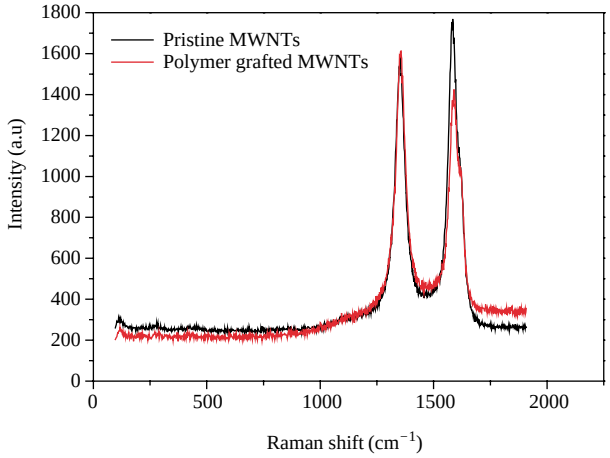

Fig. 1. Raman spectra of carbon nanotubes.

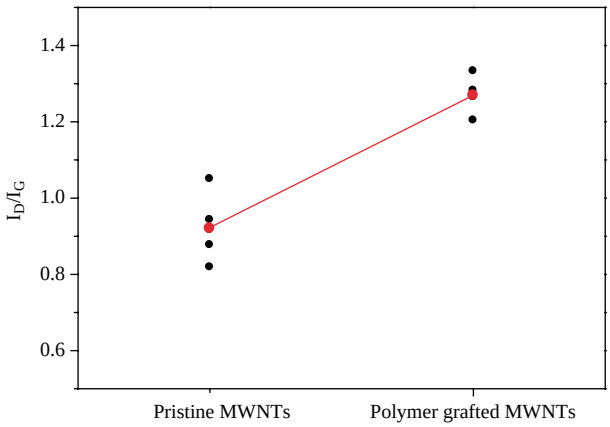

Fig. 2. The intensity ratio between D-band and G-band of carbon nanotubes.

of these MWNTs shifted the peak to a lower frequency (1,279 cm^{-1}). Similarly the peaks of G-band appeared at 1,592 cm^{-1} (pristine MWNTs), and 1,599 cm^{-1} (MWNT-*g*-P (St-*co*-MAH)) respectively. On considering the intensity ratio between D-band and G-band (I_D/I_G), it increases from 0.92 (pristine MWNTs) to 1.27 (MWNT-*g*-P (St-*co*-MAH)) implying the generation of surface defects due to a grafting reaction (Fig. 2).

It is known that the decomposition of CNTs can be realized by thermal decomposition. In this study, we used TGA to determine the relative amount of grafted polymer of MWNT-*g*-P (St-*co*-MAH). Fig. 3 shows the TGA traces for the MWNTs and MWNT-*g*-P (St-*co*-MAH) under nitrogen. The weight losses corresponding to the pristine purified MWNTs and MWNT-*g*-P (St-*co*-MAH) (10, 20, and 30

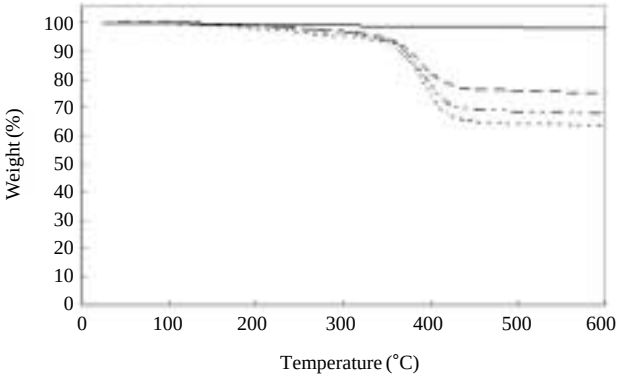

Fig. 3. TGA curves of the pristine MWNTs (a) and polymer grafted MWNTs (radiation dose: 10 kGy (b), 20 kGy (c) and 30 kGy (d)).

