Multiwalled Carbon Nanotube-Reinforced Poly(vinyl chloride)

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Summary: Multiwalled carbon nanotube (MWCNT)-reinforced poly(vinyl chloride) (PVC) was prepared via a simple adsorption method in an aqueous system. MWCNTs possessing negatively charged carboxyl groups at their tips and sidewalls introduced during the purification process were dispersed in water with the cationic surfactant, cetyltrimethylammonium bromide, using ultra-sonication. Then, PVC microspheres, which have a negative charge in water at pH 7.0, were added to the aqueous MWCNTs dispersion. As a result, the MWCNTs were stably and strongly adsorbed on the surface of the PVC microspheres by electrostatic interaction. Furthermore, the dispersivity of the MWCNTs in the PVC remained high, even when we manufactured the MWCNT-adsorbed PVC microspheres in the form of solution cast films. The PVC/MWCNTs nanocomposite exhibited a marked increase in its electrical conductivity, in spite of the relatively low MWCNT content (2.9 wt%). The composite films also showed an improvement in their mechanical properties, such as their tensile strength and Young's modulus.

Keywords: carbon nanotubes; electrical conductivity; nanocomposite; poly(vinyl chloride)

Introduction

Poly(vinyl chloride) (PVC) is one of the most popular and important plastics, whose consumption demand is the second largest among all plastic materials.[1,2] PVC products are widely employed for many uses in construction, electronics, automobiles, food packaging and other markets, because PVC has desirable properties such as good chemical resistance, low moisture absorption, dimensional stability, high mechanical strength and self-extinguishing flame characteristics. However, PVC is rarely processed by itself. It usually requires the incorporation of various additives, due to its low thermal stability and high susceptibility to generate static electricity.[3–5]

Carbon nanotubes (CNT) are one of the most promising candidates for the design of novel ultrahigh strength polymer composites. It is believed that the high aspect ratio, mechanical strength, and electrical and thermal conductivity of CNTs enhance the overall performance of many CNT-filled composites and open up new applications.[6–8] These high performance polymer composites demand the uniform dispersion of the CNTs in the polymer matrix without their aggregation; therefore, a strong interfacial interaction is needed. Recently, a great deal of attention has been paid to the modification of CNTs via chemical, electrochemical and plasma treatment for the purpose of obtaining their uniform dispersion in the polymer matrix.[9–11]

In this study, nanocomposite microspheres were prepared by adsorbing the oxidized MWCNTs on the surfaces of PVC microspheres in water containing an ionic surfactant. The MWCNTs were negatively charged by the chemical oxidation procedure, and the PVC microspheres presented a negative charge in water at pH 7. The films produced from the PVC/MWCNT

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composite microspheres were characterized in terms of their mechanical, electrical and morphological properties.

Experimental Part

Materials

PVC microspheres (LS080S), synthesized by suspension polymerization, were supplied by LG Chem. Ltd., Korea. The cetyltrimethylammonium bromide (CTAB) used as a surfactant was purchased from Aldrich, USA. The MWCNTs (Iljin Nanotech Co., Korea), which were used in this study, were synthesized by a thermal chemical vapor deposition (CVD) method.

Purification of MWCNTs

The purity of the as-received MWCNTs was 96%. To remove the impurities in the MWCNTs, they were treated with 3 M HNO_3 at 60 °C for 12 h, followed by refluxing them in 5 M HCl at 120 °C for 6 h. The purity of the acid-treated MWCNTs was measured to be 99% using thermogravimetric analysis (TGA, TA instruments, Q50, U. K.). These acid-treatments are known to introduce carboxylic and hydroxyl functional groups onto the surface of the MWCNTs.[12] The oxidized MWCNTs were filtered and washed with a large amount of deionized water and then vacuum-dried at room temperature overnight.

Preparation of Dispersed MWCNT Solution

The purified MWCNTs were dispersed in deionized water. CTAB was employed as a surfactant. The concentrations of the surfactant and MWCNTs were 0.3 and 0.02 wt%, respectively. Ultrasound was then applied to the dispersion of MWCNTs for 8 h at 25 °C using an ultrasonic generator (Kyungill Ultrasonic Co., Korea) having a nominal frequency of 28 kHz and a power of 600 W.

MWCNT-adsorbed PVC Microspheres

The PVC microspheres were added to an excess quantity of the aqueous MWCNT dispersion to ensure that a sufficient amount of MWCNTs was adsorbed onto the PVC microspheres.[7,13] The MWCNT-adsorbed PVC microspheres were then washed by centrifuging them in deionized water four times at 4000 rpm for 30 min at 4 °C and then dried in an oven at 60 °C.

