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# Nanocomposites based on vapor-grown carbon nanofibers and an epoxy: Functionalization, preparation and characterization

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ABSTRACT

Vapor-grown carbon nanofibers (VGCNF) were functionalized with amine-containing pendants via a Friedel–Crafts acylation reaction with 4-(3-aminophenoxy)benzoic acid. The resulting $H_2N$-VGCNF was treated with epichlorohydrin, followed by sodium hydroxide solution to afford N,N-diglycidyl-modified VGCNF that is designated as epoxy-VGCNF. Subsequently, epoxy-VGCNF was dispersed in an epoxy resin (Epon 862) with the aid of acetone and sonication. After acetone had been removed under vacuum from the mixture, curing agent "W" was added to epoxy-VGCNF/Epon 862 mixture, which was then poured into molds and cured at 250 °F (121 °C) for 2 h and 350 °F (177 °C) for 2 h to form a series of epoxy/fVGCNF samples; fVGCNF designated for "functionalized VGCNF" was used to denote our belief that all epoxy functions have reacted in the resulting nanocomposites. The VGCNF content was increased from 0.10 to 10.0 wt%. For comparison purposes, the pristine VGCNF or pVGCNF (0.1–5.0 wt%) was also used in the in situ polymerization of Epon 862 and curing agent "W" to afford another series of epoxy/pVGCNF samples. The epoxy-VGCNF showed a better dispersion in the epoxy resin than pVGCNF according to SEM results. Both the tensile moduli and strengths of epoxy/fVGCNF nanocomposites are higher than those of epoxy/pVGCNF. The additive effect of VGCNF on glass-transition ($T_g$) was discussed in terms of thermal analysis results. The thermal stability of the nanocomposites was investigated by thermogravimetric analysis (TGA).

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## 1. Introduction

It is well known that carbon nanotube (CNT) or carbon nanofiber (CNF) exhibits superior elastic moduli and strengths as well as high electrical and thermal conductivities, which are important for developing advanced multifunctional nanocomposites [1,2]. Therefore, they are being actively investigated with respect to their structural reinforcement, energy/electron transport or storage capabilities, and interactions with electromagnetic waves as well as the efficient ways to transfer their outstanding properties to the polymeric matrices. CNFs, which are more economical than CNT's (about 3–500 times cheaper than CNT), are typically produced by a vapor-phase catalytic process in which a carbon-containing feedstock (e.g. $CH_4$, $C_2H_2$, $C_2H_4$ etc.) is pyrolyzed in the presence of small metal catalyst (e.g. ferrocene, $Fe(CO)_5$ etc.) and have an outer diameter of 60–200 nm, a hollow core of 30–90 nm, and length on the order of 50–100 μm [3,4]. It follows that having aspect ratios (length/diameter) of greater than 800 should make them useful as nano-level reinforcement for polymeric matrices. Furthermore, since their inherent electrical and thermal transport properties are also excellent, there are many

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14. ABSTRACT

**Vapor-grown carbon nanofibers (VGCNF) were functionalized with amine-containing pendants via a Friedel?Crafts acylation reaction with 4-(3-aminophenoxy)benzoic acid. The resulting H2N-VGCNF was treated with epichlorohydrin, followed by sodium hydroxide solution to afford N,N-diglycidyl-modified VGCNF that is designated as epoxy-VGCNF. Subsequently epoxy-VGCNF was dispersed in an epoxy resin (Epon 862) with the aid of acetone and sonication. After acetone had been removed under vacuum from the mixture curing agent ??W? was added to epoxy-VGCNF/Epon 862 mixture, which was then poured into molds and cured at 250 F (121 C) for 2 h and 350 F (177 C) for 2 h to form a series of epoxy/fVGCNF samples; fVGCNF designated for ??functionalized VGCNF? was used to denote our belief that all epoxy functions have reacted in the resulting nanocomposites. The VGCNF content was increased from 0.10 to 10.0 wt%. For comparison purposes, the pristine VGCNF or pVGCNF (0.1?5.0 wt%) was also used in the in situ polymerization of Epon 862 and curing agent ??W? to afford another series of epoxy/pVGCNF samples. The epoxy-VGCNF showed a better dispersion in the epoxy resin than pVGCNF according to SEM results. Both the tensile moduli and strengths of epoxy/fVGCNF nanocomposites are higher than those of epoxy/pVGCNF. The additive effect of VGCNF on glass-transition (Tg) was discussed in terms of thermal analysis results. The thermal stability of the nanocomposites was investigated by thermogravimetric analysis (TGA).**

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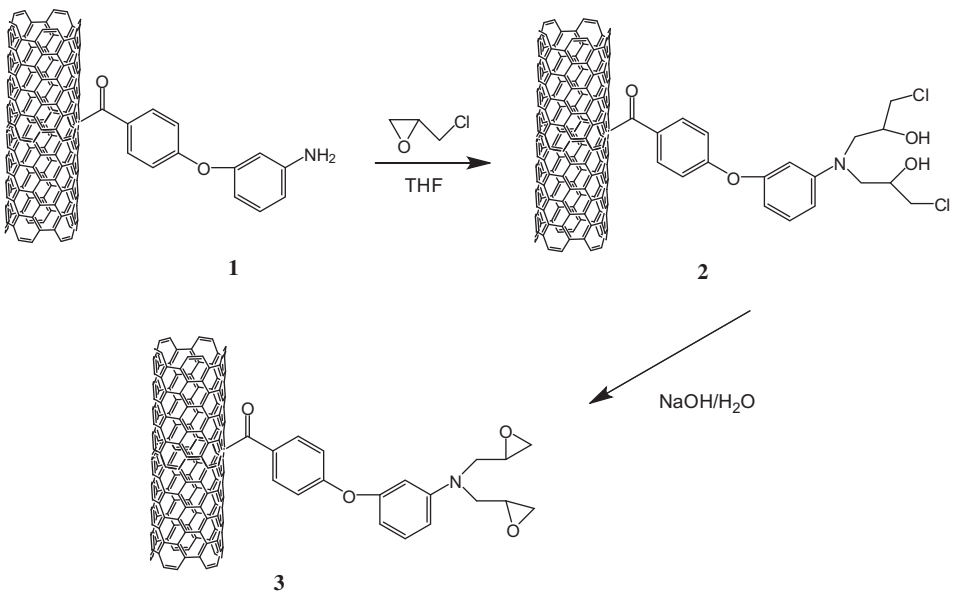
innovative possibilities for tailoring their polymer matrix composites into cost-effective, multifunctional materials. Thus, many studies related to the enhancement of the mechanical properties of an epoxy matrix by the introduction of CNF have been conducted [5–7]. Efforts to achieve homogeneous dispersion of CNFs in epoxies via chemical methods using strong acids such as sulfuric acid and nitric acid [8–10] or more elaborated schemes [11,12] have been investigated. However, strong/oxidizing acid treatment entails harsh reaction conditions, and has often brought about structural damage to CNTs, which would dramatically decrease the conductivity and mechanical properties of CNTs.

