ACS APPLIED MATERIALS & INTERFACES
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Electrical Conductivity Enhancement of Polymer/Multiwalled Carbon Nanotube (MWCNT) Composites by Thermally-Induced Defunctionalization of MWCNTs

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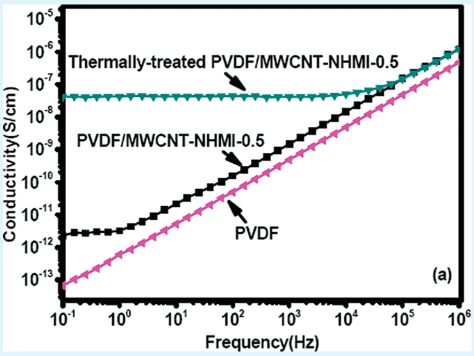
ABSTRACT: We report a thermally-induced increase of electrical conductivity of polymer/multiwalled carbon nanotube (MWCNT) composites using Diels–Alder-adduct-modified MWCNTs as additives. Thermal treatments of the composites induce the defunctionalization of the modified MWCNTs through retro-DA reaction, consequently to recover the electrical conductivity of MWCNTs and to increase the conductivity of PVDF/MWCNT composites. For the composites possessing 0.5 wt % of MWCNTs, thermal treatment increases the electrical conductivity from 2×10^{-12} S cm^{-1} to 4×10^{-8} S cm^{-1} and significantly reduces the value of percolation threshold. Meanwhile, the thermal treatment does not alter the mechanical properties of the composites.

KEYWORDS: carbon nanotube, electrical conductivity, composite, Diels–Alder reaction, poly(vinylidene fluoride)

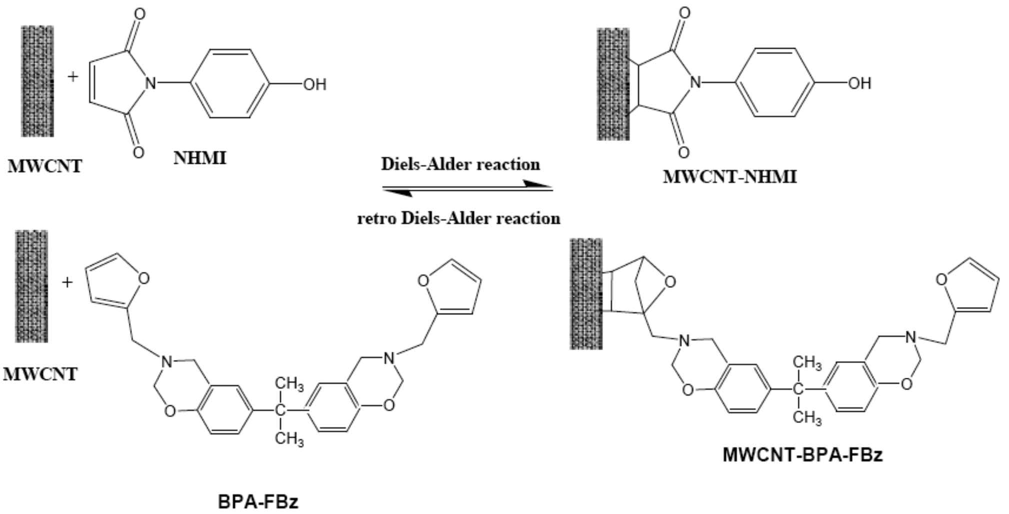


Many applications of polymeric materials, such as electrodes, electrostatic dissipation, electromagnetic radiation shielding, and conductive adhesive, require electrical conductivity. Addition of electrically conductive fillers to polymers could effectively increase the electrical conductivity of polymers. Carbon nanotubes (CNTs) exhibit metallic or semiconducting characteristics. The properties of CNTs depend on the diameters, lengths, specific surface area, and surface conductivity of CNTs.[1] Hence, CNT is a promising material for preparation of electrically conductive polymeric materials. For example, catalytically-grown CNTs dispersed in an epoxy matrix showed a percolation threshold at a 0.04 wt % loading of CNTs. The composite had a matrix conductivity of about 10^{-4} S cm^{-1}.[2] An effective method to form a percolating network of CNTs is use of aligned CNTs as the conductive additives.[3−6] Nevertheless, preparation of aligned CNTs as well as their polymeric composites employ complicated synthetic routes. As a result, this method is limited while being applied to the conventional polymer processing methods (solution and molten processes).

