Effects of Multiwalled Carbon Nanotubes Functionalization on the Morphology and Mechanical and Thermal Properties of Carbon Fiber/Vinyl Ester Composites

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S *Supporting Information*

ABSTRACT: Multiwalled carbon nanotube (MWCNT)/carbon fiber (CF)/vinyl ester (VE) laminate composites have been fabricated in this study. Pristine MWCNTs were treated with acid solution, which formed numerous oxygen-containing functional groups onto their surface, resulting in COOH-MWCNTs. Thereafter, acrylic functional groups were grafted onto the COOH-MWCNTs to generate acryl-MWCNTs. Three types of MWCNTs (pristine MWCNTs, COOH-MWCNTs, and acryl-MWCNTs) were used to reinforce the CF/VE-based composites. The dispersion of MWCNTs in the VE matrix and the interfacial interaction between MWCNTs and the VE matrix were investigated. Thereafter, the individual reinforcement efficiencies of these MWCNTs are compared. The flexural strength of the MWCNT/CF/VE composite with 1.0 phr acryl-MWCNTs content is 29.8% greater than that of neat CF/VE composites, and the flexural modulus of the MWCNT/CF/VE composite is 9.9% higher than that of neat CF/VE composites. Compared with neat CF/VE composites, 1.0 phr acryl-MWCNT/CF/VE composites exhibit an approximately 19.9 °C increase in glass transition temperature (T_g). The coefficients of thermal expansion significantly decreased from 47.2 ppm/°C of the neat CF/VE composites to 35.6 ppm/°C of the acryl-MWCNTs/CF/VE composites with 1 phr acryl-MWCNT content. This study provides a method for developing acryl-MWCNT/CF/VE composites with good dispersion of MWCNTs in VE matrix and strong interfacial interaction between the MWCNTs and VE matrix for enhancing the stress transfer from VE matrix to CF reinforcement.
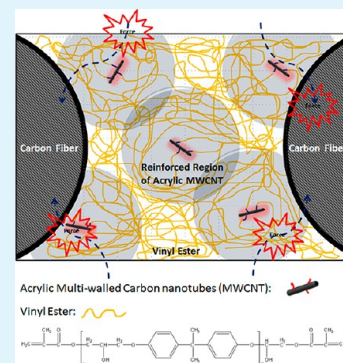
KEYWORDS: *carbon nanotubes, carbon fibers, polymer–matrix composites (PMCs), mechanical properties, thermal properties*

1. INTRODUCTION

Wind power has attracted significant attention in industries and science due to the flourishing development of green energy. The wind energy industry exhibits significant growth opportunities for composite material suppliers and wind turbine manufacturers. Market researchers predict that the global market of composite materials for wind turbine production will reach US$3.95 billion by 2014. Advanced composite wind blades should possess excellent mechanical properties, weatherability, and dimension stability, since they require enough durability to persist in a harsh environment.[1−3]

Manufacturers in the wind power industry recently started using vinyl ester (VE) resin blades rather than epoxy resins since VE resins possess high mechanical properties and good processability. Moreover, VE resins exhibit superior properties including excellent corrosion resistance, low curing shrinkage, and low cost. Wind blades can be constructed from VE composites, employed glass (GF), or carbon fibers (CF). Numerous countries are developing large-sized[4] offshore wind turbines, which require a higher strength and durability. CFs

possess a high stiffness, high tensile strength, low weight, high chemical resistance, high temperature tolerance, and low thermal expansion, which is superior to GF. Therefore, CF composites are expected to have larger applications in wind blade production.[2,5−10]

The main limitation of composites is that polymers possess low mechanical properties. Hence, various reinforcements were used to reinforce the polymer to solve this problem and resulted in improved mechanical properties.[11−13] Carbon nanotubes (CNTs) possess unique nanostructures and excellent physical properties that can reinforce polymer matrixes in various applications.[5,14−16] However, two main issues limit the reinforcing efficiency of CNTs in a polymer matrix: (1) poor dispersion of CNTs in the polymer matrix and (2) weak interfacial interactions between the CNTs and polymer matrix. Therefore, the development of new carbon
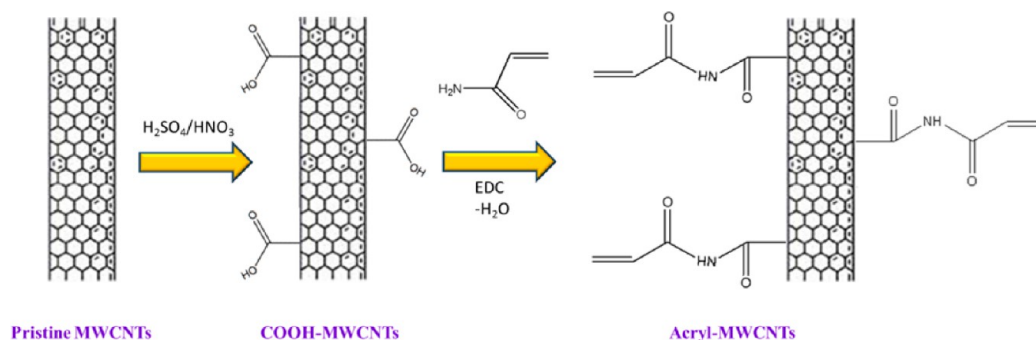
Figure 1. Scheme of the procedure for modification of MWCNT.

nanofiller materials or modification methods for CNTs for different polymer composites is a critical issue.[4,11,14,16−19]

Chen et al. indicated that the incorporation of multiwalled carbon nanotubes (MWCNT) into VE excessively reduces the polymerization degree and cross-linking density of VE resin.[20] Yang et al. showed the dispersions of MWCNTs in VE with eight different dispersing agents, and a suitable dispersing agent was identified using a centrifugation technique.[21] Zhu et al. indicated that the short MWCNTs dispersed in VE resins were used to manufacture glass fiber reinforced plastic (GFRP), which improved the interlaminar shear strength.[9] Liao et al. indicated that the incorporation of carbon nanotubes into GFRP/VE were examined, which provides an approach for improving shock strength and toughness.[5] Despite numerous related studies, the achievement of both dispersion and interfacial interaction of MWCNTs dispersed in CF/VE-based composites has seldom been discussed.

