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Use of TX100-dangled epoxy as a reactive noncovalent dispersant of vapor-grown carbon nanofibers in an aqueous solution

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ABSTRACT

The dispersion of carbon nanotubes (CNTs) into individual particles or small bundles has remained a vexing problem that limits the use of the excellent properties of CNTs in composite applications. Noncovalent functionalization is an attractive option for changing the interfacial properties of nanotubes because it does not destroy the nanotube grapheme structure. In this study, a new reactive copolymer, epoxy-toluene diisocyanate-Triton X-100 (EP-TDI-TX100) was successfully synthesized, which is shown to be highly effective in dispersing vapor-grown carbon nanofibers (VGCNFs) into individual or small bundles, as evidenced by transmission electron microscopy (TEM) and UV-vis absorption spectra. The strong π - π interaction between VGCNFs and EP-TDI-TX100 was revealed by Raman spectra and the covalent reaction between curing agent was confirmed via Fourier transform infrared spectroscopy. For an effective dispersion, the optimum weight ratio of EP-TDI-TX100 vGCNFs is 2:1. The maximum VGCNF concentration that can be homogeneously dispersed in an aqueous solution is approximately 0.64 mg/mL. The EP-TDI-TX100 molecules are adsorbed on the VGCNF surface and prevent reaggregation of VGCNFs, so that a colloidal stability of VGCNF dispersion can be maintained for 6 months.

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1. Introduction

Vapor-grown carbon nanofibers (VGCNFs) [1-3], as well as carbon nanotubes (CNTs) [4–6], have attracted a considerable amount of attention owing to their exceptional mechanical, thermal, and electrical properties, as well as their potential for a variety of biological applications, are promising materials for not only mechanelectronic, electrochemical devices, and biological ical. components. CNTs have better mechanical properties, smaller diameters, and lower density [1,7]. However, VGCNFs are an excellent alternative for the more expensive CNT because of their availability and relatively low price. Typically, the average crosssectional diameter of VGCNF is 80 nm. Therefore, VGCNFs are also referred to as multi-walled carbon nanotubes (MWCNTs) with very large diameters [1,2]. Unfortunately, synthesized VGCNFs invariably exist in the aggregated form and are held together tightly as hundreds of individual tubes (due to strong van der Waals forces and a large aspect ratio [8]. One of the key challenges is the processing or engineering of VGCNFs for potential applications as electronic components or conductive polymer composites [2,9]. In addition, the unique growth mechanism of VGCNFs results in a chemically inactive graphite sheet surface [10], as well as lower of surface functional group concentrations, and poor infusion with matrix materials such as polymers and ceramics [11,12]. However, the effective utilization of VGCNFs in composite applications strongly depends on the ability of VGCNFs to disperse homogeneously throughout the matrix without destroying the integrity of VGCNFs as well as on having an excellent interfacial adhesion. Therefore, it is essential to modify the surface structure of VGCNF to enhance the dispersibility of VGCNFs into raw materials.

Noncovalent functionalization is particularly attractive because of the possibility of adsorbing various groups onto the CNT surface without disturbing the π electron system of the graphene sheets. It is a useful method in tuning the interfacial properties of nanotubes [13,14]. In the last decades, noncovalent functionalization by surfactants or polymers has been widely used in the preparation of both organic and aqueous solutions to obtain high weight fraction of individually dispersed CNTs. Previously, studies included the following (1) surfactants, such as sodium dodecyl sulfate (anionic surfactant) [15,16], cetyltrimethylammonium bromide (cationic surfactants) [6], and polyoxyethylene octylphenylether (Triton X-100, non-ionic surfactant) [6]; and (2) polymers, such as Pluronic [17], polyvinyl pyrrolidone [18,19], and Gum Arabic [20]. The noncovalent functionalization of CNTs lowers the CNT surface tension, effectively preventing the formation of aggregates. Furthermore, surfactant-treated CNTs overcome the van der Waals attraction though electrostatic and steric repulsive forces [21].

