Characterizations on the Amidized Multiwalled Carbon Nanotubes Grafted with Polyaniline via *In Situ* Polymerization

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ABSTRACT: A multiwalled carbon nanotubes (MWCNTs) were carboxylated after refluxing with sulfuric and nitric acids. These attached carboxylic acid groups were further condensated with *o*-phenylene diamine into amide catalyzed by dicyclohexyl carbodiimide (DCC). The obtained amidized MWCNTs were *in situ*-polymerized with aniline monomers to graft a conducting polyaniline (PANI) onto MWCNT (ES-*g*-MWCNTs) through the polymerization occurring in the ortho- and meta-positions. The reduced conductivity of the MWCNT after carboxylation can be recovered after grafting with PANI, which owns a strong λ_{max} at the near infrared region due to the extended conjugation from MWCNTs to PANI. Transmission electronic microscopic pictures show a gradual broadening of the MWCNT diameter after carboxylation, amidization, and polymerization. The weight loss from the thermogravimetric thermograms due to the carboxylations of MWCNTs, amidized MWCNTs, and the PANI grafted MWCNTs into CO_2 can be used to estimate the degree of carboxylation, amidization, and grafting of PANI. The degree of carboxylation of MWCNT calculated from ESCA spectrum is around 23% close to that estimated from TGA thermogram. The doping level of redoped PANI-grafted MWCNT is found to be 27.78% much less than the maximum 50% of neat PANI. © 2011 Wiley Periodicals, Inc. J Appl Polym Sci 124: 5270–5278, 2012

Key words: multiwalled carbon nanotube; polyaniline; conjugation

INTRODUCTION

Carbon nanotubes (CNTs) are known to be good reinforcement materials for high performance, multifunctional composites, because of their extraordinary properties such as excellent Young's modulus, high electrical conductivity, and thermal stability.[1] But with little solubility in common solvents due to its extremely insoluble, nonfusible nature, their applications are significantly restricted.[2] The insolubility comes from either the lack of functional groups or the presence of the strong orbital-orbital overlapping interactions between aromatic rings of the CNTs, leading to the nonisolable aggregation by common physical methods. The lack of functionalities and aggregation can be solved through surface functionalization to improve their solubility in common solvents or polymer matrix. Even though the dispersibility in a polymer matrix can be improved by surface functionalization, the bulk conductivity of the CNT/polymer composite is still low due to the disconnection, noncontinuity of the CNTs at the matrix when their concentration are still low. To increase the conductivity of the CNT/composite by increasing the ratio of expensive CNTs in the matrix to create more interconnections in the polymer matrix would sacrifice other properties of the resultant composite. These problems can be solved simultaneously by surface functionalizing with a soluble, dispersible conducting polymer, which can not only improve the dispersibility of CNTs in solvents, compatibility with polymer matrix but also be able to maintain the conductivity of the CNT/composite even when a low ratio of CNT is input.

Recently, extensive efforts have been made to prepare functional CNT composites by grating with polyaniline (PANI), to keep the high conductivity of CNT and improve its solubility in either hydrophobic solvent like NMP after dedoping into EB.[3] On the PANI side, the grafting on CNTs can improve its own heat-resistance and allows the CNTs modified

PANI to be melt-mixed with matrix polymers that can only be processed at high temperature without inducing any thermal degradation of PANI itself. Sun et al.[4] prepared a CNT solution with aniline monomers as solvent before polymerization. Cochet et al.,[5] Zengin et al.,[6] and Feng et al.[7] obtained a CNT/PANI composite by *in situ* polymerizing aniline onto CNT surface. These efforts were made to prepare a PANI covered CNT by *in situ* polymerization in the absence of any covalent-bonding between them. The weak physical bonds between CNT and PANI disconnected the interconjugation, resulting in the limited improvement on the conductivity of the hybrid material and increasing the possibility of delamination, separation of PANI from CNTs during processing or mixing. Therefore, it is necessary to prepare a PANI grafted CNT through a real covalent-bonding to firmly catch the grafted PANI to extend the conjugation from the CNT to PANI to obtain a composite with high conductivity with less CNT incorporated.

p-phenylenediamine (PDA) was first to used to modify the surface of the multiwalled CNT (MWCNT) by reacting with its surface acylchloride group into amide.[8,9] It was claimed the left unreactive aromatic amino-group of grafted PDA can polymerize into a dangling PANI molecule with aniline monomers. However, it is very possible that both of the amine groups of PDA can be captured by the highly reactive acylchloride, and it leads to the more insoluble, crosslinked MWCNT. Besides, the PDA was usually found in the polymerization of a small molecular weight PANI as the chain growing inhibitor.[10–17] Therefore, PDA with one end connected to MWCNT is less possible to polymerize with aniline monomers through the para-position.

In this study, we used *ortho*-phenylenediamine (ODA) to replace PDA and the amide can be obtained directly from the condensation reaction of the MWCNT carboxylic acid and amine of ODA in the presence of dicyclohexyl carbodiimide (DCC) catalyst instead of turning carboxylic acid groups of MWCNT into acylchloride, which was then treated by amine to become amide. Therefore, the crosslinking between MWCNT can be avoided and the obtained amidized MWCNT[18,19] can be polymerized with aniline monomers into grafted PANIs. Furthermore, many specific behaviors will be found due to the interconjugation between the PANI and MWCNT. Most importantly, the high conductivity of MWCNT can be preserved even after grafting with PANI, which also owns conductivity.

