

Electrical Behavior of Polyurethane Composites with Acid Treatment-Induced Damage to Multiwalled Carbon Nanotubes

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ABSTRACT: We have studied the electrical conductivity and percolation threshold of polyurethane (PU) composites filled with multiwalled carbon nanotubes (MWCNT) purified by increasing immersion time in aqueous solutions of either nitric acid or a mixture of nitric and sulfuric acids at 80°C. The MWCNT crystallinity peaks after 2 h of treatment, which enables the PU composites to enhance the percolation threshold and electrical conductivity in the conductive network formation region. MWCNT treated under either a milder or severer acidic condition deteriorate the electrical behavior of the composites, since MWCNT are poorly dispersed in the PU matrix in the former condition,

but lost their intrinsic electrical conductivity due to the partial destruction of their crystalline structure in the latter. Therefore, the acid treatment needs to be carefully controlled to effectively purify the MWCNT, maintain the crystalline structure without further damage, and thereby improve the electrical behavior of PU/MWCNT composites. © 2007 Wiley Periodicals, Inc. *J Appl Polym Sci* 106: 110–116, 2007

Key words: polyurethane/MWCNT composites; acid treatment-induced damage; electrical conductivity; percolation

INTRODUCTION

Multiwalled carbon nanotubes (MWCNT) are permanently electrically conductive with an electrical conductivity of $\sim 1.85 \times 10^3$ S/cm.¹ Compared with carbon black or carbon fiber as conductive reinforcements, polymeric composite containing MWCNT can form a conductive path at an extremely low content owing to their high aspect ratio of 100–1000 and high specific surface areas. Therefore, their use in various applications, such as antistatic film and electromagnetic shielding materials, has long been anticipated. However, pristine CNT has poor compatibility with most organic solvents and binders, which results in poor dispersion and poor connectivity between the CNT and polymer matrix.²

To overcome the incompatibility of the CNT with polymer and eventually to improve the properties of the CNT-filled polymer composites to enable their practical application, many research efforts have been

made to modify the MWCNT surface.^{3–10} However, the acid treatment should precede the modification of the CNT surface, in which the impurities, such as metallic catalyst and carbonaceous materials in the CNT bundles, are removed and the CNT surface is functionalized with carboxylic acid mainly at the open end tip. In addition, nonhexagonal structures like pentagon, heptagon, and Stone-Wales defect (i.e., 5-7-7-5 defect) exist as CNT defects, which allow their network curvature^{11,12} to be attacked during refluxing the web-like deposits in the concentrated acidic solutions because of their chemical reactivity. The presence of many defects in a nanotube under strong treatment condition may allow the preexisting defective sites to act as origin points for the destruction of the CNT crystalline structure.

It is well known that the CNT surface defect density is related to band energy.¹³ CNT structural defects can reduce the effective band overlap and thus carrier density, leading to an increase in their electrical resistivity.¹³ Furthermore, the CNT damage caused by the strong acid treatment may reduce the conductance of the CNT themselves, and thus decrease the electrical conductivity of the CNT/polymer composites as previously reported.¹⁴ Since defective sites are inevitably accompanied by CNT synthesis, the acid treatment condition needs to be optimized, so that the CNT damage caused by the acid is mini-

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mized and the electrical conductivity of the polymeric composites is enhanced.

The present study focused on the electrical properties of the polyurethane (PU) composites filled with MWCNT oxidized by various conditions of acid treatment. First, the MWCNT is purified with increasing immersion time in 40% aqueous solutions of either nitric acid or a mixture of nitric and sulfuric acids at 80°C. We report the change in electrical conductivity and percolation threshold of the PU/MWCNT composites according to the acid treatment condition of the CNT. The difference in the electrical behavior of the PU/MWCNT composites is discussed in terms of the CNT damage and the degree of CNT dispersion in the PU matrix caused by the acid treatment of the CNT.

EXPERIMENTAL

Materials

Linear polyurethane (PU, Irostick S9815, Huntsman, Germany) dissolved in methyl ethyl ketone (MEK) was used as the matrix with a density of about 1.20 g/cm³ at 25°C. The as-received MWCNT (Iljin Nanotech, Korea), synthesized by a catalytic CVD with the carbon content of 95%, were used in this study. The MWCNT is 10–50 μm long, 10–20 nm in diameter, and had a density of ~ 1.83 g/cm³. Benzalkonium chloride (Junsei Chemical, Japan) was used as a cationic surfactant for all the compositions. MEK was used as an organic solvent for the preparation of MWCNT/surfactant suspension.

