TOUGHENING OF EPOXY COMPOSITES WITH REDUCED SINGLE-WALLED CARBON NANOTUBES

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1. Introduction

The one-dimensional structure of single walled carbon nanotubes (SWCNT), their low density, high aspect ratio and extraordinary mechanical, electrical and thermal properties make them particularly attractive as reinforcing fillers for multifunctional composite materials. Due to their high crystallinity and high aromaticity, SWCNT are substantially chemically inert and exist as ropes or bundles due to strong van der Waals interactions. These yield poor dispersion/exfoliation and poor interfacial bonding with matrices. Hence, a great challenge in SWCNT/polymer composites has been and continues to be the efficient transfer of nanotube properties into a polymer matrix. Most of the focus on epoxy/CNT composite systems has been on bi-dentate resins such as the well-known diglycidyl ether of bisphenol-A (DGEBA). However, many aerospace materials and other high-performance applications require tri-dentate or tetra-dentate epoxies due to their favourable mechanical properties such as high modulus and thermal stability, coupled with low shrinkage on curing. Here we demonstrate that negatively charged SWCNT (r-SWCNT) obtained upon reduction with alkali metal naphthalides react readily at room temperature with epoxide containing moieties. This surface modification allows better dispersion and improved affinity with different epoxy matrices. The mechanical properties of a bi-dentate (West System 105 Epoxy resin, Bisphenol-A), tri-dentate (Huntsman MY0510, triglycidyl p-amino phenol,) and a commercial epoxy system were evaluated upon addition of r-SWCNT.

2. Experimental section

SWCNT were synthesized by the two-laser method developed at NRC-SIMS as reported previously.[1] The procedure to reduce (negatively charge) and disperse SWCNT was similar to the method originally described by Penicaud *et al* [2] and later by Martinez-Rubi *et al*.[3] All reactions were conducted under nitrogen. In a typical integration protocol a suspension of r-SWCNT in THF was carefully transferred under nitrogen to a 250 mL flask and centrifuged for 30 min, the excess of sodium naphthalide was discarded and the r-SWCNT re-suspended in dry THF, centrifuged again to remove any residual sodium naphthalide, and re-suspended in 70 mL of dry THF using a sonication bath for 30 min. The desired amount of epoxy monomer was dried under vacuum at 80 ºC. The stable suspension of r-SWCNT in THF was added under nitrogen to the epoxy monomer and mixed by energetic shaking and bath sonication for 30 min. The THF was removed at room temperature by sparging the mixture with nitrogen for 2 hours and with air overnight, then dried in a vacuum oven at 80 ºC for 2 hours.

Using the methods described above, 20 kg of the SWCNT-modified epoxy system (consisting of 4 epoxy resins, 2 catalysts, one plasticizer and one hardener) were also prepared. A prepreg tow processing technique was used to impregnate unidirectional carbon fiber tape using a commercial-scale solvent-free prepregging technique based on hot melt processing.

3. Chemistry of reduced SWCNT and epoxide derivatives

SWCNT can be exfoliated by reduction with an alkali metal through electron transfer mediated by alkali-naphthalene-tetrahydrofuran complexes.[2] As the SWCNT charge negatively, they exfoliate as result of electrostatic repulsion and can form stable suspensions in polar solvents. In addition, r-SWCNT have higher nucleophilic character than neutral or unfunctionalized SWCNT (u-SWCNT) and hence exhibit higher reactivity towards various reagents.[3] They can react readily at room temperature with epoxide-containing molecules such as epibromohydrin as represented in Fig. 1. The covalent modification of the nanotube surface has been confirmed by Raman spectroscopy and thermogravimetric analysis (TGA). The reaction of reduced SWCNT with epibromohydrin (Fig. 2) leads to an increase in the D-band intensity, indicating side-wall functionalization. TGA of functionalized SWCNT in inert atmosphere showed a 30 wt% loss upon heating to 900, another indication of the attachment of functional groups to the SWCNT.

In a similar way r-SWCNT can readily react at room temperature with epoxy resins when they are blended together in inert atmosphere. Under these conditions the ring opening of the epoxide group supports propagation of the nucleophilic reaction to the next epoxy resin molecule by alkoxide groups creating a direct connection to the resin backbone, as shown in Fig. 3 for the tri-dentate epoxy resin (MY0510). The reaction propagates until the alkoxide is neutralized, usually though hydrolysis. This reaction ensures excellent interface compatibility and maintains the stability of the dispersion once the solvent is removed and the alkoxide moieties have hydrolyzed.

