

The effects of surface modifications of multi-walled carbon nanotubes on their dispersibility in different solvents and poly ether ether ketone

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Abstract

The effects of surface modifications of multi-walled carbon nanotubes (MWCNTs) on their dispersibility in different solvents and poly (ether ether ketone) (PEEK) have been studied. MWCNTs were treated by mixed acids to obtain acid-functionalized MWCNTs. The acid-functionalized MWCNTs were modified with six different chemical agents separately, 1,6-diaminohexane, hexadecyl trimethyl ammonium bromide, silane coupling agent 3-aminopropyltriethoxysilane, anhydrous sulfanilic acid and ethanolamine. MWCNT/PEEK composite films were fabricated in order to explore systematically the dispersibility of differently modified MWCNTs in PEEK as well as in different solvents. The morphology and structures of MWCNTs and the compatibility between MWCNTs and PEEK have been investigated. It was observed that the MWCNTs modified with anhydrous sulfanilic acid have an excellent dispersion in the PEEK grafted by sulfonic acid groups and that the MWCNTs modified with ethanolamine are also dispersed well in pure PEEK. The results herein provide useful insights into the development of MWCNT/PEEK composites for a wide variety of applications.

Keywords: Surface chemistry; polymer; composite.

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1. Introduction

Carbon nanotubes (CNTs) continue to attract a great deal of interest in polymer reinforcement owing to their outstanding mechanical, electrical and thermal properties, nanoscale dimensions, low mass density, excellent physical characteristics and high aspect ratio [1-4]. A good dispersion of CNTs in a polymer matrix is the key to improve the properties of CNT/polymer composites. However, the preparation process of CNT/polymer composites is hindered by the poor solubility of CNTs and their strong tendency to aggregate and form bundles. Several methods for the preparation of CNT/polymer composites, such as solution mixing [5], melt blending [6] and in situ polymerization [7], have been proposed. Some other strategies for distribution of CNTs through matrices have also been reported to improve the interactions between CNTs and polymers. The mechanism of these strategies includes attaching either functional groups or polymer derivatives onto CNTs' surfaces [8, 9], and dispersing CNTs in compatibilizing agents [10]. A common functionalization approach is to use an oxidation process in which CNTs are oxidized with strong acids [11], such as nitric, sulfuric acid or a mixture of both acids, in order to generate oxygen-containing surface groups (mainly hydroxyl, carbonyl and carboxyl) that can react with functional groups or polymer derivatives subsequently.

Poly (ether ether ketone) (PEEK) is a semicrystalline thermoplastic polymer and a kind of high performance engineering material, which has been chosen as the polymer matrix for high performance composites owing to its excellent thermal stability, chemical resistance and mechanical properties [12]. PEEK has been employed in a wide range of commercial and industrial applications, such as medicine, electronics and transport industries (automobile and aerospace) [13]. Many studies on the functionalization of CNTs and the synthesis of CNT/PEEK composites have been carried out over the last decade. Deng et al. studied the nanocomposites of MWCNT and PEEK [14], Song et al. worked with sandwich-like single-walled carbon nanotube (SWCNT) paper/PEEK composites [15], and Diez-Pascual et al. prepared SWCNT/PEEK composites incorporating polysulfones-I [4], polysulfones-II [16] and polyetherimide (PEI) [10] as compatibilizers, separately. Some progresses in surface modifications of CNTs and CNT/PEEK composites have also been made. However, few detailed reports on the influence of modification methods on the dispersibility of MWCNTs in different solvents and the compatibility between MWCNTs and PEEK in composite films can be found. Furthermore, little information is available in an investigation of the composite properties with a higher percentage (more than 10 wt%) of CNTs [17, 18].

This article aimed to fill the knowledge gap and investigated the effects of different surface modifications of MWCNTs on their dispersibility in different solvents and PEEK systematically. The specimens at an identical MWCNT concentration of 20 wt% were prepared by solution blending in an organic solvent. A comprehensive characterization was carried out to study the morphology and structures of MWCNTs/PEEK composite films and to explore a potential improvement in dispersion of differently modified MWCNTs in PEEK matrix.