Acid treatment

Aqueous solutions of nitric acid and a mixture of nitric and sulfuric acids at a ratio of 1 : 3 by volume were used for the MWCNT purification. The acid treatment of MWCNT was performed by increasing the immersion time from 1 to 4 h at an acidic concentration of 40% at 80°C. First, 5 g of MWCNT was suspended in 250 mL solution and refluxed under a given set of treatment conditions. The treated MWCNT was filtered and washed subsequently with acetone and distilled water, until a pH of 7 was achieved. The MWCNT oxidized with nitric acid and with the mixture of nitric and sulfuric acids was designated as NX-MWCNT and MX-MWCNT, respectively, where X is the acid treatment time.

Sample preparation

Acid-treated MWCNT (X-MWCNT) was first suspended in MEK/surfactant solution in an ultrasonic bath at room temperature for 3 h, where the surfactant content was fixed at 0.6 wt % as the ratio to the

amount of MWCNT. The PU/MEK solution was poured into a dilute MWCNT suspension, and the mixture was again mechanically homogenized at 10,000 rpm for 10 min. After filtering and completely evaporating the solvent in the mixture in a vacuum oven at 70°C for 12 h, the mixture was fully roll-milled at 80°C for 10 min. The roll-milled mixture was pressed at 100°C for 15 min to obtain the specimens.

Measurements

The infrared spectra of the MWNTs pressed with KBr were recorded up to 4000 cm⁻¹ using a Fourier transform infrared spectrometer (FTS-60, Bio-Rad, USA). The bonding structure of the carbon nanotubes was analyzed by confocal micro-Raman spectroscopy at 532 nm Ar⁺-laser with 7.0 mW intensity (NRS-3000, Jasco, Japan). Around 20 mg of MWCNT were pressed in a sample holder with 1 mm diameter and 2 mm depth for measuring Raman. The microstructures of X-MWCNT were investigated by using high resolution transmission electron microscope (HRTEM; JEM-4010, JEOL, Japan) operated at an accelerating voltage of 400 kV. The fractured surfaces of the conductive PU/MWCNT composites were observed by using field emission scanning electron microscope (FESEM, S-2700, Hitachi, Japan). AC conductivity of the PU/MWCNT composites was measured by dielectric analyzer (DEA; GmbH CONCEPT40, Novocontrol, Germany) in the frequency range of 10⁻¹ to 10⁶ Hz at room temperature. The specimens used to measure the AC conductivity were disk-shaped, with a diameter of 40 mm and a thickness of 0.5–1.0 mm. The disk-shaped specimens were silver-pasted to minimize the contact resistance between the specimens and the Au-coated electrodes. The silver paste (Dotite electroconductives D-550 type, Fujikura Kasei, Japan) consisted of silver, acryl resin, and toluene, and had a volume resistivity of less than 10⁻⁵ Ω cm. The conductive data were acquired by averaging the measured values for more than five specimens.

RESULTS AND DISCUSSION

Figure 1 shows the FT-IR spectra of the pristine MWCNT, the N1- and M2-MWCNT. The characteristic peak is found at around 1630 cm⁻¹ indicated by the arrow for N1- and M2-MWCNT, which could be assigned to the C=O stretching vibrations in the carboxylic groups. The characteristic peak observed for the oxidized MWCNT could be found in all the acid-treated MWCNT independently of the type of acid aqueous solution and treatment time, but there was no difference in peak intensity. Raman spectra were compared for MX-MWCNT and pristine MWCNT as shown in Figure 2. It is clear that the D and G bands

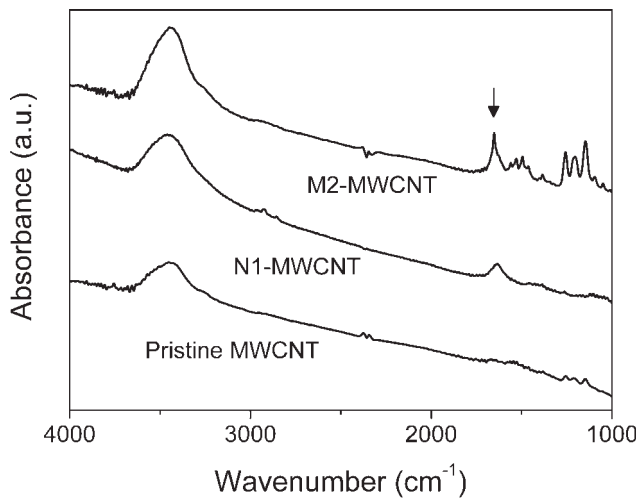


Figure 1 Comparison of FT-IR spectra of pristine MWCNT, N1-, and M2-MWCNT.