In this study, pristine MWCNTs were treated with H_2SO_4/ HNO_3 solution, resulting in MWCNTs with the COOH functional group, i.e., (COOH-MWCNT). The COOH-MWCNTs were further reacted with acrylamide to fabricate the acryl-functionalized MWCNTs (acryl-MWCNT). The nanofillers of pristine MWCNTs, COOH-MWCNTs, and acryl-MWCNTs were introduced to reinforce CF/VE composites. Following the fabrication of MWCNT/CF/VE composites, the dispersion and interfacial strength of the composites were investigated. The acryl-MWCNT/CF/VE composites exhibited molecular level dispersions of acryl-MWCNTs in the CF/VE-based composites and constructed strong, hierarchical, and covalently bonded interphase structures between the acryl-MWCNTs and VE. The acryl-functionalized MWCNTs prevented MWCNTs from aggregation and achieved covalent bonds with VE as a medium for transferring stress from VE to CF. The acryl-MWCNTs/CF/VE composites exhibit a significant enhancement in mechanical and thermal properties compared to the CF/VE composites, indicating that the combination of acryl-MWCNTs with the vinyl group is valuable in the manufacture of CF/VE-based composites. Acryl-MWCNT/CF/VE composite materials exhibit superior performances which have significant potential for a vast range of applications especially in the wind turbine blade.

2. EXPERIMENTAL SECTION

2.1. Materials. MWCNTs (trade name: Ctube 100) were obtained from the CNT Co. Ltd., Incheon, Korea. The diameter of MWCNTs is 10−50 nm, and the length is 1−25 μm. VE resin used in this study is a bisphenol A type vinylester, SW901, and methyl ethyl ketone peroxide (MEKPO) was supplied by Swancor Ind. Co., Ltd. Nantou,

Taiwan. Acrylamide (AAm), N-(3-dimethylaminopropyl-N-ethylcarbondiimide) hydrochloride (EDC), and tetrahydrofuran (THF) were obtained from Acros Organics Co., Belgium. Nitrate acid (HNO_3) and sulfuric acid (H_2SO_4) were received from Showa Chemical Co., Tokyo, Japan. The carbon fiber woven fabrics (3K, Toray Co.) used in this study were polyacrylonitrile (PAN) based and were supplied by Strong Solid Enterprise Co., Taiwan.

2.2. Modification of MWCNT. Carbon nanotubes were treated with a mixture of H_2SO_4 and HNO_3 with a weight ratio of H_2SO_4 to HNO_3 of 3:2. The weight ratio of the mixed acid to MWCNTs is 250:1 by stirring at 50 °C for 24 h to obtain acid-modified MWCNT. After acid treatment, MWCNTs were washed using deionized water, filtered (this process was repeated several times until the pH of the percolate reached 7), and dried at 100 °C. Functionalization of MWCNTs with acid treatment was assigned as COOH-MWCNTs. After acid treatment, carbon nanotubes with carboxylic acid group were further functionalized by acrylamide/EDC/THF (weight ratio of acrylamide to EDC to MWCNT is 1:1:2) solution, which were reacted at room temperature and stirred for 48 h to yield acryl-MWCNTs. Figure 1 depicts the scheme of modification of MWCNT.

2.3. Preparation of MWCNT/CF/VE Composites. Pristine MWCNTs, COOH-MWCNTs, and acryl-MWCNTs were used to fabricate MWCNTs/CF/VE composites, respectively. VE was blended with various phrs (parts per hundred parts of VE resin by weight) of nanofiller (0, 0.25, 0.5, 0.75, and 1.0 phr). In order to obtain a uniform dispersion of nanofillers in the VE resin, VE resin and nanofillers were mixed by a mechanical mixer and stirred at 25 °C for 15 min and then mixed by a three roll mixer over 15 cycles. In order to have further well-dispersed MWCNTs in the VE matrix, MWCNTs were dispersed in the VE matrix by ultrasonication for 10 min and degassed for 1 h in a vacuum oven at 40 °C. MEKPO was introduced into the system at content of 1 wt % after degassing and mixed using a high speed shear mixer (ARE-250, Thinky, Japan) for 5 min at 3000 rpm. Twelve piles of carbon fiber woven fabrics were immersed in solutions by hand-lay-up then transferred into a hot press (sandwich mold) at 150 °C and 1500 psi for 3 h. The laminated composites with a thickness of 3 mm contains a fiber weight fraction ranging between 67% and 69%. The weight fraction of fiber in laminate composites was measured by the burning off test method (according to ASTM D3171 method).