2. Experimental approaches

2.1 Materials

Parent MWCNTs (p-MWCNTs), obtained from Chengdu Institute of Organic Chemistry, China, have an outer diameter of 30-50 nm, an inner diameter of 5-12 nm, length of 10-20 μ m and purity of greater than 95%. PEEK (450G) was provided by Jilin Zhongyan High Performance Engineering Plastic Co., Ltd with physical properties of $d_{25^{\circ}\text{C}}=1.26\text{ g/cm}^3$, $T_g\sim 143\text{ }^{\circ}\text{C}$ and $T_m\sim 343\text{ }^{\circ}\text{C}$. Sulfuric acid (H_2SO_4) of 98% purity and nitric acid (HNO_3) of 65% purity were purchased from Taiyuan Chemical Reagent Factory, China. 1,6-Diaminohexane of 99% purity was supplied by Chengdu Kelong Chemical Reagent Factory, China. Hexadecyl trimethyl ammonium bromide (HTAB) of 99% purity was provided by Tianjin Damao Chemical Reagent Factory, China. Silane coupling agent 3-aminopropyltriethoxysilane (KH550; 97% purity) was obtained from Tianjin Dongliqi Tianda Chemical Reagent Factory, China. Anhydrous sulfanilic acid of 99.8% purity was purchased from Tianjin Fuchen Chemical Reagent Factory, China. N,N-Dicyclohexylcarbodiimide (DCC) of 99.5% purity was supplied from Aladdin Chemistry Co., Ltd. Ethanolamine of 99% purity was purchased from Tianjin Fuyu Chemical Co., Ltd, China. N,N-Dimethylformamide (DMF) of 99.5% purity was provided by Tianjin Bodi Chemical Co., Ltd, China.

2.2 Surface Modifications of MWCNTs

An acidic treatment on MWCNTs in strong acids was employed to explore the possibility of opening the tubes and enhancing of their reactivities. The purpose was to introduce oxygen-containing groups onto the surfaces of MWCNTs for a further reaction with some specific functional groups or polymer derivatives, which can eventually improve the dispersion of MWCNTs in PEEK matrix. The following six approaches in surface modifications of MWCNTs were carried out to study their effects on dispersibility.

2.2.1 Synthesis of acid-functionalized MWCNTs

A suspension of 3.0 g of p-MWCNTs in 240 ml of H₂SO₄/HNO₃ (3:1 v/v) was sonicated at 50 °C for 2 hours. The mixture was diluted in deionized water and kept for 12 hours. The supernatant was removed and the sediment was rinsed with water until neutral. The resulting solid was dried in a vacuum oven at 80 °C for 24 hours, and then labelled as a-MWCNTs, as shown in Fig. 1(a).

2.2.2 Grafting of 1,6-Diaminohexane to MWCNTs

A mixture of solution was prepared by filling 1.0 g of a-MWCNTs, 26.0 g of 1,6-Diaminohexane and 1.0 g of DCC into a 250-ml three-necked round bottom flask. The mixture was stirred in oil-bath at 90 °C for 36 hours. Then, the product was washed with anhydrous ethanol for several times. Finally, the powder was dried in vacuum oven at 80 °C for 24 hours and marked as d-MWCNTs, as shown in Fig. 1(b).

2.2.3 Synthesis of MWCNTs modified by HTAB

Both a-MWCNTs (0.5 g) and HTAB (0.14 g) were added into 100 ml of deionized water and kept under stirring at 30 °C for 35 minutes, then the solution was sonicated at 50 °C for 30 minutes. The reaction product was washed by anhydrous ethanol and dried under vacuum at 80 °C for 24 hours, and was named h-MWCNTs, as shown in Fig. 1(c).

2.2.4 Preparation of MWCNTs modified by KH550

Firstly, 0.3 g of a-MWCNTs, 1 ml of KH550, 25 ml of deionized water and 75 ml of anhydrous ethanol were mixed in a 250-ml three-necked round bottom flask and stirred in water-bath at 60 °C for 6 hours. Secondly, the resulting solid was washed by anhydrous ethanol, dried in vacuum oven at 80 °C until its weight remained unchanged, and marked as k-MWCNTs, as shown in Fig. 1(d).

2.2.5 Grafting of anhydrous sulfanilic acid to MWCNTs

This grafting process was carried out in the following four steps. Firstly, 0.3 g of a-MWCNTs, 0.1 g of DCC and 75ml of anhydrous ethanol were added into a three-necked round bottom flask and sonicated at 50 °C for 20 minutes. Then, 0.3 g of anhydrous sulfanilic acid in 75ml of deionized water was added into the flask. Thirdly, the mixture was stirred in water-bath at 50 °C for 10 hours. Finally, the obtained product, named s-MWCNTs, as shown in Fig. 1(e), was washed with anhydrous ethanol and water separately and dried under vacuum at 80 °C for 24 hours.

