

HSP STUDY ON THE DISPERSION AND INTERFACIAL ADHESION OF FUNCTIONALIZED SWNTS IN EPOXY COMPOSITES

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Abstract

Carbon nanotubes (CNTs) are considered as highly potential reinforcement material for the epoxy composites. However, the dispersion of CNT into epoxy is a big challenge due to the tiny scale and large aspect ratio. Surface functionalization is one of the ways that could change the compatibility between CNTs and epoxy matrix hence to change the dispersion of CNTs. The effect of functionalization was investigated by the XPS. The CNTs were dispersed in a solvent and mixed with the epoxy resin during the preparation of nanotube/epoxy composites, ultrasonic treatment and shear mixing is included to aid the dispersion. In this study, the compatibility of the CNTs with different functionalization and the polymer or the solvent is measured by using Hansen solubility parameters (HSP). The compatibility influences both the dispersion and the interfacial adhesion. The dispersion is tested by Dynamic Light Scattering (DLS) and light optical microscopy. The results of the dispersion of CNTs in epoxy are explained by HSP theory. The interfacial adhesion was evaluated using Raman spectroscopy and measuring the shift of the 2D band when applying a strain on the sample. Again the results are compared with the HSP results. This suggests an application of HSP to predict the properties of carbon nanotubes filled epoxy composite.

1 Introduction

Epoxy is widely used as the matrix material in high-technology structural composite application which requires high strength, stiffness and durability. CNTs have been found to possess excellent mechanical properties [1], and they have been regarded as the most promising reinforcement for the next generation of high performance composites. Hence the CNT reinforced epoxy composites have attracted enormous interests due to the exceptional properties of these two materials, especially for the potential applications in industry.

However, developing composites with CNTs as reinforcement is confronted with many challenges, the two of the largest challenges are the poor dispersion of agglomeration and weak interfacial bonding between CNTs and epoxy. CNTs tend to form agglomerates because of nanoscale size of the diameters of CNTs, and van der Waals attractions between CNTs. The interface controls the degree of interaction between the filler and matrix. The combination of the slipping in the bundle and the weak interface bonding results in inefficient load transfer and lead to the decreasing of the mechanical properties of the CNT reinforced composite. The interface between CNT and epoxy changes through functionalization, and the dispersion, de bundling of CNTs, and interfacial adhesion between CNT and epoxy are also expected to be improved.

Surface affinity between CNT and polymer strongly influences the performance of the composite. Hence, improving the surface affinity has been one of the most significant factors for effectively improving composites performance. Until now, there are very few ways to evaluate the surface affinity between polymer and CNTs. Hansen solubility parameters (HSP) theory has been applied in polymer-solvent evaluations, polymer plasticizing and so on. In this work, purified and functionalized SWNT with HNO₃, dodecylamine (DDA) and dichlorocarbene were added as the reinforcement into epoxy composites. Three different solvents with varying solubility parameters were chosen to investigate the function of solvents on the properties of composites. The compatibility was determined by HSP method. The dispersion of the CNT in the solvent was characterized by Dynamic Light Scattering (DLS) and light optical microscopy (LOM) was used for the composites. The strain transfer at the interface is studied by Raman spectroscopy. It is shown that the functionalization of SWNTs efficiently improved the strain transfer from epoxy to SWNTs.

2 Materials and testing methods

2.1 Surface functionalization of SWNTs and epoxy composites fabrication

The SWNTs were purchased from Bucky USA, Inc. fabricated by CCVD method.

Purified SWNTs and HNO₃ functionalized SWNTs was prepared according to our previous report[2].

DDA functionalized SWNTs: 2g dodecyl amine (DDA) was added to 200mg HNO₃ functionalized SWNTs, and the mixture was held at 90°C for 4 days. Then the mixture washed with ethanol 3-5 times and tetrahydrofuran (THF) 1-2 times to remove the remaining DDA and filtered through 0.45µm filter. And finally the powder was dried at 100°C for 24hrs.