However, mere grafting PANI, which is doped by mineral acids onto MWCNT cannot improve its solubility too much since this kind of PANI is not soluble in common organic solvents. Therefore, we will try to replace the doping acid from mineral ones to sulfonic acid with long alkyl chains to improve solubility of PANI grafting MWCNT in the organic solvents, which makes possible mixing MWCNT in other polymer matrix.

EXPERIMENTAL

Sample preparations

Preparation of carboxylated-MWCNTs (c-MWCNTs)

One gram of MWCNTs ($\sim$ 10 nm from Seedchem Company, China) was carboxylated with a 100 mL coacid (H_2SO_4 : HNO_3 = 3,653,061) in ultrasonic for 24 h at 50°C. The obtained mixture was filtered and the filtered cake was washed with deionized water and methanol alternatively until pH value is approaching seven, and dried in an oven for 24 h at 60°C. The obtained MWCNTs are called c-MWCNTs and the degree of carboxylation was estimated to be around 23% based on the results obtained from ESCA spectrum.

Preparation of amidized MWCNTs (a-MWCNTs)

The 0.1 g c-MWCNTs, 10 g DCC, and 20 g (0.185 mol) ODA were mixed in 200 mL dimethyl formamide (DMF) mixture under ultrasonication for 72 h at 70°C, then filtered with polytetrafluroethylene filter paper to remove the nonreacted ODA and the cake was collected and washed with DMF then methanol until the filtrate became clear. The amidized MWCNT cake named as a-MWCNT was dried in a vacuumed oven for at least 24 h at 60°C, and the degree of amidization is estimated to be 17.63% according to ESCA spectrum.

Preparation of emeradine salt-grafted MWCNTs (ES-g-MWCNTs)

Twelve g of distilled aniline monomer (0.132 mol) was added and stirred with a suspension of 0.1 g a-MWCNTs in 200 mL, 1M HCl until the suspension became homogenous followed by the addition of aqueous solution of ammonium persulfate (7.33 g in 30 mL deionized water) and stirred for 3 h at 0–5°C. Finally, the filter cake was collected by filtration and dedoped in excess of 1M ammonium aqueous solution overnight to remove protonic acids of grafted or ungrafted PANIs and ultrasonicated in *n*-methylpyrrolidone (NMP) to remove the ungrafted/free EB (emeraldine base) type of PANI, which is more soluble in NMP compared to EB type of grafted PANI that linked with MWCNT. The obtained filter cake, which is EB grafted on MWCNT, is named as EB-*g*-MWCNTs and was redoped with excessive *n*-dodecylbenzenesulfonic acid (DBSA) in toluene and filtered, the filtered cake was washed with isopropanol several times to remove the free DBSA. The entire preparation procedures are depicted in Scheme 1. The degree of EB-grafting will be less than 17.63%, which is the degree of amidization, and the real
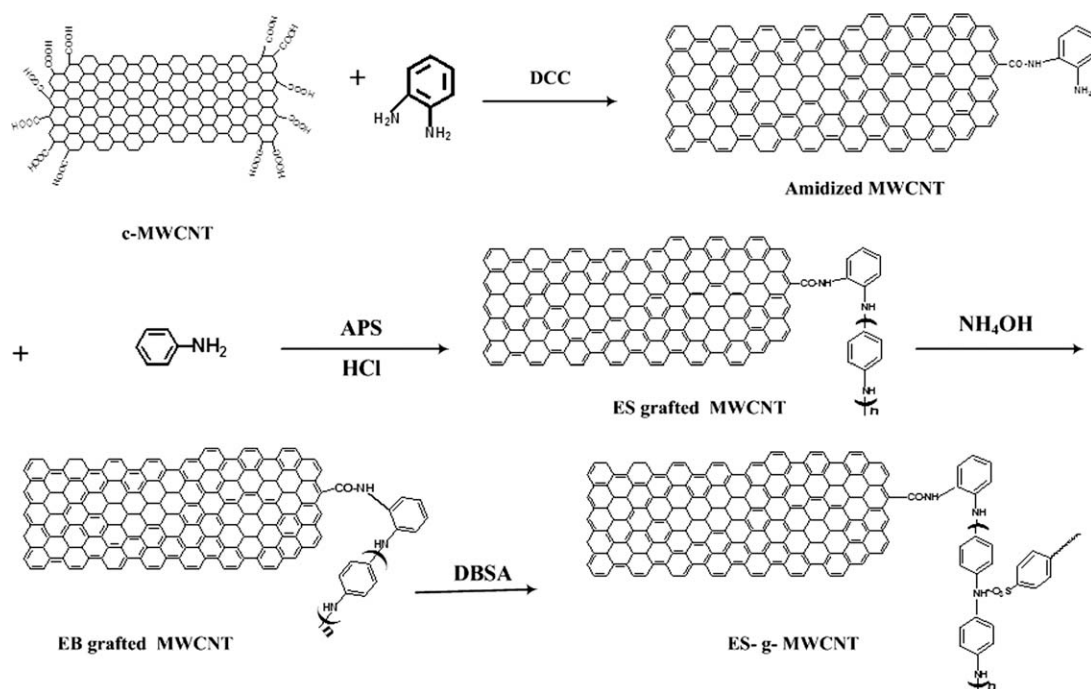
Scheme 1 Overall reaction schemes from c-MWCNT to ES-*g*-MWCNT.

grafting degree is not available since the molecular weight of the grafted EB is not measurable.

