

# Effect of Surfactant Functionalization of Multi-walled Carbon Nanotubes on Mechanical, Electrical and Thermal Properties of Epoxy Nanocomposites

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**Abstract:** The present paper compares the mechanical, electrical and thermal properties of epoxy nanocomposites (prepared by solution blending method) by adding four different multi-walled carbon nanotubes (MWCNTs), which are pristine, cationic, anionic and non-ionic surfactant functionalized MWCNTs, respectively. This investigation focused on the effects of dispersion of MWCNTs on the physical properties. Systematical characterization on the dispersion of MWCNTs in different solvents were did via UV-Vis spectrophotometer. The Hansen solubility parameters (HSPs) and dispersion of MWCNTs in solvent and epoxy were both changed after surfactants introduced especially for the non-ionic surfactant. Finally, mechanical, fracture toughness, electrical and thermal properties of epoxy composites were found can be improved because of good dispersion of MWCNTs (especially non-ionic surfactant).

**Keywords:** Carbon nanotubes, Surfactants, Epoxy resin, Composites, Physical properties

## Introduction

Carbon nanotubes (CNTs) with ultra-high length to diameter ratio has been often regarded as the fillers to form nanocomposites with multifunctional characteristics in many fields because of its superior mechanical, electrical and thermal properties [1,2]. Epoxy has been widely applied to aerospace and painting industry owing to excellent adhesion, heat resistance and mechanical properties [3-7]. Researchers attempted to incorporate CNTs into epoxy, but the results are always unsatisfactory, because of the poor dispersion of CNTs in epoxy matrix [8-12].

Two significant strategies for enhancing the dispersion of CNTs are developed, such as covalent and noncovalent functionalization. Covalent functionalization [11,13-15] is often considered as an efficient method to disperse CNTs and introduce different functional groups on the surface of CNTs via chemical reaction. However, harsh chemical reaction results in the destruction of CNTs  $\pi$ -bonds, and thus declines the intrinsic electrical, thermal and mechanical properties of CNTs. Another method is noncovalent functionalization [16-18]. It adsorbs the dispersants on the CNTs surface via noncovalent interaction, like  $\pi$ - $\pi$  stacking and Van der Waals' force, without disrupting  $\pi$ -electron conjugated structure of CNTs. Many efforts have been devoted to noncovalently disperse CNTs using surfactants due to its amphiphilicity [19-22].

Based on experiments, some researchers concluded that the physical properties of CNTs/epoxy composites can be significantly improved by adding surfactants [10,23]. Surfactants are usually divided into three kinds: as cationic, anionic and non-ionic surfactant. Valeria La Saponara and his coworkers [24] used diamine and two surfactants (TritonX-100 (non-ionic) and cetyl pyridinium chloride

(CPC, cationic)) to disperse CNTs and investigate on the effects of a low-cost treatment of CNTs on the tensile fatigue and impact damage sensing of epoxy composites. They revealed that diamine/CPC-based epoxy composite is superior, due to improved mechanical performance, higher resistance to fatigue and impact damage and increased damage sensitivity. In addition, the work on using non-ionic TritonX-100 to improve the dispersion of CNTs and mechanical, fracture, electrical conductivity and thermo-mechanical of epoxy composites was conducted by Yan Geng *et al.* [10]. Shima Ghorabi and his colleagues [23] systematically compared the effect of three different surfactants (cationic hexadecyl-trimethyl-ammonium bromide, anionic sodium dodecyl sulfate and non-ionic TritonX-100) on mechanical properties of epoxy composites. They found that TritonX-100/MWCNTs/epoxy showed the best mechanical property due to the good dispersion of TritonX-100/MWCNTs and strong interfacial interaction between CNTs and epoxy.

In the above studies, the dispersion of CNTs in different solvents was not thoroughly studied. They only studied the dispersion of CNTs in a certain solvent which was used to prepare epoxy composites by solution blending. Hansen solubility parameters (HSPs) method can help investigate the dispersion of CNTs in solvents, which were mentioned in our previous articles [25,26]. In addition, dynamic light scattering (DLS) has been applied to quantitatively characterize the dispersion of CNTs in solvents by comparing hydrodynamic size particle ( $Z$ -average), polydispersity index (PDI) of CNTs [25-28]. Ultraviolet and visible (UV-Vis) spectrophotometer can also quantitatively characterize the dispersion of CNTs by comparing the sedimentation rate (SR) of CNTs, which was reported by Wang *et al.* [29]. Based on the UV-Vis, HSPs of the CNTs can be calculated. In the three-dimensional space, a sphere represents the solute of a material, the HSPs of the material is the center of the sphere, and its radius ( $R_0$ )

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is the maximum tolerance of the material. The good solvents are included within the sphere and bad solvents are out of the sphere. Until now, the effect of surfactant functionalization on the HSPs of CNTs has rarely been reported. In addition, it is worthwhile to further investigate the relationship between the dispersion of MWCNTs and the mechanical, electrical and thermal properties of epoxy composites.

