Supercritical carbon dioxide-assisted silanization of multi-walled carbon nanotubes and their effect on the thermo-mechanical properties of epoxy nanocomposites

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Abstract

Supercritical carbon dioxide was employed as the solvent for the functionalization of multi-walled carbon nanotubes (MWCNTs) with an epoxy-capped silane. The silanization protocol was found to be a suitable green alternative to traditional routes that rely on organic solvents for grafting nearly monolayers of silane molecules onto the nanotube surfaces. The addition of silanized MWCNTs to a model epoxy markedly increased its $T_g$, and measurements of the network cooperativity length scale linked this change to a reduction in polymer segment mobility. Composites filled with low loading levels of both pristine and silanized MWCNTs exhibited significantly higher strain at break and toughness than the neat epoxy, and the greatest improvements were observed at low loading levels. SEM analysis of the composite fracture surfaces revealed that nanotube pullout was the primary failure mechanism in epoxy loaded with pristine MWCNTs while crack bridging predominated in composites containing silanized MWCNTs as the result of strong interfacial bonding with the matrix. The elevated $T_g$ and toughness achieved with small additions of silanized MWCNTs promise to extend the engineering applications of the epoxy resin.

Graphical abstract
1. Introduction

Carbon nanotubes (CNTs) possess extraordinary electrical, mechanical, and thermal properties, which, coupled with their extremely high aspect ratios, makes them ideal candidates for the reinforcing phase in polymer nanocomposites. A tremendous amount of research has been devoted to processing and characterizing CNT composites with mixed results. Dramatic increases in the thermo-mechanical and electrical properties of thermosets and thermoplastics have been observed [1], [2], [3], [4] and [5]. However, CNT additions have also been reported to have minor or even deleterious effects on polymer properties as the result of poor dispersion [6], [7] and [8]. Covalent functionalization of the nanotube surface has emerged as a popular method of not only improving dispersion, but also promoting a strong interface between the CNT and matrix. Hundreds of functionalization reactions have been developed, and incorporation of these modified nanotubes into polymer matrices with compatible reactive sites has produced composites with outstanding thermo-mechanical properties. Recent expansion in the industrial synthesis of multi-walled carbon nanotubes (MWCNTs) has led to a dramatic decrease in price, and today huge quantities of high quality MWCNTs are available for less than $200/kg. The changing economic situation has opened the door for pervasive use of MWCNT composites in many engineering applications; however, challenges in dispersing the nanotubes uniformly in matrix materials on a large scale remains an unresolved problem. While covalent functionalization of MWCNTs represents a rational solution, almost all of the reactions developed to date are not well-suited for large scale operations due to long processing times, poor yield, safety hazards, and environmental concerns. As a result, alternative functionalization strategies are needed for MWCNTs to find widespread application in polymer composites.

One potential solution involves the use of organosilanes, which have two different types of reactive groups per molecule—a hydrolyzable group (Si-OR) that can condense with hydroxyl functionalities on the surface of a filler and another type of functional group capable of reacting with the matrix material (X). Silanes have been used as adhesion promoters in composite manufacturing for decades because they are inexpensive, non-toxic, and available with functionalities to match nearly any polymer matrix material [9] and [10]. Recently, several silanization reactions have been adapted to modify MWCNTs for use in epoxy composites with promising results [11], [12] and [13]. Epoxy matrices containing MWCNTs functionalized with 3-aminopropyltriethoxysilane (APTES) have exhibited markedly higher thermo-mechanical properties. For example, Lee and coworkers reported that the addition of 0.2 wt% APTES-modified MWCNTs to an epoxy resin increased its flexural modulus by 23% and $T_g$ by 11.5 °C [11], [12] and [13]. Lee and Rhee have also shown that APTES modified MWCNTs disperse more readily in epoxies and improve their wear resistance to a greater extent than pristine MWCNTs [11], [12] and [13]. Similar improvements in tribological, thermal, and mechanical properties have been observed for epoxies filled with nanotubes functionalized with 3-glycidoxypropyltrimethoxysilane (GPTMS) [14], [15], [16] and [17], and Kim and coworkers