Although for this reaction the level of covalent connection is rather difficult to determine quantitatively, consistent results were found to be possible by controlling the reaction conditions and processing.

This integration strategy was also used to prepare composites with a bi-dentate epoxy resin commercialized under the name WEST System 105 Epoxy resin as well as a proprietary epoxy resin system made of four bi-dentate epoxy resins.

4. Processing and Mechanical Properties of SWCNT/Epoxy composites

The dispersion of the uncured SWCNT/MY0510 composites at 0.2 wt% was analyzed with an optical microscope after the addition of the curing agent. Additionally, the samples were heated under the microscope to observe the stability of the dispersions during the curing process. Fig. 4 displays optical images of these composites taken at different temperatures.

The optical images showed that DDS particles (identified by circles, Fig. 4 A, B, C) are not dissolved into the epoxy at room temperature but they dissolve at around 110 ºC while inducing local SWCNT clustering and leaving transparent areas (identified by arrows). This leads to a composite with an inhomogeneous distribution of the reinforcement. On the other hand, optical images taken at different temperatures of r-SWCNT/MY0510 samples where DDS was dissolved at 100 °C before doing the analysis (Fig. 4 G, H, I) showed less re-agglomeration and hence more homogeneous dispersion even at higher temperatures. In the case of u-SWCNT/MY0510 samples, although the distribution of nanotubes was homogeneous at room temperature, (Fig. 4D) local clustering of the nanotubes occurred at higher temperature regardless the mixing conditions. This result indicates that the introduction of reduced SWCNT and their covalent attachment to the epoxy monomer helps to increase the repulsive barrier between nanotubes and maintain the stability of the dispersion, but the processing conditions also have to be controlled. Based on these results, for specimen preparation, after the addition of the curing agent, the sample was mixed at 100 °C until the DDS was completely dissolved and mixed at 10 min intervals while degassing at 120 °C in order to maintain SWCNT dispersion and avoid the formation of local clustering. At this temperature as the crosslinking reaction begins, the formation of higher molecular weight species increases the system viscosity and restricts Brownian motion enough to stabilize the nanotube dispersion against agglomeration without affecting processability.

Tensile tests were performed to determine the mechanical properties of bi-dentate and tri-dentate SWCNT/Epoxy composites containing r-SWCNT and u-SWCNT at 0.2 wt% as well as neat resin

(without SWCNT) in order to evaluate the effectiveness of this functionalization strategy. Some of these results are shown in fig. 5A and fig. 5B for SWCNT/MY0510 and SWCNT/105 epoxy composite respectively. Tensile results showed that SWCNT/MY0510 composites containing r-SWCNT enhance the ultimate tensile strength and toughness by 32 and 118% respectively without change in modulus, while the improvement in toughness for SWCNT/105 epoxy was only 9 %. Toughness improvement is a crucial step for application of these resins for development of laminates composites with improved interlaminar properties. Since these composites have not shown any significant stiffness enhancement, it is believed that the increased ductility is then most likely due to resin mobility enhancement in the presence of reduced SWCNT. In addition to the improved dispersability, the improvement in toughness observed with r-SWCNT may be attributed to grafting of epoxy oligomers to the SWCNT wall (Fig. 3), which acts as both a dispersing agent and a covalent matrix binding agent. The reaction represented in Fig. 3 could form a less reticulated, softer structure at the SWCNT/matrix interface which could increase matrix mobility at the interface.

5. Mechanical Properties of SWCNT/Epoxy System Composites

An epoxy system already optimized for toughness through incorporation of conventional modifiers (a plasticizer) was chosen as the epoxy matrix. Two batches of r-SWCNT-integrated epoxy system with loadings of 0.1 wt % and 0.2 wt % were prepared for resin fracture toughness measurements (K_{Ic}). A commercial prepregging unit was used to impregnate unidirectional carbon fiber tape with the epoxy system containing 0.1 wt % of r-SWCNT. In order to evaluate the effects of r-SWCNT on the ability of the laminate to resist interply delamination, both Mode I (G_{Ic}) and Mode II (G_{IIc}) interlaminar fracture toughness tests were performed on both nano-modified and baseline laminate.