2.4. Characterization and Instruments. Transmission electron microscope (TEM) observations were conducted using a JEM-2100 microscope (JEOL Limited, Tokyo, Japan) with 200 kV. A high resolution X-ray photoelectron spectrometer (XPS) (ESCA pHI 1600, Physical Electronics, Lake Drive East, Chanhassen, MN, USA) was used to detect the presence of surface elements. Thermogravimetric analyses (TGA) was performed with a Du Pont TGA 2900 analyzer from 30 to 700 °C in nitrogen (N_2) at a heating rate of 10 °C/min. The flexural strength tests were performed on the basis of the procedure of ASTM D-790 by an Instron Model 4468 universal tester, and the specimen dimensions were 70.0 mm × 12.7 mm × 3.0 mm. The scanning electron microscope (SEM) used in this study was a Hitachi S-4200 (Hitachi Limited, Tokyo, Japan) with an accelerating voltage of 15 kV. Thermal expansion coefficient of composites was characterized by a thermomechanical analyzer (Universal TA Instru-

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ments 2940 TMA V2.4E) from 30 to 200 °C in nitrogen (N_2) at a ramp rate of 10 °C/min.

3. RESULTS AND DISCUSSION

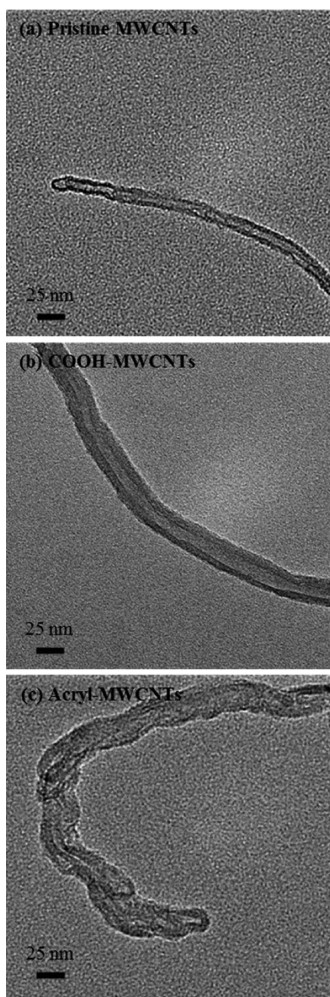### 3.1. Characterizations of Functionalized MWCNTs.

Figure 2. TEM images of (a) pristine MWCNTs, (b) COOH-MWCNTs, and (c) acryl-MWCNTs.

Figure 2 shows the TEM images of pristine MWCNTs (Figure 2a), COOH-MWCNTs (Figure 2b), and acryl-MWCNTs (Figure 2c). Figure 2a shows that the outer diameter of pristine MWCNTs is 11 nm, which is in accordance with the information provided by the manufacturer (diameter: 10−50 nm) . The morphology of the pristine MWCNTs consists of a layer-by-layer graphitic structure with close distances between the interspaces of walls. The morphology of the COOH-MWCNTs (Figure 2b) shows an imperfect structure in the outermost layers, which is attributed to disordered and amorphous carbons.[16] When pristine MWCNTs are oxidized, the fundamental graphitic structures and tubular shapes are maintained; however, several graphitic layers are etched by the acid treatment. The morphology of the acryl-MWCNTs (Figure 2c) shows an apparent rough coating on the surface of the MWCNTs, which is attributed to the acryl-functionalized layer on the tube walls. This thin layer is the direct evidence

that indicates the successful and effective grafting of the acrylic functional groups onto the MWCNT walls.

The XPS analysis was used to elucidate the surface composition of the MWCNTs for further characterizing their modification and to detect the functional groups on the MWCNTs based on chemical shift observations. A survey scan was performed to examine the elemental composition of the surface of sample. The XPS survey spectra of the pristine MWCNTs, COOH-MWCNTs, and acryl-MWCNTs are shown in Figure 3. COOH-MWCNTs show a significant
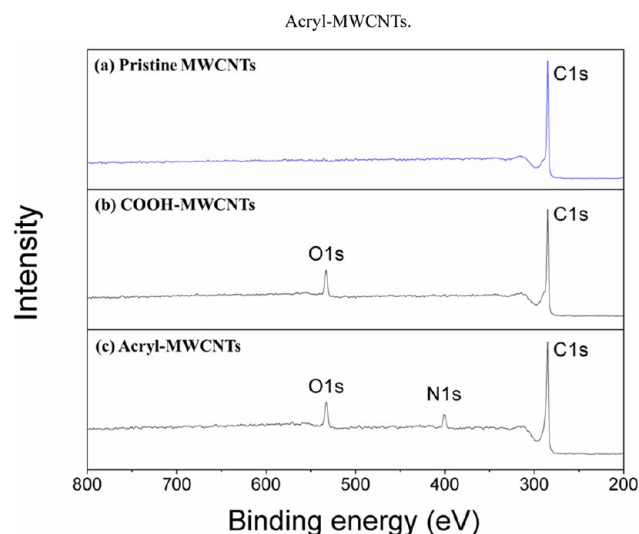

Figure 3. High resolution XPS survey scans of (a) pristine MWCNTs, (b) COOH-MWCNTs, and (c) acryl-MWCNTs.

increase in the O1s peak compared to pristine MWCNTs after acid treatment. This increased intensity in the elements is due to the oxygen-containing functional groups, which confirms the successful acidification of the MWCNTs. COOH-MWCNTs were further functionalized with acrylamide. The acryl-MWCNTs show a significant increase in the N1s peak compared to COOH-MWCNTs. This increased nitrogen peak intensity is due to the amine functional group of acrylamide which was reacted with the COOH functional groups and then was grafted onto the surface of the MWCNTs. The N1s peak confirms the successful modification of acryl-MWCNTs.