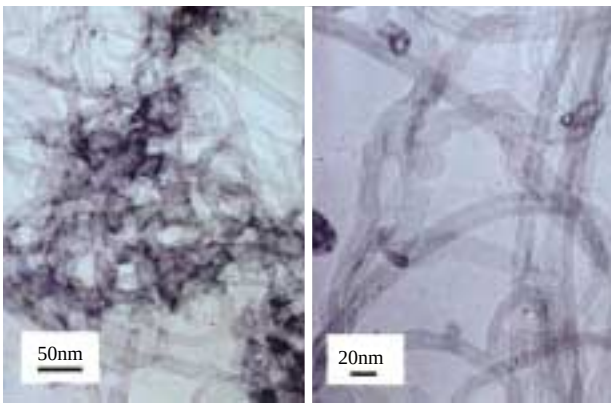

Fig. 4. TEM images of the pristine MWNTs (left) and MWNT-*g*-P (St-*co*-MAH) (right).

kGy) at 600˚C under nitrogen are 2.7, 25.3, 32.5, and 36.8 wt%, respectively. Almost all of the weight losses during fragmentation are due to the pyrolysis of grafted chain. The significant weight reduction in the region (~300~350˚C) is likely to be due to the decomposition of the polymer backbone.

The TEM images of the pristine MWNTs and MWNT-*g*-P (St-*co*-MAH) are shown in Fig. 4. Some shortened tubes can be found after a dose of 30 kGy in methanol. This can be explain by the collision of active species with carbon atoms in MWNTs may result in displacement of atoms. Therefore, some defects are formed under γ radiation, and further reaction between active species and defects finally leads to the cutting of the MWNTs (Krasheninnikov *et al.* 2004). The TEM image of MWNTs showed that the MWNTs were piled up to form large bundles and ropes, but the MWNT-*g*-P (St-*co*-MAH) was dispersed individually.

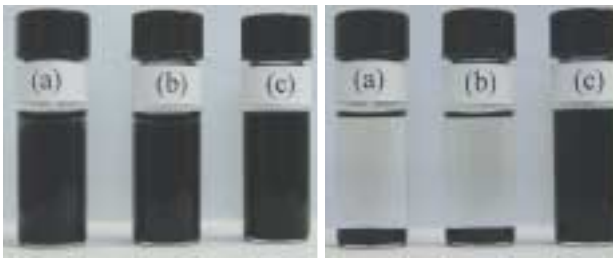

Fig. 5. Photographs of pristine MWNTs (a), irradiated MWNTs (b) and MWNT-*g*-P (St-*co*-MAH) (c) in THF before (left) and after (right) stored for 7days.

And the external diameters of MWNT-*g*-P (St-*co*-MAH) were about 19~21 nm, which were increased when compared with the MWNTs.

Pristine MWNTs cannot dissolve in THF. After radiation-induced grafting reaction, the resulting irradiated MWNTs exhibited a small solubility in THF, but a considerable sedimentation was found at the bottom of bottle after 7 days. But as shown in Fig. 5, the MWNT-*g*-P (St-*co*-MAH) showed a very good solubility in THF.

CONCLUSION

Functionalized MWNTs with styrene and maleic anhydride were synthesized via in situ radiation-induced polymerization under γ rays. The structural integrity of the nanotubes was well-maintained during irradiation. The polymer content in the functionalized MWNTs can be up to ~30% depending on the duration of irradiation. The external diameters of MWNT-*g*-P (St-*co*-MAH) were about 19~21 nm, which were increased when compared with the MWNTs and MWNT-*g*-P (St-*co*-MAH) exhibited very good solubility in THF.

ACKNOWLEDGEMENTS

This present work was supported by the Nuclear R & D program from the Ministry of Science & Technology, Korea.

REFERENCES

Chen S, Shen W, Wu G, Chen D and Jiang M. 2005. A new approach to the functionalization of single-walled carbon

nanotubes with both alkyl and carboxyl groups. *Chem. Phys. Lett.* **402**:312-317.

Dresselhaus MS, Dresselhaus G and Avouris PH. 2001. "Carbon nanotubes synthesis, structure, properties, and applications." Springer, Berlin.

Hu J, Shi J, Li S, Quin Y, Guo Z, Song Y and Zhu D. 2005. Efficient method to functionalize carbon nanotubes with thiol groups and fabricate gold nanocomposites. *Phys. Lett.* **401**:352-356.

Iijima S. 1991. Conductivity of carbon nanotubes. *Nature* **354**: 56-58.

Khabashesku VN, Margrave JL and Barrera EV. 2005. Functionalized carbon nanotubes and nanodiamonds for engineering and biomedical applications. *Diamond Relat. Mater.* **14**: 859-866.

Krasheninnikov AV and Nordlund K. 2004. Irradiation effects in carbon nanotubes. *Instrum. Methods B* **216**:355-366.

Manuscript Received: August 2, 2007
Revision Accepted: September 3, 2007