As previously mentioned, several studies have contributed to the investigation of the effect of Triton X-100 (TX100) on the



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dispersibility and other properties of CNTs. TX100 has been proven effective in dispersing individual nanotubes without compromising the nanotube graphene structure. However, TX100 has an average molecular weight of 650 g/mol. Thus, it acts as a plasticizer to the polymer matrix. Furthermore, probably due to the combined effects of the ability of TX100 to exfoliate CNTs, its interaction with the CNT walls, and its capability to desorb from the CNT surface and migrate into the polymer matrix. In addition, TX100 can migrate to the CNTs-polymer interface during and/or after the nanocomposite processing. Gerin concluded that the driving force for TX100 migration is the thermodynamic reduction of the surface free energies [22]. A high TX100 concentration in the interphase region acts as a weak boundary layer and reduces the strength of the CNTs-polymer adhesive. Thus, an excessive amount of TX100 and its migration both significantly affect the final mechanical property of the nanocomposite.

In the present study, a reactive, noncovalent polymeric dispersant for VGCNFs: diglycidyl ether of bisphenol A-toluene diisocyanate-Triton X-100 (EP-TDI-TX100, Scheme 1), was synthesized to disperse VGCNFs with TX100 and to prevent the migration of TX100 during or after processing. Moreover, EP-TDI-TX100 was synthesized to achieve high compatibility and miscibility between the modified VGCNFs and the water-based epoxy resin. This method may be used as a versatile approach to fabricating uniform VGCNF/water-based epoxy resin nanocomposites. EP-TDI-TX100 was analyzed via Fourier transform infrared (FTIR) and nuclear magnetic resonance (NMR) spectroscopy. Two series of VGCNF dispersion, one with TX100 and one with EP-TDI-TX100-dispersed VGCNFs, were fabricated. The performance of EP-TDI-TX100 in dispersing VGCNFs was assessed via transmission electron microscopy (TEM) and ultraviolet–visible light (UV–vis) absorption spectroscopy. The VGCNF/EP-TDI-TX100 interaction was analyzed via Raman spectroscopy.

2. Materials and methods

2.1. Materials

The VGCNFs (Showa Denko K. K., Japan) were fabricated through thermal chemical vapor deposition with an average diameter about



Scheme 1. Synthesis of diglycidyl ether of bisphenol A-toluene diisocyanate-Triton X-100 (EP-TDI-TX100).

80 nm [2]. The non-ionic surfactant, polyoxyethylene octyl phenyl ether (Triton X-100, supplied by Aladdin Industry, China), which has a critical micelle concentration value of 0.2–0.9 mM at 25 °C, was used. The commercially available epoxy resin (diglycidyl ether of bisphenol A, DGEBA) E-44 (epoxy equivalent ~ 213–244; supplied by Wuxi Resin Factory, China), 2,4-toluene diisocyanate (TDI, supplied by Bayer, Germany), and deuterated chloroform were obtained from commercial sources and used as received. The water-based epoxy resin used was synthesized in our laboratory from an EP/EP-TDI-TX100 emulsion using the phase-inversion technique. All dispersion experiments were performed with deionized (DI) water.

2.2. Techniques

2.2.1. EP-TDI-TX100 synthesis

In this experiment, DGEBA (3.720 g, 8 mmol) was added into a three necked-flask and stirred at 80-90 °C under vacuum (-0.08 MPa) for 30 min to eliminate moisture. After the mixture was cooled at 50 °C for 10 min, TDI (0.870 g, 5 mmol) was added dropwise into the flask under vigorous mixing. The mixture was then warmed to 70 °C and stirred for 8 h under a nitrogen atmosphere. The grafting reaction occurred between the pendant hydroxyl groups of epoxy resin and the isocyanate groups of TDI [23]. When the grafting reaction was completed, TritonX-100 (3.900 g, 6 mmol) was added dropwise to the reaction system, and the mixture was agitated for another 16 h under a nitrogen atmosphere. After the reaction was completed, the mixture was filtered and washed several times with DI water. The resulting product was dried at 80 °C under vacuum for 24 h. The copolymer (5.685 g) was obtained with a yield of 67%. This copolymer contains three structural segments: an epoxy moiety, a TDI moiety, and a TX100 segment. The reaction is shown in Scheme 1.