of MWCNT were observed at around 1340 and 1580 cm^{-1} , respectively. Raman intensities of MX-MWCNT at each band were changed from those of pristine MWCNT according to treatment time, which implies that the structure of the MWCNT is also

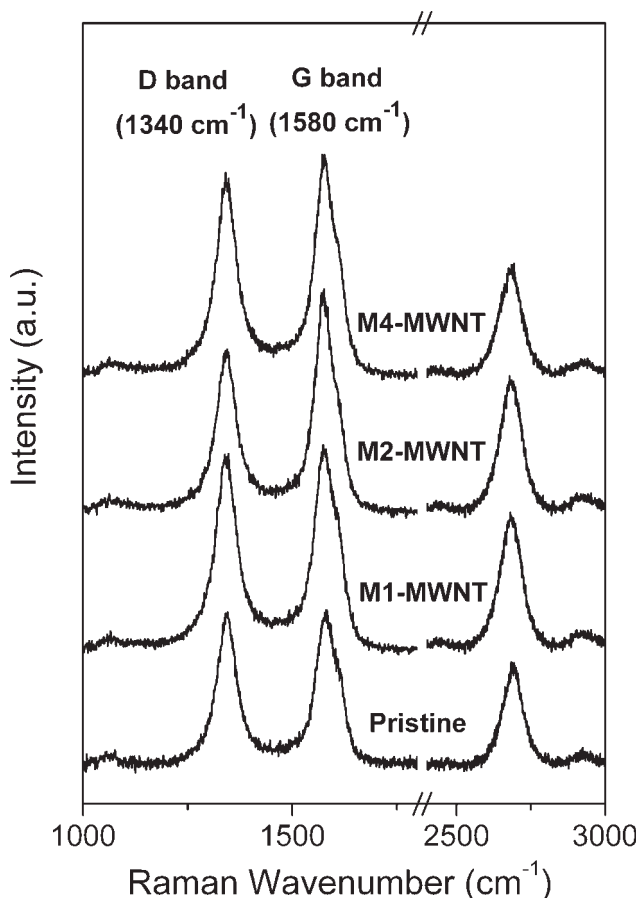


Figure 2 Raman spectra for pristine and oxidized MWCNT by a mixture of nitric and sulfuric acids.

altered by the acid treatment. Since the D band is derived from the disordered graphite structure and the G band is associated with tangential C—C bond stretching motions which originate from the E_{2g2} mode in graphite,¹⁵ the degree of disordered structure or of crystallinity can be obtained by using the ratio of the intensity at D to G band as shown in Figure 3. Intensity ratios were minimized when the pristine MWCNT were acid-treated during 2 h. This means that a better crystallinity can be provided by the acid treatment for 2 h. However, N1-MWCNT showed a higher D/G ratio than pristine MWCNT did, possibly because first the MWCNT were not sufficiently purified due to the short acid treatment time and second the imperfect ordered structure was swollen and thus changed into a disordered structure. In addition, there was no effect on increasing the degree of crystallinity with acid treatment beyond 3 h and the intensity ratio remained almost constant, being higher than the D/G ratio of the treatment time of 2 h. The mixture acid appeared to be more effective in improving the degree of crystallinity of the MWCNT at the same 2-h treatment time.