We have developed a relatively mild method to directly arylcarbonylate vapor-grown carbon nanofibers (VGCNF) via Friedel–Crafts (F–C) acylation reaction in poly(phosphoric acid) (PPA) with aromatic carboxylic acids, and also applied the technique to graft linear and hyperbranched poly(ether-ketone)s onto pristine CNF/carbon nanotube (CNT) to generate the so-called in situ nanocomposites in a one-pot fashion [13–18]. Subsequently, in addition to




**Scheme 1.** Synthesis of epoxy-VGCNF (**3**).

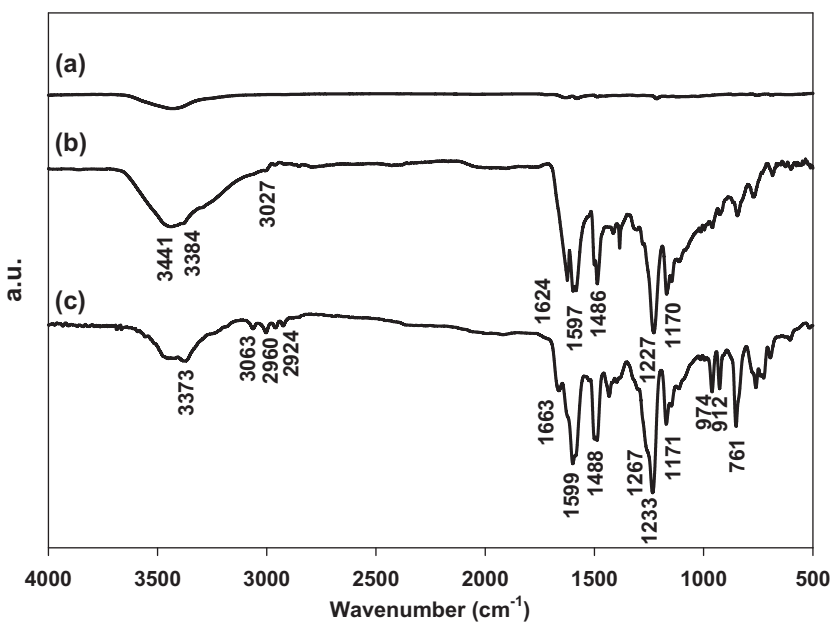



**Fig. 1.** FT-IR spectra of (a) pristine VGCNF, (b) $NH_2$-VGCNF and (c) epoxy-VGCNF.

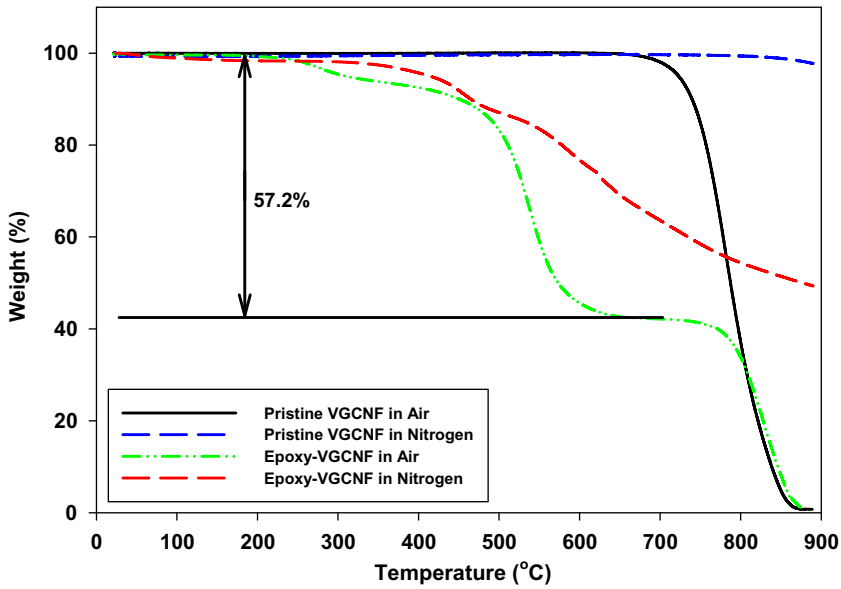



**Fig. 2.** TGA thermograms of pristine VGCNF and epoxy-VGCNF with heating rate of 10 °C/min.

extending the applicability of this functionalization method to MWNT, we also have found useful functionalities as part of aromatic pendants such as OH and $NH_2$ to be chemically unaffected in the PPA-promoted F–C acylation. Thus, when VGCNF was treated with (3-aminophenoxy)benzoic acid in PPA, $NH_2$-functionalized carbon nanofiber, i.e., $H_2N$-VGCNF, could be prepared with the degree of functionalization of ~5 atom%, and it was subsequently used to participate (co-react) in the polycondensation of 2,2-bis(phthalic anhydride)-1,1,1,3,3,3-hexafluoroisopropane (6FDA) and 1,3-bis(3-aminophenoxy)benzene (APB) to afford a series of VGCNF/polyimide nanocomposites with interesting thermal-electrical properties [19].

Glass- or carbon-fiber thermoset composites based on epoxy resins are the mainstay materials for numerous civilian and military applications. While various versions of VGCNF with organic amine pendants have been used to serve effectively as co-curing agents and property enhancers for epoxy resins [11,20–22], it would be instructive to compare the compatibility and effectiveness of the related epoxy-functionalized CNF [23] in facilitating the processing of the nanocomposites and enhancing their properties. Thus, in this work, the aromatic amine functional group attached on the $H_2N$-VGCNF surface was converted in a two-step-one-pot reaction to N,N-diglycidylamino moiety. The resulting epoxy-VGCNF co-reacted in situ with epoxy monomers (Epon 862 and curing agent "W"), resulting in a series of dog-bone samples, which contained epoxy-VGCNF (corresponding to 0.10–10.0 wt% of basic VGCNF). For meaningful comparison, the pristine VGCNF (0.1–5.0 wt%) was also used in the in situ polymerization of Epon 862 and curing agent "W" to afford another series of dog-bone samples.

**Table 1**
Elemental analysis data for pristine and functionalized VGCNF.

| Sample | Elemental analysis | C (%) | H (%) | N (%) | O (%) |
|---|---|---|---|---|---|
| Pristine | Calcd | 100 | 0 | 0 | 0 |
| VGCNF | Found | 99.02 | 1.01 | <0.20[a] | <0.10[a] |
| Epoxy- | Calcd[b] | 82.96 | 3.22 | 2.48 | 11.33 |
| VGCNF | Found | 83.43 | 3.07 | 2.67 | 11.56 |

[a] Less than detection limit.

[b] The molecular formula of $C_{19}H_{18}NO_4$ is based on the assumption that for every 100 carbon there are five 4-[3-bis(3,4-diglycidy)aminophenoxy]benzoyl groups attached, according to TGA (air) result. The molecular formula of 4-[3-bis(3,4-diglycidyl)aminophenoxy]benzoyl group are $C_{195}H_{90}N_5O_{20}$. The calculation is based on the following equation: Theoretical weight loss at 700 °C $= \frac{n\times MW_{epoxy}}{100\times W_c + n\times MW_{epoxy}} \times 100$ where $n$ is the number of 4-[3-bis(3,4-diglycidy)aminophenoxy]benzoyl groups attached to VGCNF every 100 carbon. $MW_{epoxy}$ is the molecular weight of 4-[3-bis(3,4-diglycidy)aminophenoxy]benzoyl group, which is 2822.65. $W_c$ is the atomic weight of carbon, which is 12.01. When $n$ is equal to 5, theoretical weight loss at 700 °C is 57.2% based on above equation. This value is in good agreement with the weight loss at 700 °C (57.4%).

## 2. Experimental

### 2.1. Materials

Vapor-grown carbon nanofibers (VGCNF, PR-19-HT) were obtained from Applied Science Inc. (ASI), Cedarville, OH, USA via an Air Force contract. The carbon nanofibers had a typical diameter of 50–200 nm and lengths varying from 50 to 100 μm [24]. Both Epon 862 (a bis-phenol F epoxy) and "Epi-Cure" curing agent W were purchased from Miller-Stephenson Chemical Company, Inc. All other reagents and solvents were purchased from Aldrich Chemical Inc. and used as received, unless otherwise specified.