2.2.6 Grafting of ethanolamine to MWCNTs

In this grafting process, 0.3 g of a-MWCNTs and 0.1 g of DCC were added in 75ml of anhydrous ethanol and sonicated in an ultrasound bath at 50 °C for 20 minutes. Subsequently, a solution of 0.3 ml of ethanolamine in 75 ml of anhydrous ethanol was added into a flask where the solution and a-MWCNTs suspension were mixed and the reaction was allowed to proceed under magnetic stirring at 50 °C for 10 hours. Finally, the reaction mixture was washed with anhydrous ethanol and water

separately and dried under vacuum at 80 °C for 24 hours to obtain the product marked as e-MWCNTs, as shown in Fig. 1(f).

2.3 Preparation of MWCNT/PEEK composite films

It has been well known that the compatibility between MWCNTs and PEEK plays a key role in the properties of the MWCNT/PEEK composites. Therefore, the dispersion of p-MWCNTs and the six types of modified MWCNTs in PEEK was investigated. Because sulfonic acid groups were grafted on the surfaces of MWCNTs in the preparation process of s-MWCNTs, sulfonated PEEK (SPEEK), as shown in Fig. 1(g), was also prepared by grafting sulfonic acid groups onto PEEK using H₂SO₄ in order to improve the compatibility between s-MWCNTs and PEEK.

2.3.1 Preparation of MWCNT/ PEEK composite films

In the preparation process of composite films in DMF, p-MWCNTs or each of the six types of modified MWCNTs (a-MWCNTs, d-MWCNTs, h-MWCNTs, k-MWCNTs, s-MWCNTs and e-MWCNTs) were mixed with PEEK separately. Each kind of 0.1g MWCNTs was submerged in 10 ml of DMF and sonicated in an ultrasound bath for 30 minutes. The pure PEEK (0.4 g) was dissolved in 10 ml of DMF and kept under stirring for 30 minutes. Subsequently, the polymer solution and MWCNT suspension were mixed and sonicated for 1 hour. The composite films were formed on a glass slide and dried under vacuum at 60 °C for 48 hours.

2.3.2 Preparation of s-MWCNT/ SPEEK composite films

The preparation process of s-MWCNT/SPEEK composite films was the same as that of MWCNT/PEEK composite films. Prior to the preparation, PEEK powder was dried in an oven at 120 °C for 12 hours to remove any absorbed moisture. Then, 2.5 g of PEEK and 100 ml of H₂SO₄ were added into a three-necked round bottom flask and agitated with a magnetic stirrer at 30 °C for 16 hours. The solution was dispersed in 500 ml of ice water, remained under magnetic stirring for 1 hour and kept for 24 hours. The product was washed with deionized water until neutral and dried in the vacuum oven at 80 °C for 24 hours.

The schematic views of the experiments are shown in Fig. 1 and the abbreviated product names obtained in the process of experiments are listed in Table 1.

2.4 Materials characterization

2.4.1 Scanning electron microscopy

The morphology of p-MWCNTs, all modified MWCNTs obtained from six different methods shown in Table 1 and the composite films was observed with a

JSM-6700F scanning electron microscope (SEM, acceleration voltage: 0.5~3.0 kV, beam intensity: $10^{-13}\sim 2\times 10^{-9}$ A, operated at 10 kV). The samples were coated with gold (Au) in an evaporator to avoid charging during electron irradiation.

2.4.2 Dispersion of MWCNTs in different solvents

The dispersion of p-MWCNTs and differently modified MWCNTs in deionized water, ethanol and DMF was studied with a Nikon D700 optical camera. The photographs were taken twice, first, immediately after ultrasonic treatment maintained for 30 minutes, and second, after sitting for 48 hours.

2.4.3 Fourier transform infrared (FT-IR) spectroscopy

The surface functional groups of p-MWCNTs and modified MWCNTs were characterized using a TENSOR 27 FT-IR spectrometer. Spectra were recorded at a spectral resolution of 1.5 cm^{-1} , and two scans were collected for each sample in the range of $4000\text{-}600\text{ cm}^{-1}$.

2.4.4 Raman spectroscopy

The Raman spectra of MWCNTs were carried out using an InVia Laser Micro-Raman spectrometer (British Renishaw Company), with a spectral region of 200 nm-1000 nm and a spectral resolution of 1 cm^{-1} . At least two different spectra for each sample were recorded in the range of $1000\text{-}2000\text{ cm}^{-1}$.