Figure 4 shows the frequency dependence of the AC conductivity (σ_{AC}) of the PU composites filled with M2-MWCNT measured at 25°C. The change in σ_{AC} provides information about the overall connectivity of the conducting network and is categorized into three behaviors by means of the size and distribution of the conductive clusters: the dielectric region, percolation transition region, and conductive path formation region.¹⁶ The composite in which the conductive network is not formed below the percolation threshold behaves as a dielectric, so that the AC conductivity increases linearly with increasing frequency. Such behavior, however, was absent in our figure and even the PU matrix showed the AC

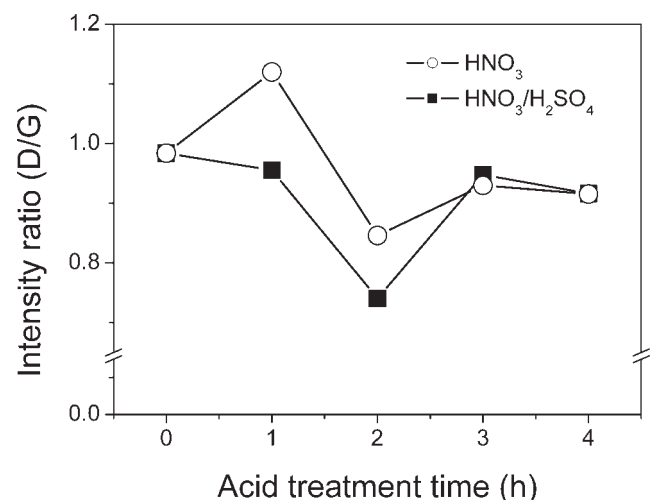


Figure 3 The ratio of Raman intensity at D to G bands as a function of acid treatment time.

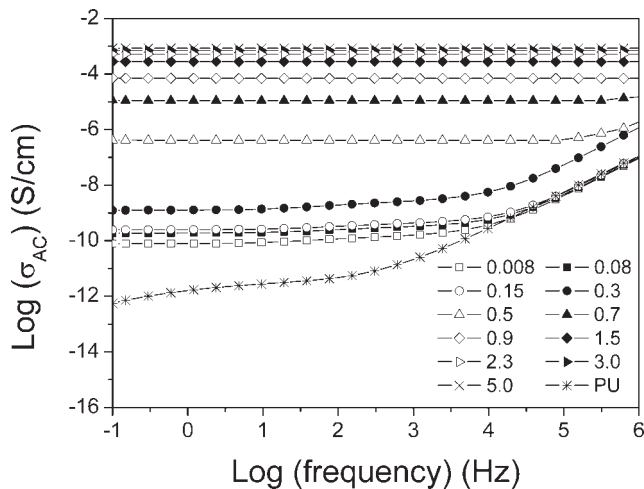


Figure 4 Change in AC conductivity of PU/M2-MWCNT composites as a function of frequency. The legend shows the weight percentage of M2-MWCNT.

conductivity deviating from the linearity. This may be attributed to the presence of unknown materials such as ion in the PU, since the ion in the polymer composite increased the imaginary permittivity, i.e., the conductivity at low frequency range. In the percolation transition region the AC conductivity was equal to the DC conductivity up to the characteristic frequency, above which the conductivity was linearly increased again. Considering the nonlinear AC conductivity of PU, the percolation transition may have occurred at the range from 0.3 to 0.7 wt % of the M2-MWCNT content. Above the percolation threshold, the conductivity remains constant at a given frequency range as shown in the conductivity of the M2-MWCNT composites with more than 0.9 wt % of MWCNT.

The DC conductivity can be deduced from the AC conductivity when the frequency tends to zero. Figures 5 and 6 compare the DC conductivity of the NX- and MX-MWCNT composites as a function of the MWCNT content obtained from the results of AC conductivity. The conductivity abruptly increased at a characteristic MWCNT content, termed the percolation threshold, in all cases, as shown by the arrow in each figure. However, it should be noticed that not only the percolation threshold occurred at different MWCNT content depending on the acid treatment time and the acid solution, but also that the composites in the region of the conductive path formation showed different conductivity even at the same MWCNT content, although at a loading level of less than the critical content, the conductivity of all the composites showed an order of 10^{-10} to 10^{-9} S/cm.

In classical percolation theory, the dependence of the σ_{DC} of the composites on the MWCNT content (p)

above the percolation concentration (p_c) can be described by a scaling law of the form.¹⁷

$$\sigma_{DC} \approx \sigma_0(p - p_c)^t \quad \text{for } p > p_c \quad (1)$$

where σ_0 is a fitted constant and t the critical exponent. To obtain the fitting parameters in eq. (1), non-linear curve fittings of the results obtained in Figures 5 and 6 were performed for $p > p_c$. The best-fitted results are listed in Table I, where the critical exponents t were determined from the slope of the least-square on the plot of $\log(p - p_c)$ versus $\log(\sigma_{DC})$. The fitting curves were also plotted as the solid line in the Figures.

