

Electrical Properties of PVdF/PVP Composite Filled with Carbon Nanotubes Prepared by Floating Catalyst Method

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Abstract : The multi-wall carbon nanotubes (MWNTs) with graphite crystal structure were synthesized by the catalytic decomposition of a ferrocene-xylene mixture in a quartz tube reactor to use as the conductive filler in the binary polymer matrix composed of poly(vinylidene fluoride) (PVdF) and poly(vinyl pyrrolidone) (PVP) for the EMI (electromagnetic interference) shielding applications. The yield of MWNTs was significantly dependent on the reaction temperature and the mole ratio of ferrocene to xylene, approaching to the maximum at 800 °C and 0.065 mole ratio. The electrical conductivity of the MWNTs-filled PVdF/PVP composite proportionally depended on the mass ratio of MWNTs to the binary polymer matrix, enhancing significantly from 0.56 to 26.7 S/cm with the raise of the mass ratio of MWNTs from 0.1 to 0.4. Based on the higher electrical conductivity and better EMI shielding effectiveness than the carbon nanofibers (CNFs)-filled coating materials, the MWNTs-filled binary polymer matrix showed a prospective possibility to apply to the EMI shielding materials. Moreover, the good adhesive strength confirmed that the binary polymer matrix could be used for improving the plastic properties of the EMI shielding materials.

Keywords : carbon nanotubes, conductive filler, polymer matrix, PVdF/PVP composite, electrical conductivity, EMI shielding effectiveness.

Introduction

Since the discovery of carbon nanotubes (CNTs) by Iijima¹ in 1991, a lot of academic and industrial researches have been intensively performed to investigate the potential applications of CNTs as noble materials available in the extensive industrial field. CNTs are a kind of tubular carbon nanofibers (CNFs) and have unique mechanical and electrical properties due to their seamless graphite-sheet structure with high aspect ratio. Among the various CNTs, multi-wall carbon nanotubes (MWNTs) are regarded as prospective substitute materials for nanosized reinforcement, since they possess significantly high aspect ratio and good axial strength.^{2,3} Up to date, CNTs have been mainly synthesized by arc discharge,^{4,5} laser ablation,^{6,7} solar technique,⁸ catalytic decomposition⁹ or electrolysis.¹⁰

Recently, CNFs-filled polymer composites have attracted considerable research attentions because of high stiffness, good mechanical strength and excellent electrical conductivity at low filler concentration. The polymer composites coated

with CNFs are usually prepared by dispersing CNFs into single polymer matrix, for example, poly(vinyl alcohol) (PVA) or poly(vinylidene fluoride) (PVdF), and well suited for the EMI (electromagnetic interference) shielding applications.¹¹⁻¹³ In order to apply the CNFs-filled polymer composites for the EMI shielding material, it is indispensable to improve the electrical conductivity of the composites, since the EMI shielding effectiveness is directly dependent on the electrical conductivity.¹² According to the percolation theory, the electrical conductivity in the composites is very sensitive to the content of CNFs filler.^{14,15}

In this research, the CNTs-filled polymer composite was synthesized using MWNTs as the conductive filler prepared by the floating catalyst method to examine the influence of fabrication factors, including content and type of filler, and heat treatment conditions, on the EMI shielding properties. The influences of decomposition temperature and the mole fraction of ferrocene in xylene on the yield and morphology of MWNTs were also investigated. In particular, the binary polymer mixture prepared by blending PVdF with poly(vinyl pyrrolidone) (PVP) was used as the polymer matrix to improve the plastic properties of the final polymer composites along with EMI shielding efficiency.

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Experimental

MWNTs were synthesized through the catalytic decomposition of a ferrocene-xylene mixture in a quartz tube reactor. Ferrocene was chosen as the source of Fe catalyst and the MWNTs nucleated and grew on the surface site of the vaporized catalyst. Xylene was used as both the hydrocarbon source for MWNTs and the solvent of ferrocene.¹⁶ The reactant solution was prepared by dissolving approximately 3.0 to 10.0 mol% of ferrocene in xylene and continuously introduced into the tubular reactor using a syringe pump after vaporization at 200 °C in the front part of the reactor. The detailed experimental set-up adopted was described elsewhere.¹⁷ The temperature of reaction zone in the reactor was controlled from 650 to 900 °C. After 3 h of the reaction time, carbon deposits were formed on the quartz reactor wall and most of the deposits were confirmed as MWNTs by HRTEM (high resolution transmission electron microscope) analysis. The yield of MWNTs deposited on the reactor was calculated by dividing the mass of carbon deposits with the mass of carbon contained in the ferrocene-xylene mixture for the reaction time.