Dichlorocarbene functionalized SWNTs: 100mg of as received SWNTs were dried at 110°C for 8 hours to remove the absorbed water, then SWNTs was ultrasonicated in 6ml chloroform for 1h, 40g of potassium tert-butoxide is dissolved in 60ml THF, and surrounded by dry ice-ethanol solution in order to keep the temperature around -75°C. Then the purified SWNTs/chloroform suspension was added into the potassium tert-butoxide /THF drop by drop. Hereafter, the mixture was poured in to ice and finally the mixture was washed with water 3-5 times to removed potassium chloride and washed with ethanol 3 times and once with THF to remove butanol and other chemicals. And finally the powder was dried at 100°C for 24hrs.

Preparation of composites: The nanocomposites were produced by the different modified SWNTs and a commercial epoxy resin Proset 117 and epoxy hardener Proset 229PF. The epoxy resin is a mixture of ether of bisphenol A, ether of bisphenol F and butanediol diglycidyl ether. The hardener consists mainly of polyoxypropyleneamine.

The purified SWNTs were dispersed in chloroform, the HNO₃ and DDA modified SWNTs were dispersed in THF, the dichlorocarbene functionalized SWNTs were dispersed in toluene for 1 hour using an 80 W ultrasonic rod generator to form a stable suspension, an ice bath was used to keep the suspension cold during sonication. The suspension was then poured into 8.955g of epoxy resin, and shear mixed for 1.5 hours at the speed of 3500 rpm. Afterwards, solvents were evaporated at 45°C. 3.045g hardener was then added to the mixture of SWNTs / resin mixture and stirred under vacuum to prevent introduction of air bubbles. Dog bone test specimens (ISO 527-2) was obtained by casting the resin/hardener mixture in a silicon mold, specimens was pre-cured at 40°C for 24 hours and post cured at 80°C for 16 hours.

2.2 Testing methods

X-ray photoelectron spectroscopy (XPS) The ESCALAB 250 XPS machine produced by ThermoFisher Scientific USA with high resolution spectrometer was used for analysis. The instrument employs monochromatic Al K α 200W as the X-ray source, and formed a spot size of 600µm on the sample. For the overall survey 200eV was used and for the high resolution

scans 30eV was used as the pass energy. The lens mode is set as LargeareaXL and the analyzer mode is CAE during analysis. Spectral data were recorded and analyzed by computer to give surface composition.

HSP In order to evaluate the HSP of the carbon nanotubes, small amount of SWNT powders were added to 20 different kinds of solvents with known HSP, the tested tubes were ultrasonicated for 6hrs to form suspension, and then the suspensions were left for observation. HSP experiment is based on the observation of the interaction or absence of interaction between the studied materials and solvents with known HSP [3]. The difference of interaction is used to divide the solvents into two groups, “good” and “bad” solvents. “Good” solvents interact strongly with the material, while the “bad” solvents give little interaction. In this case, the degree of sedimentation is used to divide solvents into “good” or “bad”. The data were processed by a Matlab program to determine the HSP and radius of the sphere for the tested materials.

Dynamic Light Scattering (DLS) The SWNT/solvent suspension (0.1mg/mL) after tip sonication was analyzed by Zetasizer Nano ZS from Malvern Instruments using DLS to characterize the dispersion of SWNTs in solvents. The Zetasizer Nano ZS illuminates the particles with laser and measures the rate of the intensity of scattered light and calculated the size of the particles. The software calculates the particle size according to the ISO standard 13321:1996(E). The average Hydrodynamic particle diameter (Z-average) is calculated by the Zetasizer software by determination of the rate of diffusion.

Light optical microscope (LOM) The dispersion of carbon nanotubes in epoxy matrix was characterized by using LOM on thin composite sections, which were ground from the bulk dog bone specimens.