3. Results and discussion

3.1 Morphology of unmodified and modified MWCNTs

The morphology of parent and modified MWCNTs was analyzed by SEM. Fig. 2 presents typical SEM micrographs of p-MWCNTs and all MWCNTs modified with six different methods. As shown in Fig. 2(a), p-MWCNTs were accumulated loosely with entangled feature and large tube gaps while each nanotube had a uniform pipe diameter. From Fig. 2(b), it can be seen that after the acid treatment, a-MWCNTs became shorter and denser. It is suggested that carboxyl groups were grafted on the surfaces of tubes [19]. Figs. 2(c)-(g) show that the sole-dispersibility of modified MWCNTs was obviously improved to different extent with different treatments, compared with that of a-MWCNTs. In the case of d-MWCNTs as shown in Fig. 2(c), the mechanism that the grafting of 1,6-diaminohexane to MWCNTs improves the sole-dispersibility of MWCNTs is probably because 1,6-diaminohexane increases the gaps among nanotubes because the stereo-hindrance effect in 1,6-diaminohexane can weaken the hydrogen bonds on MWCNTs which are created in the process of acid treatment [20]. In the case of h-MWCNTs as shown in Fig. 2(d), HTAB formed an effective electrostatic layer on the surfaces of nanotubes. The electrostatic repulsion, steric hindrance and Van der Waals force between the nanotubes were balanced [21],

as a result, h-MWCNTs were found well dispersed. Fig. 2(e) shows that k-MWCNTs had better sole-dispersibility than a-MWCNTs as shown in Fig. 2(b). The possible reasons could be given. The ethoxyl groups of KH550 were subjected to hydrolysis into hydroxyl groups, which further partly reacted with the hydroxyl groups on the surfaces of MWCNTs to form Si-O-C bonds, and partly undergone intermolecular dehydration to form Si-O-Si bonds. A flexible organic layer was introduced on the surfaces of MWCNTs by combining Si-O-C bonds with Si-O-Si bonds. Thus, a large stereo-hindrance effect between the nanotubes was induced to prevent the aggregation of MWCNTs [22]. As shown in Fig. 2(f), the surfaces of s-MWCNTs were rougher and the structures of nanotubes became wormlike, which indicates that the sulfonic acid groups were grafted on the surfaces of MWCNTs. In Fig. 2(g), e-MWCNTs showed no entanglement or agglomeration owing to grafting of amino groups on the surfaces of MWCNTs [20]. In general, it can be seen in Fig. 2 that after different treatments for surface modifications, the sole-dispersibility of k-MWCNTs, s-MWCNTs and e-MWCNTs is superior to that of a-MWCNTs, d-MWCNTs and h-MWCNTs.

3.2 Dispersion of MWCNTs in different solvents

Photographs of MWCNTs' dispersion in different solvents (water, ethanol and DMF) are shown in Fig. 3. It can be seen that the modified MWCNTs had the nearly identical dispersibility in water at once after the ultrasonic processing. After 48 hours, three different scenarios were observed. Firstly, p-MWCNTs deposited obviously in water at the bottom of sample bottle (e) owing to the Van der Waals force among nanotubes. Secondly, the dispersion of MWCNTs in bottles (c) and (d) changed slightly. Finally, the dispersibility of a-MWCNTs and s-MWCNTs had no change. When the used solvent was ethanol, the colour of solution in sample bottle (e) was lighter than that in the other bottles after an ultrasonic process. After 48 hours, the upper solution in bottles (c) and (e) became clearer than before and the MWCNTs deposited at the bottoms of two bottles while the color of solution in the other bottles barely changed. The dispersibility of seven samples in DMF was almost identical when the ultrasonic treatment was just finished. After the samples had been kept for 48 hours, the dispersibility of d-MWCNTs and k-MWCNTs changed considerably while the others changed little. The unexpected dispersibility of p-MWCNTs in ethanol and DMF could be due to the chemical groups grafted on the surfaces of nanotubes in the preparation process of p-MWCNTs. The poor dispersion of d-MWCNTs and k-MWCNTs in all three solvents indicates that grafting amino groups (-NH₂) to MWCNTs has little effect on the MWCNTs' dispersion no matter in water, ethanol or in DMF. The h-MWCNTs had a better dispersion in all three

solvents (water, ethanol and DMF). This is because of the electrostatic layer on the surfaces of nanotubes formed by HTAB, which may produce electrostatic repulsion to counteract gravity force of nanotubes and Van der Waals force between them [21, 25]. It is evident that both a-MWCNTs and s-MWCNTs had a super dispersion in all three solvents because of the organic functional groups which were grafted to MWCNTs in the modification process, such as carboxyl groups (-COOH) [23] and sulfonic groups (-SO₃H). The e-MWCNTs' dispersion in water showed little change after 48 hours. This is probably due to the hydroxy or carboxyl groups of MWCNTs. It is suggested that the ether linkages formed by the hydroxyl groups on the surfaces of nanotubes [25] lead to the excellent dispersibility of e-MWCNTs in ethanol and DMF.