Characterization

Infrared (IR) spectroscopy

The characteristic functional groups of all samples of KBR tablets were characterized by Fourier transform infrared (FTIR) spectroscopy. The FTIR spectra were recorded on an IFS3000 v/s FTIR spectrometer at room temperature.

Ultraviolet-visible-near infrared (UV–vis-NIR) spectroscopy

UV–vis-NIR spectra were measured with a Hitachi U-2001 UV–vis spectrometer and DTS-1700 NIR Spectrometer.

Measurement

Conductivity

Samples used in electrical conductivity measurements were pressed into a uniform circular shape by applying a hydraulic pressure of about 10 MPa, and the electrical conductivity was measured by a standard four-probe method on a milliohm meter (Lutro MO-2001) at room temperature.

Transmission electronic microscopy (TEM)

Samples for taking field emission transmission electron microscope by a HR-AEM (Hitachi FE-2000)

with an accelerating voltage of 15 kV were prepared by dispersing samples in water or toluene, which was then dropped on carbonic-coated copper grids for TEM measurement.

Thermogravimetric analysis (TGA)

Samples were given a thermal gravimetric analysis by a TA SDT-2960 at 10°C/min, under purging N_2.

Electron spectroscopy for chemical analysis (ESCA)

The different binding energy spectra of C_{1s} of EB-*g*-MWCNTs, which were used to estimate the percentage of carboxylic, amine and amide groups, were analyzed by an ESCA instrument of Fison (VG)-Escalab 210 using Al Kα X-ray source at 1486.6 eV. The pressure in the chamber was maintained under 10^{-6} Pa or lower during the measurement. A tablet sample was prepared by a stapler. The binding energies of the C_{1s} around 285 eV were recorded.

RESULTS AND DISCUSSION

Dispersibility in solvents

The neat MWCNTs were able to disperse in water after surface modification in mixed strong acids granted with surface carboxylic acid groups, comparing Figure 1(a) with (b). A subsequent amidization with ODA in the presence of DCC (Scheme 1) can change its hydrophilic behavior to hydrophobic one. After amidization, the a-MWCNT became
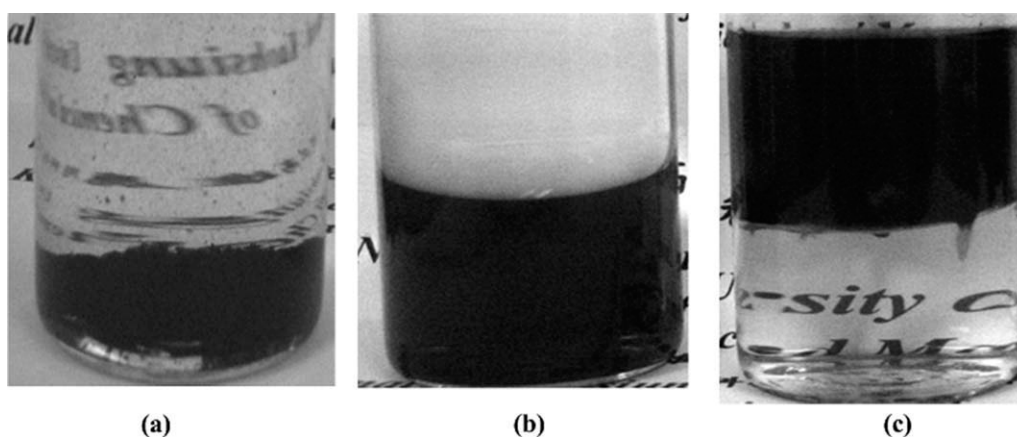
Figure 1 Optical pictures of (a) sedimentation of neat MWCNTs in pure water, (b) c-MWCNTs dispersed in lower phase of water and toluene mixture, and (c) a-MWCNTs dispersed in upper phase of water and toluene mixture.

toluene dispersible but not water dispersible any more according to Figure 1(b,c). The c-MWCNTs can be dispersed in lower water phase in a vial containing upper toluene and lower water phases as seen in Figure 1(b). Figure 1(c) illustrates that the a-MWCNTs were dispersed in the upper toluene phase when hydrophilic carboxylic acid were converted into hydrophobic amide groups. The improved solubility in toluene for a-MWCNT significantly revealed that the already linking ODA to the MWCNT surface via condensation with —COOH of c-MWCNT and the degree of amidization was higher enough to convert hydrophilic c-MWCNT to hydrophobic a-MWCNT.

## Characterization on surface modification by IR-spectroscopy

c-MWCNT and a-MWCNT were both characterized by IR spectra, which demonstrate the carbonyl groups of carboxylic acid and amide in Figure 2, respectively. Figure 2(a), an IR spectrum of neat MWCNTs, illustrates only the strong band of benzene ring and no significant carbonyl group around 1700 cm^{-1} can be seen. After carboxylation in the mixed acids, a carbonyl band at around 1710 cm^{-1} appears in Figure 2(b), assigned as the carbonyl group of —COOH. Further reaction with ODA in the presence of DCC, the IR-spectrum of the obtained a-MWCNTs is shown in Figure 2(c) in which a significant band of amide carbonyl group can be found at around 1680 cm^{-1} next to the weak absorption band of the carbonyl of —COOH, indicating most of the —COOH groups have been converted into amides. The obtained a-MWCNTs were then covalent-bonded with PANI by *in situ* polymerization and became PANI-grafted MWCNTs according to the mechanism depicted in Scheme 2, which indicates the initiation occurred at the left (unreacted) *ortho-*

amine of ODA and did not interfere with the connected MWCNT.