An explicit trend in which the higher the degree of crystallinity of the MWCNT the lower the percolation threshold of the composites was observed for all composites, except the M4-MWCNT. In addition, the fitted constant, σ_0 , and the conductivity at 5 wt % of the MWCNT exhibited higher values, regardless of the solution used when the MWCNT had the minimum intensity ratio D/G as shown in Figure 3. The fitted

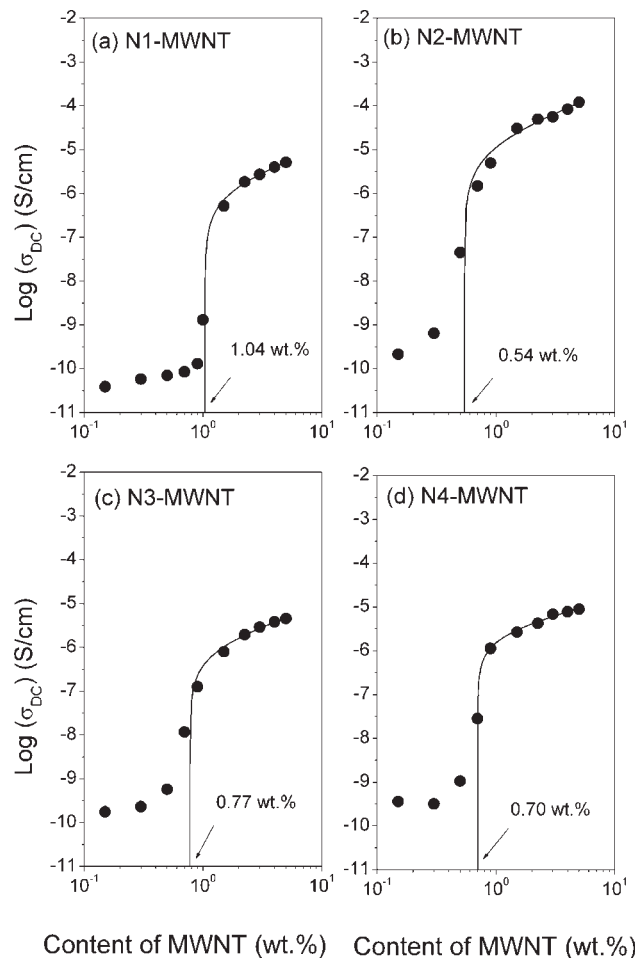


Figure 5 DC conductivity of (a) N1-, (b) N2-, (c) N3-, and (d) N4-MWCNT composites with the MWCNT content. The percolation threshold is also shown in each figure.

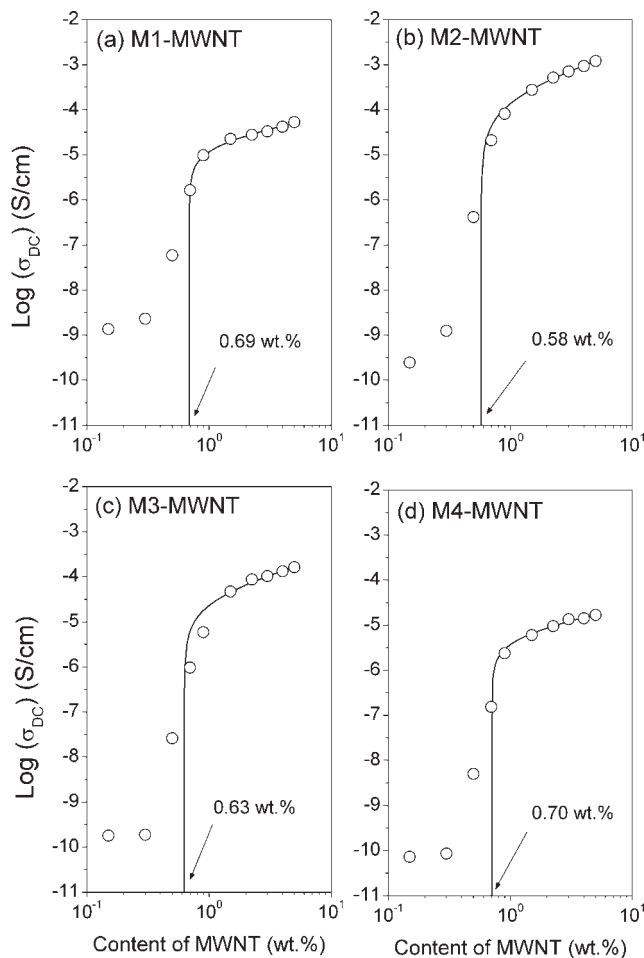


Figure 6 DC conductivity of (a) M1-, (b) M2-, (c) M3-, and (d) M4-MWCNT composites with the MWCNT content. The percolation threshold is also shown in each figure.