Stain transfer Composites were tested in Renishaw Invia Raman Microscope with 632.8nm excitation focused through X5 objective lens. The small dog-bone specimens were loaded in a custom-made tensile test rig placed on the microscope table. The laser polarization was parallel to the loading direction and an analyzer also parallel to the load direction was used – the so called VV geometry. The specimen was gradually loaded up to different strain and Raman spectra were taken at each strain level.

3 Results and discussion

3.1 XPS of functionalized SWNTs

High resolution XPS spectra for purified, HNO₃, DDA and dichlorocarbene functionalized SWNTs are shown in Figure 1. The raw XPS data for each SWNT were analyzed to determine the peak locations and areas in relation to specific binding energies which best fit the data.

In C1s level spectra, the main peak at 284.8eV is corresponding to C1s C-graphite peak in SWNT[4]; additional photoemission present at higher binding energies indicates the presence of carbon atoms bonded to other functional groups.

For the purified SWNTs, the binding energy peak at 286.1eV[5] is attributed to atmospheric oxidation resulting from the SWNT purification process. The O1s peak at 532.9eV for the purified SWNTs is represent the –C=O group.

For the HNO₃ functionalized SWNT sample, the binding energies at 286.1 and 287.7 eV represent the –C-O and O-C=O contributions, respectively. The O1s peak at 533.5eV for the HNO₃ functionalized SWNTs is represent the O–C=O group[6].

DDA functionalized SWNTs, beside the main C-C is at 284.8eV[4], the second peak at 285.7eV shows the C-N bond in the amine (CH₂-NH₂) group[7], and the third peak at 288.5eV shows the also the C-N contributions[8]. The DDA functionalization is further confirmed in the N1s spectrum with two peaks at 397.6eV and 400.0eV which are attributed to the carboxylic acid amine base reaction. As expected, no N1s peaks were observed in the purified SWNTs, but for the HNO₃ functionalized SWNTs a small N1s peak was observed

maybe introduced by nitric acid. These XPS results are consistent with other SWNT studies presented in the literatures [8; 9].

For the dichlorocarbene functionalized SWNTs, beside the peak at 284.8eV[4], the peak at 285eV and a smaller peak at 289.8eV were attributed to the presence of C-C bond and sp³ carbons from organic chlorocarbons (C-Cl) respectively. Apart from that, the presence of Cl2p peak at 200.2eV on the dichlorocarbene functionalized SWNTs further ascertained the success of the reaction. The O1s peak at 530.1eV and 532.2eV for the dichlorocarbene functionalized SWNTs corresponding to the C-O and H-O-H group.

Based on the XPS results, the C1s, O1s and N1s peak areas for SWNTs were determined. The atomic concentration of each element provided a quantitative measure of the extent of functionalization[9]. The concentration values are given in Table 1. The higher surface oxygen content 11% for the carboxylic acid functionalized SWNTs, in comparison to that of the purified SWNTs 3.1% is evidence of COOH groups, other carbonyl groups and absorbed water on the SWNT surface. For the DDA functionalized SWNTs, the oxygen content at the surface slight decreased from 11% to 8.1%, at the same time the nitrogen content increased to 2.4% indicates that large number of COOH groups reacted with DDA in acid-base reaction, but also left other carbonyl groups unattached. The oxygen content (11.2%) and chlorine content (0.5%) increased as the purified SWNTs were functionalized by dichlorocarbene, but the reason for the increased oxygen content is unclear.