Table 1 summarizes the fracture toughness of the bulk resins and laminates. For both nano-modified batches, the addition of r-SWCNT resulted in a reduction in resin fracture toughness (12 - 20%) as compared to the neat epoxy system. One possible explanation for this reduction is the addition of plasticizers. Plasticizers cause an increase of fracture toughness versus unmodified epoxy through a crack pinning mechanism. Optimization of the plasticizer content therefore results in maximizing crack-pinning effectiveness. Although the addition of SWCNT can also potentially enhance the fracture toughness of an epoxy system via various mechanisms such as fiber bridging, they can also reduce the effectiveness of the soft nano-particles (SNP) additives by deviating cracks away from these plasticizers through the weaker resin-SWCNT interface. Contrary to the bulk fracture toughness results, the addition of r-SWCNT enhances both Mode I and Mode II interlaminar fracture results (Table 1). Mode I interlaminar initiation toughness values were found to be lower than propagation values. This is believed to be caused by the fact that the first incremental delamination starts from the end of the Teflon insert and it is only after the crack begins to propagate that toughening mechanisms such as fiber bridging begin to act, increasing the energy required to grow the crack further. For Mode II fracture toughness results, Increases of 12% and 27% were measured for precracked (PC) and non-precracked (NPC) coupons, respectively, upon addition of r-SWCNT. The improvements reported for both Modes I and II are in agreement with recent findings already published in the literature [4].

References

[1] C. T. Kingston, Z. J. Jakubek, S. Denommee, B. Simard, “Efficient laser synthesis of single-walled carbon nanotubes through laser heating of the condensing vaporization plume”, *Carbon*, Vol. 42, pp 1657, 2004.

[2] A. Penicaud, P. Poulin, A. Derre, E. Anglaret, and P. Petit “Spontaneous dissolution of a single-Wall carbon nanotube salt”. *Journal of American Chemical Society*, Vol. 127, pp 8-9, 2005.

[3] Y. Martínez-Rubí, J.W. Guan, S. Lin, C. Scriver, R.E. Sturgeon, and B. Simard **“**Rapid, controllable and scalable covalent functionalization of single-walled carbon nanotubes at room temperature”. *Chemical Communications*, Vol. 48, pp 5146-8, 2007.

[4] H. Qian, E.S. Greenhalgh, M.S.P. Shaffer, A. Bismarck. “Carbon nanotube-based hierarchical composites: a review”. J. Mater. Chem. Vol. 20 pp 4751–62, 2010. 2010;

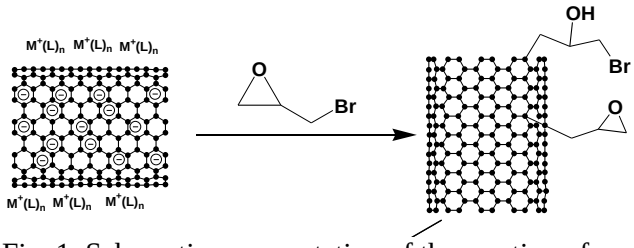

Fig. 1. Schematic representation of the reaction of reduced SWCNT with epibromohydrin.

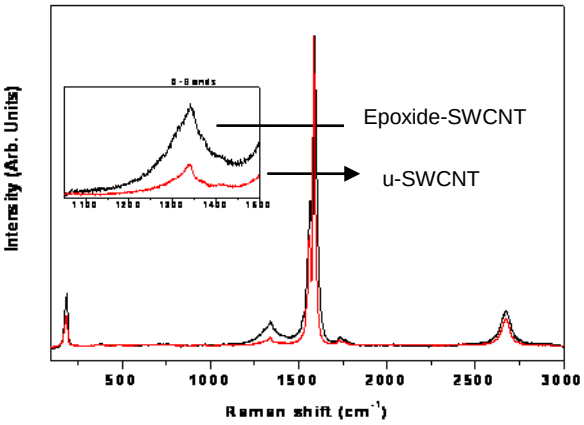

Fig. 2. Raman spectra of unfunctionalized (u-SWCNT) and epoxide functionalized SWCNT

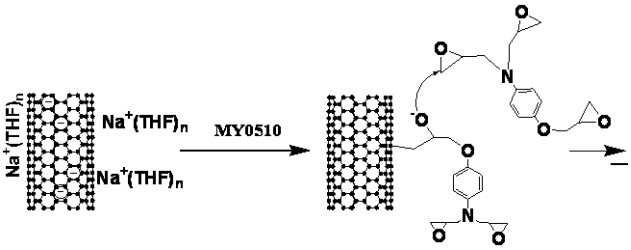

Fig. 3. Schematic representation of the reaction of r-SWCNT with the epoxy resin monomer MY0510 and the secondary crosslink propagation.