A detailed analysis of the XPS spectra provides clear evidence that MWCNTs are chemically modified. The C1s core level spectra of the pristine MWCNTs are presented in Figure 4, and the major peaks of the pristine MWCNTs appeared at 284.5 eV (C=C), 285.2 eV (C−C), and 290.5 eV (π−π*), which are attributed to their graphitic structure.[16,22] COOH-MWCNTs possess a significant degree of oxidation in a similar manner to numerous oxygen-functional groups such as the C−OH (286.5 eV) and O−C=O (288.9 eV).[17,22] Oxygen-containing functional groups on the MWCNTs can provide significant possibilities for further chemical modification. The XPS results show that an additional peak appeared at 287.3 eV for the acryl-MWCNTs, which originates from the N−C=O bonds.[18] The N−C=O peak suggests that the acrylamide monomer attaches onto the COOH-MWCNT surface by the nucleophilic attack of amine group on the COOH groups, which further alters the surface properties of the COOH-MWCNTs. Furthermore, the
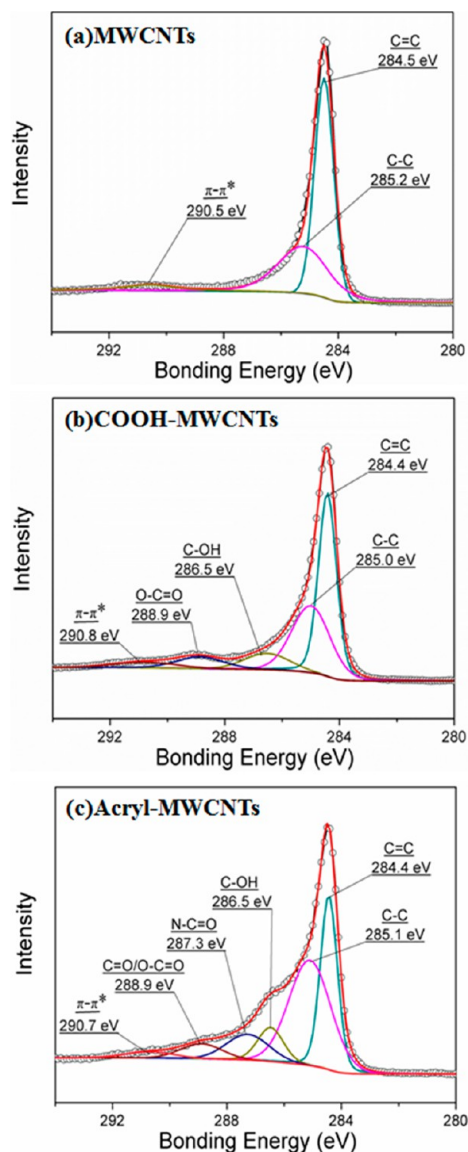
Figure 4. High resolution C1s XPS spectra of (a) pristine MWCNTs, (b) COOH-MWCNTs, and (c) acryl-MWCNT.

Figure 5. TGA curves of MWCNTs, COOH-MWCNTs, and acryl-MWCNTs (heating rate of 10 °C/min, in nitrogen).

presence of N−C═O bonds is beneficial to the expected structures of acryl-MWCNTs as shown in Figure 1.

TGA is a useful method for determining the quantity of organic substances grafted on MWCNTs. Figure 5 shows the typical TGA thermograms which indicate the weight losses of pristine MWCNTs, COOH-MWCNTs, and acryl-MWCNTs. A slight weight loss occurs below 700 °C for pristine MWCNTs, which is caused by the extensively graphitized structure. However, the extensively graphitized structure starts to oxidize at higher temperatures of approximately 800 °C.[22] The acid-treated COOH-MWCNTs exhibit significantly different weight loss curves compared to the thermal decomposition behavior of the pristine MWCNTs. A significant weight loss occurs from 125 °C, which is caused by the decomposition of acid-treated oxygen-containing functional groups (the concentration of COOH functional group on COOH-MWCNTs was exhibited in the Supporting Information). The acryl-MWCNTs show an apparent degraded curve between 125 and 500 °C (refer to the TGA data of acrylamide in the Supporting Information), which is attributed to the thermal degradation of
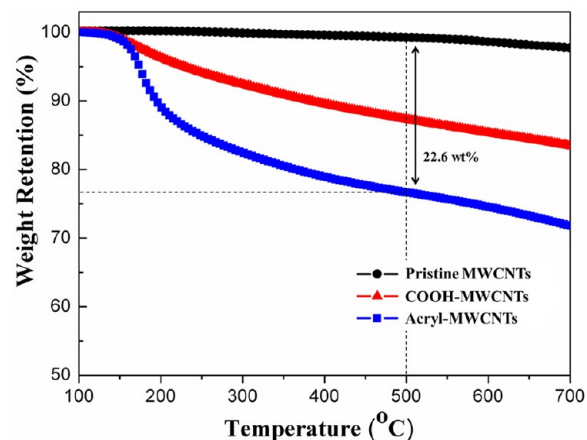
the grafted acrylamide on the surface of the acryl-MWCNTs and the residual unreacted oxygen-containing substances. Furthermore, the acryl-MWCNTs exhibit a slight weight loss between 500 and 700 °C, which is caused by the defects in the MWCNT structure (disordered and amorphous carbons) after modification.[22] Compared to the TGA curve of pristine MWCNTs at 500 °C, the TGA curve of the acryl-MWCNTs shows that the organic content and the residual unreacted oxygen-containing substances of the acryl-MWCNTs is approximately 22.6 wt %, which indicates that the grafting of acrylic functional groups onto the MWCNTs is successful.