The obtained PANI-g-MWCNTs were dedoped with ammonia water and converted into EB type of PANI whose IR spectrum is in Figure 2(d) and was compared with that of c-MWCNTs in Figure 2(b) and neat EB in Figure 2(e). Strong benzenoid and quinoid bands can be seen at around 1600 and 1500 cm^{-1} for EB-g-MWCNTs and neat EB in Figure 2(d,e). Compared with Figure 2(b) of c-MWCNTs and Figure 2(e) of neat EB, the IR-spectra of a-MWCNTs [Fig. 2(c)] and EB-g-MWCNTs [Fig. 2(d)] also demonstrate insignificant bands of 1685 cm^{-1} of unpolymerized amide and of 1660 cm^{-1} due to the presence of the dihexylcyclourea, which is the by-product of DCC. To improve the solubility and conductivity of EB-g-MWCNTs, it was redoped with DBSA, which can behave as both dopant and dispersing agent in organic solvent, the obtained MWCNTs are designated as ES-g-MWCNTs and the
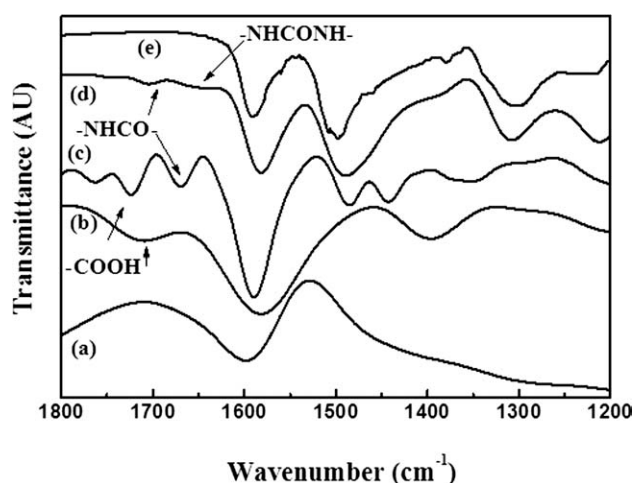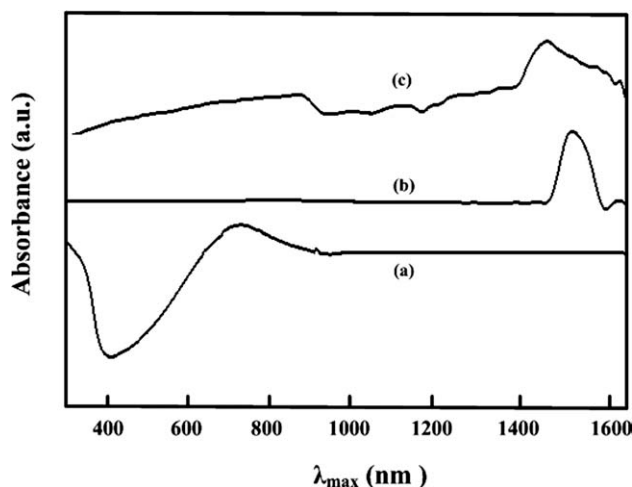

Figure 2 IR-spectra of (a) neat MWCNTs, (b) c-MWCNTs, (c) a-MWCNTs, (d) EB-g-MWCNTs, and (e) neat EB.
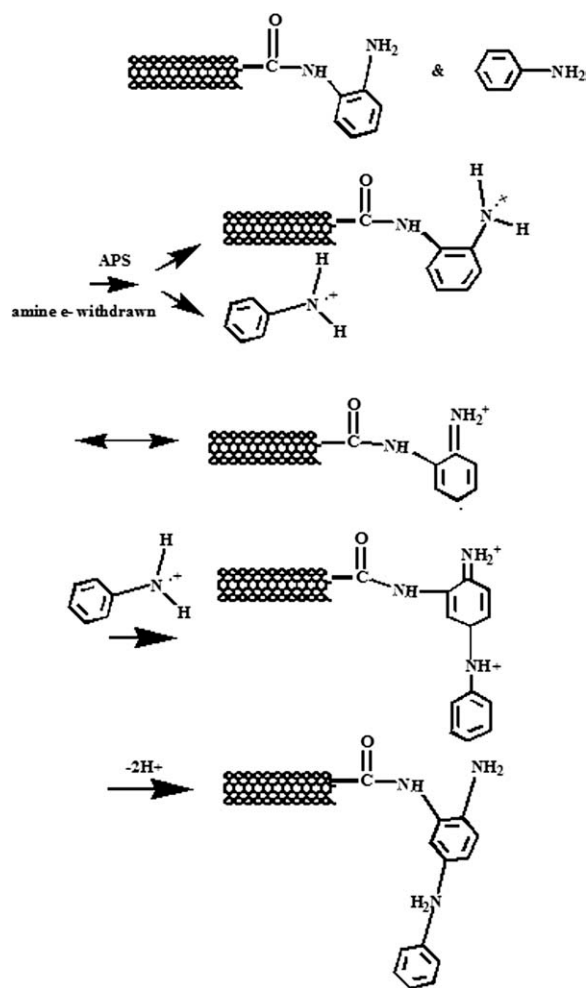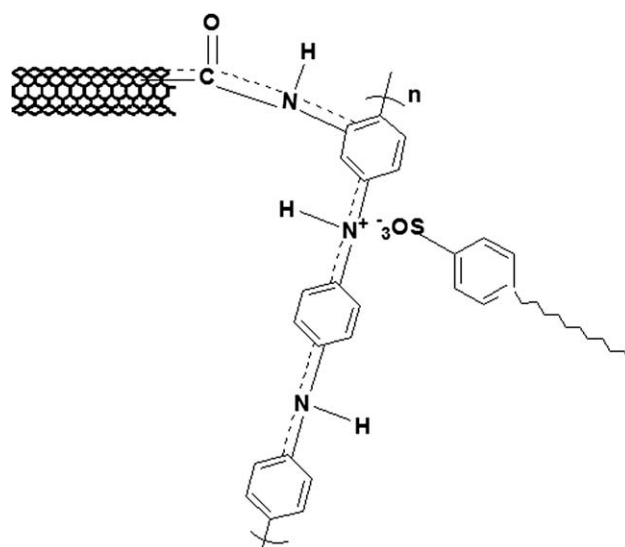
Scheme 2 Polymerization of aniline monomer on a-MWCNT.