2.2.2. Fourier transform infrared spectroscopy (FTIR)

The FTIR spectra of pure epoxy resin, TX100, EP-TDI-TX100, and cured EP-TDI-TX100 were recorded on a Nicolet 5700 attenuated total reflection Fourier transform infrared (ATR-FTIR) instrument (Thermo Electron Corp., USA) with a resolution of 4 cm⁻¹.

2.2.3. Nuclear magnetic resonance spectroscopy (NMR)

The ¹H NMR measurements were performed on an AVANCE AV 400 MHz Digital FT-NMR spectrometer operating at 400 MHz using deuterated chloroform (CDCl₃) as a solvent at 25 °C.

2.2.4. Preparation of VGCNF/EP-TDI-TX100 dispersion

The mixture of VGCNFs (0.2 g) and EP-TDI-TX100 was stirred to homogeneity in a flask at 25 °C, and DI water droplets (15 mL) were then added to the mixture. The EP-TDI-TX100/VGCNF ratios ranged from 0.25:1 to 6:1 by weight. After stirring for 6 h, 35 mL of cold DI water was added to the flask and the mixture then was stirred for another 18 h. After the maximum dispersion was achieved, the VGCNF dispersions were bottled. The process of making VGCNF/TX100 dispersions was the same as the VGCNF/EP-TDI-TX100 dispersions.

2.2.5. UV-vis spectroscopic measurements

VGCNF dispersions in the EP-TDI-TX100 and TX100 solution were characterized using a UV-vis spectrophotometer (TU-1901, PGeneral, China) operating between 190 and 900 nm. After UV-vis characterization, the dispersion mentioned in Step 2.2.4 was collected. The blank used was the original EP-TDI-TX100 and TX100 solutions under the same conditions as the samples.

2.2.6. Evaluation of the centrifuged VGCNF dispersion stability via visual observation

Pristine VGCNFs, VGCNF/EP-TDI-TX100, and VGCNF/TX100 solutions with different surfactant/VGCNF ratios by weight were prepared. To obtain a clearer observation of the dispersion property and dispersion stability of VGCNF in solution, with or without surfactant treatment, the VGCNF solutions were first centrifuged at 3000 rpm for 20 min, using an Anke TGL-16C with a Sepatech rotor (8 cm), to remove the catalyst particles and the remaining VGCNFs aggregates. The supernatant was collected from the dispersion and then left standing for different times (immediately, 1 day to 7 days, and even 6 months). Finally, the homogeneity was evaluated through visual observation and UV-vis spectroscopy.

2.2.7. Raman spectroscopy

The Raman spectra were obtained at room temperature under ambient conditions using a LabRam HRUV Raman spectrometer (LabRam HRUV, JDbin–yvon Inc., France). The excitation source was a 514 nm Ar^+ ion laser, and the optical power at the sample position was maintained at 10 mW.

2.2.8. Scanning electron microscopy (SEM)

Pristine VGCNFs and the fracture surface of VGCNFs nanocomposite samples were observed under a field emission scanning electron microscopy (Ultra 55, Zeiss, Germany). High vacuum conditions were applied, and a secondary electron detector was used for image acquisition.

2.2.9. Transmission electron microscopy (TEM)

The TEM dispersion states of VGCNFs with and without treatment were examined using a transmission electron microscope (JEM-2100F, JEOL, Japan) operated at 200 kV and by monitoring the stability of the VGCNF suspensions. The two dispersions were deposited onto the carbon-coated copper grids by drop-casting without ultrasonication. These dispersions were then dried in vacuum for TEM observation. In addition, the solutions were diluted 10 times prior to casting.

3. Results and discussion

3.1. Synthesis and characterization of EP-TDI-TX100

The formation of the EP-TDI-TX100 polymer network is shown in Scheme 1. The structures of the synthesized EP-TDI-TX100 were determined from the attenuated total reflectance (ATR)-FTIR spectra. Fig. 1 shows a new stretching vibration absorption peak of the C=O group at 1730 cm⁻¹ and a bending vibration absorption peak of the N-H group at 1535 cm⁻¹ in curve (c) and (d), respectively, and these peaks confirm that a grafting reaction occurred between the hydroxyl groups of the epoxy resin (or TX100) and the isocyanate groups of TDI [23]. The stretching vibration absorption peak of the epoxy group at 915 cm⁻¹ can also be observed in curve (c), indicating that the epoxy groups. The signal of epoxy at 915 cm⁻¹ vanishes when excessive concentrations of the curing agent were added to EP-TDI-TX100. This disappearance suggests that a curing reaction occurred between EP-TDI-TX100 and the curing agent (Fig. 2d).