Preparation of PVC/MWCNT Composite Films

The film-type samples were prepared by solution casting the MWCNT-adsorbed PVC microspheres in N,N-dimethylformamide (DMF) at 80 °C. The solution cast film was processed to form films with a thickness of 0.3 mm for the purpose of measuring the electrical conductivity and mechanical properties of the composite

Characterization

The morphology of the microspheres and films was observed using field emission scanning electron microscopy (FESEM, S-4200, Hitachi, Japan) at an accelerating voltage of 15 kV after precoating the sample with a homogeneous Pt layer by ion sputtering (Hitachi, E-1030). The amount of MWCNTs adsorbed on the microspheres was calculated using thermogravimetric analysis (TGA, Polymer Lab., TGA1000, U. K.) by scanning from 20 to 900 °C at a heating rate of 20 °C/min under a nitrogen atmosphere. The electrical conductivity of the PVC and PVC/MWCNT composite was measured at room temperature using an Agilent 4339B high resistance meter. The tensile properties of the nanocomposite films were determined by a universal test machine (UTM, Model 4200, Instron, USA) according to ASTM D 638 at room temperature. The zeta potentials were measured in deionized water at pH 7.0 using a electrophoretic light scattering spectrophotometer (ELS-8000, Otsuka Electronics, Japan).

Results and Discussion

The as-received PVC microspheres were commercially available materials that were synthesized by suspension polymerization. Their degree of polymerization was

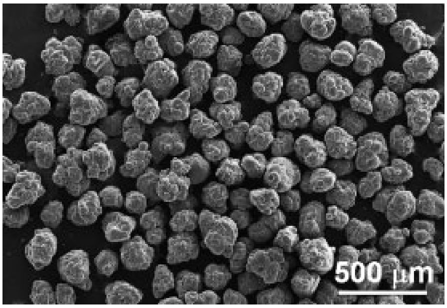

Figure 1.
FESEM image of pure PVC microspheres which were suspension-polymerized.

820 ± 30 and their average particle size was 92.1 ± 15.8 μm. Because of the effect of the suspension polymerization, the PVC microspheres that we used possessed a very rough and porous surface which results from the agglomeration of the primary particles.

The PVC microspheres were added to an aqueous dispersion of oxidized MWCNTs, which was sonicated for 7 h to help the relatively large PVC microspheres come into contact with the MWCNTs. When the MWCNTs were adsorbed onto the PVC microspheres, the supernatant of the MWCNT dispersion turned into a clear solution. Figure 2 shows the change in color of the MWCNT dispersion. Whereas the initial MWCNT dispersion was jet-black, as shown in the left vial, the solution became quite transparent after the MWCNTs were adsorbed onto the PVC microspheres, as shown in the right vial.

Figure 2.
An aqueous dispersion of the MWCNTs with CTAB (left) and a sedimentation of the MWCNTs-adsorbed PVC microspheres (right).

Figure 3 illustrates the surface morphology of the MWCNT-adsorbed PVC microspheres. The individual MWCNTs were strongly and stably adhered to the surface of the PVC microspheres (Figure 3b). The adsorbed MWCNTs did not separate from the PVC microspheres even when ultrasound was applied to them for a long time. Interestingly, we observed that the MWCNTs were rarely adsorbed on a relatively flat surface, but rather were almost always adsorbed on a rough surface (Figures 3b and 3c). We suggest that both electrostatic and physical interactions affected the adsorption of the MWCNTs on the polymeric surfaces. Polymers produced by suspension polymerization usually have a rough and irregular surface, which comes from the aggregation of the primary particles (<∼400 nm) during the suspension polymerization. Each of the MWCNTs has a peculiar bent structure. We conjectured that these bent MWCNTs might have been caught on the rough surface of the PVC particles. To verify this hypothesis, we performed the same experimental procedure with PVC films fabricated by solution casting, but few MWCNTs were found on the flat films (Figure 4).

As previously reported by many researchers, MWCNTs oxidized through a purification process possess carboxyl groups at their ends and sidewalls, with the result that they are negatively charged in water.[14,15] Using zeta potential measurements, we confirmed that the MWCNTs dispersed using CTAB were positively charged, while the oxidized MWCNTs were negatively charged, as shown Table 1. Otherwise, the aqueous PVC colloid exhibited a negative zeta potential at pH 7. We suggest that the negatively charged PVC microspheres in water attracted the positively charged MWCNTs stabilized using the cationic surfactant, CTAB, by electrostatic interaction.