**Keywords**

- Carbon nanotubes;
- Composites;
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have demonstrated that the improvements in thermo-mechanical properties are the result of stronger interfacial interactions between the nanotubes and the matrix [14], [15], [16] and [17]. While silanization has been shown to improve the properties of MWCNT-epoxy composites, the reactions commonly used to functionalize the nanotubes are not easily scaled.

Traditional silanization is performed in aqueous solution, during which the Si-OR bonds rapidly hydrolyze into silanols which can condense with hydroxyl groups on the filler surface or self-condense to form stable Si–O–Si bonds. Because the self-condensation reaction is favored, aqueous deposition leads to grafting of oligomeric or polymeric siloxane molecules onto the filler surface. This can be problematic for nanoparticles because the deposited oligomer can approach the size scale of the nanoparticle and significant entanglement of adjacent siloxane chains causes particle agglomeration [18]. As a result, monolayer deposition is often preferred when the nanoparticles are to be used in composite applications. This is usually achieved through a direct condensation reaction of the Si-OR group with hydroxyl groups on the particle’s surface under anhydrous conditions in an organic solvent. Such an approach for monolayer grafting of silanes onto oxidized MWCNTs has been reported [19]. While this route affords the versatility of silane end-group chemistry, it requires that the MWCNTs be refluxed in organic solvents for very long periods of time making it undesirable for industrial reactions.

Supercritical carbon dioxide (scCO₂) has emerged as an alternative to organic solvents for silanization reactions and offers the benefits of being non-flammable, non-toxic, naturally abundant, relatively inert, and a good solvent [20]. It is especially attractive for reactions involving nanoparticles because scCO₂ has low viscosity and lacks surface tension, allowing it to wet out even complicated and porous structures including the interstitial surfaces of an agglomerate [21], [22], [23], [24], [25] and [26]. Successful monolayer silanization of several inorganic nanoparticles including hydroxyapatite, [26] and [27] TiO₂ [26], [27] and [28], and hectorite [27] have been reported. In addition to being simple, these reactions do not produce any solvent waste because the CO₂ is removed upon depressurization post-reaction. Since 60–80% of the capital and operating costs of industrial chemical reactions are typically tied to purification and separation of the desired product from solvents and byproducts [29], the ease of solvent removal is a serious advantage.

The advantages afforded by supercritical fluids have sparked efforts to use scCO₂ as the solvent in reactions to functionalize MWCNTs. Capitalizing on the fact that organometallics are generally soluble in scCO₂, Wai and coworkers decorated nanotubes with a variety of metals including Pd, Ni, Cu, Rh, Ru, and Pt by dissolving metal–β-diketone precursors in scCO₂ before reducing them with hydrogen in the presence of MWCNTs [30], [31] and [32]. Metal oxides have also been deposited on the surface of MWNCTs by using scCO₂ as an antisolvent to precipitate polar nitrate precursors from cosolvents such as methanol and ethanol and subsequently thermally decomposing the nitrates into oxides. Following this approach, nanotubes have been coated with Co₃O₄ [33], Eu₂O₃ [34], Al₂O₃ [35], Fe₂O₃ [36], and ZrO₂ [37] nanoparticles. In addition to decoration with inorganic materials, several reports have recently focused on functionalization of MWCNTs with organic molecules. The gas-like diffusivity of scCO₂ has enabled the noncovalent coating of the exterior (and in some cases the interior) of nanotubes with small molecules such as pyrenes [38] as well as polymers including, polystyrene [39], polyethylene [40], poly(2, 4-hexadiyne 1,6-diol) [41], poly(ethylene glycol) [42], polypyrrole
[43], poly(N-vinyl carbazole) [44], and poly(methyl vinyl ether-alt-maleic anhydride) [45]. Covalent functionalization of MWCNTs in scCO$_2$ is also possible. Yue and coworkers functionalized SWCNTs with amino ethyl methacrylate and subsequently reacted the nanotubes with PMMA in scCO$_2$ via a free radical route [46], and Nguyen and Shim used scCO$_2$ to facilitate further functionalization of vinyl-terminated MWCNTs with a biocompatible polymer, 2-hydroxyethyl methacrylate [47]. This paper extends that work by demonstrating that scCO$_2$ is a suitable solvent for covalent silanization reactions, which have important industrial and scientific applications. A two-step approach of oxidizing MWCNTs with gas-phase O$_3$ followed by silanization in scCO$_2$ is employed to graft silane monomers to the nanotube surface. This functionalization protocol is free of organic solvents and acids and requires only non-toxic reagents. A solventless processing route is then used to incorporate the silanized MWCNTs (s-MWCNTs) into a model epoxy and the effects of functionalization on the network structure and thermo-mechanical properties are investigated.