The PVdF/PVP solution was prepared by stirring the mixture containing 3-7 wt% of PVdF homopolymer (Kryer 731, ELF Atochem.), 3-7 wt% of PVP and 80-88 wt% of *N*-methyl-2-pyrrolidone (NMP, Micropure EG, ISD Technologies) at 60 °C for at least 30 min. The MWNTs crushed mechanically beforehand were fed into the PVdF/PVP/NMP solution and the resulting mixture was homogenized at 600 rpm for 30 min by a mechanical stirrer (Art-Micra D-8, Art Co.). The final mixture obtained was coated into the size of 15 cm by 30 cm with the thickness of 400-600 μm using a coating machine (CNI Robotics Co.). The thickness of the coating materials was decreased to 40-60 μm after drying.

The morphology of the MWNTs filler was analyzed using SEM (Leica S440), and the structure was confirmed from TEM (JEM-200EX II) and HRTEM (JEM 3000F) images. The electrical conductivity of fillers was measured from the electrical resistance of samples in the stainless steel cylinder under a constant pressure of 10,000 psi using a digital multimeter (HI Tester 3220, Hioki Co.) and an automatic four-probe system (CMT-SR2000N, Chang Min Tech. Co.) was used for measuring the electrical conductivity of the coating materials.¹⁸ The EMI shielding effectiveness was determined according to ASTM D4935 using a HP-8720C apparatus. In addition, X-ray diffraction analysis of the fillers was carried out with an XD-D1 system (Shimadzu) using $\text{CuK}\alpha$ radiation and the adhesive strength of the final coating materials was measured by using cross-cut test according to ISO 2409.¹⁹ The sample for the adhesive strength was prepared by pressing 100 pieces of coating materials on a plastic substrate and the adhesive strength was defined as the number of the pieces remaining on the plastic substrate after detaching with cel-

lophane tape.

Results and Discussion

Synthesis and Characterization of MWNTs. The influence of the reaction temperature on the yield and morphology of MWNTs is shown in Figures 1 and 2, respectively. The MWNTs were synthesized at a flow rate of 1 mL/h of the reactant solution and with 3 h of the reaction time. As presented in Figure 1, the yield of MWNTs was increased with the increase of the reaction temperature up to 800 °C. However, the yield was decreased sharply with the further increase of temperature. These results indicated that the reaction temperature below 700 °C was too low for the MWNTs to form graphitic structure and that the increase of amorphous carbon caused by the decomposition of xylene at high reaction temperature above 800 °C resulted in the reduction of the yield.²⁰ These phenomena were also confirmed from the SEM images of MWNTs taken with the reaction temperatures, as typically given in Figure 2. It can be seen that the MWNTs were well-graphitized at about 800 °C and not covered by amorphous carbon. Therefore, in the present work, the reaction temperature was maintained at 800 °C as the optimal temperature for synthesis of MWNTs.

The yield of MWNTs was also influenced by changing the mole ratio of ferrocene to xylene and the maximum yield was obtained at 0.065 mole ratio of ferrocene to xylene. Typical TEM and HRTEM images of MWNTs produced at this mole ratio with the optimal reaction temperature are given in Figure 3, which reveals well the MWNTs have tubular structure with uniform diameter and wall thickness. Interestingly, as the mole fraction of ferrocene increased, the MWNTs became shorter and thicker and the Fe catalyst was found to be attached to the tip as well as the inside of the growing MWNTs. These results indicated clearly that

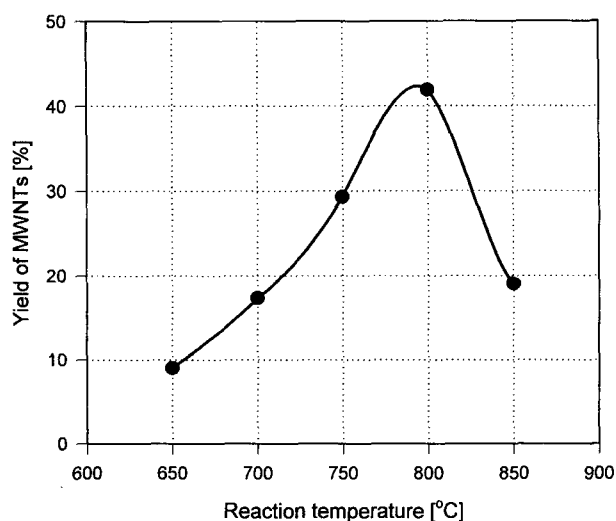


Figure 1. Effect of reaction temperature on yield of MWNTs.