### 2.2. Instrumentation

Infrared (IR) spectra were recorded on a Nicolet Nexus 470 Fourier transform spectrophotometer. Elemental

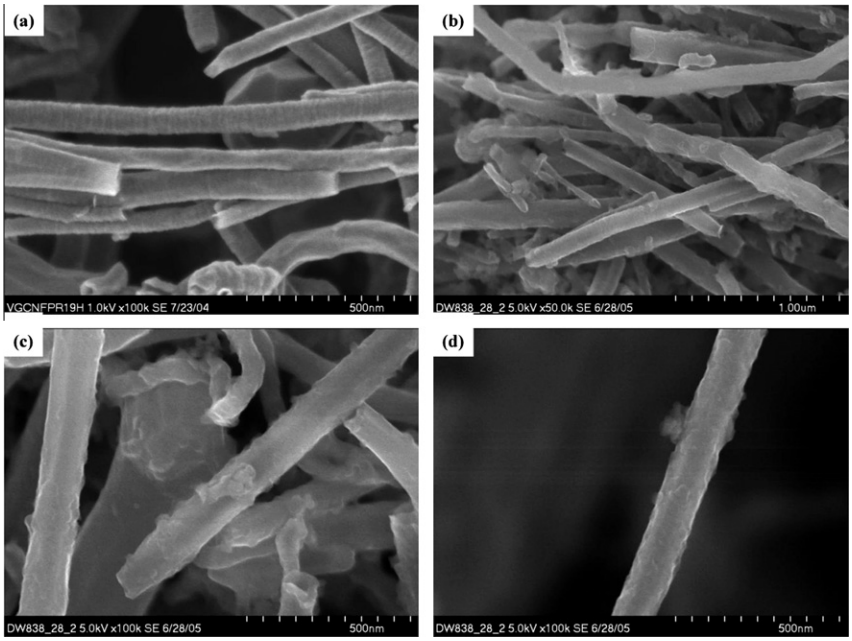
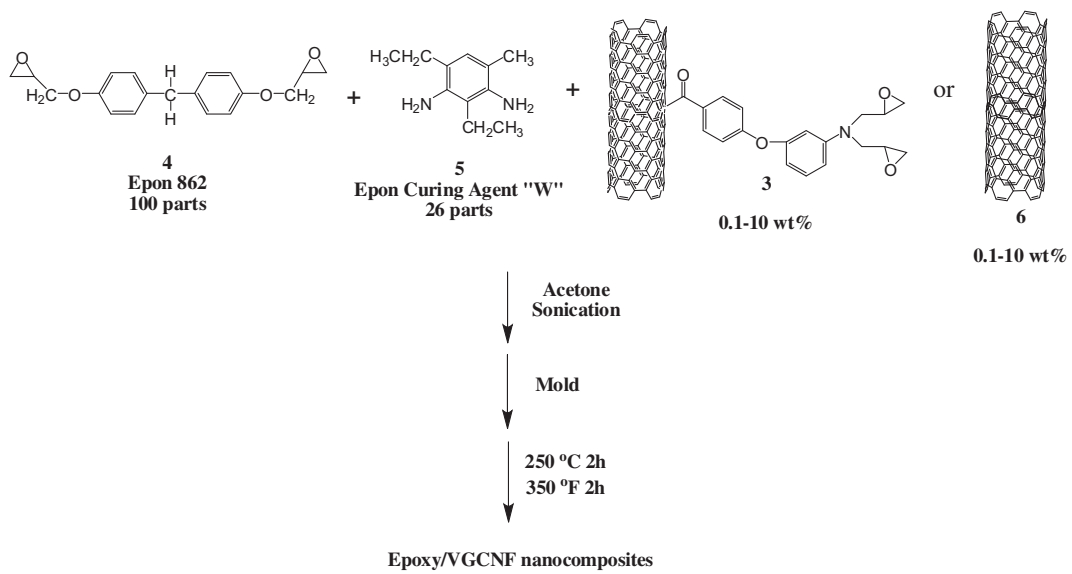



**Fig. 3.** SEM images of (a) as-received VGCNF (×100 k); (b) epoxy-VGCNF (×50 k); (c) epoxy-VGCNF (×100 k) and (d) epoxy-VGCNF (×100 k).




**Scheme 2.** Preparation of epoxy/VGCNF nanocomposites.

analysis and mass spectral analysis were performed by System Support Branch, Materials Directorate, Air Force Research Lab, Dayton, Ohio. Differential scanning calorimetry (DSC) analysis were performed in nitrogen with a heating rate of 10 °C/min using a Perkin-Elmer model 2000 thermal analyzer equipped with differential scanning calorimetry cell. Themogravimetric analysis (TGA) was conducted in nitrogen ($N_2$) and air atmospheres at a heating rate of 10 °C/min using a TA Hi-Res TGA 2950 themogravimetric analyzer. The scanning electron microscope (SEM) used in this work was Hitachi S-520. Sonication was conducted at 20 kHz with a 600 W-power using Ace Glass GEX 600-5 Ultrsonic Processor. Tensile strength and modulus were measured using a hydraulic load frame from MTS (Model# 312.11).

### *2.3. Functionalization of VGCNF with 3-aminophenoxy-4-benzoic acid (1, $H_2N$-VGCNF)*

Compound **1** was prepared according to previously reported procedure [19].