The structures of the synthesized EP-TDI-TX100 were further confirmed via ¹H NMR spectroscopy. The complete assignment of the proton signals is shown in Fig. 2. In the ¹H NMR spectrum of EP-TDI-TX100, the sharp resonance centered at 3.64 ppm (peak a) is attributed to methylene protons of PEO [24]. Furthermore, resonance signals at 1.89 ppm (peak b) are assigned to the NH protons of —OCONH— groups [23]. The peaks at 6.82 ppm (peak c) and 7.14 ppm (peak d) are attributed to the aromatic protons of the



Fig. 1. ATR-FTIR curves of (a) pristine epoxy, (b) Triton X-100, (c) EP-TDI-TX100, and (d) cured EP-TDI-TX100.



bisphenol A moiety of epoxy resin. Moreover, the peak at 1.63 ppm (peak g) corresponds to the methyl protons. The glycidyl terminal group is characterized by five peaks in the range of δ = 2.74 ppm to 4.66 ppm range (ranges e and f) [25]. These results indicate that the as-synthesized EP-TDI-TX100 exhibits the expected structure.

3.2. Solubility of the EP-TDI-TX100-functionalized VGCNF

Fig. 3 shows the extracted VGCNF concentrations of the centrifuged supernatant of the VGCNF/EP-TDI-TX100 and VGCNF/TX100 dispersions prepared at different EP-TDI-TX100 (and TX100) to VGCNFs mass ratios (from 0.25:1 to 6:1) via the same method. The VGCNFs were dispersed well in DI water with EP-TDI-TX100 and TX100 through intensive stirring. A clear dependence of the surfactant to VGCNF mass ratio on the amount of dispersed VGCNFs is observed in the VGCNF/EP-TDI-TX100 or VGCNF/ TX100 supernatant. The minimum mass ratio of EP-TDI-TX100 to VGCNFs to achieve a good dispersion is 0.25, indicating that EP-TDI-TX100 is a highly efficient dispersant for VGCNFs. The VGCNF concentration initially increases with the EP-TDI-TX100 to VGCNF mass ratio and then decreases when the mass ratio reaches 2:1. This result suggests that 2:1 is the optimal mass ratio in preparing the VGCNF/EP-TDI-TX100 dispersion. The highest VGCNF concentration of a stable VGCNF supernatant is approximately 0.64 mg/ mL and 0.37 mg/mL for the VGCNF/EP-TDI-TX100 dispersions (using 2:1 EP-TDI-TX100 to VGCNF mass ratio) and VGCNF/ TX100 dispersions (using 4:1 TX100 to VGCNF mass ratio), respectively. The results suggest that approximately one-tenth of TX100 that was modified by the epoxy resin is sufficient dispersion the



Fig. 3. VGCNF solutions concentrations prepared using different EP-TDI-TX100 (and TX100) to VGCNF mass ratios.

same amount of VGCNFs compared with pristine TX100. In addition, surfactants to VGCNF mass ratios of the centrifuged VGCNF/ TX100 supernatants (C_S/C_V) are always higher than that of the centrifuged VGCNF/EP-TDI-TX100 supernatants. Furthermore, the VGCNFs started to precipitate out of the VGCNF/TX100 supernatant in just a few hours. The VGCNF concentrations and surfactants of the centrifuged supernatants are summarized in Table 1.

The addition of low concentrations of EP-TDI-TX100 has a positive effect on VGCNF debundling. However, the VGCNF concentration of VGCNF supernatants decreases when the EP-TDI-TX100 to VGCNF mass ratio is higher than 2:1. For example, the dispersive efficiency is insufficient when an excessive amount of EP-TDI-TX100 is added for VGCNF dispersion. This result can be attributed to a bridging mechanism: polymeric surfactant molecules are adsorbed onto the surfaces of adjacent nanotubes, thus bridging the molecules together [26]. The bridging effect can promote the reaggregation of the dispersed VGCNFs in the solution, which can lead to sedimentation during the centrifugation process. Therefore, the VGCNF concentration is rapidly decreased when the EP-TDI-TX100 to VGCNF mass ratio above 2:1.