3.3 The chemical structures of unmodified and modified MWCNTs

An identification of the chemical groups on the MWCNT surfaces was conducted through FT-IR spectroscopy. The spectra of p-, a-, h-, s- and e-MWCNTs are compared in Fig. 4. It can be seen that p-MWCNTs show little relevant features except the band around 3430 cm⁻¹ and 1560 cm⁻¹. It is suggested that the band around 3430 cm⁻¹ is the O-H stretching caused by the preparation process of p-MWCNTs, and the band at 1560 cm⁻¹ is assigned to the C=C stretching of the main structures of the MWCNTs [26]. As shown in Fig. 4, a-MWCNTs present a broad absorption at 3430 cm⁻¹ attributed to the O-H stretching of the carboxylic groups while the band around 1640 cm⁻¹ corresponds to the C=O stretching vibration [9]. The bands at around 2920 cm⁻¹ and 2850 cm⁻¹ are ascribed to C-H stretching vibrations, and the C-H bending of methylene groups occurs at around 1410 cm⁻¹. The spectra of h-MWCNTs are similar to those of a-MWCNTs. This indicates that their chemical structures are similar. The absorption around 1630 cm⁻¹ is related to the vibration of the N-H in-plane deformation in primary amine groups, suggesting that the sulfonic acid groups of anhydrous sulfanilic acid has been grafted on the surfaces of MWCNTs. Regarding the spectra of e-MWCNTs, the new band around 3380 cm⁻¹ can be observed, assigned to asymmetrical N-H stretching vibrations. It is suggested that ethanolamine has been grafted on the surfaces of MWCNTs.

Raman spectra of the p-MWCNTs and modified MWCNTs were investigated to analyze possible changes in the bands due to the CNT disaggregation. Two features can be seen in Fig. 5: the D-band induced by dispersive disorder around 1350 cm⁻¹ and the tangential modes or G-band near 1580 cm⁻¹ [27-29]. The Raman spectra of MWCNTs in Fig. 5 also show that the MWCNTs after treatments resulted in modifications in the D/G intensity ratio (I_D/I_G). The I_D/I_G value of p-MWCNTs was close to 0.72, and that of a-MWCNTs was 0.86. Such an increase of I_D/I_G indicates that considerable defects were produced on the surfaces of MWCNTs. As a result, it is

easier to graft chemical groups on the surfaces of MWCNTs to improve the compatibility between MWCNTs and PEEK matrix. After the further treatments, the I_D/I_G values of s- and e-MWCNTs were reduced to 0.83 and 0.74 respectively. These decreased I_D/I_G values of s- and e-MWCNTs suggest that the functional groups grafted on the surfaces of MWCNTs probably increase the sole-dispersibility of MWCNTs, which correlates well with the SEM observations of MWCNTs as shown Fig. 2.

3.4 The compatibility between MWCNTs and PEEK

SEM was employed to observe the surface morphology of composite films and qualitatively visualize the dispersion state of the carbon nanotubes in the PEEK matrix. It is well known that achieving a good distribution of the filler in polymer matrix is a rather difficult task because p-MWCNTs have a strong tendency to gather together and form bundles [4]. Fig. 6 shows typical micrographs of MWCNT/PEEK composite films with a concentration of 20 wt% MWCNTs. It can be seen that a small amount of p-MWCNTs were dispersed in PEEK while some agglomerated nanotubes were observed in the p-MWCNT/PEEK composite film as a result of the strong agglomerating tendency of the nanotubes. Fig. 6(b) shows that a-MWCNTs either floated on the surface of PEEK or existed independently in the cracks of PEEK owing to the agglomerating tendency of a-MWCNTs. Figs. 6(c) and (e) show that both d- and k-MWCNTs agglomerated distinctly in PEEK. Although grafting amino groups ($-NH_2$) to MWCNTs can enhance the adhesive force between MWCNTs and PEEK, the dispersibility of both d- and k-MWCNTs in DMF is still poor. This poor dispersibility led to reduce compatibility between MWCNTs and PEEK when MWCNT/PEEK composite films were fabricated using solution blending method with DMF as a solvent. It can be clearly seen in Fig. 6(d) that h-MWCNTs and PEEK were formed into micro spheres because HTAB could inhibit the growth of the product in one dimensional direction. These small particles assembled into a submicron spherical product spontaneously in order to reduce the surface free energy [30, 31]. Fig. 6(f) shows that in s-MWCNTs/PEEK composite films, s-MWCNTs agglomerated evidently and could not be dispersed well in PEEK while s-MWCNTs were uniformly dispersed in SPEEK as shown in Fig. 6(g). This indicates that grafting sulfonic acid groups ($-SO_3H$) on the surfaces of MWCNTs cannot improve the compatibility between MWCNTs and PEEK matrix. By contrast, after grafting $-SO_3H$ to PEEK, s-MWCNTs have a better dispersion in SPEEK owing to the hydrogen bonding interactions between the sulfonic acid groups on the surfaces of s-MWCNTs and SPEEK. It can be seen in Fig. 6(h) that the compatibility between e-MWCNTs and PEEK was as good as that between s-MWCNTs and SPEEK. It is suggested that