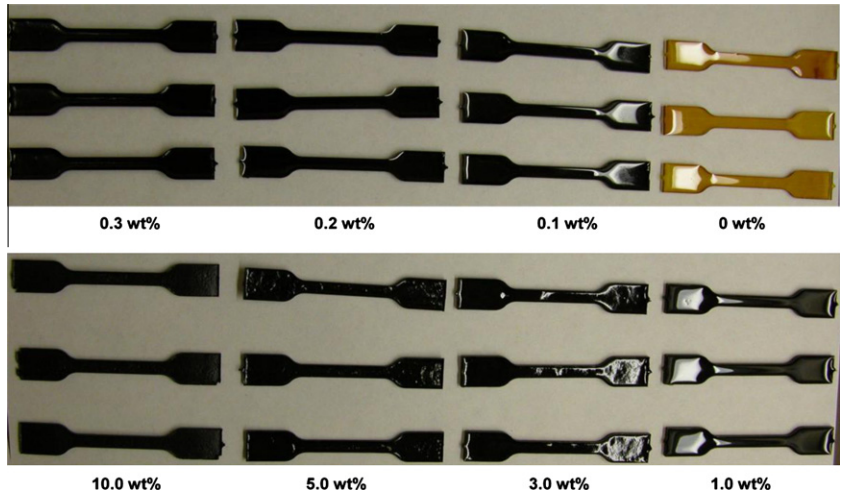



**Fig. 4.** Epoxy/fVGCNF dog-bone samples.

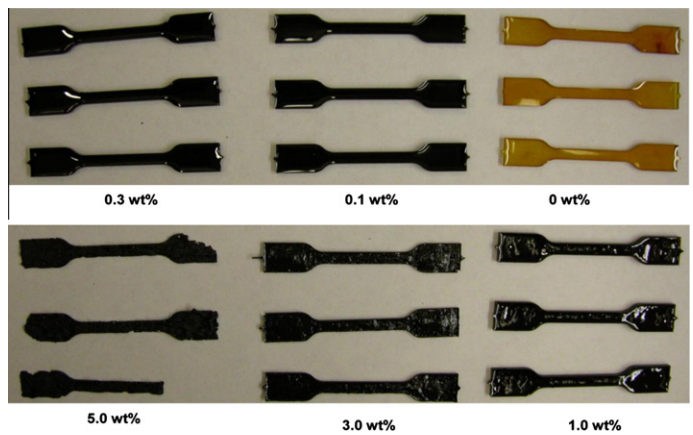



**Fig. 5.** Epoxy/pVGCNF dog-bone samples.

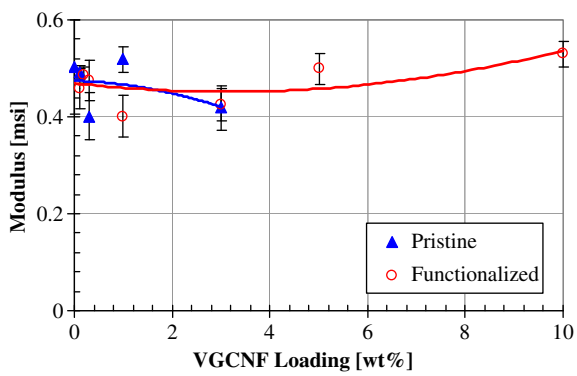



**Fig. 6.** Moduli of epoxy/VGCNF nanocomposites vs. VGCNF contents.

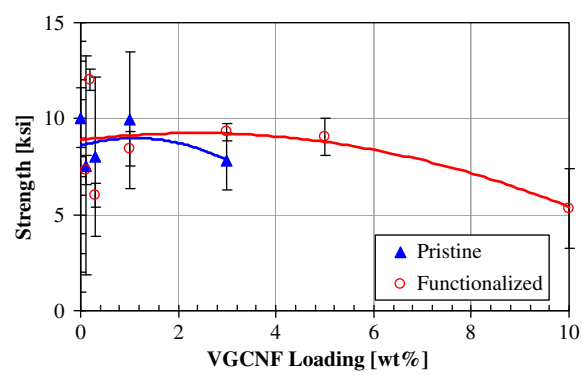



**Fig. 7.** Tensile strengths of epoxy/VGCNF nanocomposites vs. VGCNF contents.

### *2.4. Synthesis of epoxy-VGCNF (**3**)*

Into a 250 mL three-necked, round-bottomed flask equipped with a magnetic stir-bar, nitrogen inlet, $H_2N$-VGCNF (0.5 g) and THF (50 mL) were added, and the mixture was sonicated for 10 min until VGCNF was dispersed homogeneously in THF. Epichlorohydrin (5.0 g, 53.8 mmol)

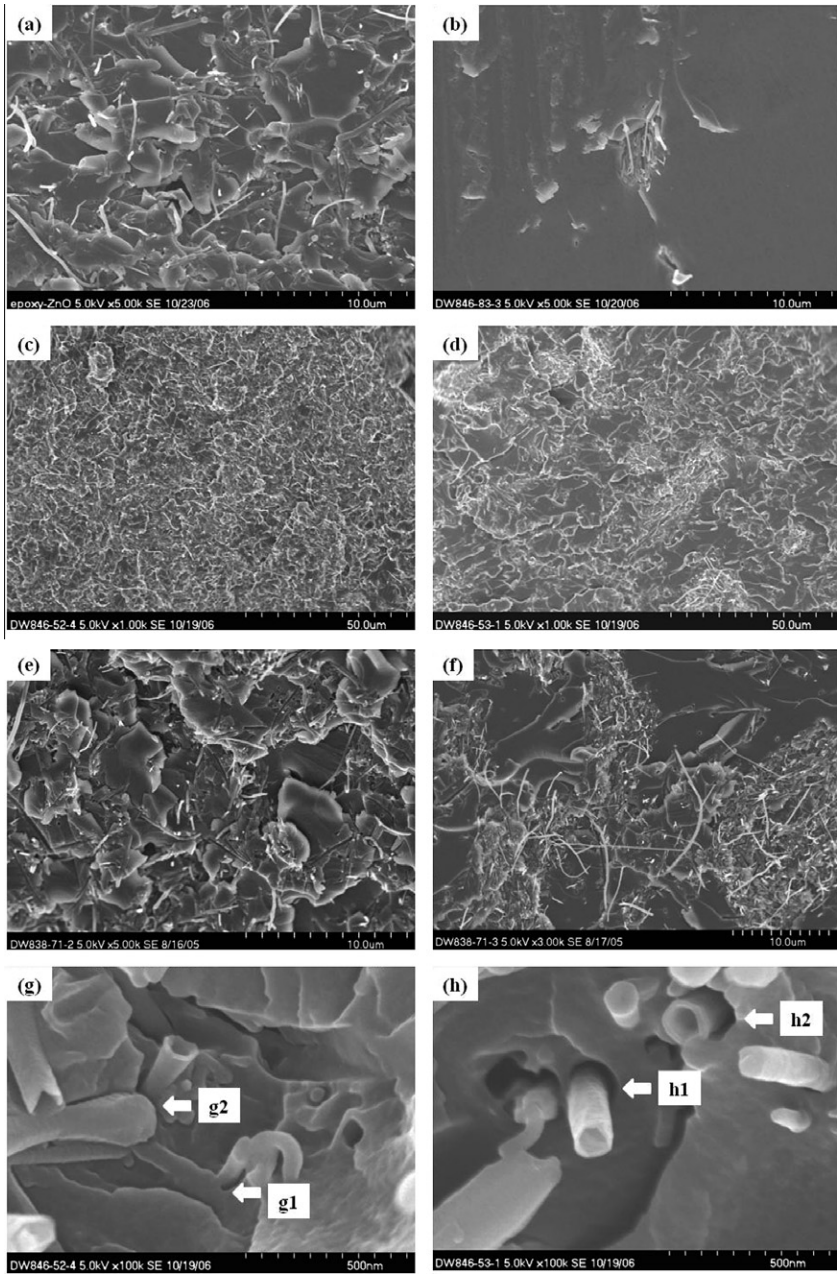



**Fig. 8.** SEM images of (a) 0.1 wt% epoxy/fVGCNF(×5 k); (b) 0.1 wt% epoxy/pVGCNF(×5 k); (c) 5 wt% epoxy/fVGCNF(×1 k); (d) 5 wt% epoxy/pVGCNF(×1 k); (e) 5 wt% epoxy/fVGCNF(×5 k); (f) 5 wt% epoxy/pVGCNF(×5 k); (g) 5 wt% epoxy/fVGCNF(×100 k) and (h) 5 wt% epoxy/pVGCNF nanocomposites(×100 k).

was then added. The resulting mixture was agitated and refluxed under dry nitrogen for 3 d. The reaction mixture was then allowed to cool to room temperature. Sodium hydroxide solution (50 wt%, 5.20 g, 65 mmol) was added, and the mixture was agitated under dry nitrogen at room temperature for 3 d. Finally, it was poured into water and the black precipitate was collected and washed with a large amount of water until pH reach neutral. The product was dried under vacuum at 50 °C for 24 h to afford 0.48 g (93%) of a black powder. Anal. Calcd. for $C_{195}H_{90}N_5O_{20}$: C, 82.96%; H, 3.22%; N: 2.48%. Found: C, 83.43%; H, 3.07%; N: 2.67%. FT-IR (KBr, $cm^{-1}$): 3373, 3063, 2960 (CH), 2924 ($CH_2$), 1663 (ketone carbonyl), 1599, 1488, 1233 $\nu_{asym}$ (Ar–O–Ar), 1267 $\nu_{sym}$ (epoxy; C–O–C), 1171, 974, 912 $\nu_{asym}$ (epoxy; C–O–C), 761.

### *2.5. Representative procedure of preparation of VGCNF/epoxy nanocomposites (epoxy resin with 5.0 wt% VGCNF load)*

Epoxy-VGCNF (2.629 g) or pristine VGCNF (1.125 g) was dispersed into Epon 862 (20.0 g) by sonicating in acetone (50 mL). Acetone was removed under vacuum at room