2. Experimental details

2.1. Materials

Multi-walled carbon nanotubes (MWCNTs) with an average diameter of 10 nm and purity greater than 90% were supplied by Kumho Petrochemical Co (Seoul, South Korea). An epoxy-capped silane, 3-(Glycidyloxypropyl) trimethoxysilane (GPTMS), was purchased from Gelest, Inc. (Morrisville, PA). Composites were fabricated with a diglycidyl ether of bisphenol A, Epon 828, and triethylenetetramine (TETA) curing agent supplied by Momentive Specialty Chemicals (Houston, TX).

2.2. Methods

2.2.1. MWCNT functionalization

As-received MWCNTs were first oxidized with gas-phase ozone in a fluidized bed for 10 min to obtain primarily hydroxyl functionality using an optimized reaction reported previously [48]. The oxidized MWCNTs (o-MWCNTs) were further functionalized according to Fig. 1. Reactions were conducted by placing 100 mg o-MWCNTs, 100 μL GPTMS, and 200 g scCO$_2$ into a Parr reactor (model 452HC3), heating the contents to 60 °C (pressure ~ 1500 psi), and stirring for 20 h. Post-reaction, the MWCNTs were washed with toluene to remove any excess silane, a step which could be omitted during industrial production through the design of a reaction chamber which allows for filtration and washing with liquid or supercritical carbon dioxide. The treated MWCNTs were then heated to 110 °C in an oven and held isothermally for 30 min to promote condensation of the silanols with hydroxyl groups on the o-MWCNT surface. Samples functionalized in this manner will be referred to as s-MWCNTs.
2.2.2. Nanocomposite processing

Epoxy nanocomposites were prepared with p-MWCNTs and s-MWCNTs using the following procedure. MWCNTs were weighed and added to Epon 828 resin. In the case of s-MWCNTs, TGA measurements were performed to determine the MWCNT weight fraction, which was used to correct for the actual weight of MWCNTs needed to achieve a given loading. The epoxy-MWCNT mixture was subjected to sonication with a horn (Fisher, sonic dismembrator model 100) in 30 s intervals for a total of 2 min at a power of 40 W and 2 min at 80 W followed by sonication in a bath (Emerson, Branson Model 1800) at 60 °C for 30 min. The mixture was allowed to cool, and a stoichiometric amount of TETA hardener was added. A two-axis planetary mixer (Kurabo, Mazerustar) was then used to thoroughly mix the resin components and remove trapped air bubbles before the resin was cast into a mold and allowed to cure at room temperature for 3 h. The gelled solid was subsequently heated to 80 °C for 1 h followed by a post-cure at 120 °C for 1 h in accordance with the resin manufacturer's recommendation.