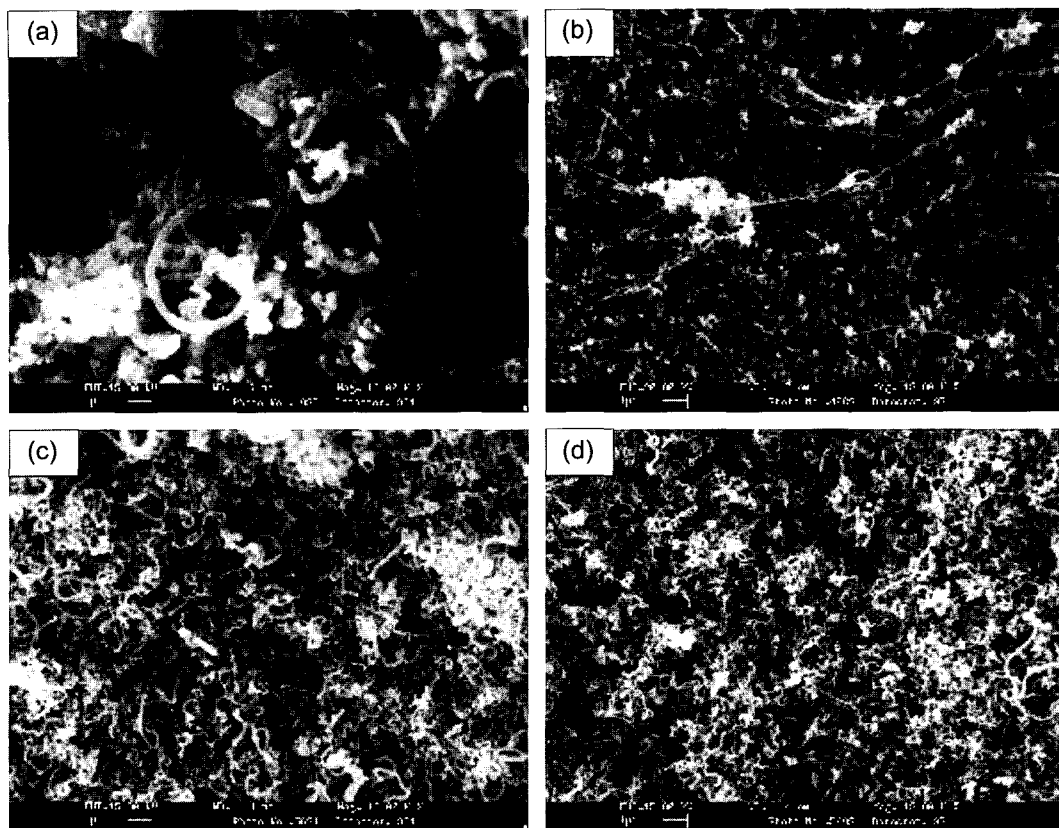


Figure 2. Morphology of MWNTs observed by SEM at different reaction temperatures. (a) 750°C, (b) 800°C, (c) 850°C and, (d) 900°C.