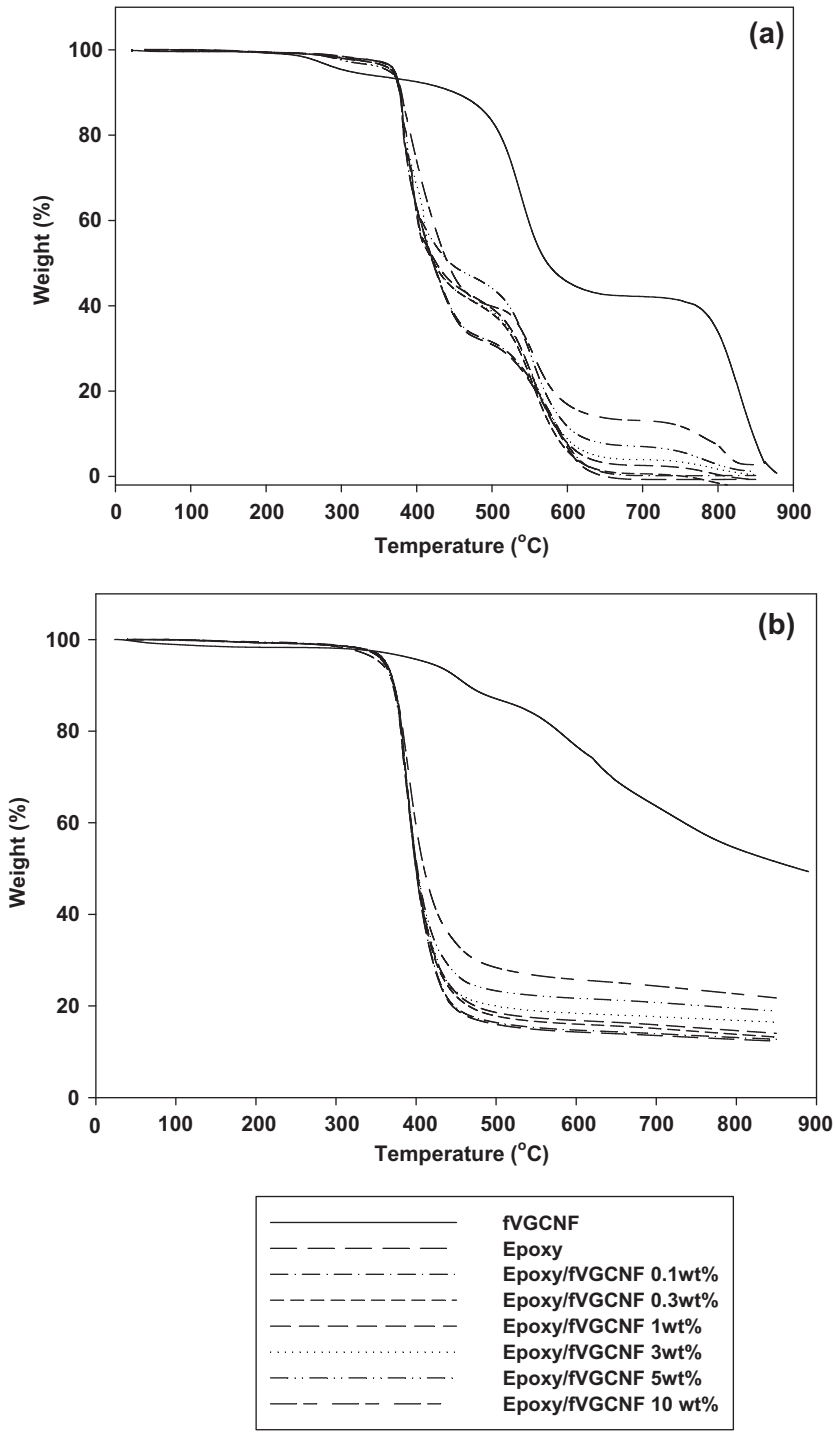



**Fig. 9.** TGA thermograms of epoxy/fVGCNF at heating rate of 10 °C/min (a) in air and (b) in nitrogen.

temperature. Then the curing agent "W" (5.2 g) was added. The viscous mixture was agitated for 30 min. The resulting viscous mixture was poured into dog-bone molds. The sample molds were placed into vacuum at 50 °C for 2 h to remove the bubbles formed. Finally, the dog-bone samples were heated using a 30-min temperature ramp from room temperature to 250 °F for 2 h, followed by a 30-min ramp from 250 to 350 °F for 2 h under $N_2$ atmosphere in an oven. They were allowed to cool to room temperature and released from silicone molds.

**Table 2**
Thermal properties of epoxy/fVGCNF nanocomposites.

| | DSC | | | | TGA | | | | |
|---|---|---|---|---|---|---|---|---|---|
| | | | | | In nitrogen | | In air | | |
| VGCNF (wt%) | $\Delta H$ (J/g) | $T_p$ (°C) | $T_{onset}$ (°C) | $T_g$[a] (°C) | $T_{d5\%}$[b] (°C) | Char[c] (%) | $T_{d5\%}$[b] (°C) | Char[c] (%) | Char[d] (%) |
| 100 | – | – | – | – | >900 | 99.7 | 723 | 98.1 | 4.9 |
| 0 (0) | 415 | 194 | 148 | 137 | 362 | 12.3 | 370 | 0.21 | 0.20 |
| 0.1 (0.23)[e] | 442 (442)[f] | 194 | 130 | 138 | 364 | 12.7 | 371 | 0.19 | 0.19 |
| 0.3 (0.69)[e] | 457 (458)[f] | 206 | 133 | 141 | 360 | 13.2 | 367 | 0.53 | 0.32 |
| 1.0 (2.33)[e] | – | – | – | 134 | 361 | 14.0 | 368 | 2.53 | 0.78 |
| 3.0 (6.99)[e] | – | – | – | 131 | 363 | 16.5 | 365 | 3.91 | 0.43 |
| 5.0 (11.6)[e] | 471 (496)[f] | 215 | 136 | 129 | 360 | 18.9 | 363 | 6.99 | 1.5 |
| 10.0 (23.3)[e] | – | – | – | 109 | 355 | 21.7 | 370 | 13.1 | 2.7 |

[a] Inflection in baseline on DSC thermogram obtained in $N_2$ at a heating rate of 10 °C/min.
[b] Temperature at which 5% weight loss recorded on TGA thermogram obtained at a heating rate of 10 °C/min.
[c] Char yield at 700 °C.
[d] Char yield at 850 °C.
[e] The values for the wt% based on epoxy-VGCNF are in the parenthesis.
[f] Normalized values are in the parenthesis.

## 3. Results and discussion

### 3.1. Synthesis and characterization of epoxy-VGCNF

VGCNF used in this work had been thermally stripped at temperatures up to 3000 °C to graphitize any amorphous carbons. It is a complex mixture comprised of multi-walled carbon nanotubes with straight, helical, nested and bamboo configurations, of which the latter two are dominant. While the bamboo configuration is similar to that of the straight, multi-walled nanofibers, except for the presence of nodes (defect sites) along their lengths, the nested CNF, also known as fish-bone type, has an orientation similar to that of a stack of Dixie cups with a hollow core and the defect sites at the "cup rims" [25,26]. We believe that VGCNF were functionalized with amine-containing pendants at the defect sites via a Friedel–Crafts acylation reaction with 4-(3-aminophenoxy)benzoic acid to afford $H_2N$-VGCNF (**1**) with ca. 5 atom% functionalization [19a]. The resulting $H_2N$-VGCNF was subsequently treated with epichlorohydrin to form the open-chain intermediate **2**, which was directly converted to oxirane (epoxy) ring using sodium hydroxide aq. solution to afford the epoxy-containing product, epoxy-VGCNF (**3**, Scheme 1). Compound **3** exhibits the symmetrical of epoxy ring at ~1270 $cm^{-1}$ and asymmetrical $\nu$(C–O–C) at 912 $cm^{-1}$ as well as the associated aliphatic C–H bands at 2959 and 2924 $cm^{-1}$ (Fig. 1). The vibration band of carbonyl group in epoxy-VGCNF was unexpectedly shifted, but still within the range, from 1624 $cm^{-1}$ (in $H_2N$-VGCNF) to 1663 $cm^{-1}$. The very weak band at 3373 $cm^{-1}$ on top of the broad $\nu$(OH) band (due to difficult-to-remove water of crystallization in KBr) could be attributed to the presence of small amount of secondary amine.

The pristine VGCNF exhibited excellent thermal stability in both air and nitrogen as shown in Fig. 2. However, epoxy-VGCNF started to lose weight at 253 °C in air, and 234 °C in nitrogen, respectively, due to the decomposition of organic epoxy groups. The TGA curve taken in air showed a two-stage degradation. Epoxy-VGCNF lost 57.2% of weight between 250 and 700 °C, attributable to the loss of arylcarbonyl substituents, with 42.8% of residue at 700 °C due to VGCNF. Based on TGA and element analysis results (Table 1 and Fig. 2), we concluded that there were approximately five arylcarbonyl groups covalently attached to the nanofiber surface for every 100 carbon sites. SEM reveals that the pristine VGCNF exhibits smooth textures such as stacked Dixie cups on the surface whereas the rough surfaces of the functionalized VGCNF are clearly indicative of modification with organic moieties (Fig. 3).