constant should actually have the same conductivity to the MWCNT themselves, about 10^3 S/cm,¹ but it is always underestimated because of the contact resistance among the MWCNT in spite of the formation of percolation network. Therefore, the high values of the fitted constant and the conductivity in the percolation path formation region imply that the better MWCNT

dispersion in the PU matrix and the higher degree of crystallinity can be achieved by suitable acid treatment of the MWCNT.

Figure 7(a) shows the optical microscopic image of the N1-MWCNT filled composite. The N1-MWCNT is not dispersed well enough, resulting in the formation of many aggregates of the N1-MWCNT in many places. Besides, since the condition of purifying the NX-MWCNT at 80°C for 1 h was not enough to remove the amorphous carbon in the MWCNT bundles, to open the end cap, and thus to functionalize the end tip of the MWCNT with the carboxylic acid as observed in Figure 7(b), the N1-MWCNT composites showed the highest percolation threshold in the given composite systems and a very low value of conductivity at the concentration of 5 wt % of the MWCNT, as confirmed in Figure 5 and Table I. In Figure 7(b), the black and white arrows indicate the end tip and amorphous carbon, respectively.

Figure 8(a) compares the degree of dispersion of the M2-MWCNT in PU composite, in which few aggregates were found and the MWCNT were well dispersed. Figure 8(b) shows the HRTEM image of M2-MWCNT. No defects or impurities are evident. Not only have most walls maintained their intrinsic shape, but the tangles have disappeared without extraordinary damage. Since the M2 treatment condition was successful in removing impurities, functionalizing the MWCNT end tip and obtaining the highest degree of crystallinity, it is seen that a lower percolation threshold and the highest electrical conductivity in the region of the conductive path formation were observed.

Actually, we could not find any macroscopic difference in the degree of MX-MWCNT dispersion in any of the measured composite systems. All the composites showed well-dispersed MX-MWCNT in the PU matrix in the same manner as shown in Figure 8(a). Nevertheless, to show the different behavior in the electrical conductivity may be due to the MWCNT damage caused by strong acidic condition. HRTEM images of M4-MWCNT are shown in Figure 8(c–e). The very strong oxidative condition of M4 caused

TABLE I
Comparison of Percolation Threshold in the Composite Systems

| MWCNT | σ_0 (S/cm) | p_c (wt %) | t | Conductivity at 5 wt % of MWCNT (S/cm) |
|----------|-----------------------|------------------|-----------------|--|
| N1-MWCNT | 1.46×10^{-6} | 1.037 ± 0.08 | 1.06 ± 0.07 | 5.13×10^{-6} |
| N2-MWCNT | 3.00×10^{-5} | 0.540 ± 0.19 | 1.30 ± 0.09 | 1.22×10^{-4} |
| N3-MWCNT | 1.35×10^{-6} | 0.773 ± 0.09 | 1.03 ± 0.03 | 4.55×10^{-6} |
| N4-MWCNT | 3.42×10^{-6} | 0.702 ± 0.03 | 1.00 ± 0.07 | 8.82×10^{-6} |
| M1-MWCNT | 2.00×10^{-5} | 0.687 ± 0.03 | 1.00 ± 0.06 | 5.30×10^{-5} |
| M2-MWCNT | 3.00×10^{-4} | 0.578 ± 0.05 | 1.11 ± 0.04 | 1.21×10^{-3} |
| M3-MWCNT | 5.00×10^{-5} | 0.625 ± 0.09 | 1.30 ± 0.09 | 1.62×10^{-4} |
| M4-MWCNT | 7.41×10^{-6} | 0.702 ± 0.02 | 1.00 ± 0.03 | 1.69×10^{-5} |