The dispersion of CNTs in polymer matrix alters much on the conductivities of polymer/CNT composites.[6−10] Huang and Terentjev[11] studied the effect of processing parameters on the dispersion of CNTs in poly(dimethylsiloxane) (PDMS) and the electrical conductivities of the CNT/PDMS composites. Nevertheless, the strong van der Waals forces and physical entanglements make CNTs have less compatibility with polymers, resulting in the poor dispersion of CNTs in polymer matrix for the polymer/CNT composites fabricated through the solution and molten processes.[12,13] A general method to increase CNT's solubility in organic solvents and compatibility with polymers is organomodification of CNTs. Noncovalent modification might not obviously alter the intrinsic electronic properties of CNTs, as not changing the sp^2 structure of CNTs.[14] Nevertheless, physical modification of CNTs usually results in relatively weak and unstable products. On the other hand, chemical modification[14−17] usually involves the sp^2 structure of CNTs in modification reactions so as to reduce their electrical conductivity. This limits the efficiency of using CNTs to improve the electrical conductivity of polymer/CNT composites. Pan et al. reported that an annealing process is effective to increase the electrical conductivities of CNT/polypropylene composites.[18] In the annealing process, re-aggregation of CNTs to form a CNT network in the polymer matrix have attributed to the electrical conductivity jump of the composites. On the other hand, CNT aggregation might be harmful to the mechanical properties of the composites. Hence, a method to increase the electrical conductivity of polymer/CNT composites and maintain their mechanical properties is attractive. In this study, we report a general approach to increase the electrical conductivity of CNT/polymer composites without sacrificing their mechanical properties. Multiwalled carbon nanotubes (MWCNTs) functionalized with small molecules through Diels–Alder (DA) reaction have been prepared[19] for preparation of poly(vinylidene fluoride) (PVDF)/MWCNT composite. Thermal treatment of the composite (containing 0.5 wt % of functionalized MWCNTs) induces the defunctionalization of MWCNTs through retro-DA reaction, and results in an electrical conductivity jump from 2×10^{-12} S cm^{-1} to 4×10^{-8} S cm^{-1}. The value of percolation threshold is significantly reduced.

Received: May 5, 2011
Accepted: June 6, 2011
Published: June 06, 2011

Scheme 1. Functionalization and Defunctionalization of Multiwalled Carbon Nanotubes through Diels−Alder (DA) and Retro-DA Reactions



N-(4-Hydroxyphenyl)maleimide (NHMI)[20] and bis(3-furfuryl-3,4-dihydro-2*H*-1,3-benzoxazinyl)isopropane (BPA-FBz)[21] have been utilized to modify MWCNTs through DA reactions. The maleimide group of NHMI and furan group of BPA-FBz are reactive toward the C═C groups of MWCNT surfaces (Scheme 1). The preparation and characterization of the functionalized MWCNTs were reported in our previous work.[19] The contents of NHMI and BPA-FBz in the functionalized MWCNTs measured with a thermogravimetric analyzer (Thermal analysis TA-TGA Q500) are 8.2 and 20.7 wt %, respectively. NHMI and BPA-FBz could provide the functionalized MWCNTs dispersion ability in common organic solvents and compatibility between the functionalized MWCNTs and polymer matrix. In this work, the compatibility might be accomplished with polar−polar interaction and hydrogen bond between PVDF and the functionalized MWCNTs. Moreover, the maleimide group of NHMI and the benzoxazine group of BPA-FBz could polymerize in the thermal treatment process to avoid the presence of free NHMI or BPA-FBz molecules in the final PVDF/MWCNT composites. In the preparation of PVDF/MWCNT composites, certain amounts of MWCNT-NHMI or MWCNT-BPA-FBz were added to a PVDF solution of *N*,*N*-dimethylformamide (5 wt %), respectively. The solutions were put in an ultrasonic bath for 1 h to disperse MWCNTs homogeneously and then were cast on glass plates. After drying at 100 °C for 24 h, self-standing PVDF/MWCNT composite films were obtained for tests. The MWCNT contents of the samples are 0.5, 1.0, and 1.5 wt %. The electrical conductivity of the composite films were measured according to the reported method.[17] As shown in Figure 1, pristine PVDF film showed a conductivity of about 7×10^{-14} S cm^{-1} at 0.1 Hz. Addition of 0.5 wt % of MWCNT-NHMI to PVDF slightly increase its conductivity to 2×10^{-12} S cm^{-1}. The small amount of MWCNT-NHMI is not sufficient enough to make the PVDF/MWCNT composite film being electrically conductive. The sample containing 1.5 wt % of MWCNT-NHMI showed a conductivity of about 5×10^{-8} S cm^{-1}. The conductivity of PVDF/MWCNT-NHMI composite films increases with increasing in their MWCNT-NHMI contents. This is similar to the results reported to other polymer/MWCNT composites.