2.2.3. Characterization

Thermogravimetric analysis (TGA, Q50, TA Instruments) in air at 20 °C/min heating rate was used to determine the amount of silane grafted onto the surface of functionalized MWCNTs. Functional groups present in as-received and silanized MWCNTs were identified with Fourier-transform infrared spectroscopy (FTIR). The nanotubes were thoroughly mixed with potassium bromide and pressed into a pellet before data acquisition with a Bruker IFS66V spectrometer utilizing a Michelson interferometer. Changes in the surface chemistry of s-MWCNTs were probed with X-ray photoelectron spectroscopy (XPS) using a Physical Electronics 5500 Multitechnique system with a monochromatic Al Kα radiation source, and CasaXPS software was employed for data processing.

The rheological properties of epoxy/MWCNT suspensions were measured using an AR2000ex stress-controlled rheometer (TA Instruments) configured with 25 mm diameter parallel plates. All tests were performed with a 0.75 mm gap size at 25 °C according to the following procedure. MWCNTs were sonicated in Epon 828 using the same protocol outlined for nanocomposites.
processing. After cooling, 0.3 mL of the nanotube dispersion was transferred to the parallel plates and held for 3 min at 25 °C before a stepped steady state flow test was conducted from 0.01 to 100 s⁻¹.

Dynamic mechanical analysis (DMA, Q800, TA Instruments) of nanocomposite samples was performed in three-point bending mode to probe thermo-mechanical properties. Samples with dimensions of 25 mm × 6 mm × 1.5 mm were tested at a fixed frequency of 1 Hz during temperature sweeps from 20 to 200 °C with a heating rate of 3 °C/min. The glass transition temperature ($T_g$) of each sample was determined by the peak of the tan δ curve. Heat capacity measurements of cured samples were conducted by differential scanning calorimetry (DSC, Q2000, TA Instruments) at 10 °C/min in nitrogen using a sapphire standard for calibration. The mechanical properties of nanocomposites at room temperature were evaluated by tensile testing with an Instron universal testing machine (Model 5569) equipped with a 50 kN load cell and video extensometer. Dog-bone shaped samples were machined according to the recommendations in ASTM D638 (Type V) and tested at a crosshead speed of 5 mm/min. At least 5 samples were tested per batch to determine average properties. The fracture surfaces of samples were examined post-tensile testing with a scanning electron microscopy (SEM, FEI Quanta 200) to evaluate the nanotube dispersion and correlate the fracture morphologies with mechanical properties. Images were collected at 8 kV accelerating voltage and 10 mm working distance.