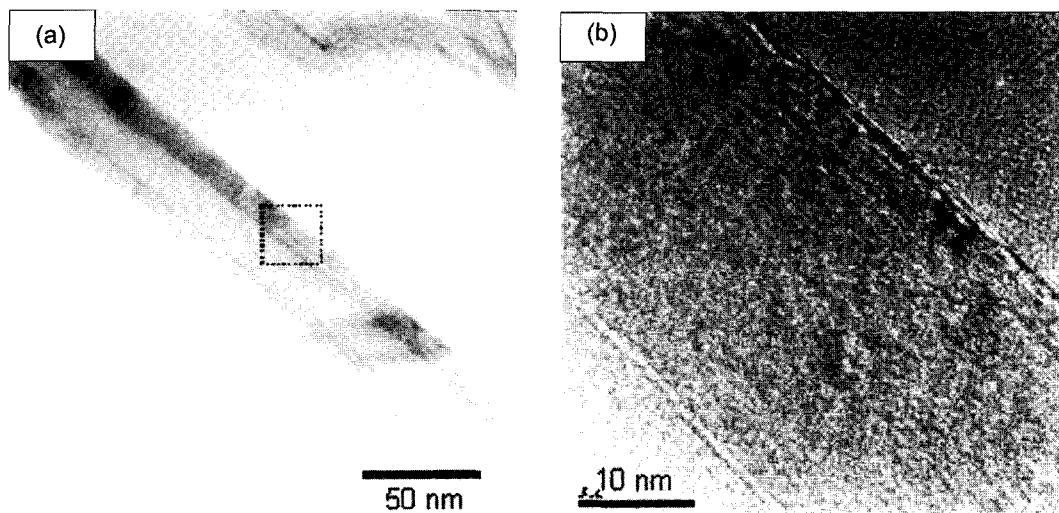


Figure 3. TEM and HRTEM images of a MWNT synthesized at 800°C and 0.065 mole ratio of ferrocene to xylene. (a) TEM and (b) HRTEM.

with increasing the mole fraction of ferrocene, the metal catalyst existed in the form of clusters with high surface area rather than fine particles in the reactor, thereby resulting in short and thick MWNTs.

The XRD pattern of MWNTs is compared with that of CNFs¹³ in Figure 4 to identify the degree of crystalline structure. Based on the main peaks detected at 26° and 46° of 2θ, the XRD patterns revealed that both of them closely

matched with the graphite crystal structure.²¹ However, the characteristic peak intensity at 26° of the MWNTs was narrower and higher than that of CNFs, which indicated that the degree of crystalline order in the MWNTs was more well-developed than that in CNFs, thereby resulting in the higher electrical conductivity.

Electrical Properties of MWNTs-filled PVdF/PVP Composite. The variation in electrical conductivity of the binary polymer composite filled with MWNTs is given in Figure 5 as a function of the MWNTs content in the polymer matrix. The MWNTs content is expressed as the mass ratio of MWNTs to the binary polymer matrix. In the current work, the binary polymer matrix system was selected to enhance mechanical strength and EMI shielding effectiveness of coating materials by combining the physical and electro-

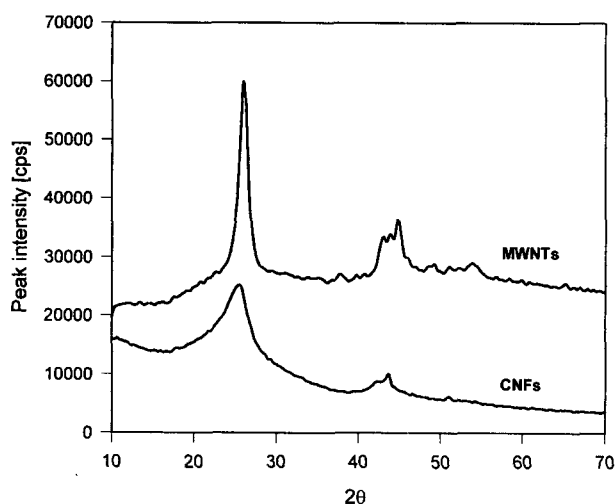


Figure 4. Typical XRD patterns of MWNTs and CNFs.

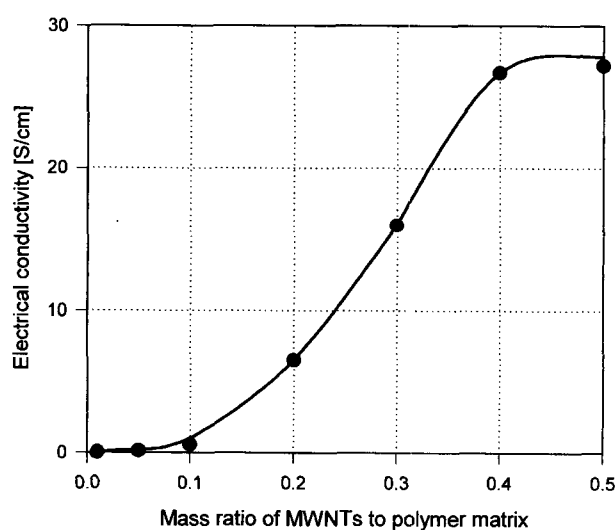


Figure 5. Effect of MWNT content on electrical conductivity of PVdF/PVP composite.

chemical properties of PVdF with those of PVP. Since PVdF has relatively high conductivity as well as good mechanical strength,^{22,23} it has been extensively applied as the noble materials in various industrial areas, such as conductible polymer, secondary cell, and capacitor. In addition, PVP is also widely employed as a bonding agent or additive to improve strength and toughness.