good dispersibility in toluene was found to allow us to carry out other characterizations starting with the toluene solution.

Figure 3 UV–vis-NIR spectra of (a) neat ES, (b) c-MWCNTs, and (c) ES-g-MWCNTs.

Scheme 3 Interconjugation between MWCNT and grafted polyaniline.

UV-vis-NIR spectroscopy and conductivity

In Figure 3(a), no absorption peak at the NIR region (1000–1700 nm) can be seen for DBSA doped PANI in toluene. The λ_{max} at around 800 nm in Figure 3(a) is designated as the polaron–bipolaron transition of protonic acid doped PANI, indicating a limited conjugation of PANI itself. The c-MWCNT dispersed in water demonstrated a λ_{max} at around 1580 nm in Figure 3(b), resulting from the presence of a super-conjugated, polyaromatic surface of MWCNT. For ES-g-MWCNTs, a tremendous red shift of λ_{max} from 800 to 1480 nm in Figure 3(c) was found for PANI, illustrating that conjugation could be extended from the MWCNT surface to the grafted PANI chains through the amide bridges. The broader band of it is due to not all carboxylic acid groups of the c-MWCNT were amidized or grafted with PANI, which retained some of the feature of c-MWCNT owns λ_{max} at around 1580 nm. The interconjugation from MWCNT to grafted PANI described in Scheme 3 is another evidence confirming that PANI was linked onto the MWCNT surface by covalent-bonding. From Table I, we understand that the interface conjugation can also improve the conductivity of MWCNTs to 2.46 S/cm from 0.051 S/cm of c-