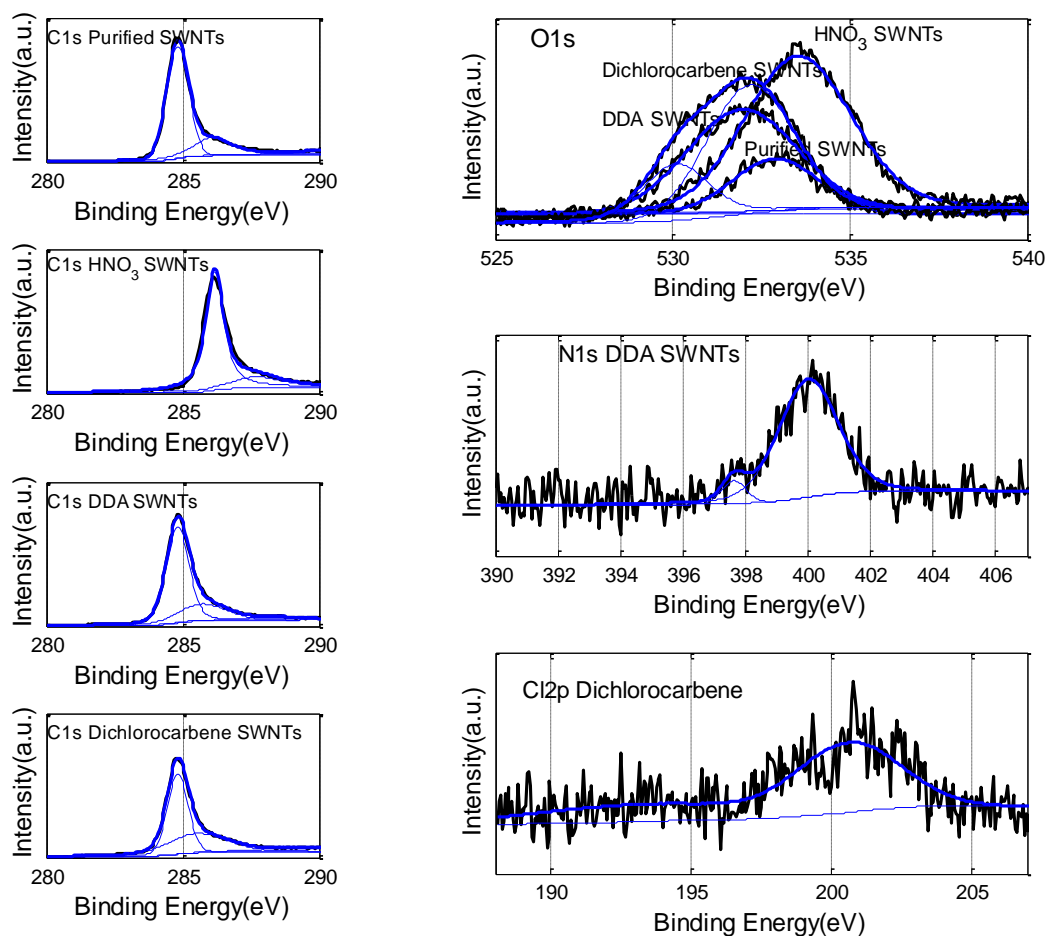


Figure 1. XPS results (C1s, O1s, N1s and Cl2p peaks) of different SWNTs

Materials	C1s%	O1s%	N1s%	Cl2p%
Purified SWNT	96.84	3.16		
HNO ₃ SWNT	87.48	11.01	1.51	
DDA SWNT	89.54	8.1	2.36	
Dichlorocarbene SWNT	84.5	11.18	1.28	0.49