3. Results and discussion

3.1. Silanization

Functionalization of the nanotubes was confirmed by TGA, FTIR, and XPS analyses. Fig. 2 shows the thermal degradation behavior of p-MWCNTs, o-MWCNTs, and s-MWCNTs. While p-MWCNTs and o-MWCNTs are stable up to 400 °C, s-MWCNT exhibit weight loss (~6 wt%) from 200 to 400 °C corresponding to the decomposition of silane molecules [14]. FTIR confirmed reaction of the methoxy group of the silane monomer with hydroxyl groups on the MWCNTs, and a comparison of p-MWCNT, o-MWCNT, and s-MWCNT spectra is given in Fig. 3. The sharp band at 1384 cm⁻¹ and broad peak centered around 1100 cm⁻¹ are prominent features in the o-MWCNT spectrum and are attributed to bending of hydroxyl groups and C–O stretching vibrations, respectively [19]. After silanization, the intensity of these peaks decreases significantly, signifying reaction of methoxy groups with hydroxyl moieties on the nanotube surfaces. Three other bands appear after silanization in the range from 880 to 1110 cm⁻¹ that are not present in the p-MWCNT or o-MWCNT spectra. Theses peaks at 880 cm⁻¹, 1020 cm⁻¹, 1110 cm⁻¹, are attributed to absorption by Si–OH, Si–O–Si, and Si–O–C bonds, respectively [49] and [50]. While the reaction was run using dry CO₂, the presence of Si–O–Si and Si–OH moieties following silanization suggests that some water was present, likely on the surface of the MWCNTs.
XPS was used to further characterize the silane grafting process. The survey scans presented in Fig. 4a show the average surface composition of p-MWCNTs, o-MWCNTs, and s-MWCNTs. The peaks in each spectrum have been normalized to their respective C1s bands at 285 eV to allow for direct comparison. Almost no oxygen (~0.5 at%) is present on the surface of p-MWCNTs, as can be seen from the low intensity of the O1s band at 532 eV. Oxidation introduces a significant number of hydroxyl groups and yields an overall composition of about 7.5 at% oxygen on the MWCNT surfaces. Silanization further increases the oxygen content and peaks appear at 102 eV and 152 eV due to Si2p and Si2s photoelectrons, respectively, which confirms the presence of silane molecules [16] and [51].
High resolution scans of the Si2p peak were obtained to better understand the bonding environment of the silanes and a representative spectrum is given in Fig. 4b. Two peaks centered at 102.1 eV and 103.1 eV were required to fit the spectrum, indicating two distinct chemical states of silicon. The band at 102.1 eV corresponds to silicon bonded to oxygen and the MWCNT surface while the peak at 103.1 eV derives from silicon bonded to oxygen and the silicon atom of another silane monomer [52]. The presence of Si–O–Si bonds indicates that partial hydrolysis of the silane molecules occurred and is in agreement with the FTIR results discussed earlier. However, only a small number of silane monomers underwent self-condensation relative to the number of GPTMS molecules that reacted with the o-MWCNT surface. Comparison of the fitted peak areas reveals that approximately 77% of the Si atoms were grafted to the MWCNT surface while 23% were bonded to another silane molecule.

Rheological measurements indicate that functionalization affects the interaction of nanotubes with epoxy resin. Fig. 5 compares the viscosity of neat Epon 828 with that of resin containing 0.5 wt% p-MWCNTs and s-MWCNTs as a function of shear rate. The neat resin behaves as Newtonian fluid with viscosity independent of shear rate. The addition of both p-MWCNTs and s-MWCNTs increases the resin viscosity and induces shear thinning behavior. However, the higher viscosity of epoxy containing s-MWCNTs suggests that these nanotubes are either more highly dispersed or interact more favorably with the resin than p-MWCNTs [53] and [54].
In order to test the effectiveness of functionalization in improving nanocomposite properties, composites were prepared using model epoxy system consisting of Epon 828 and TETA. Fig. 6 and Fig. 7 summarize the thermo-mechanical behavior of nanocomposites made with p-MWCNTs and s-MWCNTs, respectively. The addition of p-MWCNTs increased the glassy modulus of the epoxy slightly at all loading levels while the rubbery modulus plateaued at nearly the same value for the neat epoxy and all composites. Composites containing s-MWCNT also exhibited marginally higher glassy moduli than the neat epoxy and had slightly higher rubbery moduli as well. The elevated rubbery plateau modulus of s-MWCNT composites may be due to increased cross-linking density. While a stoichiometric ratio of amine to epoxide groups was maintained in the resin mixture, the addition of s-MWCNTs introduces a slight excess of epoxide groups, which can react with –OH moieties present in cured portions of the network. Such a reaction would increase the cross-link density relative to the neat epoxy. Analysis of the curing exotherm by DSC revealed that the heat of reaction increases by a small amount with the addition of s-MWCNTs relative to the neat epoxy (Table S1). This suggests that the composites do indeed have a higher cross-link density than the neat resin, although the magnitude of the change is not large enough to account for the $T_g$ increases observed in the present study alone. Therefore, the elevated $T_g$s observed at low loadings of s-MWCNTs are likely due to both a slight increase in crosslink density and confinement of network segments near s-MWCNTs.
The insets in Fig. 6 reveal the significant changes observed in tan δ of the nanocomposites, and the tan δ peak temperature was used to define the $T_g$. The $T_g$ of the epoxy increased from 136 °C to around 142 °C upon introduction of 0.1 wt% and 0.2 wt% p-MWCNTs. Higher loading levels caused only minor increases in the $T_g$, which may be due to limited polymer-MWCNT interaction as the result of agglomeration of the nanotubes. Dramatic increases in the $T_g$ of composites containing s-MWCNTs were seen at low loading levels. At 0.1 wt% s-MWCNT loading, the composite $T_g$ increased 18 °C relative to the neat epoxy to 154 °C. The addition of greater amounts of s-MWCNTs led to progressively lower $T_g$s, though they were still much higher than the neat epoxy with values of 149 °C, 147 °C, and 143 °C for 0.2 wt%, 0.5 wt%, and 1.0 wt% loading, respectively.