The electrical conductivity of the final binary polymer composite was proportionally dependent on the mass ratio of MWNTs. The electrical conductivity was increased from 0.56 to 26.7 S/cm with the raise of the mass ratio from 0.1 to 0.4. However, when the mass ratio of MWNTs went over 0.4, the electrical conductivity was almost independent of the MWNTs content and the viscosity of the PVdF/PVP/NMP solution was observed to be too high to fabricate uniform coatings. As a result, the conductivity did not increase with a further raise of filler content. On the other hand, when the mass ratio of MWNTs was decreased from 0.05 to 0.01, the electrical conductivity of the coating materials dropped sharply from 10^{-1} to less than 10^{-4} S/cm.

Table I shows the electrical conductivities of carbon nanofibers (CNFs) and nanotube (MWNTs) fillers, along with those of their composites when the mass ratio of filler to various matrixes, such as PVA, PVdF, and PVdF/PVP, has the same value of 0.4. As compared the conductivity of fillers, the value of the MWNTs was about 14 times higher than that of CNFs, which seemed to be caused by the higher degree of crystalline order. The type of the polymer matrix also had an influence on the conductivity of the final composite and the PVdF/PVP polymer had a superb effect on the conductivity. Although a dispersant had to be introduced to get homogeneous dispersion for the case of PVA matrix,¹² the CNFs-filled PVA composite was found to have very low conductivity of 0.033 S/cm. However, relatively good homogeneous dispersion of the fillers in both PVdF and PVdF/PVP matrix could be obtained by only mechanical mixing. When PVdF was used as a single polymer matrix and filled with CNFs and MWNTs, the electrical conductivity of the coating materials was significantly improved from 0.65 to 9.8 S/cm by changing the fillers. This improvement resulted from the conductivity difference between the fillers. The conductivity of coating materials was further enhanced

Table I. Electrical Conductivities of Nanofiber and Nanotube Fillers and Their Composites

Matrix	Filler	Conductivity of Filler at 10,000 psi (S/cm)	Conductivity of Coating Composites (S/cm)
PVA	CNFs	5.5	0.033
PVdF			0.65
PVdF	MWNTs	75	9.8
PVdF/PVP			26.7

Table II. Effect of PVdF/PVP Ratio on Electrical Conductivity and Adhesive Strength of Final Composite

PVdF/PVP (wt ratio)	Filler	Film Uniformity	Electrical Conductivity (S/cm)	Adhesive Strength
0/100	MWNTs	Good	9.5	100
30/70	MWNTs	Good	17.8	100
50/50	MWNTs	Good	26.7	100
70/30	MWNTs	Good	13.3	96
100/0	MWNTs	Good	9.8	0

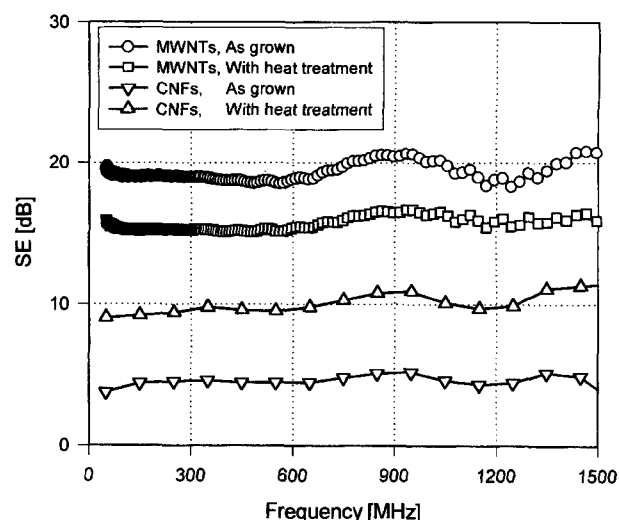
up to 26.7 S/cm by introducing the binary PVdF/PVP matrix instead of PVdF matrix. These results implied obviously that the binary polymer composite filled with MWNTs could be prospective EMI shield material since the shielding effectiveness was proportional to the electrical conductivity.²¹