### 3.2. Preparation of VGCNF/epoxy nanocomposites

Epoxy-VGCNF (corresponding to 0.10–10.0 wt% of basic VGCNF composition) and the pristine VGCNF (0.1–5.0 wt%) were mixed with Epon 862 and curing agent W with the aid of both acetone and sonication. The viscous mixtures were poured into the silicone "dog-bone" molds and cured to afford a series of epoxy/epoxy-VGCNF nanocomposites (designated as epoxy/fVGCNF) and a series of epoxy/pristine VGCNF nanocomposites (designated as epoxy/pVGCNF) as shown in Scheme 2. While epoxy-VGCNF could be mixed with epoxy up to 10 wt% (Fig. 4), the maximum content of the pristine VGCNF was 3 wt%. The mixture containing 5 wt% of pristine VGCNF was too viscous to be processed. As a result, only broken dog-bone samples were obtained (Fig. 5).

### 3.3. Mechanical properties of epoxy/VGCNF nanocomposites

The tensile properties of two series of nanocomposites were tested and shown in Figs. 6 and 7. The tensile moduli of epoxy/fVGCNF samples are similar to the neat resin up to 5 wt%. The sample containing 10 wt% epoxy-VGCNF shows a 15% of modulus increase compared with the neat resin (0.54 msi vs. 0.47 msi). However, for the samples in which the pristine VGCNF was blended with epoxy, their moduli continue to decrease from 0.54 msi (neat resin) to 0.42 msi for 3 wt% VGCNF/epoxy samples, which corresponds about 11% lower than the modulus of neat epoxy resin cured under the same conditions. The tensile strength of the epoxy/fVGCNF composites would increase up to 6% when the VGCNF content was increased from 0 to 3 wt%.

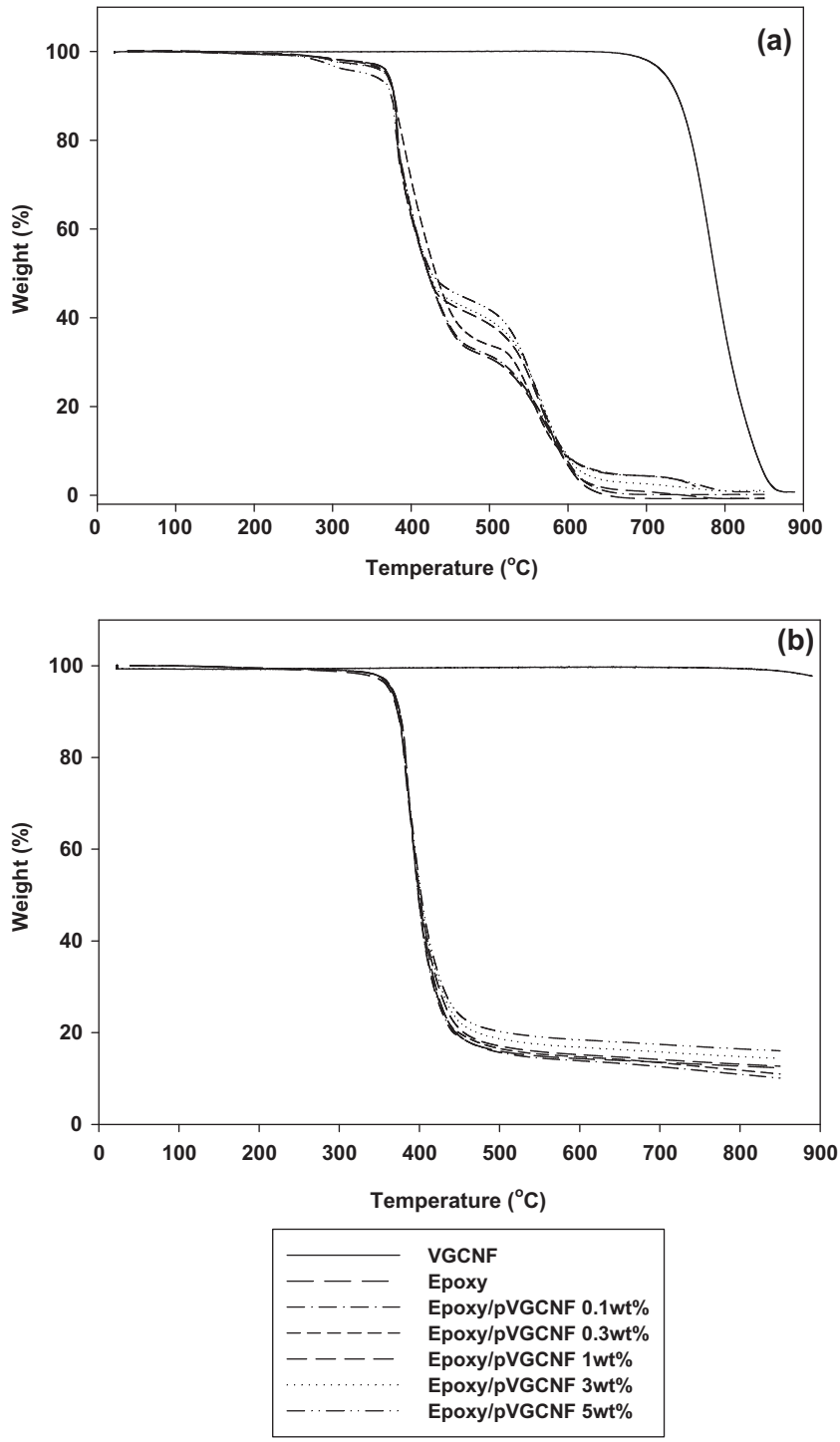



**Fig. 10.** TGA thermograms of epoxy/pVGCNF at heating rate of 10 °C/min (a) in air and (b) in nitrogen.

After that, the strength value would decrease as the VGCNF content was further increased to 10 wt%. The tensile strength of the pristine epoxy/pVGCNF composites would show similar trend. Albeit their strength values would only increase to about 3% for 1 wt% epoxy/pVGCNF sample, and decrease thereafter. Therefore, the functionalized VGCNF shows better improvement of mechanical properties for epoxy than the pristine one.

**Table 3**
Thermal properties of epoxy/pVGCNF nanocomposites.

| | DSC | | | | TGA | | | | |
|---|---|---|---|---|---|---|---|---|---|
| | | | | | In nitrogen | | In air | | |
| VGCNF (wt%) | $\Delta H$ (J/g) | $T_p$ (°C) | $T_{onset}$ (°C) | $T_g$[a] (°C) | $T_{d5\%}$[b] (°C) | Char[c] (%) | $T_{d5\%}$[b] (°C) | Char[c] (%) | Char[d] (%) |
| 100 | – | – | – | – | >900 | 99.7 | 723 | 98.1 | 4.9 |
| 0 | 415 | 194 | 148 | 137 | 362 | 12.3 | 370 | 0.21 | 0.20 |
| 0.1 | 416 (416)[f] | 194 | 148 | 142 | 365 | 10.1 | 371 | 0.33 | 0.19 |
| 0.3 | 418 (419)[f] | 193 | 144 | 140 | 366 | 10.9 | 369 | 0.46 | 0.39 |
| 1.0 | – | – | – | 138 | 362 | 12.7 | 368 | 0.93 | 0.74 |
| 3.0 | – | – | – | 137 | 364 | 14.4 | 367 | 2.65 | 1.11 |
| 5.0 | 398 (419)[f] | 195 | 145 | 136 | 365 | 16.0 | 343 | 4.78 | 2.45 |

[a] Inflection in baseline on DSC thermogram obtained in $N_2$ at a heating rate of 10 °C/min.
[b] Temperature at which 5% weight loss recorded on TGA thermogram obtained at a heating rate of 10 °C/min.
[c] Char yield at 700 °C.
[d] Char yield at 850 °C.
[f] Normalized values are in the parenthesis.