Cetyl pyridinium chloride (CPC, cationic), sodium deoxycholate (NaDC, anionic) and polyethylene glycol octylphenol ether (TritonX-100, non-ionic) are chosen to disperse multiwalled carbon nanotubes (MWCNTs) because they have been proven to enhance the dispersion of MWCNTs [10,24,30]. In addition, we systematically characterized the dispersion of MWCNTs in different solvents via UV-Vis spectrophotometer and reported effect of surfactant functionalization on the HSPs of MWCNTs. Based on the above results, we chose tetrahydrofuran as the dispersion solvent to prepare epoxy composites by solution blending. The dispersion of MWCNTs in tetrahydrofuran and epoxy was further evaluated by DLS and confocal laser scanning microscopy (CLSM), respectively. The effect of the dispersion of MWCNTs on the mechanical, electrical and thermal properties of epoxy composites was also characterized.

## Material and Methods

### Materials

The pristine MWCNTs with diameter of 10-20 nm and length of 10-30  $\mu\text{m}$  was purchased from XFNANO (Nanjing, China) and used without further purification. Cetyl pyridinium chloride (CPC, Amresco, America), sodium deoxycholate (NaDC, Amresco, America) and polyethylene glycol octylphenol ether (TritonX-100, Deng Feng, Tianjin) were used to noncovalently functionalize MWCNTs, which were also used as reinforcements to compare with pristine MWCNTs, respectively. The epoxy resin (CYD128) and curing agent (593) used as the composite's matrix was supplied from Baling Petrochemical Co., Ltd. (Hunan, China).

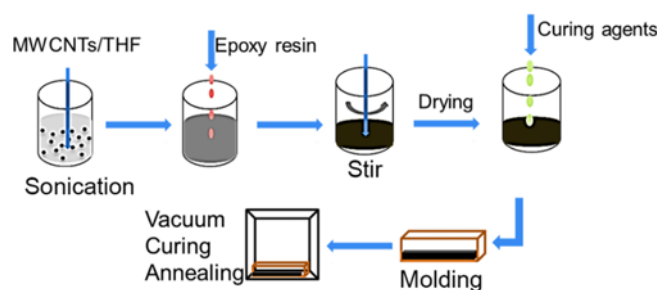
### Functionalization of MWCNTs

The surfactants/MWCNTs solutions were prepared at Table 1. Firstly, MWCNTs and surfactants (1CMC) were mixed into 10 ml of aqueous solution with a weight ratio of

**Table 1.** Preparation of the surfactants/MWCNTs solution

Surfactants	Surfactant type	CMC <sup>a)</sup> (mol/l) at 25 °C	Surfactants weight (mg)	MWCNTs weight (mg)	Water volume (ml)
CPC	Cationic	$9 \times 10^{-4}$	4	4	10
NaDC	Anionic	$6 \times 10^{-3}$	30	30	10
TritonX-100	Non-ionic	$2 \times 10^{-4}$	2	2	10

<sup>a)</sup>CMC is the critical micelle concentration of surfactant.



**Figure 1.** Fabrication routing of MWCNTs/epoxy composites.

1:1, sonicated (SONICS VCX800) for 30 min and in ultrasonic bath for 1 h, followed by centrifugation at 5000 rpm for 30 min with a high speed freezing centrifuge (KDC-140HR, Anhui). Finally, the supernatant was dried at 60 °C for 24 h to get the CPC/MWCNTs, NaDC/MWCNTs and TritonX-100/MWCNTs powders.

### Preparation of Composites

Fabrication flowchart of MWCNTs/epoxy composites was schematically illustrated in Figure 1. To disperse MWCNTs, 40 mg MWCNTs was sonicated in tetrahydrofuran (THF) at 160W for 1 h. Then 16.667 g epoxy resin was added into the MWCNTs/THF suspension, and vigorously stirred for 15 min. Afterwards the solvent THF was evaporated at 60 °C for 72 h. Then hardener (3.333 g) was added to the mixture of MWCNTs/epoxy resin (the resin/hardener weight ratio is 5:1) and stirred to form MWCNTs/resin/hardener mixture. The mixture was cast in a silicon mold and the samples were degassed under vacuum before curing at room temperature for 24 h. Finally, the samples were obtained by secondary curing heated from 20 °C to 60 °C and kept at 60 °C for 24 h by heating rate at 1 °C/min. Functionalized MWCNTs/epoxy (CPC/MWCNTs/epoxy, NaDC/MWCNTs/epoxy and TritonX-100/MWCNTs/epoxy) were also obtained by the same process.

## Experimental

### Functionalization of MWCNTs

The morphology of the pristine MWCNTs and functionalized MWCNTs was characterized by Scanning Electron Microscopy (SEM, MIRA3LMH, TESCAN, a.s.).

Fourier transform infrared spectrometer (FTIR, VERTEX70, Germany Bruker Co., Ltd.) was employed to characterize the functionalization of MWCNTs.

Raman spectrometer (Renishaw Invia) characterized the structural defects of MWCNTs with or without surfactants.

### The Dispersion of Pristine MWCNTs and Functionalized MWCNTs in 24 Solvents

To evaluate the dispersion of MWCNTs in a solvent, we designed a simple and understandable method via UV-Vis

spectrophotometry. The specific steps are as follows: MWCNTs powders were sonicated in a certain solvent for 2 min to form 25  $\mu\text{g}/\text{mL}$  MWCNTs/solvent suspension, followed by measuring the absorption of the suspension at 600 nm on UV-Vis spectrophotometry (UV-1800PC, Meipuda, Shanghai) every half hour. The measures last for 3 h (the time counted as in turn: 0, 0.5, 1, 1.5, 2, 2.5, 3) and the absorption of the suspension were counted as in turn: A1, A2, ..., A7. In the 2D coordinate systems, the time and absorption were used as x-coordinate and y-coordinate, respectively. And the slope of the line was the sedimentation rate (SR) of MWCNTs in the solvent. The SR is index of dispersion of MWCNTs in the solvent.