On the other hand, thermal treatments of the samples at 160 °C for 3 h result in a dramatic increase in their conductivities. The thermally-treated PVDF/MWCNT-NHMI-0.5 film has a conductivity of 4×10^{-8} S cm^{-1}, which is much higher than that of the untreated film (2×10^{-12} S cm^{-1}). Meanwhile, the conductivity of the thermally-treated PVDF/MWCNT-NHMI-1.5 film is 8×10^{-7} S cm^{-1}, which is 16 times the conductivity of the untreated PVDF/MWCNT-NHMI-1.5 film. Thermal treatment effectively increases the electrical conductivities of the PVDF/MWCNT composites. Moreover, Hong and Hwang[9] reported that PVDF/MWCNT composites showed a critical MWCNT content of about 3 wt % for conductivity saturation. A similar result was reported in our previous paper.[17] Show and Itabashi[8] reported that it needed 5 wt % of MWCNT to make PTFE/MWCNT composites become electrically conductive. As a result, it is noteworthy that in this work only 0.5 wt % of modified-MWCNTs is sufficient for PVDF showing certain electrical conductivity. The high electrical conductivities of the thermally-treated PVDF/MWCNT composite films render them being suitable for electromagnetic interference (EMI) and other applications.[10]

Functionalization of MWCNTs with NHMI is performed through DA reaction. DA reaction is thermally reversible. The DA adduct, MWCNT-NHMI, could carry out retro-DA reaction at high temperatures to regenerate the precursors (NHMI and MWCNT) utilized in the DA reaction. The performance of retro-DA reaction and the regeneration of MWCNT and NHMI have been demonstrated in our previous work.[19] As a result, thermal treatment of PVDF/MWCNT-NHMI composite films induces the defunctionalization of MWCNT-NHMI through the retro-DA reaction so as to recover the high electrical conductivity of MWCNTs and to increase the electrical conductivity of PVDF/MWCNT composites. The method combined of the use of DA-adduct-functionalized MWCNTs in preparation of polymer/MWCNT composites and the thermal treatment process is highly effective for preparation of electrically conductive polymer/MWCNT composite materials which have relatively low MWCNT contents.

Another DA-adduct functionalized MWCNT (MWCNT-BPA-FBz) has also been prepared to re-check the effect of