### 3.4. Scanning Electron Microscopy (SEM)

SEM images of 0.1 and 5 wt% epoxy/fVGCNF composites show a homogenous dispersion of VGCNF in the epoxy matrix (Fig. 8a, c and e) while the 0.1 and 5 wt% epoxy/pVGCNF composites display nanofiber aggregates and phase separation between VGCNF and epoxy (Fig. 8b, d and f). Although the SEM image of epoxy/fVGCNF shows good adhesion between VGCNF and epoxy in some area, for example, in **g1** region as indicated by a white arrow in Fig. 8g due to the covalent bonding of epoxy matrix with VGCNF, in other area, the poor interfacial interaction between VGCNF and epoxy can also be seen (e.g. **g2** region). For epoxy/pVGCNF the grossly poor adhesion (i.e., appearance of detachment) between VGCNF and the epoxy matrix is evident in whole region, as shown in Fig. 8h. Therefore, the combination of better dispersion and adhesion of epoxy/fVGCNF composites probably have contributed to their higher mechanical properties than those of the epoxy/pVGCNF composites.

### 3.5. Thermal properties

The pristine VGCNF exhibited an expectedly high thermal stability, with 5 wt% weight loss ($T_{d5\%}$) occurring at 723 °C in air, and at temperatures higher than 900 °C in nitrogen. Epoxy/fVGCNF displayed $T_{d5\%}$ in the range of 363–370 °C in air and 355–364 °C in nitrogen, respectively (Fig. 9 and Table 2). Epoxy/pVGCNF displayed $T_{d5\%}$ in the range of 343–371 °C in air and 362–366 °C in nitrogen, respectively (Fig. 10 and Table 3). Unlike PEK/VGCNF nanocomposites, which all showed a two-stage degradation in air, both epoxy/fVGCNF and epoxy/pVGCNF samples exhibited a three-stage degradation. The aliphatic component of epoxy matrix started to degrade around 350 °C, following the decomposition onset temperature of aromatic component at 450 °C. After epoxy had been thermooxidatively stripped off, the amount of residues at 700 °C was taken as the original amount of VGCNF. Excellent agreement was obtained between the theoretical and experimental values for all the epoxy/pVGCNF compositions (Table 3). However, the experimental amounts of residues for the epoxy/fVGCNF samples at 700 °C are higher than theoretical values, probably due to the carbonization of the grafted epoxy onto the VGCNF surface (Table 2).

The glass-transition ($T_g$) temperatures of epoxy/fVGCNF and epoxy/pVGCNF samples were determined by DSC. The samples were heated to 300 °C in the DSC chamber in the first run, and then cooled to ambient temperature at 10 °C/min under nitrogen purge. Then the samples were heated to 300 °C at 10 °C/min in the second run. The $T_g$'s were calculated based on mid-point of change in slope on the second heating run. In a previous work, we observed the $T_g$'s of *m*-polyetherketone (*m*PEK) increased gradually with VGCNF contents after *m*PEK had been grafted onto VGCNF. This is consistent with the rationale that the attachment of flexible *m*PEK chains to VGCNF had occurred [14]. In a separate work, we also observed that the $T_g$'s of the CP2 polyimide/VGCNF films increased at low VGCNF contents, and gradually decreased at higher VGCNF contents [19a]. In this work, we observed such similarly unusual thermal behaviors for both epoxy/fVGCNF and epoxy/pVGCNF samples. The glass transition temperature of the neat epoxy is 137 °C. The $T_g$ values of 0.1 wt% and 0.3 wt% epoxy/fVGCNF samples were 138 and 141, an increase of 1 and 4 °C, respectively. As the VGCNF contents were incrementally increased from 0.3 to 10 wt%, the $T_g$'s of epoxy/fVGCNF samples would decrease from 141 to 109 °C (Table 2 and Fig. 11a). The $T_g$ trend of epoxy/pVGCNF samples was similar to that of epoxy/fVGCNF. The $T_g$ of 0.1 wt% epoxy/pVGCNF sample increases from 137 °C (neat epoxy) to 142 °C. Then, the $T_g$ decreased to 140 °C for 0.3 wt% epoxy/pVGCNF sample, and further decrease to 136 °C as VGCNF contents increase to 5 wt% (Table 3 and Fig. 11b). While the $T_g$ increase in both series of the nanocomposites at low VGCNF content could be attributed to the reinforcement effect of VGCNF on the polymer chains, it is unclear as to the reasons for the significantly and consistently lower $T_g$ values of the epoxy/fVGCNF nanocomposites at higher VGCNF content (∼>1 wt%).

As we suspect that VGCNF might have interfered with the curing process of epoxy resin at the rate that the increase of VGCNF content (especially in the case of epoxy-VGCNF) through adsorption of epoxy monomers and especially amine curing agent, which resulted in lower cross-link density and uneven distribution of cross-linked sites in the