When the mass fraction of MWNTs and NMP in the PVdF/PVP solution was fixed at 0.04 and 0.86, respectively, the influence of PVdF-PVP composition on the electrical conductivity and adhesive strength of coating materials are presented in Table II. The electrical conductivity was significantly affected by the PVdF/PVP ratio and the maximum conductivity was observed at 50/50 wt%. PVdF is known as a semi-crystalline polymer, which means it has both crystalline and amorphous phase.²² According to the report by Chen and Hong,²³ the crystalline phase of PVdF was experimentally observed to be influenced by the added amount of PVP as PVdF was blended with PVP. Only when the content of PVP and PVdF was same each other, the crystalline phase of PVdF disappeared completely and the binary blend became amorphous and miscible. Based on this result, it could be speculated that the maximum electrical conductivity of the final composite at 50/50 wt% of PVdF and PVP resulted from the entire conversion into amorphous phase in the polymer matrix. The adhesive strength of the composite coatings was magnificently improved by the introduction of PVP and the satisfactory adhesive strength was obtained if the PVP content was over 50 wt%.

Figure 6 shows the EMI shielding effectiveness (SE) of the PVdF/PVP composite filled with MWNTs at the mass ratio of 0.4 and the PVdF composite filled with the same contents of CNFs. The fillers were introduced with and without heat treatment. The heat treatment was conducted in N₂ atmosphere at 1,100 °C for 1 h. The SE was calculated using Eq. (1) in the range of 10 to 1500 MHz, where P_i and P_t mean the power of the incident and transmitted wave, respectively.²⁴

$$SE \text{ (dB)} = 10 \log (P_i/P_t) \quad (1)$$

Regardless of the frequency of the electromagnetic wave

**Figure 6.** EMI shielding effectiveness of MWNTs- and CNFs-filled composites with and without heat treatment of the filler.

and the heat treatment of fillers, the SE of the coating materials with MWNTs was always higher than that with CNFs. The SE of CNFs/PVdF composite increased from about 4 to 10 dB by the heat treatment of CNFs. However, contrary to the case of the CNFs-filled composite, the SE of MWNTs-filled composite was considerably decreased from about 20 to 15 dB by the heat treatment of MWNTs. Generally, the SE of EMI shielding material is dependent on electrical conductivity and specific surface area of the filler. According to previous reports on the heat treatment of CNFs-filled coating materials,^{12,18} the electrical conductivity of the filler increased but the specific surface area decreased with increasing heat treatment temperature and time. The decrease in the surface area was explained by the surface rearrangement and porosity loss of CNFs. The electrical conductivity of the coating materials maximized with the mild heat treatment at 1,100 °C for 1 h and then decreased with the further increase of heat treatment temperature and time. It was concluded that as an EMI fillers property, large specific surface area was desirable and a more important factor than the conductivity. The reduced SE of MWNTs-filled composite with the heat treatment of filler might be caused by the decrease in the specific surface area of the filler. The specific surface area of MWNTs was reduced by 4-5% after the heat treatment.

Conclusions

The MWNTs was synthesized by the catalytic decomposition of a ferrocene-xylene mixture and used as the conductive filler to investigate the effects of the preparation conditions on the EMI shielding properties of the binary polymer composite made up with PVdF and PVP. The binary polymer matrix was chosen to examine the possibility to apply to the

coating materials for improving the plastic property as well as the EMI shielding effectiveness. The reaction temperature and mole fraction of ferrocene in xylene were varied to find the optimal conditions for the yield and morphology of MWNTs. The maximum yield was obtained at 800 °C of reaction temperature and 0.065 mole ratio of ferrocene to xylene, and the MWNTs had good graphite crystal structure.

The electrical conductivity of the binary polymer composite was affected by the mass ratio of MWNTs to the polymer matrix, increasing from 0.56 to 27.2 S/cm with the raise of mass ratio from 0.1 to 0.5, which seem to saturate at the mass ratio of MWNTs over 0.4. The electric conductivity of the MWNTs-filled PVdF/PVP composite was 26.7 S/cm at the mass ratio of 0.4, whereas that of the CNFs-filled PVdF composite was 0.65 S/cm at the same filler content. While the EMI shielding effectiveness of CNFs-filled composite was improved by the heat treatment of filler at 1,100 °C for 1 h from about 4 to 10 dB, the EMI shielding effectiveness of MWNTs-filled composite was dropped from about 20 to 15 dB by the heat treatment at the same condition. The MWNTs-filled binary polymer composite also showed good adhesive strength.

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