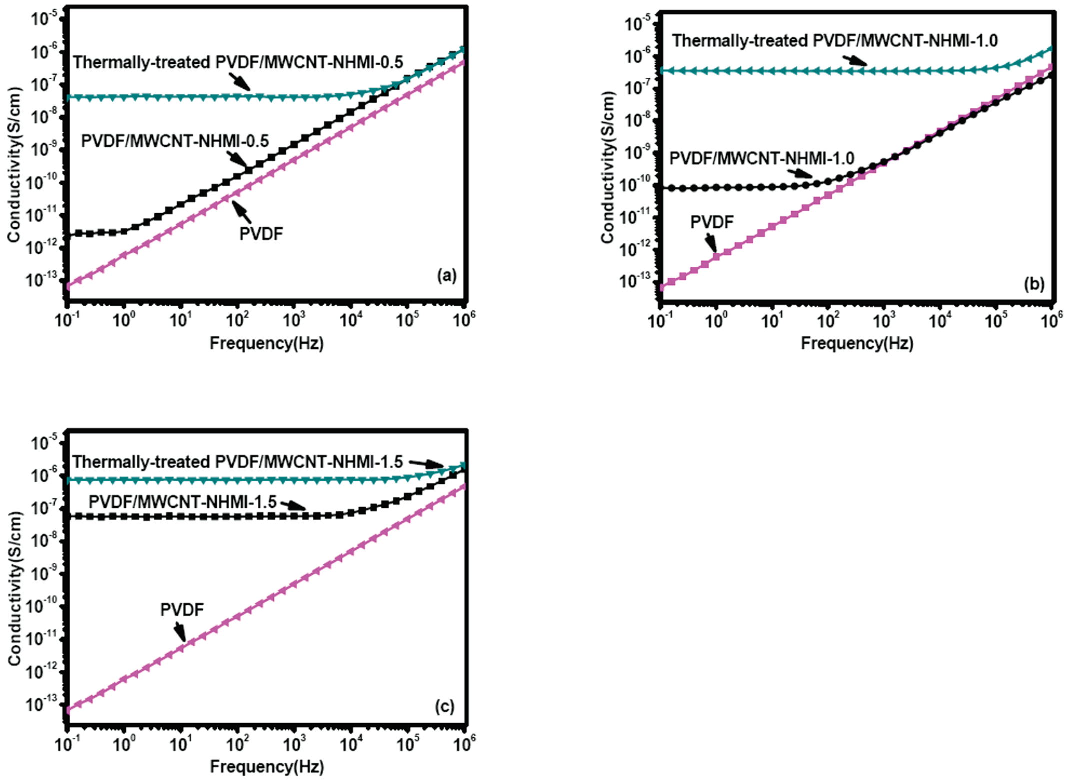


Figure 1. Electrical conductivity measurements of PVDF film and PVDF/MWCNT-NHMI composites films containing (a) 0.5 wt %, (b) 1.0 wt %, and (c) 1.5 wt % of MWCNT-NHMI. Thermally-treated samples have been heated at 160 °C for 3 h.

thermally-induced electrical conductivity jump. As shown in Figure 2, addition of MWCNT-BPA-FBz to PVDF shows relatively poor ability to enhance the electrical conductivity of PVDF, due to the relatively high organic content of MWCNT-BPA-FBz. Nevertheless, their conductivities have been significantly enhanced after thermal treatment. While being heated at 160 °C for 3 h, PVDF/MWCNT-BPA-FBz-0.5 (containing 0.5 wt MWCNT-BPA-FBz) demonstrates an electrical conductivity of about 8×10^{-8} S cm^{-1}, which is comparable to the value of thermally-treated PVDF/MWCNT-NHMI-0.5 (4×10^{-8} S cm^{-1}). Increasing in the MWCNT-BPA-FBz contents also increase the conductivities of the PVDF/MWCNT-BPA-FBz composites. As a result, thermally-induced defunctionalization of MWCNT-BPA-FBz also results in the electrical conductivity jump of PVDF/MWCNT-BPA-FBz films. It is noteworthy that thermally-treated PVDF/MWCNT-BPA-FBz-1.5 shows a conductivity of 1×10^{-7} S cm^{-1}, which is lower than the value of the MWCNT-NHMI-based analogue. Besides defunctionalization of MWCNTs, dispersion of functionalized-MWCNTs in PVDF matrix still plays an important role in their electrical conductivities.[7]

PVDF/MWCNT composite film containing 1.0 wt % of the unmodified MWCNT (PVDF/MWCNT-1.0) has also been prepared as a reference. The conductivities of the sample before and after thermal treatment are included in Figure 2. PVDF/MWCNT-1.0 has an electrical conductivity of about 4×10^{-9} S cm^{-1}, which is higher than the conductivities of PVDF/MWCNT-NHMI-1.0 and PVDF/MWCNT-BPA-FBz-1.0. The relatively high conductivity of PVDF/MWCNT-1.0 indicates its relatively poor dispersion in PVDF so as to form MWCNT connections in PVDF matrix for electrical conduction. Moreover, the thermally-treated PVDF/MWCNT-1.0 still exhibits an increased conductivity of about 1.0×10^{-8} S cm^{-1}. As the thermal treatment on PVDF/MWCNT-1.0 would not induce the chemical change of MWCNTs (no retro-DA reaction occurrence), the increase in the conductivity is attributed to the re-aggregation of MWCNTs.[18] Nevertheless, the conductivity of the thermally-treated PVDF/MWCNT-1.0 is not as high as the conductivities of the corresponding samples possessing modified MWCNTs. It is therefore concluded that functionalized MWCNTs disperse in PVDF matrix more homogeneously to result in the relatively low conductivity. With thermal treatment, the well-dispersed functionalized MWCNTs form effective MWCNT networks with a small amount of MWCNTs, hence resulting in the relatively high conductivities of the thermally-treated PVDF/MWCNT-NHMI-1.0 and PVDF/MWCNT-BPA-FBz-1.0 samples.

Figure 3 shows the scanning electrical microscopy images (SEM, Hitachi S-4800 field-emission SEM) of the PVDF/MWCNT composites. MWCNT bundles, especially MWCNT-NHMI, embed in the PVDF matrix, as shown in the SEM images. As a result, both of MWCNT-NHMI and MWCNT-BPA-FBz have high compatibility to PVDF. Thermal treatment induces some changes of the morphologies of the PVDF/MWCNT composites. Some MWCNTs stand out the fractural surfaces, indicating the relatively poor compatibility between MWCNTs and PVDF matrix in the thermally-treated samples. The morphological change is attributed to the thermally-induced defunctionalization of MWCNT-NHMI and MWCNT-BPA-FBz. Thermal treatment might enhance the formation of a MWCNT connected network in the composite contributing to the increase in their electrical conductivity.