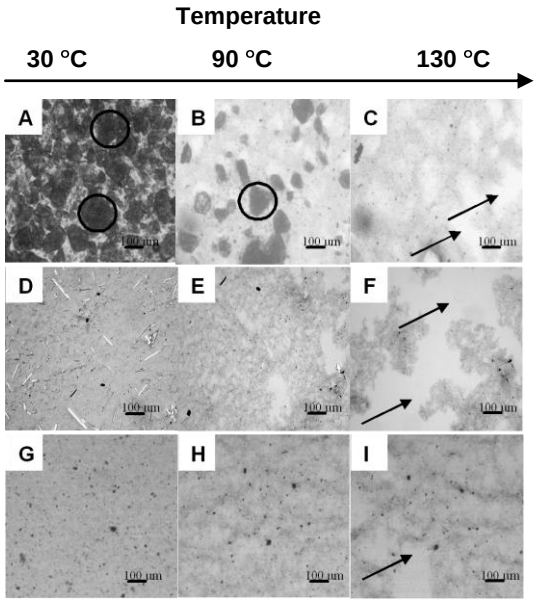

Fig. 4. Optical images of the uncured SWCNT/MY0510 composites at different temperatures; A, D and G at 30 ºC; B, E and H at 90 ºC and C, F and I at 130 ºC. The top and bottom rows of images correspond to r-SWCNT composites and the middle row to u-SWCNT.

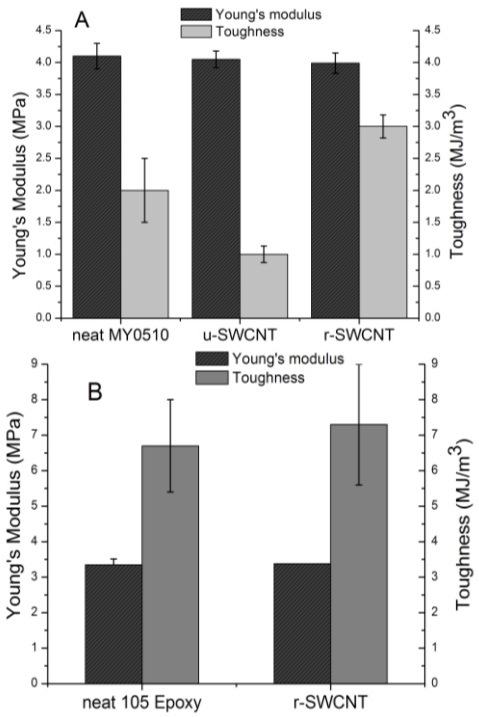

Fig. 5. Summary of mechanical properties obtained from tensile tests for (A) SWCNT/MY0510 and (B) SWCNT/105 epoxy composites.

Table 1. Comparison summary of mechanical testing of neat and nano-modified resin and their laminates

Properties	Baseline Sample	r-SWCNT 0.1 wt% (% change)	r-SWCNT 0.2 wt% (% change)
K_{Ic}	2.27±0.25 MPa.m$^{0.5}$	1.99±0.32 MPa.m$^{0.5}$ (-12.9%)	1.83±0.33 MPa.m$^{0.5}$ (-19.3%)
G_{Ic} Initiation	314±18 J/m^2	323±41 J/m^2 (+3.0%)	—
G_{Ic} Propagation	343±7 J/m^2	387±6 J/m^2 (+13.0%)	—
G_{IIc} Non precracked	1.79±0.24 KJ/m^2	2.01±0.13 KJ/m^2 (+12.4%)	—
G_{IIc} Precracked	1.10±0.13 KJ/m^2	1.41±0.08 KJ/m^2 (27.4)	—