The results from the TEM, XPS, and TGA clearly indicate that the MWCNTs were successfully functionalized by the acid treatment and acrylic functionalization processes. This study shows an effective method for altering the surface properties of MWCNTs. The effective dispersion of modified MWCNTs in the VE polymeric matrix is expected which provides a strong interphase for improving the reinforcement in CF/VE-based composites compared to pristine MWCNTs.3.2

3.2. Mechanical Properties of the MWCNTs/CF/VE Composites. This study compared the flexural strengths and moduli of pristine MWCNTs, COOH-MWCNTs, and acryl-MWCNTs in CF/VE-based composite at various MWCNT contents (0.25, 0.5, 0.75, and 1 phr) to investigate their reinforcement effects. Five samples were tested for each composite. Flexural strengths and moduli of composites are shown in Figure 6 and Table 1. Flexural strength of composite increases from 368.3 to 406.8 MPa (approximately increases 10.4% over neat CF/VE composites), and the flexural modulus increases from 45.5 to 47.8 GPa (approximately increases 5.1% over neat CF/VE composites) when the pristine MWCNT content increased from 0 to 0.5 phr. Moreover, as the pristine MWCNT content increases from 0.5 to 0.75 and 1.0 phr, the flexural strength of the pristine MWCNT/CF/VE composite decreased slightly; a similar trend is observed for their flexural modulus. When the filler reaches a critical content, the distance between any two MWCNTs is very short so that van der Waals forces become significant, and the MWCNTs may agglomerate and entangle (as can be seen from SEM images of Figure 7a,b), which reduce the effective contact area of the MWCNTs between VE polymer matrix. Consequently, the reinforcement between MWCNTs and VE polymeric matrix is weakened and results in a lower reinforcing efficiency.
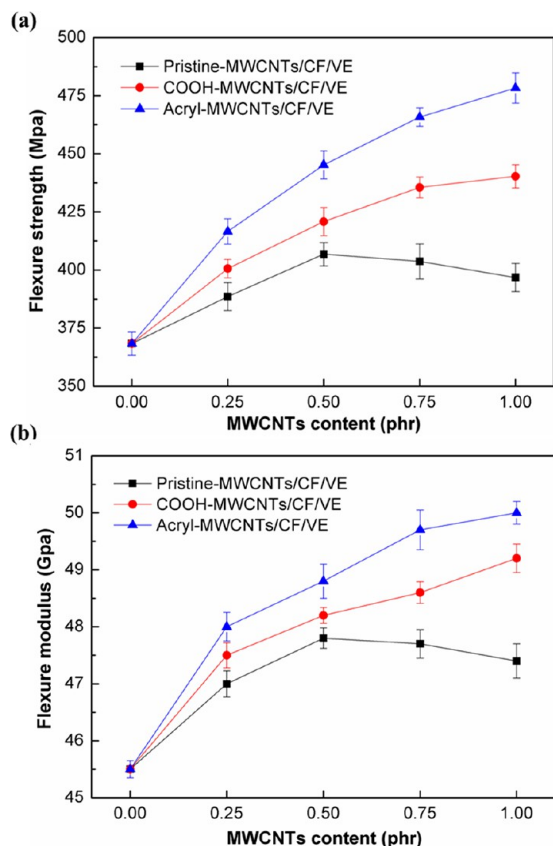
Figure 6. (a) Flexure strength and (b) flexure modulus of MWCNTs/CF/VE composites.

Table 1. Mechanical Properties of the MWCNTs/CF/VE Composites

sample	flexure strength (Mpa)	flexure modulus (Gpa)
neat CF/VE	368.3 ± 5.1	45.5 ± 0.1
0.25 phr pristine MWCNTs/CF/VE	388.6 ± 5.9	47.0 ± 0.2
0.5 phr pristine MWCNTs/CF/VE	406.8 ± 4.8	47.8 ± 0.1
0.75 phr pristine MWCNTs/CF/VE	403.7 ± 7.6	47.7 ± 0.2
1.0 phr pristine MWCNTs/CF/VE	396.8 ± 6.2	47.4 ± 0.3
0.25 phr COOH-MWCNTs/CF/VE	400.6 ± 4.9	47.5 ± 0.2
0.5 phr COOH-MWCNTs/CF/VE	420.8 ± 6.1	48.2 ± 0.1
0.75 phr COOH-MWCNTs/CF/VE	435.5 ± 4.6	48.6 ± 0.1
1.0 phr COOH-MWCNTs/CF/VE	440.3 ± 5.2	49.2 ± 0.2
0.25 phr Acryl-M WCNTs/CF/VE	416.6 ± 5.6	48.0 ± 0.2
0.5 phr acryl-M WCNTs/CF/VE	445.2 ± 5.9	48.8 ± 0.2
0.75 phr acryl-MWCNTs/CF/VE	465.8 ± 3.8	49.7 ± 0.3
1.0 phr acryl-MWCNTs/CF/VE	478.3 ± 6.6	50.0 ± 0.1