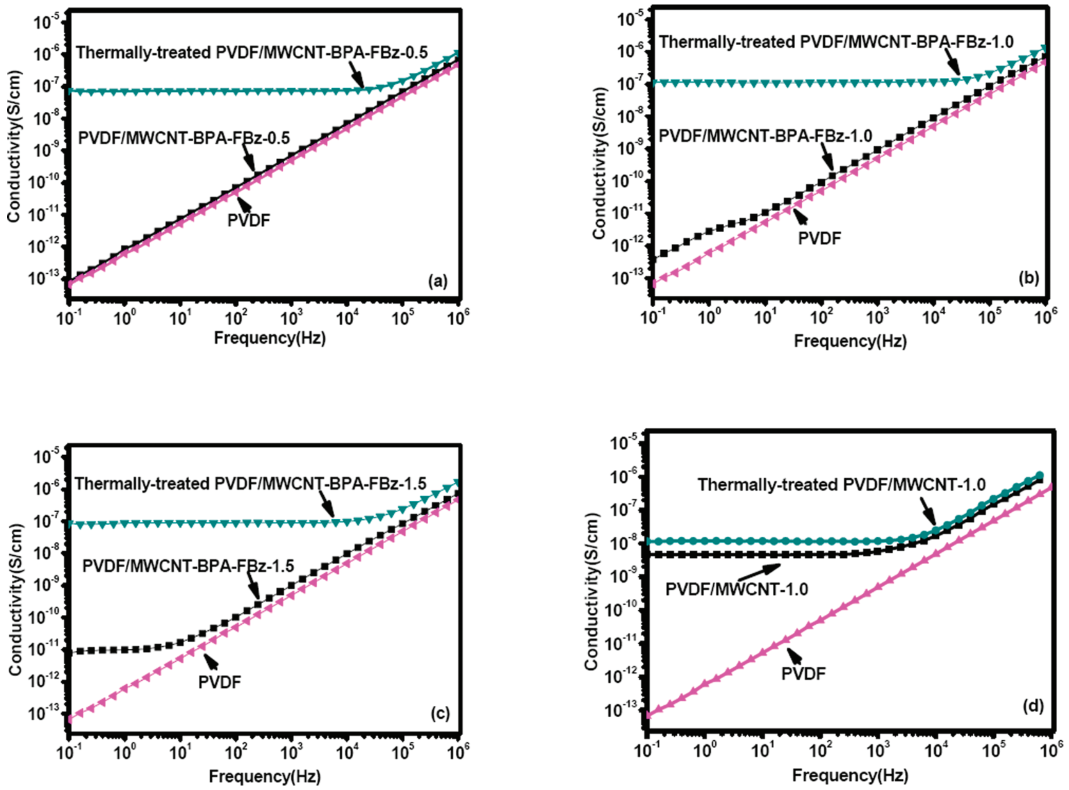


Figure 2. Electrical conductivity measurements of PVDF film and PVDF/MWCNT-BPA-FBz composites films containing (a) 0.5 wt %, (b) 1.0 wt %, and (c) 1.5 wt % of MWCNT-BPA-FBz. Plot (d) showing the data of PVDF/MWCMT containing 1.0 wt % of unmodified MWCNT for comparison. Thermally-treated samples have been heated at 160 °C for 3 h.