Large SR means the poor dispersion of MWCNTs in the solvent; oppositely, when the SR is small, MWCNTs dispersed well in the solvent. To find the excellent dispersion solvent of pristine MWCNTs, it need to be dispersed in 24 solvents using the above method, respectively. Likely, the dispersion of functionalized MWCNTs was also evaluated by the same method.

To verify the accuracy and feasibility of the above method, we observed the dispersion picture of four different MWCNTs in 24 solvents left for 3 h after sonication.

### Hansen Solubility Parameters (HSPs) of Pristine and Functionalized MWCNTs

Based on the UV-Vis results, Hansen solubility parameters (HSPs) of the MWCNTs were calculated by our software [25,26], which could reflect the solubility and dispersion of MWCNTs in solvents.

### Dispersion of MWCNTs in THF and Epoxy Matrix

Dynamic Light Scattering (DLS) technique was also employed to evaluate the dispersion of pristine and functionalized MWCNTs in THF by Malvern zeta nano 90 system.

Because the epoxy has good transmissivity, the dispersion of MWCNTs in epoxy matrix was analyzed by confocal laser scanning microscopy (CLSM, NikonC2 plus, ShanHai). In the micrograph, the black spot is the agglomeration of MWCNTs, the white is the epoxy matrix. All the composites were ground to a thickness of 0.4 mm-0.5 mm.

### Mechanical, Electrical and Thermal Testing

Mechanical properties of all specimens were measured by a tensile tester (Instron 5966, America). The crosshead speed was 2 mm/min at room temperature. Five specimens were tested for each epoxy nanocomposites.

Electrical properties (resistivity) of specimens were measured by high-impedance tester (Agilent 4339B).

Thermal characterization was performed using a Q100 DSC (TA Instruments Inc., Delaware). Specimens (8-9 mg) were heated from 20-250  $^{\circ}\text{C}$  and kept for 20 min and then cooled to 20  $^{\circ}\text{C}$  and kept for 5 min at a heating or cooling rate of 10  $^{\circ}\text{C}/\text{min}$ . The glass transition temperature ( $T_g$ ) was

showed on the second heating process. All DSC scans were sealed in the aluminum pan under  $\text{N}_2$  atmosphere.

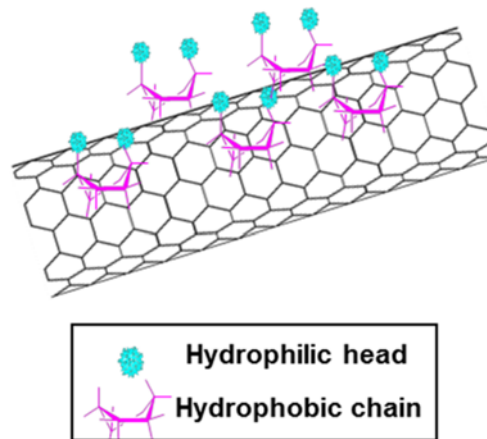
## Results and Discussion

### Functionalization of MWCNTs

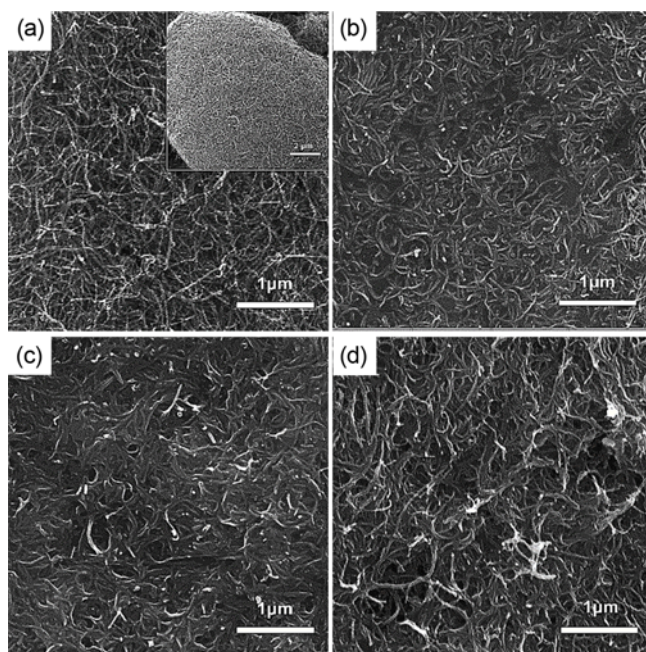
Schematic diagram of surfactants functionalize MWCNTs was shown in Figure 2. Hydrophobic carbon chain of surfactants interacted with MWCNTs through Van der Waals forces or  $\pi$ - $\pi$  interaction. Their opposite end remained free and provided the water solubility, which is in touch with the solvents and epoxy matrix.