Table 1. The atomic concentration of the different SWNTs by XPS

3.3 HSP

Solvents	δd^a	δp^a	δh^a	Purified SWNTs		HNO ₃ SWNTs		DDA SWNTs		Dichlorocarbene SWNTs	
				S ^b	RED	S ^b	RED	S ^b	RED	S ^b	RED
Methanol	15.1	12.3	22.3	0	4.17	1	0.90	0	3.74	0	1.40
Ethanol	15.8	8.8	19.4	0	3.42	1	0.62	0	2.90	1	1.00
2-propanol	15.8	6.1	16.4	0	2.76	1	0.53	0	2.15	0	0.64
Acetone	15.5	10.4	7	0	1.52	1	0.70	0	1.51	1	0.75
Tetrahydrofuran	16.8	5.6	8	0	1.20	1	0.84	1	0.73	1	0.64
Cyclohexanone	17.8	6.3	5.1	0	0.98	0	1.13	0	1.00	0	1.00
Ethyl acetate	15.8	5.3	7.2	0	1.00	1	0.84	1	0.53	0	0.53
Toluene	18	1.4	2.0	0	5.44	0	1.62	1	1.17	1	1.32
Dimethylformamide	17.4	13.7	11.3	1	2.58	1	0.69	0	2.45	1	1.12
Diethylethenamine	14.6	3.7	1.9	1	0.55	0	1.36	0	1.00	1	1.00
Dicloromethan	18.2	6.3	6.1	0	1.20	0	1.11	0	1.10	0	1.00
Chloroform	17.8	3.1	5.7	1	1.00	0	1.24	0	0.72	1	0.97
Tetrachloromethane	17.8	0	0.6	0	1.10	0	1.79	0	1.42	0	1.46
Hexane	14.9	0	0	0	1.00	0	1.73	0	1.40	0	1.31
Decahydronaphthalene	18.8	0	0	0	1.40	0	1.91	0	1.74	0	1.63
Benzene	18.4	0	2	0	1.23	0	1.73	0	1.38	0	1.43
Xylol	17.8	1	3.1	1	0.95	0	1.54	1	1.00	0	1.22
Acetonitrile	16	12.8	6.8	0	1.86	1	0.80	1	2.88	0	1.00
Tetrachloroethylene	18.3	5.7	0	0	1.00	0	1.63	0	1.61	0	1.47
Trichlorethylene	16.6	15.3	21.7	0	1.00	0	1.29	1	0.81	0	1.62

The HSP are in units of MPa^{1/2}

a Refs.[10; 11]

b S represent the solubility. "1" and "0" stand for the good and bad solvent, respectively.

Table 2. Hansen solubility parameters and RED values of SWNT in various solvents

In Table 2, the solubility of each SWNT in various solvents is displayed and RED values are calculated. The smaller RED values the better the solvent is for dispersion. The RED value for purified SWNTs in chloroform is 1. THF is selected for HNO₃ and DDA functionalized SWNTs, and the RED values are 0.84 and 0.73. The RED for dichlorocarbene functionalized SWNTs dispersed in toluene is 1.32 which is larger than 1.

Materials	δd	δp	δh	r	RED
Purified SWNT	16.0	4.3	2.1	5.2	2.06
HNO ₃ SWNT	14.8	10	13.7	9.8	1.22
DDA SWNT	16	2.9	6.0	5	2.02
Dichlorocarbene SWNT	14.2	5.2	11.2	9.5	1.33
Epoxy resin	20.0	8.9	7.7	9.0	0.00

Table 3. Hansen solubility parameters calculation of Relative Energy Difference (RED) for SWNTs and Epoxy resin

Table 3 illustrates the RED values calculated with respect to SWNTs, the epoxy resin are taken as the solvent in the calculation. The results indicate that the HNO₃ and dichlorocarbene functionalized SWNT have the best physical surface affinity with epoxy resin; the RED values are 1.22 and 1.33. The purified and DDA functionalized SWNT have inferior physical affinities with the higher RED values of 2.06 and 2.02.

3.4 Dispersion (DLS and LOM)

Table 4 illustrates the Dynamic Light Scattering (DLS) data for SWNTs in the solvent used for composite fabrication. By comparing the particle size, the DDA modified SWNTs dispersed in THF exhibited the smallest Z-average particle diameter of 699 nm. The dichlorocarbene functionalized SWNTs in toluene giving the largest Z-average particle diameter of 1659 nm which indicate that the agglomerates are large.

Compared with the HSP results in Table 2, the DDA SWNTs dispersed best in THF and the RED value is also the smallest. However, in most cases, RED values could just be an indication, because the calculation of the HSP method is not very accurate as in these cases it is impossible to create a sphere that includes all the good solvents and exclude all the bad.