As the acid treated COOH-MWCNT content in the composite increased from 0 to 1.0 phr, the flexural strength and modulus of COOH-MWCNT/CF/VE composite increased from 368.3 MPa and 45.5 GPa to 440.3 MPa (approximately increased 19.5% compared to neat CF/VE composites) and 49.2 GPa (approximately increased 8.1% over neat CF/VE composites), respectively. The reinforcing efficiency of the well-dispersed COOH-MWCNTs is significantly higher than that of pristine MWCNTs, which is consistent with the SEM observations (as shown in SEM images of Figure 7c,d). However, the interphase between the
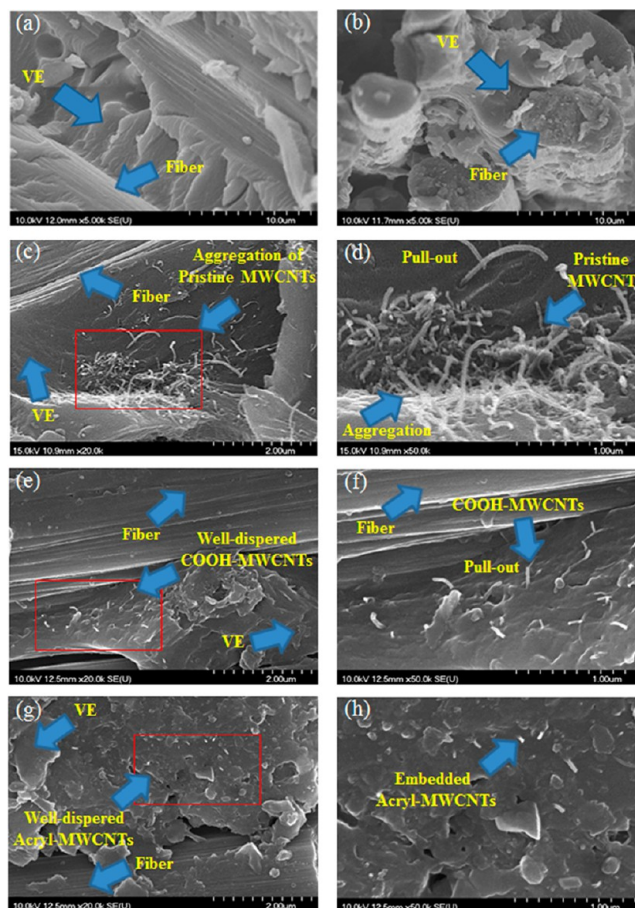

Figure 7. SEM images of a fractured surface of (a) and (b) neat CF/VE (×5k), (c) 0.75 phr pristine MWCNTs/CF/VE (×10k), (d) 0.75 phr pristine MWCNTs/CF/VE (×50k), (e) 0.75 phr COOH-MWCNTs/CF/VE (×10k), (f) 0.75 phr COOH-MWCNTs/CF/VE (×50k), (g) 0.75 phr acryl-MWCNTs/CF/VE (×10k), and (h) 0.75 phr acryl-MWCNTs/CF/VE (×50k).

COOH-MWCNTs and VE polymer segment is still too weak to promote the load transfer effectively.

The flexural strength and modulus of the acryl-MWCNT/CF/VE composites containing 1 phr acryl-MWCNTs increased to 478.3 MPa and 50.0 GPa, respectively, which were increased by 29.8% and 9.9% compared to those of neat CF/VE composites, indicating that acryl-MWCNTs are highly efficient in reinforcing VE polymers and promoting the load transfer from VE polymers to CF. Compared to the increase of flexural strength of composites with functionalized MWCNTs, the composites do not exhibit great change on the moduli of composites with functionalized MWCNTs, since this study used functionalized MWCNTs to reinforce the VE matrix, enhancing the main performance of VE matrix and promoting the load transfer from VE polymers to CF. Furthermore, the weight fraction of CF was 67−69 wt % and had the highest percentage in composites. Comparing VE to CF, the CF (200−600 GPa of moduli) possesses much higher moduli than VE (3.1−3.4 GPa of moduli) polymeric matrix. Therefore, the carbon fiber had a main influence on the moduli of the composites, and the composites do not exhibit great change on the moduli of composites with MWCNT functionalization.

This significant improvement in efficiency may be attributed to the molecular-level dispersion of acryl-MWCNTs in the polymeric matrix and the formation of a strong interfacial force

between MWCNTs and the VE matrix. This strong interface may benefit from the oxygen-containing functional groups that result from the acid treatment and the vinylic functional groups on the acryl-MWCNT surface which are the free-radical polymerization with VE.

3.3. Fractured Morphology of MWCNTs/CF/VE Composites. High-resolution SEM images of the fractured surfaces of the composites (as shown in Figure 7) were used to investigate the dispersion and compatibility of the MWCNTs in the VE matrix after the flexural test. The SEM images of the CF/VE-based composites with pristine MWCNTs, as shown in Figure 7c,d, indicate that serious MWCNT agglomerations occurred due to the high degree of entanglement of the pristine MWCNTs. However, COOH-MWCNTs exhibit a better dispersion than pristine MWCNTs since there is an existence of oxygen-containing functional groups on the surface of the MWCNTs, which can promote the disentanglement of MWCNTs as shown in Figure 7e,f. Although the oxygen-containing functional groups in COOH-MWCNTs should effectively prohibit the aggregation of the MWCNTs, MWCNTs can be pulled out easily due to the weak interface between MWCNTs and VE. The SEM images of the acryl-MWCNTs as shown in Figure 7g,h indicate that there is nearly no agglomerates formed, suggesting that acryl-MWCNTs were well dispersed in acryl-MWCNT/CF/VE composites. Furthermore, the acryl-MWCNTs are embedded in the VE matrix tightly, which may improve the interfacial strength and homogeneity of acryl-MWCNT/CF/VE composites. Therefore, the surface of acryl-MWCNTs with acryl functional groups can provide reactive sites for free-radical polymerization; the higher cross-linking density can construct a strong interface to achieve a superior reinforcement efficiency by adding acryl-MWCNTs to the composites.