TABLE I
Conductivity of Various MWCNTs

Sample name	σ (S/cm)
Neat MWCNTs	8.5
c-MWCNTs	5.1×10^{-2}
Neat EB	1×10^{-6}
EB-g-MWCNTs	9.39×10^{-6}
ES-g-MWCNTs	2.46
Neat ES (DBSA doped)	7.3×10^{-3}
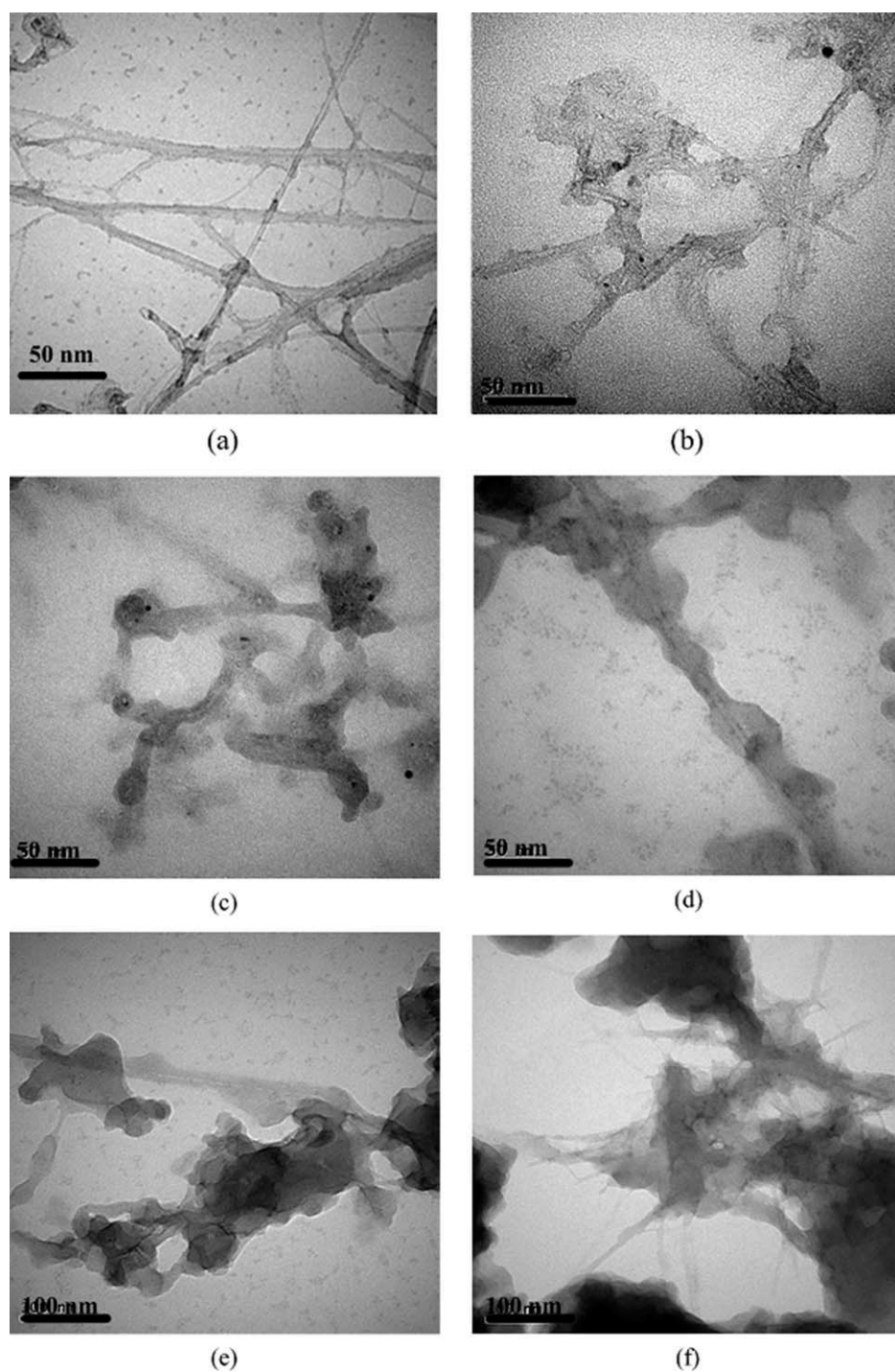
Figure 4 TEM pictures of (a) neat MWCNTs, (b) c-MWCNTs, (c) a-MWCNTs, (d) ES-*g*-MWCNTs, (e) EB-*g*-MWCNTs, and (f) ES-*g*-MWCNTs in smaller magnification.

MWCNTs whose conductivity were destroyed by carboxylation in mixed strong acids. When MWCNT was grafted with EB, its conductivity also drops sharply to 10^{-6} S/cm close to that of neat EB listed in Table I. It illustrated the MWCNTs were far away separated from each other by the entangled, long-chain EB phase. In other words, the conductivity of the separated MWCNTs can be reconnected if the entangled (seen in TEM micrograph), grafted EBs

can recover its conductivity by doping with DBSA. And the data listed in Table I proved the possibility that the conductivity of ES-*g*-MWCNTs is significantly increased to 2.46 S/cm, which is close to that of the neat MWCNT and three order higher than that of neat DBSA doped ES. Therefore, grafting MWCNT with conducting PANI can improve its solubility and compatibility in organic solvents and other polymer matrix without the sacrifice of
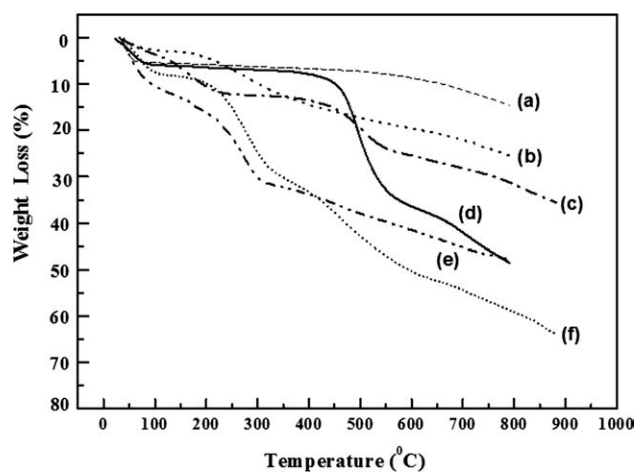
Figure 5 TGA thermograms of various types of MWCNTs and EB (a) neat MWCNT, (b)c-MWCNT, (c) EB-g-MWCNTs, (d) neat EB, (e) a-MWCNT, and (f) ES-g-MWCNT.

conductivity, which was usually found in other modifications on MWCNTs.

TEM micrographs

The TEM micrographs of neat MWCNTs, c-MWCNTs, and a-MWCNTs are illustrated in Figure 4(a–c) featured with increasing diameters after carboxylation and amidization due to surface mounting with ─COOH and ─CONH-φ-NH$_2$ groups. Figure 4(d) described the strain of ES-g-MWCNT with larger diameter after ES grafted to surface of MWCNT. Figure 4(e) is the TEM micrographs of EB-g-MWCNT, which demonstrates smaller size compared to Figure 4(f) of ES-g-MWCNT in smaller magnifications. Both of them illustrated that MWCNTs are encompassed by PANI matrix, which bind together the strains of MWCNT.