SEM images of all MWCNTs samples were presented in Figure 3. Surfactants functionalized MWCNTs avoided shortening the length of CNTs and enlarged its diameter, which indicated that MWCNTs was functionalized successfully with surfactants by physical absorption without structural destruction of MWCNTs. The dispersion of MWCNTs was improved via noncovalent functionalization in Figure 3(b-d). With surface functionalization, large aggregations of pristine MWCNTs (see inset of Figure 3(a)) disappeared. TritonX-100/MWCNTs looks loose and porous (see Figure 3(d)), while CPC/MWCNTs is formed in a compact states (see Figure 3(b)), and NaDC/MWCNTs sticks together (see Figure 3(c)).

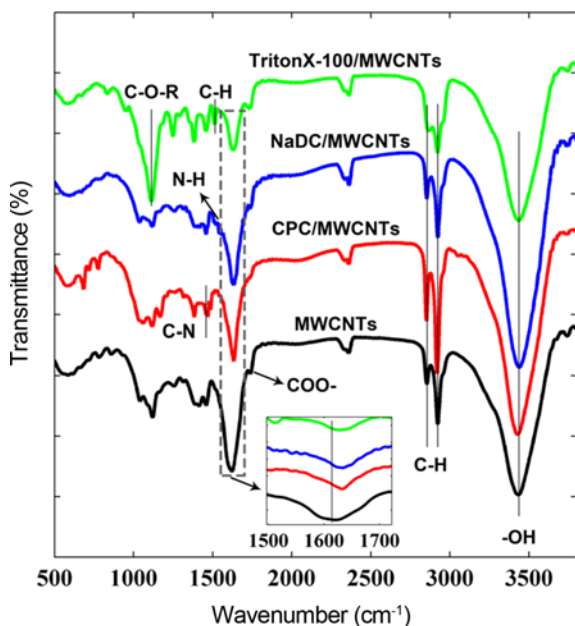
To indicate the functionalization of MWCNTs, FTIR spectra of pristine and functionalized MWCNTs were shown in Figure 4. The peak assigned to carboxyl ( $\sim 1740\text{ cm}^{-1}$ ) was observed in pristine MWCNTs spectrum [31], which indicates that pristine MWCNTs has carboxyl groups on it. The peak at  $\sim 1620\text{ cm}^{-1}$  can be assigned to the stretching vibration of C=C in aromatic ring of MWCNTs [30], it upshifted to higher wavenumber when surfactants adsorbed on the MWCNTs surface (inset in Figure 4). It may be because of the strong interaction between MWCNTs and surfactants. Peaks at wave numbers of  $2920\text{ cm}^{-1}$  and  $2850\text{ cm}^{-1}$



**Figure 2.** Schematic diagram of surfactants functionalize MWCNTs.

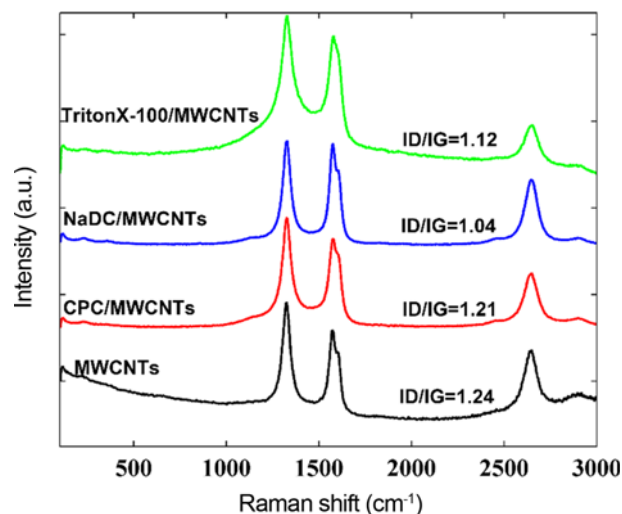


**Figure 3.** SEM images of pristine and functionalized MWCNTs; (a) MWCNTs, (b) CPC/MWCNTs, (c) NaDC/MWCNTs, and (d) TritonX-100/MWCNTs.



**Figure 4.** FTIR of pristine and functionalized MWCNTs.

appeared in all curves, which are corresponding to the C-H stretching vibration of  $-CH_3$ ,  $-CH_2$  [10,23]. Compared to the FTIR spectrum of pristine MWCNTs, a new peak at  $1470\text{ cm}^{-1}$  corresponded to stretching vibrations of C-N in CPC was observed in CPC/MWCNTs spectrum [32]. It confirms that CPC was introduced onto the side of walls of



**Figure 5.** Raman spectra of pristine and functionalized MWCNTs.

MWCNTs. Additionally, the functionalization of MWCNTs with NaDC is proved by the new peaks  $1552\text{ cm}^{-1}$  assigned to vibration of N-H [33]. Likely, a strong peak associated with the bending vibration of C-H of alkyl chain in TritonX-100/MWCNTs was observed at  $1511\text{ cm}^{-1}$  [10,34]. A band at  $1114\text{ cm}^{-1}$  shows the presence of C-O-R (ether groups) in TritonX-100 [10,30]. It can indicate that TritonX-100 successfully adsorbed on the surface of MWCNTs.