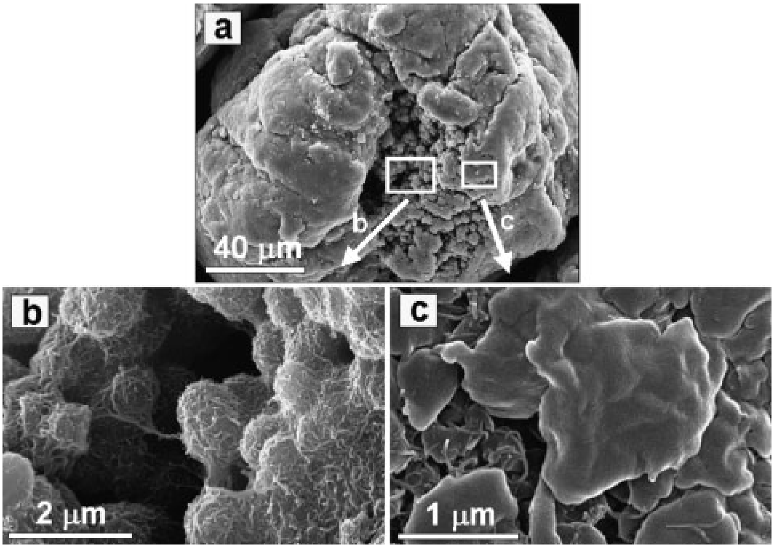

Figure 3.
FESEM images of (a) the surface morphology of the MWCNT-adsorbed PVC microspheres, and magnified (b) rough and (c) relatively flat surfaces of the MWCNT-adsorbed PVC microspheres.

The amount of MWCNTs adsorbed on the PVC microspheres was determined by TGA. Figure 5 provides a comparison of the mass loss curves for the degradation of pure PVC and the PVC/MWCNT composite in a nitrogen atmosphere. Pure PVC decomposed with the production of 6.1 wt% of residue, while the PVC/MWCNT composite left 9.0 wt% of residue which remained constant after the second decomposition. This result indicates that approximately 2.9 wt% of the MWCNTs were adsorbed on the surface of the PVC microspheres. Furthermore, we observed that the two decompositions of the MWCNT-adsorbed PVC took place at a slightly higher temperature than that of pure PVC.

The surface electrical conductivity of the PVC/MWCNT composite measured by the two probe method was $\sim 1.5 \times 10^{-4}$ S/cm, while that of pure PVC was approximately 10^{-14} S/cm. This is a noticeable difference as compared with a previously reported PVC/carbon black composite containing about 5.7 wt% of carbon black which exhibited a surface electrical resistivity of 10^4 Ω/sq.[3] The PVC/MWCNT composite films were produced by solution casting the MWCNT-adsorbed PVC microspheres. The MWCNT-adsorbed PVC

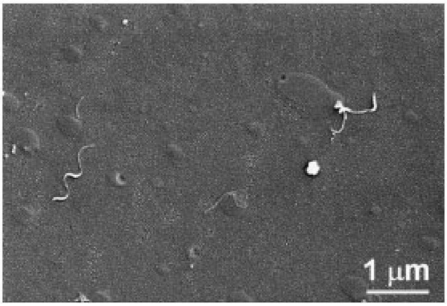

Figure 4.
FESEM image of the MWCNTs adsorbed on the PVC films prepared by solution casting.

Table 1.
Zeta Potentials of Aqueous MWCNT and PVC Dispersion at pH 7.

	zeta potential (mV)
MWCNTs	0.36
Oxidized MWCNTs	−6.23
Oxidized MWCNTs with CTAB	30.17
Pure PVC	−11.16

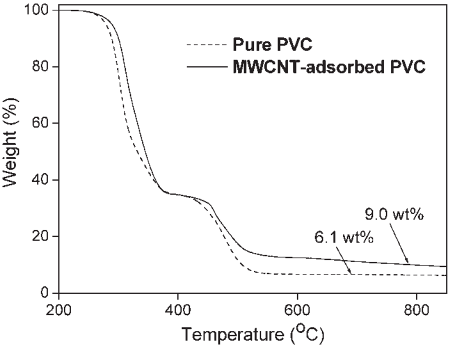

Figure 5.
TGA of pure PVC and MWCNT-adsorbed PVC in nitrogen atmosphere.