These grafted, entangled DBSA doped PANI (ES) not just maintained the high conductivity of the MWCNTs but avoid aggregation with each other, which would otherwise become intractable. The DBSA doped ES-g-MWCNT is thus dispersible in organic solvents like toluene and is ready to be mixed with polymer matrix in the same solvent to prepare a conducting MWCNT based nanocomposite.

TGA thermograms

The TGA thermograms of various MWCNTs and PANI are shown in Figure 5(a–f). Decarboxylation of ─COOH groups into ─H with the release of CO_2 at around 250°C[20] was found for c-MWCNTs in Figure 5(b), which demonstrated a similar degrading pattern to that of neat MWCNT in Figure 5(a) except the decarboxylation at 250°C. Similar behaviors were also found for a-MWCNT [Fig. 5(e)], indicating the presence of grafted carboxylic acid groups on MWCNT backbones even after amidization.

Regularly, the sharp weight loss of neat EB at 500°C in Figure 5(d) is due to the crosslinking and carbonization effects of the EB molecules, which were still found for thermogram of EB-g-MWCNTs in Figure 5(c). In Figure 5(a), there was about 6% of moisture water evaporated at 100°C and no significant weight loss until it was over 500°C. Insignificant weight loss was found to be 9% from 500 to 800°C due to the vaporization of impurities of neat MWCNTs. The EB-g-MWCNTs in Figure 5(c) demonstrated a 5% weight loss of moisture at 100°C, 6% weight loss of decarboxylation, 11% more loss from both thermal crosslinking and carbonization of grafted EBs[21–26], and final weight loss resulting from the vaporization of impurities of MWCNT from 550 to 900°C. Compared the weight loss of crosslinking and carbonization of EB-g-MWCNT to that of neat
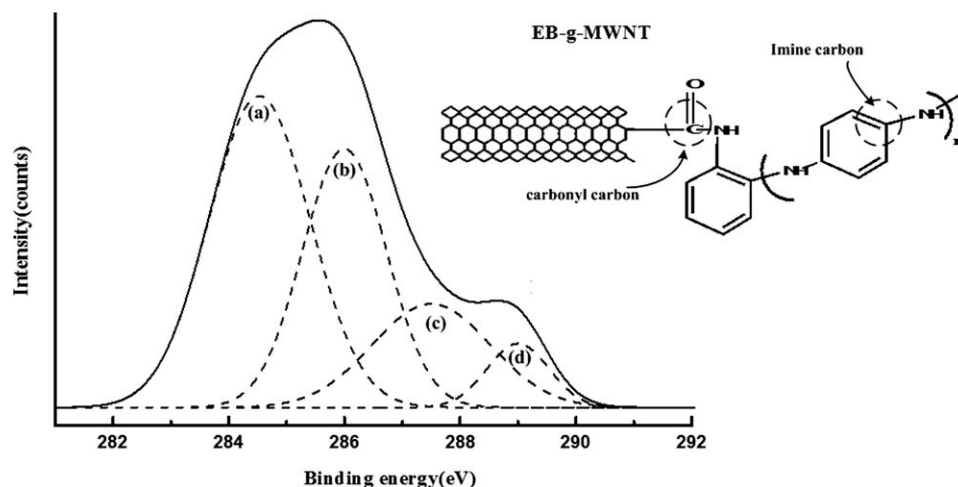
Figure 6 C$_{1s}$ ESCA spectrum of EB-g-MWCNTs. Deconvoluted peaks of various carbons (a) aromatic carbons of neat MWCNT, (b) imine carbon of ─C─NH─, (c) carbonyl carbons of amide, and (d) carboxylic carbon.

TABLE II
Various Carbons of EB-*g*-MWCNTs from ESCA

EB-*g*-MWCNTs	C=C	—C=C—NH—	O=C—OH	O=C—NH—
Binding E. (eV)	284.5	286.7	287.5	289
Absorption (%)	45.28 (a)	31.34 (b)	17.63 (c)	5.75 (d)

EB (30%) in Figure 5(d), these types of high temperature degradation, usually occurred to the EB, is not significant when it was grafted to the MWCNT backbones.

The thermogram of ES-*g*-MWCNT demonstrated the regular evaporation of moisture around 100°C and the desulfonation (debonding) of DBSA from PANI backbone at about 250°C[21,25,26] in Figure 5(f). After the desulfonation, the degradation behavior is similar to that of EB-*g*-MWCNT.

ESCA spectra

Since the binding energy graphite carbon (C=C) will increase with the substitution of polar groups like amine or hydroxyl groups, we can estimate the degree or percentage of carboxylation, amidization of the MWCNT by checking their C1s ESCA spectra. According to Figure 6 and Table II, we understand graphite carbons own the lowest binding energy of 284.5 eV and amine substituted C=C has increased the binding energy to 286.7 eV. After amidization, which converts the amine substituted, C=C to amide group by putting carbonyl group in it increased its binding energy slightly further to 287.5 eV. The highest binding energy of 289 eV listed in Table II goes to carboxylic acid group that owns both carbonyl and hydroxyl groups. The C_{1s} ESCA spectrum of EB-*g*-MWCNTs in Figure 6 was then deconvoluted into several peaks, assigning C=C of neat MWCNT, C-NH of the EB-*g*-MWCNT, O=C—NH of the a-MWCNT, and —COOH of c-MWCNT, respectively, and the percentages are listed Table II. The percentage of each carbon was calculated from integration of each deconvoluted area in Figure 6, which allowed us to estimate the percentage of C—NH groups of EB-*g*-MWCNT to be 31.34%, which can be used as the degree of PANI grafting on MWCNT. After redoping EB-*g*-MWCNT with DBSA in toluene to obtain ES-*g*-MWCNT, the percentages of ES in ES-*g*-MWCNT is calculated from the N1s ESCA spectra in Figure 7 and it should be much higher with additional complexed DBSA when comparing the upper and lower N1s ESCA spectra. Table II also shows that 5.75% of —COOH [very close to the 6% found in TGA thermogram in Fig. 5(c)] is neither consumed by amidization with ODA nor destroyed during *in situ* polymerization and the whole percentage of carboxylation of MWCNT after treating with acid