3.4. Thermal Properties of the MWCNTs/CF/VE Composites. The coefficients of thermal expansion (CTE) and glass transition temperature (T_g) of MWCNT/CF/VE composites were analyzed by TMA, which can provide information of the interfacial interaction between the VE matrix and MWCNTs (as shown in Figure 8 and Table 2). Previous studies[20,23] showed that incorporating pristine MWCNTs into polymer matrixes through blending generally decreased the thermal properties due to the presence of aggregated MWCNTs which cause an increase in viscosity and steric hindrance, that will affect the cross-linking density of a composite. The low cross-linking density in a composite leads to an increase in mobility for polymer segments. The experimental data of the pristine MWCNT/CF/VE composites in this study also showed similar results to those of previous studies.[24] The T_g and CTE of the COOH-MWCNT/CF/VE composites show better improvement compared to the pristine MWCNT/CF/VE composites. The T_g of neat CF/VE is 98.6 °C, and the T_g of the COOH-MWCNTs/CF/VE composites containing 1.0 phr COOH-MWCNTs increased to 112.2 °C. Incorporating 1.0 phr COOH-MWCNTs into the VE matrix significantly reduced the CTE from 47.6 to 40.1 ppm/°C. The T_g of the acryl-MWCNT/CF/VE composites containing 1.0 phr acryl-MWCNTs is 118.5 °C, which is significantly higher than that of neat CF/VE composites (98.6 °C). Moreover, the CTE of acryl-MWCNT/CF/VE composites containing 1 phr acryl-MWCNTs decreases significantly compared to neat CF/VE composites (from 47.6 to 35.2 ppm/°C), indicating that the incorporation of acryl-MWCNTs into the VE matrix efficiently restricts the mobility of polymer chains in the existing covalent
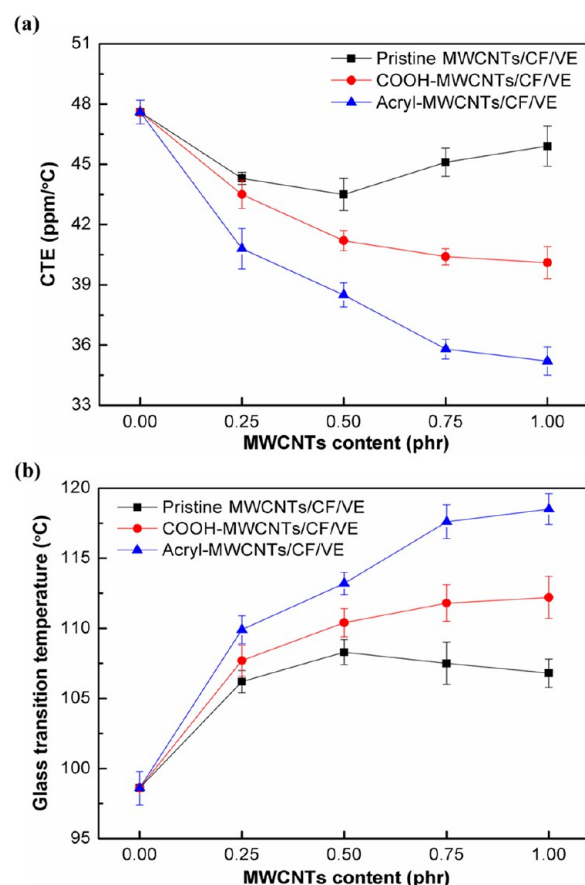

Figure 8. (a) CTE and (b) T_g of MWCNTs/CF/VE composites.

Table 2. Thermal Properties of the MWCNTs/CF/VE Composites

sample	CTE (ppm/°C)	T_g (°C)
neat CF/VE	47.6 ± 0.6	98.6 ± 1.2
0.25 phr pristine MWCNTs/CF/VE	44.3 ± 0.3	106.2 ± 0.8
0.5 phr pristine MWCNTs/CF/VE	43.5 ± 0.8	108.3 ± 0.9
0.75 phr pristine MWCNTs/CF/VE	45.1 ± 0.7	107.5 ± 1.5
1.0 phr pristine MWCNTs/CF/VE	45.9 ± 1.0	106.8 ± 1.1
0.25 phr COOH-MWCNTs/CF/VE	43.5 ± 0.7	107.7 ± 1.2
0.5 phr COOH-MWCNTs/CF/VE	41.2 ± 0.5	110.4 ± 1.0
0.75 phr COOH-MWCNTs/CF/VE	40.4 ± 0.4	111.8 ± 1.3
1.0 phr COOH-MWCNTs/CF/VE	40.1 ± 0.8	112.2 ± 1.5
0.25 phr acryl-MWCNTs/CF/VE	40.8 ± 1.0	109.9 ± 0.9
0.5 phr acryl-MWCNTs/CF/VE	38.5 ± 0.6	113.2 ± 0.8
0.75 phr acryl-MWCNTs/CF/VE	35.8 ± 0.5	117.6 ± 1.2
1.0 phr acryl-MWCNTs/CF/VE	35.2 ± 0.7	118.5 ± 1.1