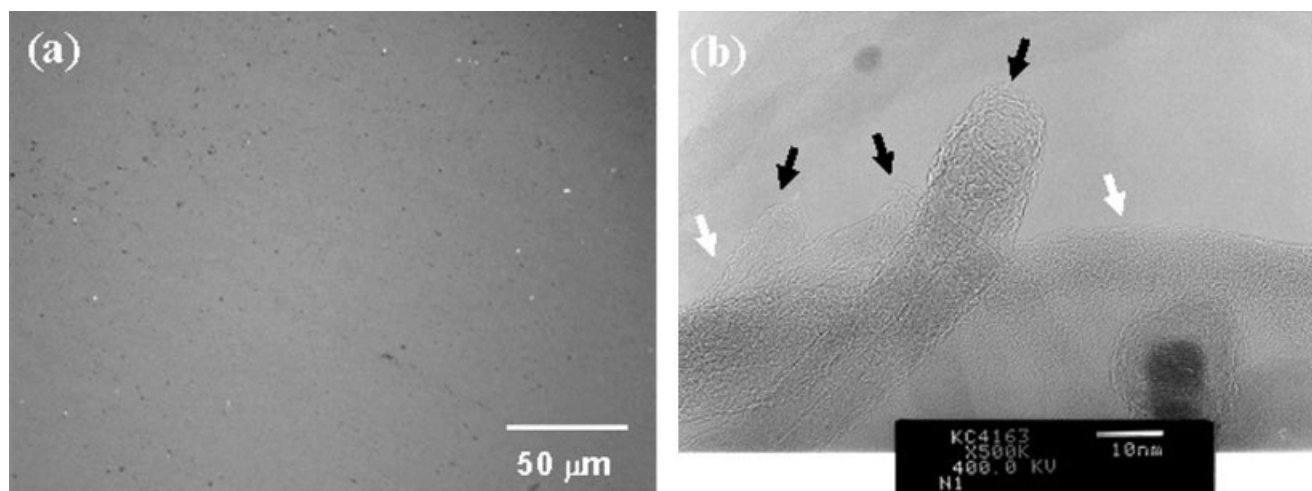


Figure 7 (a) Optical microscopic and (b) HRTEM image of N1-MWCNT-filled PU composite and N1-MWCNT, respectively.