mixtures is equal to the summation of amidization and the left carboxylic acid, which is estimated to be 23.38%.

The doping levels before (EB-*g*-MWCNT) and after doping (ES-*g*-MWCNT) were checked by N1s ESCA spectra in Figure 7. The presence of the unreacted —COOH groups contributed to some doping effect and induced the formation of some complexed nitrogen in 402 eV in the lower diagram of Figure 7. In other words, there have been already some EBs doped by carboxylic acid before doping with DBSA and the doping level was around 6.9%. However, the carboxylic doping can be replaced by stronger DBSA one when EB was redoped by DBSA according to the upper ESCA spectrum of ES-*g*-MWCNT in Figure 7, which demonstrates a complexed N in 401 eV in different binding energy from
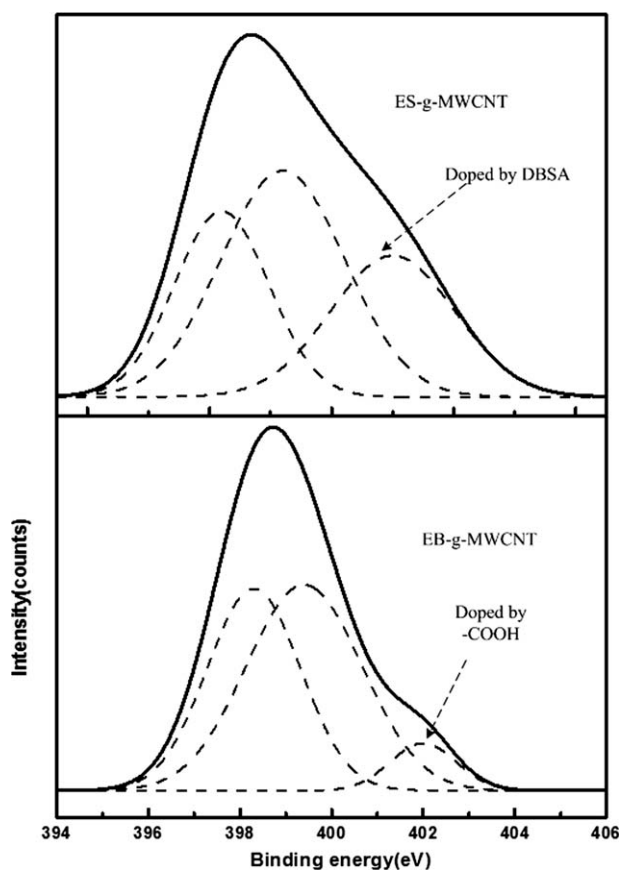

Figure 7 N_{1s} ESCA spectra of EB-*g*-MWCNTs and ES-*g*-MWCNTs with Quinoid at 398.3, Benzenoid at 399.4, and doped ammonium ion around 401–402 eV, depending on the types of protonic acids.

that of 402 eV. The doping level was found to be around 27.78% according to upper Figure 7. There are several possibilities that the doping level of ES-*g*-MWCNT is much less than fully doped level (50%). One originated from the less mobile property of the one-end tethered EB molecules that cannot be redoped easily by diluted DBSA in toluene. In addition, the insoluble nature of EB-*g*-MWCNT in toluene can effectively deterred them from getting close to toluene soluble DBSA to induce doping (acid-base neutralization). Another one may be due to the surface oxidation, which can cause the smaller level of doping as well.

CONCLUSIONS

The neat MWCNTs can be covalent-bonded with conducting PANI through *in situ* polymerization with aniline monomers after surface modification with *o*-phenylenediamine. The surface of MWCNT was first carboxylated in strong acids followed by condensating with the *o*-phenylenediamine in the presence of dicylclohexyldicarbodiimide and the left, unreacted amine can polymerize into grafted PANI. It can prevent the MWCNTs from crosslinking with each other when was grafted to MWCNT with surface acyl-chloride groups.

Besides, an interconjugation was found between the covalent-bonded PANI and MWCNT surface, leading to the strong red-shift to near-IR region for grafted PANI. The interconjugation not just retained the high conductivity of MWCNT after carboxylation but also increased its processability at high temperature with matrix polymers and dispersibility in organic solvents. For the grafted PANI, its heat resistance was greatly improved and can be processed with other matrix polymers at higher processing temperature without inducing significant degradation and losing much conductivity.

In the future, the PANI covalent-bonded MWCNT will be solvent- or melt-mixed with common polymer matrix to prepare a CNT based nanocomposite to improve its conductivity and performance.

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