the ether bond formed by the reaction between the hydroxy groups on the surfaces of nanotubes [23] has a similar structure with the ether bond of PEEK. While the reaction between -NH_2 on the surfaces of e-MWCNTs and C=O of PEEK could produce an interaction between e-MWCNTs and PEEK, the two factors lead to a good dispersibility of the e-MWCNTs in pure PEEK.

4. Conclusions

The effects of surface modifications of MWCNTs on their dispersibility in different solvents and PEEK matrix have been investigated. Based on the above results and discussion, the following conclusions can be drawn:

- i) Morphological observations of both parent and modified MWCNTs reveal that the sole-dispersibility of k-MWCNTs, s-MWCNTs and e-MWCNTs are better than that of the others.
- ii) a-, s- and e-MWCNTs have an excellent dispersion feature no matter in water, ethanol or in DMF, attributed to the chemical groups grafted onto the surfaces of MWCNTs.
- iii) SEM observations of composite films reveal an excellent compatibility between s-MWCNTs and SPEEK and a super dispersion of e-MWCNTs in pure PEEK. In particular, compared with other MWCNT/PEEK composite systems, s-MWCNTs could be dispersed well in SPEEK and e-MWCNTs had an excellent dispersion in pure PEEK.

In a short, this study suggests that it is feasible to fabricate MWCNT/PEEK composites suitable for a wide range of property requirements in applications by appropriate surface modifications of MWCNTs.

Acknowledgement

The authors acknowledge financial support from Changjiang Scholar and Innovative Research Team in University (IRT0972), National Natural Science Foundation of China (21176169), Shanxi Provincial Key Innovative Research Team in Science and Technology (2012041011), International Science & Technology Cooperation Program of China (2012DFR50460) and Research Project Supported by Shanxi Scholarship Council of China (2012-038).

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Table 1 The information of reagents used in the process of experiments.

Reagent	Purity (%)	Manufacturer
1,6-diaminohexane	99	Chengdu Kelong Chemical Reagent Factory
Hexadecyl trimethyl ammonium Bromide (HTAB)	99	Tianjin Damao Chemical Reagent Factory
Silane coupling agent KH550	97	Tianjin Dongliqu Tianda Chemical Reagent Factory
Sulfanilic acid anhydrous	99.8	Tianjin Fuchen Chemical Reagent Factory
N-N-dicyclohexylcarbodiimide (DCC)	99.5	Aladdin Chemistry Co., Ltd
Ethanolamine	99	Tianjin Fuyu Chemical Co., Ltd
N,N-dimethylformamide (DMF)	99.5	Tianjin Bodi Chemical Co., Ltd

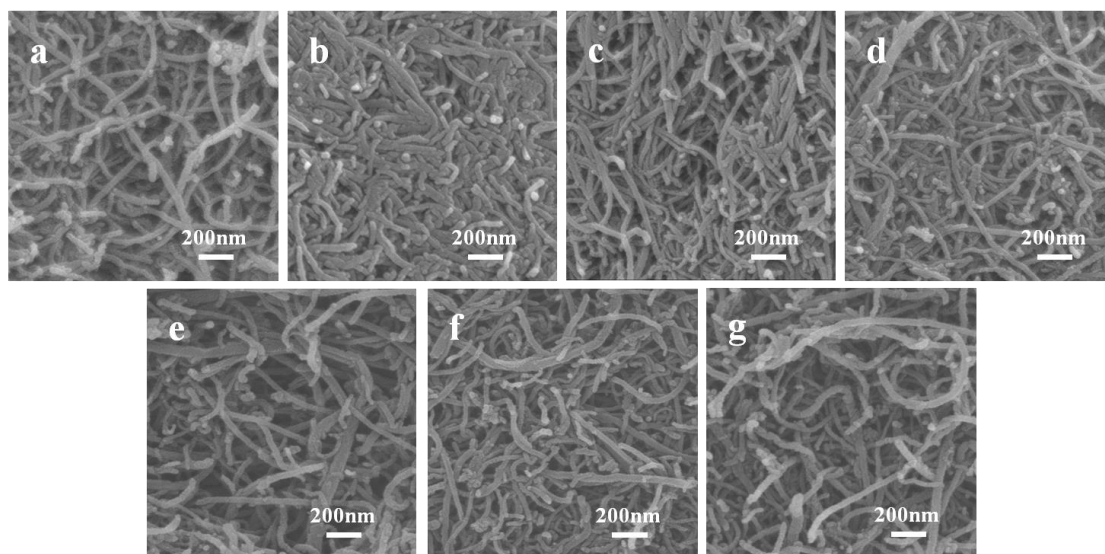


Figure 1 SEM micrographs of MWCNTs: (a) p-MWCNT_s, (b) a-MWCNT_s, (c) d-MWCNT_s, (d) h-MWCNT_s, (e) k-MWCNT_s, (f) s-MWCNT_s, (g) e-MWCNT_s.