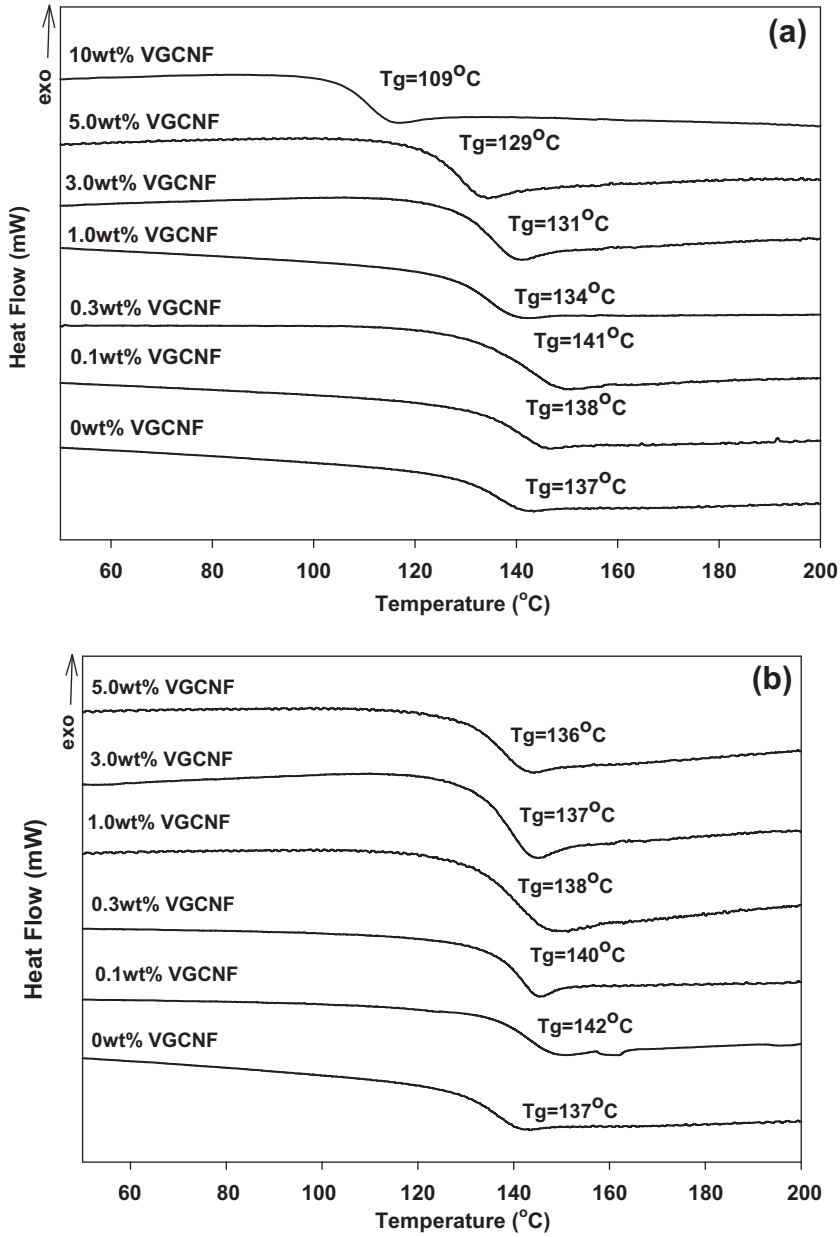



**Fig. 11.** DSC thermograms of (a) epoxy/fVGCNF and (b) epoxy/pVGCNF with heating rate of 10 °C/min.

epoxy matrix. Therefore, the curing process of the epoxy monomers containing 0, 0.1, 0.3 and 5 wt% of epoxy-VGCNF and pristine VGCNF, respectively, were monitored using DSC (Fig. 12). Compared with neat epoxy monomers during curing process, addition of 0.1 wt% epoxy-VGCNF did not change the peak temperature of exotherm (194 °C). However, its exothermal peak is broader than that of neat epoxy resin. Upon further increase in epoxy-VGCNF content from 0.3 to 5 wt%, the curing exothermal peaks not only became broader, but their peak temperatures also increased from 194 (neat epoxy) to 215 °C (Fig. 12a and Table 2). It seems at low content (0.1 wt%) epoxy-VGCNF had minimal effect on the curing temperatures. At higher content, epoxy-VGCNF delayed the curing process, which probably resulted in uneven distribution of crosslinking sites. The onset temperature of the neat epoxy is 148 °C. After epoxy-VGCNF was added into epoxy their onset temperatures decrease to between 130 and 136 °C. The exotherms of epoxy/fVGCNF are higher than the neat resin and increase with the nanofiber contents. We speculate that crosslinking densities must be much higher in the vicinity of carbon nanofibers and less abundant. Thus, the low $T_g$ values detected by DSC are associated with epoxy network further away from the carbon nanofibers, with lower crosslinking densities and more abundant. On the other hand, the pristine VGCNF show no effect on the exothermal peaks for 0.1, 0.3 and 5 wt%

epoxy/pVGCNF composites. While the exotherm of 0.1 wt% epoxy/pVGCNF composite is almost identical to the neat epoxy the exotherms of 0.3 and 5 wt% epoxy/pVGCNF composite are slightly broader than the neat epoxy (Fig. 12b and Table 3). The curing temperatures, onset temperatures and exotherms of epoxy/pVGCNF samples changes much less than the epoxy/fVGCNF samples, which may attribute their less $T_g$'s decrease than the epoxy/fVGCNF samples at higher VGCNF contents.

## 4. Conclusion

VGCNF was functionalized with epoxy groups on the surface via the reaction of a previously attached aromatic amine (~5 atom%) and epichlorohydrin and IR results confirmed high degree of conversion. Either the epoxy-functionalized or pristine VGCNFs was first premixed with an epoxy resin in various compositions, and then the molded mixtures was subject to the thermal curing to give two

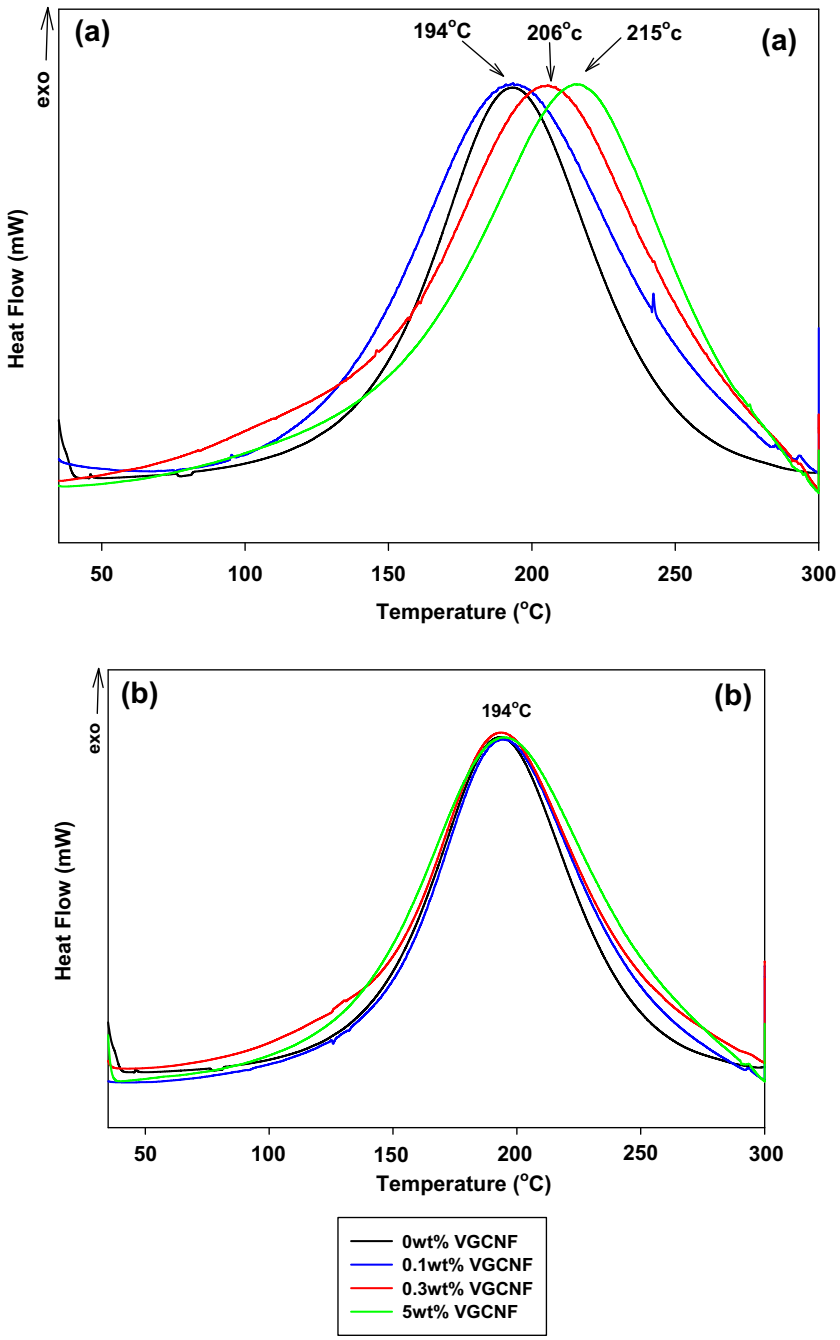



**Fig. 12.** DSC thermograms of (a) epoxy/fVGCNF and (b) epoxy/pVGCNF with heating rate of 10 °C/min during curing process.

series of epoxy/VGCNF nanocomposites. Higher amounts of epoxy-VGCNF (up to 10 wt%) were able to be mixed with epoxy matrix than the pristine VGCNF (3 wt%) since Epxoy-VGCNF was more compatible with epoxy. Both the tensile moduli and strengths of epoxy/fVGCNF nanocomposites are higher than those containing pristine VGCNF, due to their better dispersion in epoxy. Their thermal properties were studied using TGA and DSC. It is noteworthy that the $T_g$'s of both series of the nanocomposites initially increased at lower VGCNF contents, and then decreased at higher contents with more drastic decrease (up to 28 °C) for 10 wt% epoxy/fVGCNF sample. A DSC curing study indicated that the curing process of the epoxy resin in the nanocomposites was changed due to the presence (>1 wt%) of either pristine VGCNF or epoxy-functionalized VGCNF. The presence of latter apparently had an adverse effect on the glass-transition, which could be stemming from its higher affinity for the curing agent W and leading to low crosslinking densities in the bulk region away from the carbon nanotubes.

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