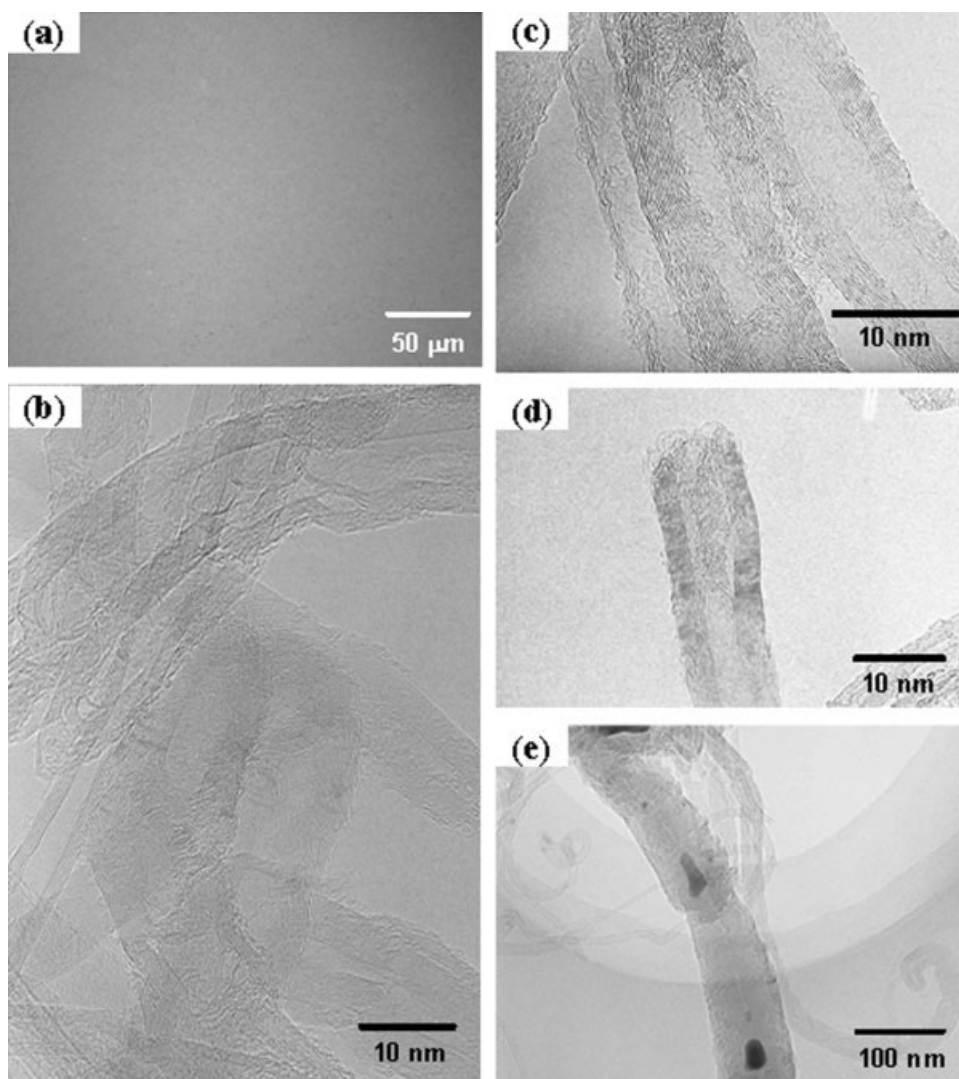


Figure 8 (a) Optical microscopic image of M2-MWCNT-filled PU composite, and HRTEM images of (b) M2-MWCNT and (c), (d), and (e) M4-MWCNT.

greater CNT damage than the other conditions. Severely thinned MWCNT with fewer tube walls can be observed in Figure 8(c). Especially, the inner tube walls had been stripped off in all M4-MWCNT compositions. The stripping of the inner walls may have originated from the propagation of the damage generated in the open end tips of the MWCNT as observed in Figure 8(d). Over time, the strong acid attacks the relatively unstable weak sites along with the inner tube wall, with the damage spreading out over the entire inside of the tube which is finally pulled down as shown in Figure 8(e), where the tube is swollen up to about 80 nm in diameter and its hollow structure is destroyed by the destruction of crystalline structure. The mixture acid confined to the inside of the destroyed tube is shown. This is the main reason why the PU/MWCNT composites that underwent acid treatment under stronger conditions showed poor electrical behavior in spite of well-dispersed MWCNT.

In summary, the acid treatment is inevitable for the purposes of purification, functionalization, and modification of CNT. To enhance the electrical properties of the PU/MWCNT composite, however, the acid treatment condition needs to be controlled to effectively purify the MWCNT bundles and to maintain the crystalline structure without further MWCNT damage. Insufficient acid treatment prevents the impurities from being removed and the MWCNT from being well dispersed in the polymer matrix. On the contrary, excessive severe acid treatment damages the crystalline structure of the MWCNT and reduces the electrical conductivity despite good MWCNT dispersion in the polymer matrix. By analyzing the electrical conductivity and percolation behavior, the relationship between the acid treatment conditions and the electrical properties of MWCNT-filled polymer composites treated with those conditions can be evaluated.

CONCLUSIONS

MWCNT is purified at 80°C in 40% of aqueous solutions of either nitric acid or a mixture of nitric and sulfuric acids, with increasing immersion time. The degree of crystallinity, as obtained from Raman spectroscopy measurements, shows a maximum for the MWCNT treated for 2 h in the mixture acid solution. Electrical conductivity is measured by a dielectric analyzer, and a percolation threshold of acid-treated MWCNT/PU composites is exactly evaluated. The

MWCNT with the maximum degree of crystallinity enables the PU/MWCNT composites to present a lower percolation threshold and the highest electrical conductivity in the region of the conductive network formation in the given composite systems. Excessive acid treatment damages the MWCNT crystalline structure, resulting in their composites showing poor electrical behavior despite good MWCNT dispersion in the polymer matrix. Since the MWCNT obtained via insufficient acid treatment are not well dispersed in the matrix or sufficiently purified such that the end tips of the MWCNT remain unopened, the composites also exhibit low conductivity and high percolation threshold. It is concluded that the acid treatment condition applied to the MWCNT must be controlled to purify effectively the impurities in the MWCNT bundles and to maintain the crystalline structure without further damage to the MWCNT for ensuring superior electrical properties of the polymer composites.

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