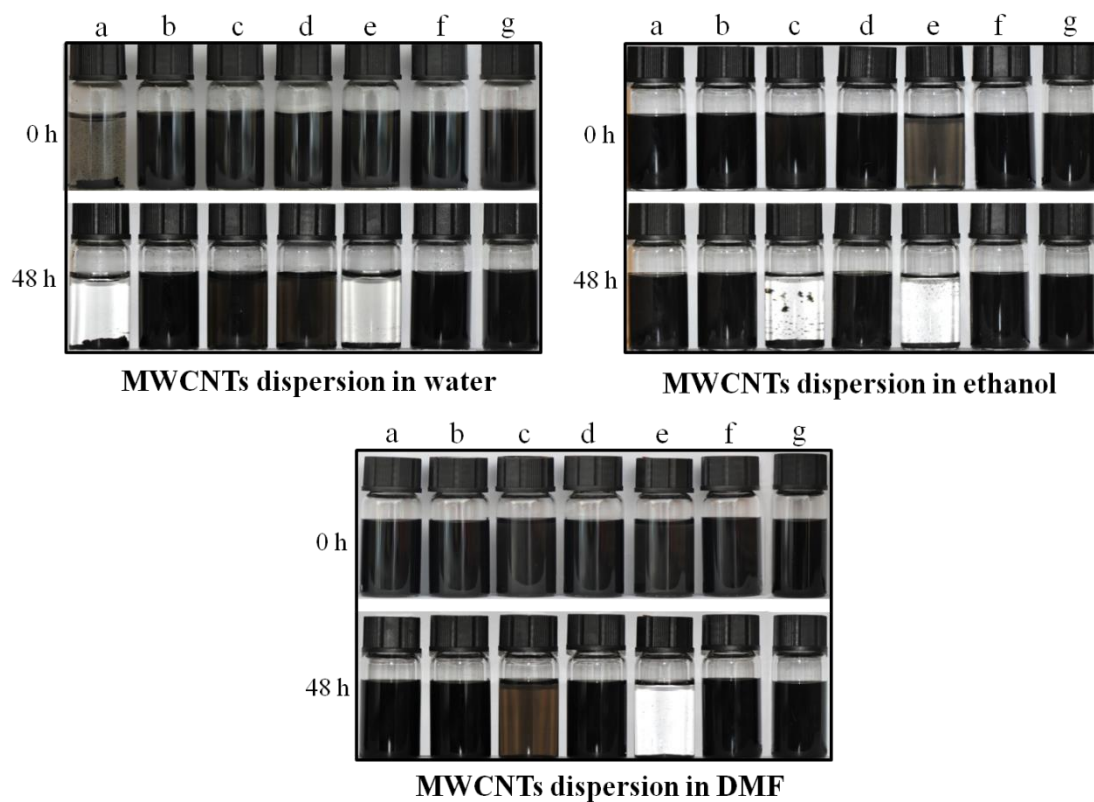


Figure 2 Photographs of MWCNTs dispersion in different solvents: (a) p-MWCNTs, (b) a-MWCNTs, (c) d-MWCNTs, (d) h-MWCNTs, (e) k-MWCNTs, (f) s-MWCNTs, (g) e-MWCNTs.

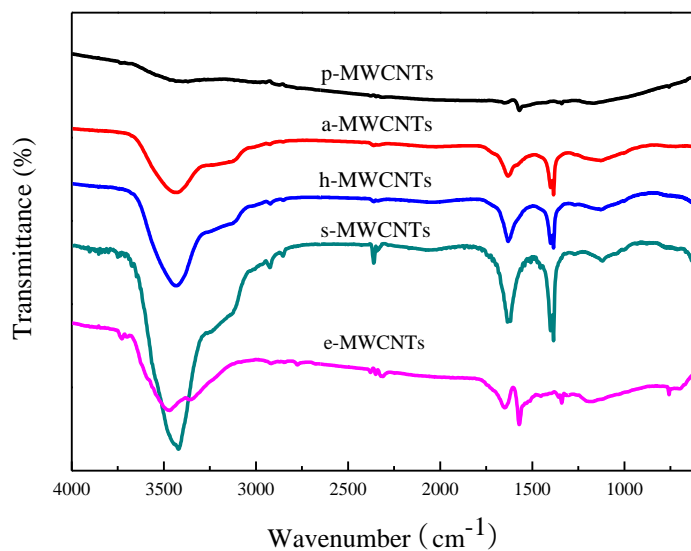


Figure 3 FT-IR spectra of p-MWCNTs, a-MWCNTs, h-MWCNTs, s-MWCNTs and e-MWCNTs.