All types of individual CNTs are active in the 200 and 1200 nm wavelength region and exhibit characteristic bands that correspond to additional absorption due to 1D van Hove singularities [27]. UV–visible absorption measurements were used to evaluate quantitatively the efficacy of the surfactant in dispersing CNTs [28]. Furthermore, as previously mentioned, VGCNFs belong to a large family of CNTs. Therefore, the dispersion of VGCNFs in aqueous EP-TDI-TX100 and TX100 solutions can be monitored via UV–vis spectroscopy.

| Table 1 |
|--|
| VGCNF and surfactant concentrations of the centrifuged supernatants. |

| Sample | C_V^{a} (mg/mL) | $C_S^{\rm b}$ (mg/mL) | C_S/C_V |
|-----------------------------|-------------------|-----------------------|-----------|
| TX100/VGCNF (0.25:1) | 0.06191 | 0.8147 | 13.16 |
| TX100/VGCNF (0.50:1) | 0.1881 | 1.905 | 10.13 |
| TX100/VGCNF (1:1) | 0.3010 | 4.466 | 14.84 |
| TX100/VGCNF (2:1) | 0.3305 | 7.246 | 21.92 |
| TX100/VGCNF (4:1) | 0.3671 | 14.42 | 39.28 |
| TX100/VGCNF (6:1) | 0.3271 | 20.31 | 62.05 |
| TX100/VGCNF (8:1) | 0.2982 | 31.35 | 105.1 |
| EP-TDI-TX100/VGCNF (0.25:1) | 0.02412 | 0.2573 | 10.67 |
| EP-TDI-TX100/VGCNF (0.50:1) | 0.1102 | 0.3501 | 3.177 |
| EP-TDI-TX100/VGCNF (1:1) | 0.2064 | 0.8006 | 3.879 |
| EP-TDI-TX100/VGCNF (2:1) | 0.6431 | 2.892 | 4.497 |
| EP-TDI-TX100/VGCNF (4:1) | 0.5985 | 6.523 | 10.90 |
| EP-TDI-TX100/VGCNF (6:1) | 0.5658 | 8.590 | 15.20 |
| EP-TDI-TX100/VGCNF (8:1) | 0.5266 | 12.83 | 24.36 |
| | | | |

^a VGCNF concentration of the centrifuged supernatant.

^b Surfactant concentration of the centrifuged supernatant.



Fig. 4. Evolution of the UV–vis spectra of aqueous 0.4 wt.% VGCNF-0.8 wt.% EP-TDI-TX100 (and TX100) solution (both samples were collected from Step 2.2.4, without centrifugation). The solutions were diluted 10 times prior to the UV–vis measurements.

Fig. 4 shows the UV-vis spectra of the VGCNF/EP-TDI-TX100 and VGCNF/TX100 solutions, after the maximum dispersion was achieved. The corresponding spectra for both solutions show a similar development, exhibiting two maximum peaks at 220 nm to 300 nm. These peaks gradually decrease from UV to near-IR, particularly in the longer wavelength range. VGCNFs exist as large aggregates in solution. Furthermore, almost no absorption is evident in the UV-vis spectrum (Fig. 4c). The area under the UV-vis spectrum (a) is larger than the area below the spectrum line (b), implying a higher number of individual VGCNF particles in the solution with EP-TDI-TX100. This observation also means that EP-TDI-TX100 has a higher efficiency in dispersing VGCNFs than TX100.