It is well known that the intensity ratio ( $I_D/I_G$ ) of the D band and G band is often used to evaluate the defect density of CNTs [10]. The D band at  $\sim 1350\text{ cm}^{-1}$  represents defects of CNTs, and the G band at  $\sim 1580\text{ cm}^{-1}$  corresponds to the sound  $sp^2$  carbon networks. Figure 5 gives the Raman spectra of pristine and functionalized MWCNTs. When MWCNTs was functionalized by surfactants, its  $I_D/I_G$  decreased in different degree. Therefore, it was inferred that the some defects of MWCNTs were coated by surfactants in some extent, so its defects were not detected. It also indicates that MWCNTs were noncovalently functionalized by physical adsorption without disturbing the structure of MWCNTs.

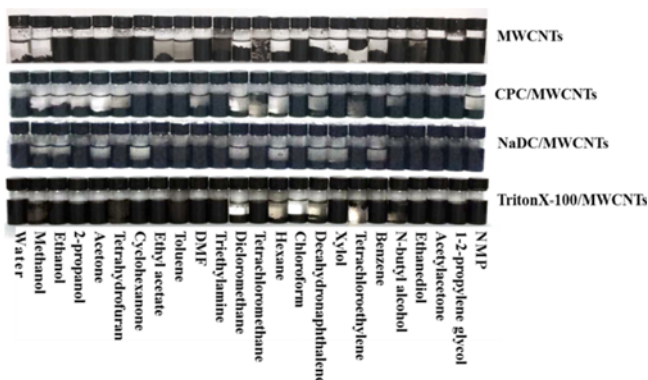
#### The Dispersion of Pristine and Functionalized MWCNTs in 24 Solvents

Table 2 illustrates the dispersion (S) and the sedimentation rate (SR) in 3 h for pristine and functionalized MWCNTs in 24 solvents. The dispersion images of four different MWCNTs in 24 solvents for 3 h were shown in Figure 6. On comparison of the SR and the dispersion images of MWCNTs, it was found that smaller SR (under 0.0281) were generally associated with the solvents with stable dispersion as indicated in Figure 6. The UV-Vis analyzed the dispersion of MWCNTs in solvent is feasible and practicable. With surfactants, the dispersion of MWCNTs in 24 solvents significantly changed. Some bad dispersed solvents such as water, ethyl acetate and toluene converted into good dispersed

**Table 2.** The dispersion and sedimentation rate of pristine and functionalized MWCNTs

No	Solvents	MWCNTs		CPC/MWCNTs		NaDC/MWCNTs		TritonX-100/MWCNTs	
		S <sup>a)</sup>	SR <sup>b)</sup>	S	SR	S	SR	S	SR
1	Water	0	0.0046	0	0.2179	1	0.0157	1	0.0058
2	Methanol	0	0.0694	1	0.0002	0	0.0336	1	0.0041
3	Ethanol	1	0.0126	0	0.2329	1	0.0030	1	0.0163
4	2-propanol	1	0.0024	1	0.0068	1	0.0016	1	0.0024
5	Acetone	1	0.0012	1	0.0070	0	0.0673	1	0.0057
6	Tetrahydrofuran	1	0.0048	1	0.0003	1	0.0004	1	0.0005
7	Cyclohexanone	1	0.0059	1	0.0031	0	0.0577	1	0.0022
8	Ethyl acetate	0	0.0879	1	0.0148	1	0.0281	1	0.0074
9	Toluene	1	0.0156	1	0.0127	0	0.0367	1	0.0106
10	Dimethyl formamide	1	0.0090	1	0.0028	1	0.0049	1	0.0018
11	Triethylamine	1	0.0021	1	0.0186	1	0.0144	1	0.0046
12	Methylene chloride	0	0.0436	0	0.3337	0	0.0322	0	0.0389
13	Tetrachloromethane	1	0.0148	1	0.0199	1	0.0146	1	0.0209
14	Hexane	0	0.1392	0	0.2938	0	0.0368	1	0.1644
15	Chloroform	1	0.0274	0	0.0289	1	0.0268	0	0.0342
16	Decahydronaphthalene	0	0.1732	0	0.0314	0	0.0284	0	0.0286
17	Xylol	1	0.0231	1	0.0056	0	0.0342	1	0.0081
18	Tetrachloroethylene	0	0.2558	1	0.1188	1	0.0335	1	0.0689
19	Benzene	0	0.0319	1	0.0110	0	0.0345	1	0.0169
20	N-butyl alcohol	1	0.0020	0	0.1127	1	0.0121	1	0.0049
21	Ethanediol	1	0.0084	1	0.0092	1	0.0046	1	0.0133
22	Acetylacetone	1	0.0018	1	0.0008	1	0.0003	1	0.0011
23	1-2-propylene glycol	1	0.0105	1	0.0022	1	0.0010	1	0.0053
24	N-methyl-2-pyrrolidone	1	0.0035	0	0.0345	1	0.0040	1	0.0155

<sup>a)</sup>S-dispersion (0 indicate the bad solvent for dispersion, 1 indicate the good solvent for dispersion) and <sup>b)</sup>SR-sedimentation rate in 3 h.