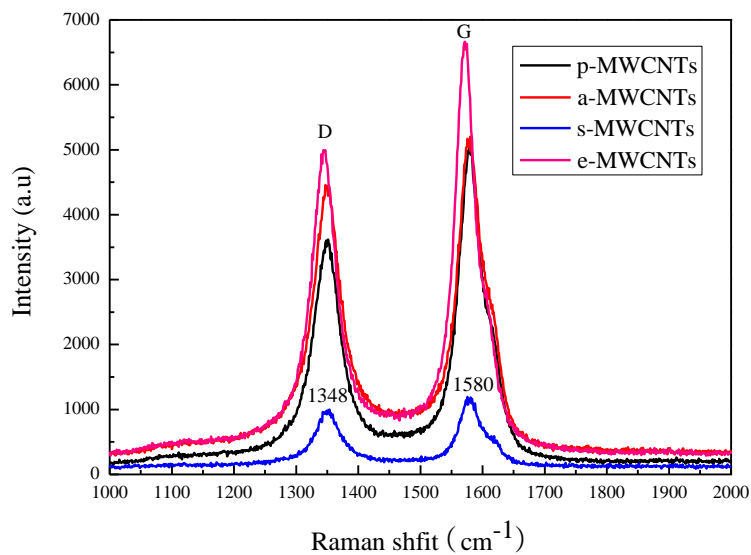


Figure 4 Raman spectra of p-MWCNTs, a-MWCNTs, s-MWCNTs and e-MWCNTs.

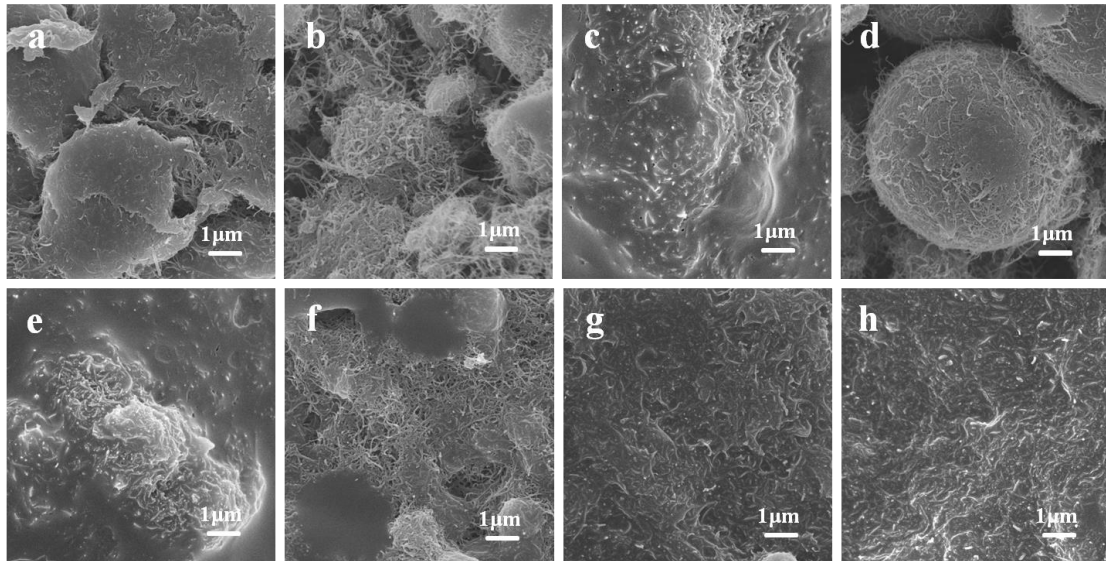


Figure. 5 SEM micrographs of MWCNTs/PEEK composite films: (a) p-MWCNTs/PEEK, (b) a-MWCNTs/PEEK, (c) d-MWCNTs/PEEK, (d) h-MWCNTs/PEEK, (e) k-MWCNTs/PEEK, (f) s-MWCNTs/PEEK, (g) s-MWCNTs/SPEEK, (h) e-MWCNTs/PEEK.