The dramatic increase in the $T_g$ of the epoxy with small MWCNT additions suggests that strong, positive interactions exist among the MWCNTs and polymer network. To further probe the nature of these confinement effects, the nanocomposite heat capacities were measured with DSC and polymer cooperativity length scales calculated according to the method of Donth [55] and [56]. Within this framework, an inhomogeneous glass composed of spatially fluctuating network mobility can be conceptually divided into several subsystems capable of rearranging their configurations independently of surrounding subsystems upon thermodynamic fluctuation. These subsystems, called cooperatively rearranging regions (CRRs), represent the number of segments that must cooperatively move in order for network relaxation to occur and their size strongly depends on temperature. The CRR volume at the glass transition, $\xi^3$, can be estimated from the mean temperature fluctuation ($\delta_T$) of an average CRR at the glass transition according to:

$$\xi^3 = \frac{k_B T_g^2 \Delta (1/C_v)}{\rho (\delta_T)^2}$$

where $k_B$ is the Boltzmann constant, $\rho$ the density, $T_g$ the glass transition temperature, and $C_v$ the heat capacity at constant volume of the composite. In practice, $C_v$ is approximated by the constant pressure heat capacity, $C_p$, measured by DSC. For all measurements, samples were first heated to 200 °C to erase thermal history, cooled at 10 °C/min to 30 °C, and finally heated to 200 °C at 10 °C/min. The heat capacity measured during the final heating cycle was used to calculate all parameters. The mean temperature fluctuation at $T_g$ was estimated using Donth's
approach, in which $\delta_T = \Delta T/2.5$ with $\Delta T$ defined as the temperature interval over which $C_p(T)$ varies by one standard deviation of the total $C_p$ change at $T_g$. [57]

The effect of various loadings of p-MWCNT and s-MWCNT on the CRR of epoxy nanocomposites is presented in Fig. 8. The neat epoxy has a slightly lower average CRR length ($\xi \sim 2.18$ nm) than composites prepared with p-MWCNTs at all loading levels ($\xi \sim 2.32$ nm). However, composites filled with s-MWCNTs exhibit a fundamentally different behavior, with $\xi$ values of 3.50 nm, 3.46 nm, 3.15 nm, and 2.79 nm for loadings of 0.1 wt%, 0.2 wt%, 0.5 wt%, 1.0 wt%, respectively. Elevation of the CRR with s-MWCNT additions is the result of both an increase in the temperatures of the glass transition and a reduction in its width, and this behavior is consistent with DMA observations. The peaks in Fig. 6 corresponding to p-MWCNT composites have similar widths as the neat resin, while the composites containing s-MWCNTs depicted in Fig. 7 are narrower with peak positions at higher temperatures. The large CRR size of the composites prepared with s-MWCNTs is attributed to covalent bonding of the silanized nanotubes with the epoxy network, which greatly restricts the mobility of its segments and necessitates the coordinated movement of many chains for relaxation to occur. The increased connectivity of the network produces a larger activation energy barrier for chain motion, which is manifested in a relatively large $T_g$.