**Figure 6.** Stability of pristine and functionalized MWCNTs in 24 solvents for 3 h.

solvents when surfactants (CPC, NaDC and TritonX-100) adsorbed on MWCNTs. Meanwhile, some good dispersed

**Table 3.** The calculated HSPs

Samples	$\delta^a)$	$\delta_p^b)$	$\delta_H^c)$	$R_0^d)$
MWCNTs	17.7	1.9	13.7	12.3
CPC/MWCNTs	15.3	6.4	7.5	9.7
NaDC/MWCNTs	17.4	2.4	13.9	11.7

<sup>a)</sup> $\delta_D$ , <sup>b)</sup> $\delta_P$ , and <sup>c)</sup> $\delta_H$  represent the dispersion, polar, and hydrogen bonding force parameters, respectively) locate in the geometrical center of the HSP sphere. <sup>d)</sup>The radius  $R_0$  of the sphere is maximum tolerance of the solvent (TritonX-100/MWCNTs has too big  $R_0$  to be calculated).

solvents turn into bad solvents, for example, acetone is a good dispersion solvent for pristine MWCNTs but it becomes bad solvents after functionalization of NaDC and CPC. Additionally, it was interesting to find that tetrahydrofuran (THF) were both good solvent for pristine and functionalized MWCNTs.

### Hansen Solubility Parameters (HSPs) of Pristine and Functionalized MWCNTs

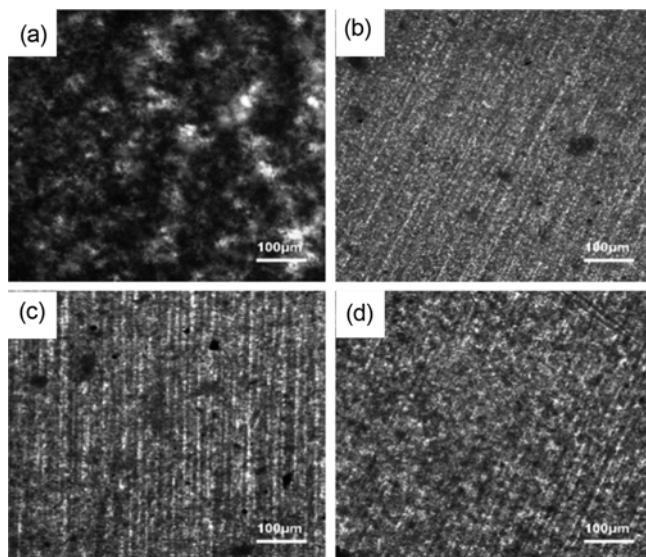
Hansen solubility parameters (HSPs) of pristine and functionalized MWCNTs were calculated by our software [25,26], as shown in Table 3. The center position of HSP sphere of MWCNTs changed after adding surfactants.  $R_0$  is the maximum tolerance of the solvent, large  $R_0$  represent MWCNTs can well disperse in more solvents. In four MWCNTs, TritonX-100/MWCNTs has the largest  $R_0$ , means that it can dispersion in more solvents.

### Dispersion of MWCNTs in THF and Epoxy Matrix

Epoxy can be dissolved in acetone, tetrahydrofuran (THF), cyclohexanone and ethyl acetate, etc [26]. All MWCNTs in tetrahydrofuran (THF) have a better dispersion than the others (Table 2). Therefore, THF was selected as the solvents for preparing epoxy composites. DLS results of pristine and functionalized MWCNTs in THF were presented at Table 4, which was analyzed by Z-Average and PDI. Small Z-Average and low PDI represent good dispersion of particles in the solvent. Z-Average and PDI of pristine and functionalized MWCNTs is very small, which confirms that MWCNTs with or without surfactants exhibit uniform

**Table 4.** The DLS results of pristine and functionalized MWCNTs in THF

Samples	MWCNTs	CPC/ MWCNTs	NaDC/ MWCNTs	TritonX-100/ MWCNTs
Z-Average (nm)	216.4	241.0	257.3	210.5
PDI	0.32	0.33	0.34	0.32



**Figure 7.** Dispersions state of pristine and functionalized MWCNTs in epoxy (black spot represents MWCNTs aggregates); (a) MWCNTs/epoxy, (b) CPC/MWCNTs/epoxy, (c) NaDC/MWCNTs/epoxy, and (d) TritonX-100/MWCNTs/epoxy.

dispersion in THF just after sonication. This is in agreement with the UV-Vis and SR results.

Figure 7 are the microscope pictures of epoxy composites. It shows the dispersion of pristine and functionalized MWCNTs in epoxy matrix. Many black spots were observed in Figure 7(a), which suggest that pristine MWCNTs has poor dispersion in epoxy matrix. Compared to MWCNTs/epoxy, less black spots were observed in Figure 7(b), (c) and (d), which demonstrates that CPC/MWCNTs, NaDC/MWCNTs and TritonX-100/MWCNTs presented good dispersion, especially TritonX-100/MWCNTs. Remarkably, TritonX-100/MWCNTs was homogeneously dispersed in the epoxy matrix. Therefore, the functionalization of surfactants helps improve the dispersion of MWCNTs in THF, further enhanced the dispersion of MWCNTs in epoxy matrix.