Materials	Solvent	Z-average (nm)
Purified SWNT	Chloroform	1015
HNO ₃ SWNT	THF	1021
DDA SWNT	THF	699
Dichlorocarbene SWNT	Toluene	1659

Table 4. DLS size measurement data for SWNTs

Figure 2 exhibits the LOM images of various SWNT/epoxy composite. The dispersion of DDA modified SWNT were homogenous in the epoxy as observed in Fig.2c, while the purified, HNO₃ and dichlorocarbene modified SWNTs were less dispersed in the epoxy composites and lots of agglomerates were observed as seen in Fig.2a,b,d.

The DDA modified SWNTs possess worse physical affinities with epoxy, however the dispersion in epoxy is very uniform compare to HNO₃ functionalized SWNTs, which is due to DDA modified SWNTs dispersed better in THF than HNO₃ functionalized SWNTs. And the bad dispersion for dichlorocarbene functionalized SWNTs is also due to the bad dispersion in toluene. Thus the dispersion of CNTs in polymer matrix was mainly influenced by the dispersibility of SWNTs in solvent.

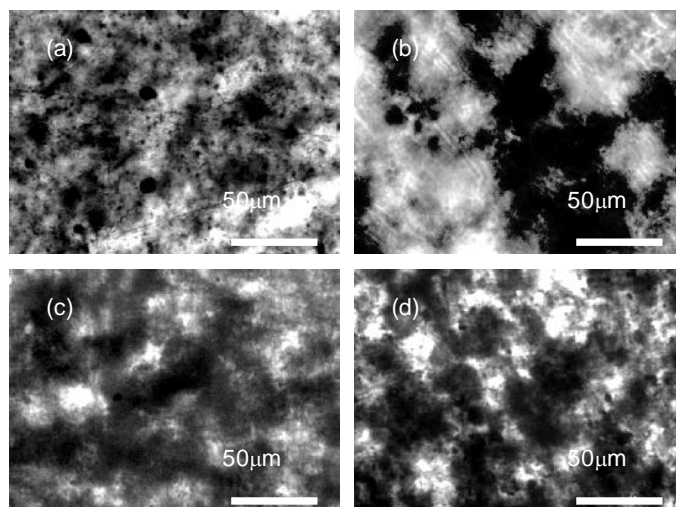


Figure 2. Light optical microscope images of (a) Purified SWNT dispersed by chloroform; (b) HNO₃ functionalized SWNT dispersed by THF; (c) DDA functionalized SWNT dispersed by THF; (d) Dichlorocarbene functionalized SWNT dispersed by Toluene in epoxy