microspheres were dissolved in DMF without any treatment such as sonication. Figure 6a shows a typical view of the fracture surfaces of the PVC/MWCNT composite. The uniformly dispersed bright dots and lines are the ends of the broken MWCNTs. The FESEM images clearly show that an even dispersion of the MWCNTs was achieved throughout the PVC matrix (Figure 6a). Moreover, a close inspection indicates that most of the MWCNTs broke apart upon failure, while a few of them were pulled out of the matrix, as shown in Figure 6a. Clearly, most of the MWCNTs are separated into individual nanotubes by the repulsive interaction among the MWCNTs and the attractive interaction between PVC and MWCNTs as well, so that they are evenly dispersed in the matrix, which is extremely important for producing CNT-reinforced polymer composites with excellent mechanical properties. In addition, other belt-like nanotubes were observed which interconnect two polymer lumps, as indicated in Figure 6b. Obviously, this appearance is caused by the presence of MWCNTs wrapped by the polymeric matrix, since their diameter is much bigger than the other broken tubes (i.e., the bright dots) mentioned above. Moreover, the middle part of the MWCNTs is smaller than the two ends adhering to the two lumps of polymeric matrix.

The electrical conductivity of the PVC/MWCNT films of 1.5×10^{-6} S/cm was still higher than that of pure PVC, and was sufficient for electrostatic charge dissipation, which requires a surface electrical conductivity in the range from 10^{-6} to 10^{-10} S/cm without degrading the other desired material properties.[16] We suggest that this results from the high dispersivity of the MWCNTs in the PVC film. Moreover, these PVC/MWCNT films showed an improvement in their mechanical properties. The PVC films became stiffer when they contained MWCNTs (Table 2). The composite films displayed an approximately 131% higher tensile strength, which increased from 15.0 to 34.7 MPa, and exhibited a 145% improvement in their Young's modulus from 481.3 to 698.2 MPa. These results indicate that the MWCNTs act as a reinforcing agent in the PVC matrix, because of their being individually dispersed in the PVC films, as mentioned above.

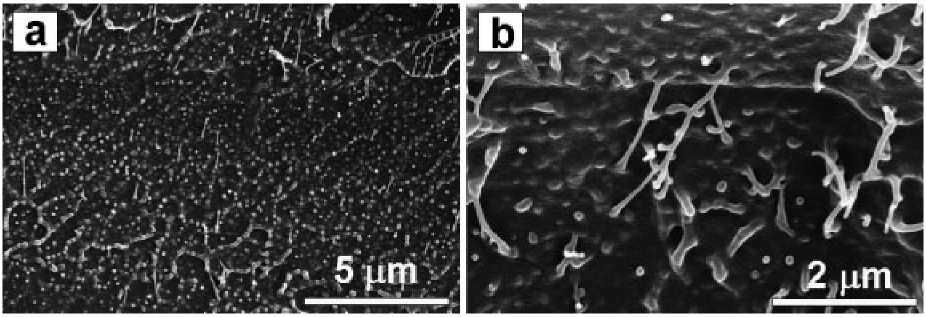

Figure 6.
FESEM images of (a) fractured surface of the PVC/MWCNT composite and (b) its magnified image.

Table 2.
Tensile Properties of PVC and PVC/MWCNT Films.

Films	Tensile strength (MPa)	Young's modulus (MPa)	Elongation at break (%)
PVC	15.0 ± 3.9	481.3 ± 55.7	7.3 ± 2.4
PVC/MWCNT (2.9 wt%)	34.7 ± 4.7	698.2 ± 89.3	4.4 ± 0.5

Conclusion

PVC is a commercial polymer which has many uses, because of its many advantages, such as its chemical resistance and self-extinguishing flame characteristics. We incorporated MWCNTs, which have outstanding thermal, electrical, and mechanical properties, into PVC. We developed a truly simple and potentially scalable process for integrating MWCNTs into synthetic polymers in an aqueous system. When PVC microspheres were added to a surfactant-stabilized aqueous dispersion of MWCNTs with sonication, MWCNT-adsorbed PVC microspheres were formed. The individual MWCNTs were strongly adsorbed on the surface of the PVC microspheres, because of both electrostatic and physical interaction. The composite microspheres contained ~2.9 wt% of MWCNTs, and showed a marked increase in their electrical conductivity, due to the MWCNTs on the surface. The MWCNTs were uniformly dispersed, even when films were fabricated from the composite microspheres by solution casting. The tensile strength and modulus of the PVC/MWCNT composite films were increased by 131% and 145%, respectively. They also demonstrated an electrical conductivity of 1.5×10^{-6} S/cm, which is sufficient for electrostatic charge dissipation. From these results, the PVC/MWCNT composites can be considered as potential electrostatic discharge materials which can overcome the disadvantages of PVC materials.

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