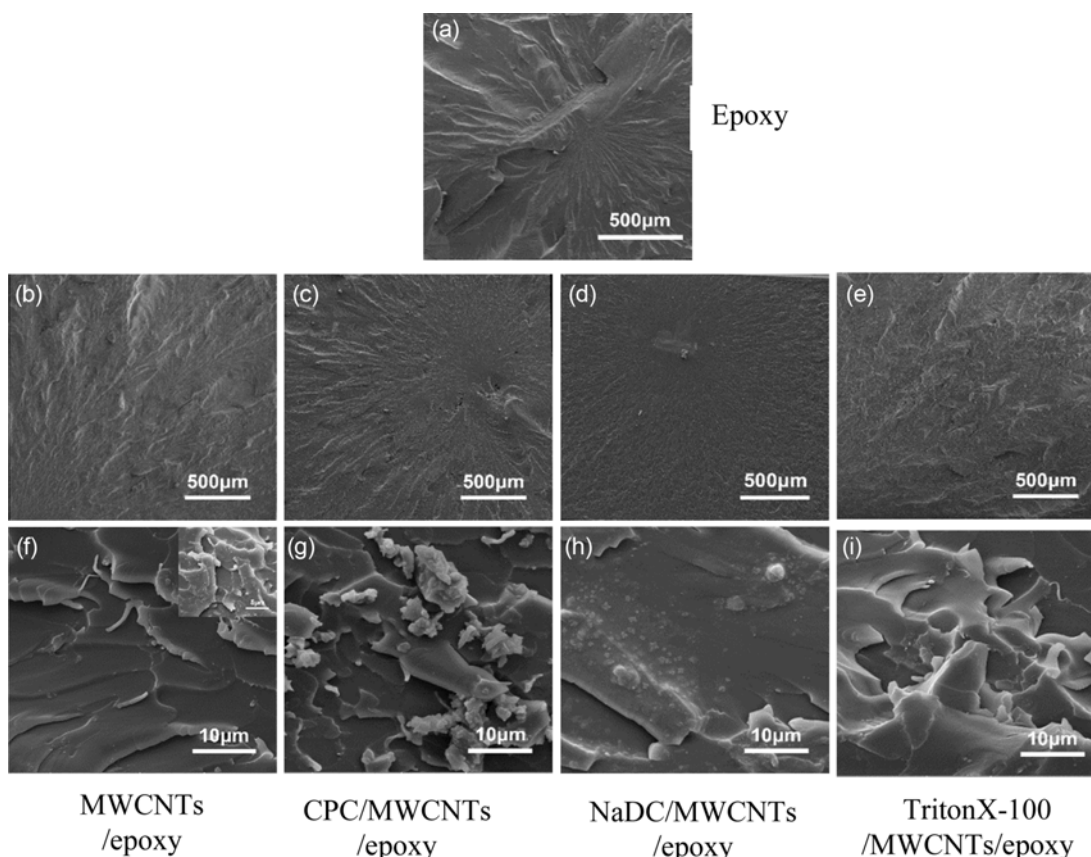
### Mechanical Properties of Epoxy and Epoxy Composites

Table 5 listed the mechanical properties of neat epoxy and epoxy nanocomposites. The elastic modulus of neat epoxy decreased after adding pristine MWCNTs due to its poor dispersion in the epoxy matrix (see Figure 7(a)). With surfactants, the elastic modulus of MWCNTs/epoxy increased due to the enhanced dispersion (Figure 7). CPC/MWCNTs/epoxy composites exhibit the highest yield strength, which can be explained by two reasons [24]: (i) amine group in CPC covalently bonds with epoxide rings of epoxy resin, increasing the compatibility of MWCNTs with epoxy (ii) the electrostatic attractions between the cationic head group of CPC and the carboxyl of MWCNTs surface (FTIR can indicate the existence of carboxyl in MWCNTs at  $\sim 1740 \text{ cm}^{-1}$ , Figure 4). The anion NaDC and non-ionic Triton X-100 are unable to create such attractions. NaDC/MWCNTs/epoxy exhibits the smallest yield strength. Therefore, it indicates that the functional groups and dispersion of MWCNTs in epoxy influenced the mechanical properties of epoxy composites.

Figure 8 presents the tensile fracture surface morphology of epoxy and epoxy nanocomposites at different magnifications. At low magnification, the regions of nucleation and propagation of cracks can be seen clearly in Figure 8(a-e). At high magnification (Figure 8(h)), NaDC/MWCNTs/epoxy exhibit a relatively smooth fracture surface, some brittle fracture features and aggregations of NaDC/MWCNTs were clearly observed, which explained its low yield strength. However, fracture surface of CPC/MWCNTs/epoxy is rough and some fragments appeared in Figure 8(g), which explained its high yield strength (Table 5). Similarly, the rough fracture surface of MWCNTs/epoxy and TritonX-100/MWCNTs/epoxy clearly explained their good yield strength. Therefore, the fracture morphology of epoxy and its composites well explain its mechanical properties

### Resistivity Analysis of Epoxy and Epoxy Composites

The resistivity of all epoxy specimens were presented in



**Figure 8.** The tensile fracture morphology of all epoxy specimens; (a) Epoxy, (b,f) MWCNTs/epoxy, (c,g) CPC/MWCNTs/epoxy, (d,h) NaDC/MWCNTs/epoxy, and (e,i) TritonX-100/MWCNTs/epoxy.