Comparing the VGCNF stabilities in a solvent is one of the most direct means to understanding the effects of the surfactant treatment. The dispersion stabilities of the VGCNF solutions prepared in water with and without EP-TDI-TX100 were evaluated through visual observation at different standing times after centrifugation (Fig. 5). The EP-TDI-TX100 treated VGCNFs exhibited an excellent stability for up to 6 months. Pristine VGCNFs underwent rapid aggregation and completely floated on water after stirring. In addition, the supernatant was transparent and colorless (Fig. 5a). The VGCNF/EP-TDI-TX100 solutions were highly stable and did not precipitate after 1 week, or even after 6 months Fig. 5 (right bottle b) at room temperature. These phenomena indicate that EP-TDI-TX100 significantly improves the VGCNF solubility in water and



Fig. 5. Time-resolved UV absorbance intensities of VGCNF (a) in water without any dispersant, (b) in the supernatant of VGCNF/EP-TDI-TX100 solution after centrifugation, and (c) in the supernatant of the VGCNF/TX100 solution after centrifugation. The left inset picture was taken after centrifugation, whereas the right picture was taken 6 months after centrifugation. The supernatants were diluted by a factor of 10 when the UV-vis measurements were performed at a wavelength of 279 nm.



Fig. 6. Dipping test to evaluate the dispersion of VGCNFs in water: (a) without any dispersant and (b) with EP-TDI-TX100.

provides long-term dispersion stability. The EP-TDI-TX100 molecules or micelles that may have been adsorbed onto the VGCNF surface not only reduced the surface tension, but also separated the lager agglomerates by overcoming the strong van der Waals interactions, to maintain good stability. However, VGCNFs started to precipitate out of the VGCNF/TX100 supernatant in just a few hours (Fig. 5 right bottle c). This precipitation corresponds to the lowering of the absorption in the UV–vis absorbance (Fig. 5 line c). The precipitate of the VGCNF/TX100 supernatant at the bottom of right bottle c is indicated by an arrow in Fig. 5. These comparative studies suggest that EP-TDI-TX100 has a considerably higher dispersing capability for VGCNFs compared with the commercial dispersant TX100.

Fig. 6 shows the results of a dipping test. The agglomerates of VGCNFs are visible on the glass rod in the absence of any dispersants (Fig. 6a). However, the glass rod appeared very uniformly coated with the VGCNF/EP-TDI-TX100 supernatant after dipping the supernatant. This result illustrates the good dispersion of VGCNFs (Fig. 6b).



Fig. 7. Raman spectra of (a) pristine VGCNFs and (b) EP-TDI-TX100/VGCNF. The sample (b) was frozen in liquid nitrogen, and the aqueous solvent was removed using a Labconco FreeZone freeze-dryer operated at 0.1 mbar and -20 °C for 48 h (EP-TDI-TX100: VGCNF mass ratio is 2:1).



Scheme 2. Schematic illustration of VGCNF dispersing by the EP-TDI-TX100 copolymer and the structure of EP-TDI-TX100.

The interaction between the copolymers and VGCNFs was investigated via Raman spectroscopy. As shown in Fig. 7, shows no significant increase in the peak intensity of the D-band (represents disorder induced character of VGCNFs at approximately 1360 cm⁻¹ [2]) in VGCNF/EP-TDI-TX100 (b) and pristine VGCNFs (a), indicating that the VGCNF graphene structure was well-protected after noncovalent functionalization with EP-TDI-TX100. Upshifts of approximately 5 cm⁻¹ were observed when comparing the G-band (corresponds to the sound sp² carbon networks of VGCNFs at about 1580 cm⁻¹ [2]) of VGCNF/EP-TDI-TX100 (b) with those of pristine VGCNFs (a). The 5 cm⁻¹ upshift can be attributed to the lose electrons of VGCNFs [29], which suggests that a molecular level interaction (π - π stacking) occurred between VGCNFs and the EP-TDI-TX100 molecules.

The higher efficiency of EP-TDI-TX100 in dispersing VGCNFs may be attributed to its distinct structure, wherein the benzene rings of the epoxy resin and Triton X-100 may have a strong π - π interaction with the VGCNFs wall. As illustrated in Scheme 2, a copolymer for steric stabilization consists of lyophobic and lyophilic blocks. In an aqueous solvent, the alkyl chains of TX100 and epoxy resin backbone may strongly interact with VGCNFs via noncovalent interactions, whereas the PEO (CH₂CH₂O) chains of TX100 interact with water through hydrogen bonds. Afterward, the copolymer-coated VGCNFs remain dispersed.