bonds between the interphases of the VE matrix and MWCNTs. The reinforcement efficiencies of the pristine MWCNTs and COOH-MWCNTs are obviously lower compared to that of acryl-MWCNTs, which is in accordance with the results from the SEM and flexural properties. Two reasons were proposed to explain the improvement in the mechanical and thermal properties of the acryl-MWCNT/CF/VE composites (as shown in Figure 9) are as follows: (1) the acryl-functionalized COOH-MWCNTs with oxygen-containing functional groups can maintain the molecular-level dispersion of MWCNTs within the VE matrix, which forms a 3D network throughout the whole polymer matrix, providing a large contact area between the MWCNTs and VE polymer and (2) the acryl-
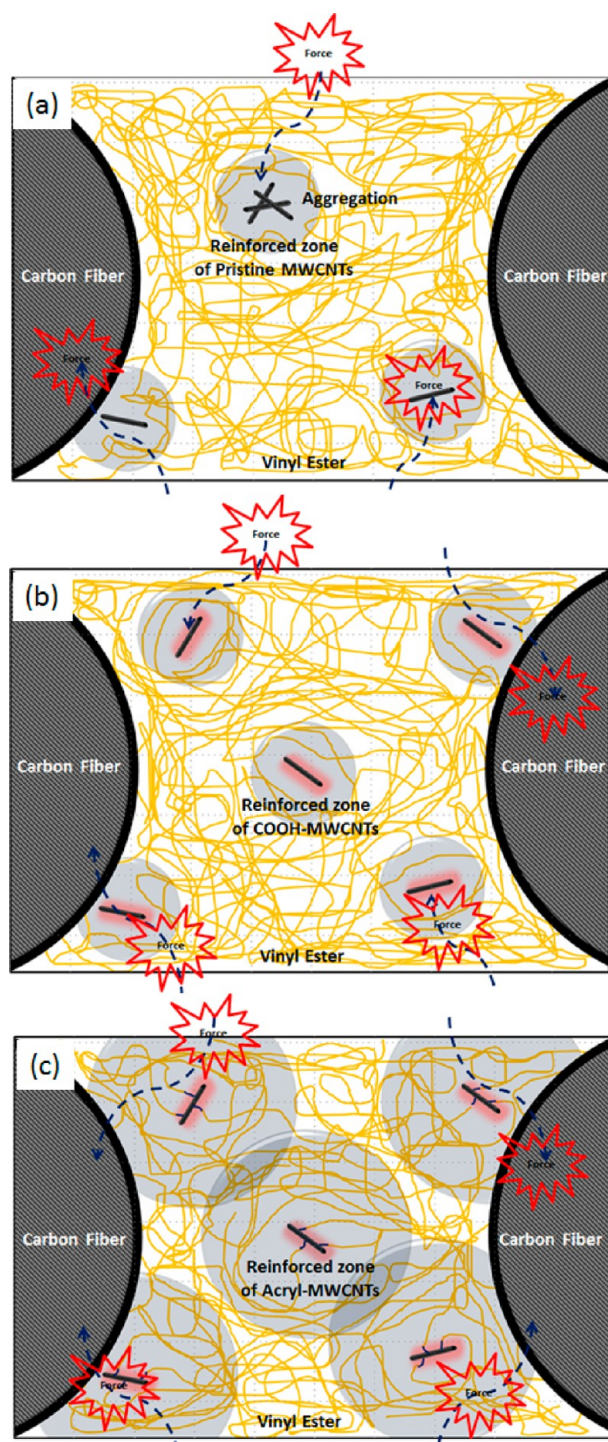
Figure 9. Proposed model of the reinforcing MWCNTs of (a) pristine MWCNTs/CF/VE and (b) COOH-MWCNTs/CF/VE and (c) acryl-MWCNTs/CF/VE composites.

functionalized surface of the MWCNTs can provide reaction sites for free-radical polymerization; the high cross-linking density can construct a hierarchical and covalently bonded interphase structure between the acryl-functionalized MWCNTs and VE, which results in a strong interfacial interaction and restrains the movement of polymer segments. The excellent reinforcement effect of acryl-MWCNTs provides a higher ability for loading the stress in the VE polymeric matrix

and has a critical role in promoting load transfer from VE polymer to CF.

4. CONCLUSION

The results of TEM, XPS, and TGA confirm the successful modification of the MWCNTs in this study. The pristine MWCNTs were oxidized with an acid treatment. The acrylic functional groups were successfully grafted onto the surfaces of the COOH-MWCNTs, forming the acryl-MWCNTs. Three types of MWCNTs (pristine MWCNTs, COOH-MWCNTs, and acryl-MWCNTs) were used to reinforce the CF/VE-based composites. The acryl-functionalized MWCNTs can participate in the free-radical polymerization of VE matrix when these were used to reinforce the CF/VE-based composites, which results in well-dispersing MWCNTs in the VE matrix and establishing a strong interfacial interaction between the MWCNTs and the VE matrix to promote the transfer of stress from the VE to CF. The results of the SEM and TMA and mechanical properties indicated that the acryl-MWCNT/CF/VE composites with 1.0 phr acryl-MWCNT exhibited an improvement of 29.8% in flexural strength and 9.9% in flexural modulus compared to neat CF/VE composites. Moreover, the CTE was decreased significantly from 47.6 ppm/°C (neat CF/VE composite) to 35.2 ppm/°C for the acryl-MWCNT/CF/VE composites with 1.0 phr acryl-MWCNT content. Furthermore, the T_g of the acryl-MWCNT/CF/VE composites containing 1.0 phr acryl-MWCNT (118.5 °C) is significantly higher than that of neat CF/VE composites (98.6 °C). The acryl-MWCNT showed the best reinforcement efficiency among three types of MWCNTs used. The acryl-MWCNT/CF/VE composites exhibit an excellent performance in mechanical properties and thermal and dimensional stability.

ASSOCIATED CONTENT

Supporting Information
Table of titration results; TGA curves of acrylamide. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes
The authors declare no competing financial interest.

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