3.5 Raman 2D band strain transfer

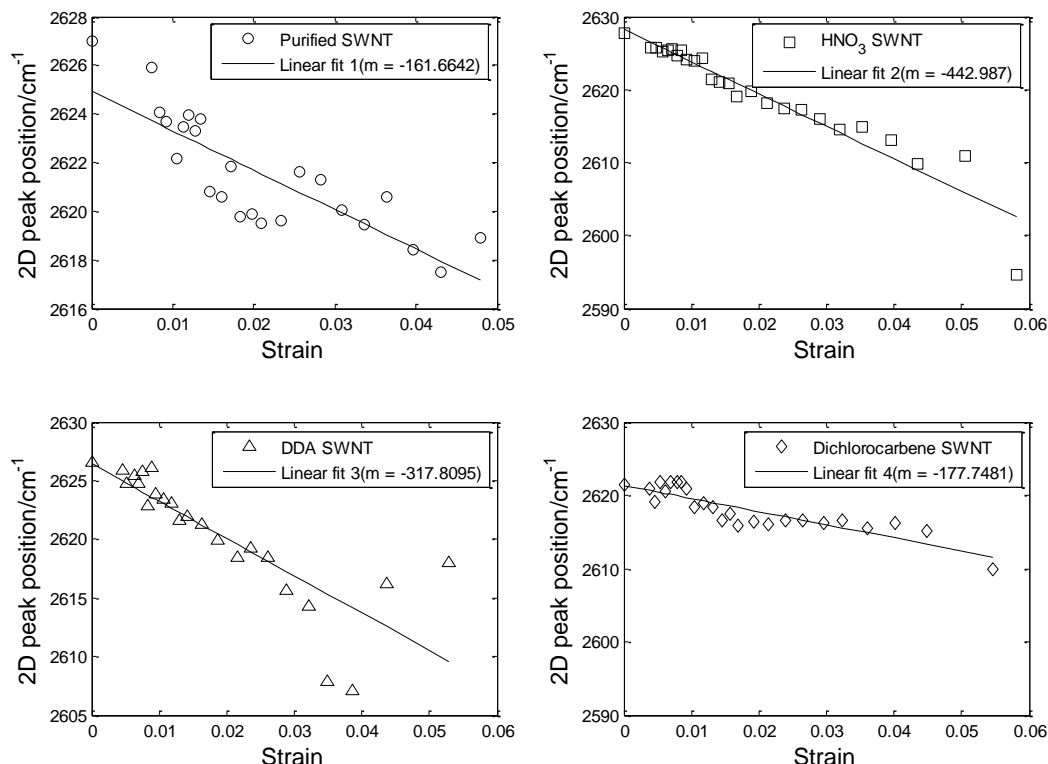


Figure 3. Raman 2D band shift of different SWNT/epoxy composites under tension

Figure. 3 shows the strain induced 2D Raman shifts in SWNT/epoxy composites under tension. The slope in the elastic regime for purified SWNTs in epoxy is $-162 \text{ cm}^{-1}/\text{strain}$, whereas it is $-443 \text{ cm}^{-1}/\text{strain}$ for HNO₃ functionalized SWNTs, $-318 \text{ cm}^{-1}/\text{strain}$ for DDA functionalized SWNTs and $-179 \text{ cm}^{-1}/\text{strain}$ for dichlorocarbene functionalized SWNTs in epoxy composites.

The higher slope of HNO₃ functionalized SWNTs/epoxy composite indicates the better interface and help strain transfer from the epoxy to SWNTs. Nitric acid treatment of SWNT is known to cause de bundling [2; 12]. The de-bundling is expected to improve the strain transfer between the matrix and the nanotubes. The HNO₃ functionalization also forms carboxyl groups at free ends of SWNTs and defect sites at the surface. The carboxyl groups form hydrogen bonds with epoxy to create a stronger interface and hence to promote better stress transfer between carbon nanotubes and matrix [13]. The hydrogen bonding could explain the good surface affinity demonstrated by HSP results.

The DDA functionalized SWNTs show less strain transfer in the epoxy composites than HNO₃ functionalized SWNTs which is due to weak surface affinity with epoxy. On the other hand the superior strain transfer compared to purified and dichlorocarbene functionalized SWNT is caused by the good dispersion by THF.

For the dichlorocarbene functionalized SWNTs, the strain transfer were not improved as expected based on the good physical affinity between the SWNTs and epoxy calculated by HSP method. The poor strain transfer can be as mentioned explained by an inferior dispersion using the toluene resulting in large bundles and agglomerated in the composite.

Conclusions

The surface functionalization extent was investigated by XPS spectra, the functional degree are: HNO₃ functionalized SWNTs > Dichlorocarbene functionalized SWNTs > DDA functionalized SWNTs > purified SWNTs. Dichlorocarbene functionalized SWNT and HNO₃ functionalized SWNT have better surface affinity than purified SWNT and DDA SWNTs with epoxy. The dispersion of the SWNTs in epoxy is mainly affected by the solvent used during the processing. The dispersion of DDA functionalized SWNTs in THF and epoxy are the most homogenous. The HNO₃ SWNTs shows the best strain transfer from matrix to carbon nanotubes due to the best surface affinity.

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