![Fig. 8: Changes in the cooperatively rearranging region length with p-MWCNT and s-MWCNT additions.](image)

Tensile testing was performed to evaluate the effect of nanotube additions on the epoxy mechanical behavior. Fig. 9 summarizes the results and reveals that optimal properties are realized at low loadings. The addition of 0.2 wt% s-MWCNTs markedly increases the ultimate tensile strength of the resin, while the same loading of p-MWCNTs has little effect. Both types of MWCNTs increase the strain at break and toughness of the epoxy, though the greatest improvements are observed for s-MWCNTs composites. Functionalization has a less pronounced impact on the Young's modulus, and Fig. 9b shows that the modulus of s-MWCNT composites is nearly the same as those of p-MWCNTs at all nanotube loadings. Elevating the loading levels of any type of MWCNT above 0.2 wt% has a deleterious effect on toughness, likely due to agglomeration of the nanotubes. The fracture surfaces of tensile test specimens were examined with SEM to compare the failure mechanisms of the neat epoxy and nanocomposites prepared with both types of nanotubes.
Fig. 9: Tensile properties of neat epoxy as well as p-MWCNTs and s-MWCNT/epoxy nanocomposites: (a) Young's modulus, (b) tensile strength, (c) fracture strain, and (d) toughness.

Large differences in the fracture behavior of p-MWCNT and s-MWCNT composites reflect the increased toughness that was observed for composites containing silanized nanotubes. Fig. 10 shows the surfaces of neat epoxy and p-MWCNT composite samples fractured via tensile testing. The neat epoxy fracture surface is smooth with few river markings, indicative of brittle failure. p-MWCNT composites contain agglomerations even at 0.1 wt% loading that become larger as the nanotube concentration is increased to 0.5 wt%. Inspection at high magnification reveals significant nanotube pullout, which is indicative of poor bonding at the MWCNT-epoxy interface. In contrast, s-MWCNT composites contained fewer agglomerations at low loadings, and microcracks were bridged with nanotubes, as shown in Fig. 11. Therefore, the increased toughness observed for s-MWCNT composites is likely due to the increased energy required to open cracks, in an analogous fashion to crazing-induced toughening in thermoplastics.
Fig. 10: Fracture surfaces of (a) neat epoxy and composites filled with (b) 0.1 wt% p-MWCNT and (c) 0.5 wt% p-MWCNT. A higher magnification image of the 0.5 wt% p-MWCNT composite (d) shows MWCNTs that have partially pulled out of the matrix (demarcated with red arrows) as well as grooves left behind from nanotubes that have been completely removed (highlighted with blue arrows).

Fig. 11: Fracture surfaces of composites filled with (a) 0.1 wt% s-MWCNT and (b) 0.5 wt% s-MWCNT. A higher magnification image of the (c) 0.5 wt% s-MWCNT composite shows nanotubes bridging cracks, which are demarcated by red arrows.

4. Conclusions

scCO\textsubscript{2} was found to be a suitable solvent for the functionalization of o-MWCNTs with GPTMS and offers a green alternative to organic solvents for grafting nearly monolayers of silane molecules onto the nanotube surfaces. The addition of s-MWCNTs to a model epoxy system markedly increased its \(T_g\), and measurements of the network cooperativity length scale confirmed that silanized nanotubes restrict polymer mobility. Composites filled with p-MWCNTs and s-MWCNTs exhibited significantly higher strain at break and toughness than the neat epoxy, and the greatest improvements were observed at low loading levels. SEM analysis of the composite fracture surfaces revealed that nanotube pullout was the primary failure mechanism in epoxy loaded with p-MWCNT while crack bridging predominated in s-MWCNT composites as the result of covalent bonding of silanated nanotubes with the matrix. The elevated \(T_g\) and toughness achieved with small additions of s-MWCNTs promise to extend the engineering applications of the epoxy resin.

References