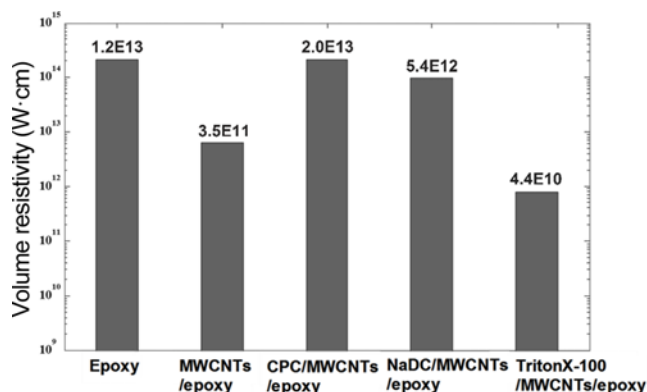
**Table 5.** The mechanical properties of neat epoxy and epoxy composites

Samples	Elastic modulus (GPa)	Yield strength (MPa)
Epoxy	3.6±0.1	67.1±12.9
MWCNTs/epoxy	3.4±0.1	56.9±15.0
CPC/MWCNTs/epoxy	3.6±0.3	75.5±2.1
NaDC/MWCNTs/epoxy	3.7±0.1	47.8±9.0
TritonX-100/MWCNTs/epoxy	3.7±0.1	68.5±6.6

Figure 9. The addition of MWCNTs significantly decreases the resistivity of epoxy. TritonX-100/MWCNTs/epoxy has smaller resistivity than that of MWCNTs/epoxy due to the good dispersion of TritonX-100/MWCNTs in epoxy (Figure 7(d)). However, NaDC/MWCNTs/epoxy and CPC/MWCNTs/epoxy show larger resistivity than that of MWCNTs/epoxy.

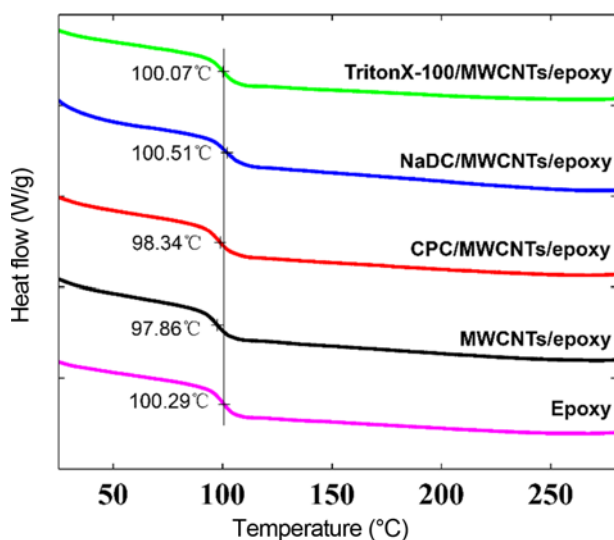
#### Thermal Analysis of Epoxy and Epoxy Composites

Glass transition temperatures ( $T_g$ ) of all the samples were obtained from DSC curves, as shown in Figure 10. The  $T_g$  of MWCNTs/epoxy was  $\sim 3^\circ\text{C}$  lower than that of neat epoxy. It



**Figure 9.** The volume resistivity of neat epoxy and epoxy composites.

was because MWCNTs increases the distance between epoxy chains and weakens the interaction between epoxy molecules, leading to the low  $T_g$  of MWCNTs/epoxy [12,35]. With the addition of surfactants,  $T_g$  of MWCNTs/epoxy shifted to higher temperature, which is in agreement with the study of Kim *et al.* [10]. It was inferred that surfactants help the formation of networks of well-dispersed and functionalized



**Figure 10.** The DSC curves of neat epoxy and epoxy composites.

MWCNTs and increase cross-linkage of the composites. NaDC/MWCNTs/epoxy has highest  $T_g$  in all of epoxy samples, which were ascribed to the networks of NaDC/MWCNTs in epoxy more limit the wave of epoxy chains.

### Conclusion

To investigate the effect of dispersion of MWCNTs on the mechanical, electrical and thermal properties of epoxy composites, we adopt three surfactants to functionalize MWCNTs noncovalently and synthesized epoxy composites by solution blending. Surfactants were adsorbed successfully on MWCNTs surface without damaging the structure of MWCNTs, and confirmed by SEM micrographs, FTIR and Raman spectra. Based on the UV-Vis analysis, we reported the effect of surfactant functionalization on the Hansen solubility parameters (HSPs) of MWCNTs. It was found that the use of surfactants changed the HSPs of MWCNTs. The dispersion of MWCNTs in THF characterized by DLS agrees with the UV-Vis results. It was found that the dispersion of MWCNTs in solvents and epoxy was enhanced with the addition of surfactants.

After surfactant functionalization of MWCNTs, epoxy exhibits improved elastic modulus and yield strength due to improved dispersion of MWCNTs, except yield strength of NaDC/MWCNTs/epoxy. The fracture mechanism can be explained by their tensile fracture morphology. TritonX-100/MWCNTs/epoxy has better conductivity than that of MWCNTs/epoxy due to its uniform dispersion in epoxy. Moreover, the glass transition temperatures ( $T_g$ ) of MWCNTs/epoxy shift a higher temperature when the surfactants functionalized MWCNTs were added into the epoxy.

With surfactants to functionalization of MWCNTs, its dispersion in solvents and epoxy were improved, and further

influences the mechanical, thermal and electrical properties of epoxy composites.

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