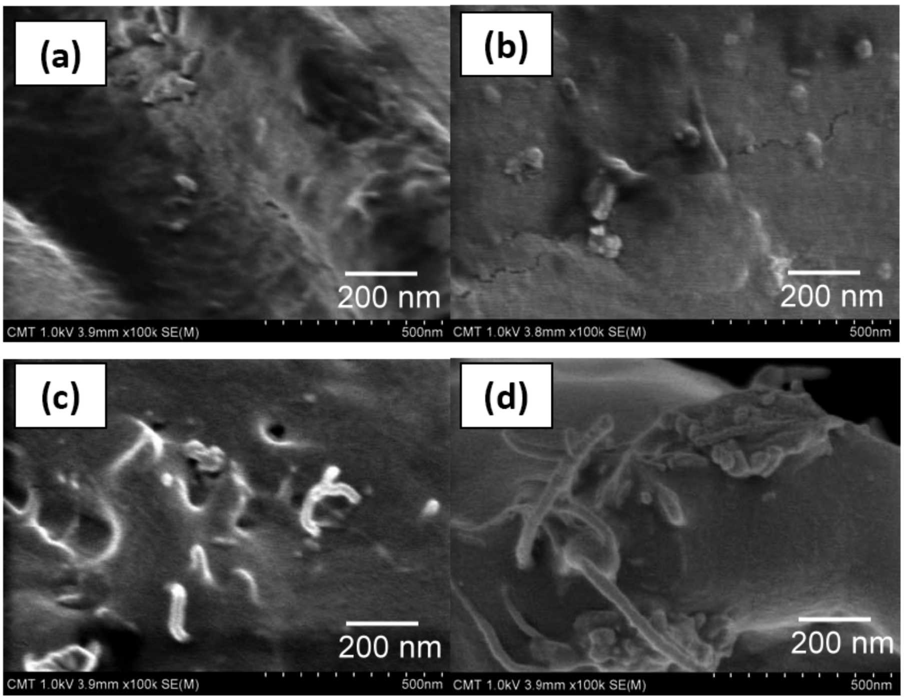


Figure 3. Cross-sectional scanning electrical micrographs of PVDF/MWCNT composites: (a) PVDF/MWCNT-NHMI-1.5, (b) PVDF/MWCNT-BPA-FBz-1.5, (c) thermally-treated PVDF/MWCNT-NHMI-1.5, and (d) thermally-treated PVDF/MWCNT-BPA-FBz-1.5.

The effect of thermal treatment on the mechanical properties of the PVDF/MWCNT composite films has been studied. Figure 4 shows the stress–strain curves of selected samples measured with an Instron (Instron 5543 analyzer at an elongation

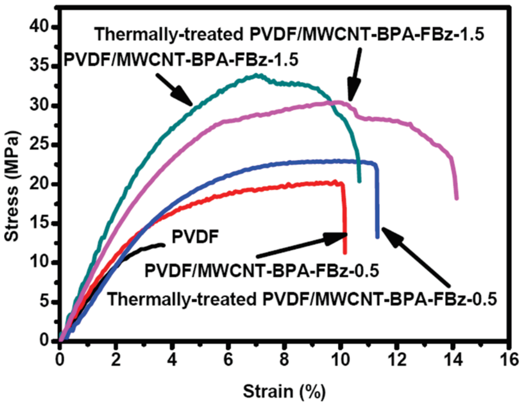


Figure 4. Stress−strain curves of PVDF film and PVDF/MWCNT-BPA-FBz composites films. Thermally-treated samples have been heated at 160 °C for 3 h

rate of 5 mm min^{-1}). Pristine PVDF film shows a tensile strength and an elongation at break of about 12.3 MPa and 3.6 %, respectively. Because of the reinforcement of MWCNTs, PVDF/MWCNT-BPA-FBz-0.5 shows better mechanical properties with a tensile strength of 20.0 MPa and an elongation at break of 9.8 %. Increases in the MWCNT contents to 1.5 wt % further enhance the tensile strength of PVDF/MWCNT-BPA-FBz-1.5 to about 31 MPa. It is noteworthy that the thermally-treated PVDF/MWCNT-BPA-FBz-0.5 sample exhibits similar stress−strain behavior in the test. The result demonstrates that thermal treatment only enhances the electrical conductivity of the composite film and not alters its mechanical properties.

In summary, we have demonstrated an effective and simple approach to reduce the percolation threshold, increase the electrical conductivity, and enhance the mechanical properties of polymer/MWCNT composite films. This approach combines the uses of DA-adduct functionalized MWCNTs and post thermal treatments of the resulting polymer/MWCNT composites. After thermal treatment, the sample possessing 0.5 wt % of functionalized MWCNT shows an electrical conductivity jump from 2×10^{-12} S cm^{-1} to 4×10^{-8} S cm^{-1} without any reduction of mechanical properties. The effects of thermal treatment on the increase in the electrical conductivity could be the recovery the conductivity of MWCNTs through retro-DA reaction and the formation of a MWCNT connected network. This approach deserves applying to other polymer matrixes for finding high performance polymer/MWCNT composites.

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ACKNOWLEDGMENT

We thank the National Science Council, Taiwan, for the financial support on this work (NSC 99-2221-E-033-007-MY3 and NSC-99-2622-E-033-008-CC3).

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