3.3. VGCNF dispersion in aqueous solvents and composites

Fig. 8 shows the overall morphology of as-grown VGCNFs using FE-SEM (a) and the highly magnified structure of an individual VGCNF using HR-TEM (b). VGCNFs have a relatively larger diameter and shorter length than CNTs and contain many impurities, such as amorphous particles, which can be seen in Fig. 8a. Such a morphological difference is attributed to the VGCNFs unique growth mechanism, which depends on the amount of catalyst employed.

The dispersion of pristine VGCNFs and EP-TDI-TX100-functionalized VGCNFs in water was further examined via TEM. Fig. 9 shows representative TEM images of pristine VGCNFs and EP-TDI-TX100 modified VGCNFs. Before the modification, VGCNFs



Fig. 8. The overall morphology of as-grown VGCNFs using FE-SEM (a) and the highly magnified structure of an individual VGCNF using HR-TEM (b).

are aggregated, bundled, and closely packed, which indicates their poor dispersibility in water (Fig. 9a). After EP-TDI-TX100 coating, the aqueous dispersibility of VGCNFs is significantly improved while retaining the VGCNF structure (Fig. 9b). The TEM images (Fig. 9d) clearly reveal that VGCNFs are covered with a coating layer, which is assumed to be EP-TDI-TX100 layered on the VGCNF surfaces. Moreover, the test results also show that the higher the EP-TDI-TX100/VGCNF mass ratio, the higher dispersion of EP-TDI-TX100 on the copper grids.



Fig. 9. TEM images of (a) pristine VGCNFs dispersed in water; (b) EP-TDI-TX100functionalized VGCNFs; (c) TEM image of pristine VGCNF; and (d) TEM image of a single VGCNF covered by a thin layer of EP-TDI-TX100. The solutions were diluted 10 times prior to casting.

The homogeneous dispersion of VGCNFs can also be deduced from the fracture surface pattern of the nanocomposite samples (Fig. 10a and b). VGCNF dispersion in the sample in Fig. 10a was achieved by directly mixing the VGCNFs with water-based epoxy resin, freeze-drying to remove the aqueous solvent, and then compressing the composite powder into films at 120 °C. On the other hand, the sample in Fig. 10b was prepared by mixing the VGCNF/



Fig. 10. SEM-images of the fracture surfaces (fractured under liquid nitrogen) of (a) sample without EP-TDI-TX100 functionalized VGCNF/water-based epoxy resin composite film and (b) with EP-TDI-TX100-functionalized VGCNF/water-based epoxy resin composite film. The VGCNF concentration is 0.2 wt.%.

EP-TDI-TX100 centrifugation supernatant with the water-based epoxy resin, followed by the same procedure used for the sample without a dispersant. Fig. 10a shows that the fracture surface contains large agglomerates. The VGCNFs in the sample in Fig. 10b are randomly, individually dispersed and incorporated well in the water-based epoxy resin. This result indicates that EP-TDI-TX100 is an efficient copolymer dispersant for VGCNFs and also implies that the EP-TDI-TX100-modified VGCNFs are compatible well with water-based epoxy resin.

4. Conclusions

This study designed and successfully synthesized EP-TDI-TX100, which is a reactive copolymer that covalently reacts with the curing agent through the side chains but strongly noncovalently interacts with the VGCNF surface, as proven via proved by FTIR and Raman spectroscopy, respectively. In addition, EP-TDI-TX100 was shown highly effective in dispersing VGCNFs without damaging the VGCNF structure. The dispersion of EP-TDI-TX100functionalized VGCNFs in water was studied via UV-vis spectroscopy and TEM. The optimum EP-TDI-TX100 to VGCNF ratio of 2:1 (by weight) is required to achieve the maximum achievable VGCNF dispersion in the aqueous EP-TDI-TX100 solution. The maximum VGCNF concentration that can be homogeneously dispersed is approximately 0.64 mg/mL. The EP-TDI-TX100 molecules are adsorbed on the VGCNF surface and prevent reaggregation. Furthermore, the colloidal stability of the aqueous VGCNFs dispersion can be maintained for 6 months. The TX100 dosage was not only preserved for VGCNFs dispersion, but also for obtaining a high concentration of modified dispersed VGCNFs with a good solubility and miscibility in water-based epoxy resin. Therefore, the proposed method is an environment friendly approach to fabricating uniform VGCNF nanocomposites.

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