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Integration of Single-Walled Carbon Nanotubes into a Single Component Epoxy Resin and an Industrial Epoxy Resin System

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SUMMARY

Single-walled carbon nanotubes (SWCNT) exhibit amongst the best mechanical, thermal and electrical properties of any known material. With their very high aspect ratios, SWCNT are well-suited to making ultra-light multifunctional structural composites. In this work, covalent chemistry is used to integrate SWCNT into a single component epoxy resin (aerospace grade MY0510) as well as an industrialized epoxy resin system for sporting goods. In particular, reduced SWCNT react directly with epoxide groups to create direct connections to the resin backbone. As the reduction process naturally exfoliates the SWCNT bundles, excellent dispersion is readily obtained. Substantial mechanical property improvements of the modified resin and carbon fibre composites have been observed through well-controlled processing. Their mechanical properties, specifically impact resistance, compression after impact strength and fracture toughness of the modified resin and fibre composites are discussed.

1. INTRODUCTION

Single-walled carbon nanotubes (SWCNT) exhibit exceptional mechanical, thermal and electrical properties, amongst the best of any known material. Combined with their very high aspect ratios, SWCNT are ideal fillers for the fabrication of ultra-light multifunctional and structural composite materials with superlative properties. Therefore, over the past decade, a huge amount of effort has been expended exploring potential applications of SWCNT in different polymer matrices including PMMA¹, vinyl ester², Nylon³, Epoxy resin⁴ etc., to enhance their mechanical properties as well as their electrical and thermal conductivities. Unfortunately, as a result of strong van der Waals interactions, high crystallinity and aromaticity, SWCNT bundle together

as ropes and have little affinity for, or compatibility with, any matrices and solvents. This makes the reinforcement of nanocomposites very challenging unless proper chemistry is employed. It is now widely accepted that chemistry is central to the proper integration of SWCNT into various matrices. Not only does chemistry address problems related to dispersion, it also resolves difficulties with interfacial compatibility. The latter is particularly important if one is seeking improvement of mechanical properties. Pénicaud *et al.* reported that SWCNT bundles can be readily exfoliated by reduction with an alkali metal such as Na, Li or K in THF through electron transfer mediated by alkali-naphthalene-THF complexes⁵. Furthermore, they concluded that the thus-reduced SWCNT dissolve spontaneously in polar aprotic solvents

such as sulfolane, dimethyl sulfoxide (DMSO), N-methylformamide (NMF), dimethylformamide (DMF), and 1-methyl-2-pyrrolidone. Indeed, these solvents do appear to dissolve reduced SWCNT and therefore, they have been used to conduct chemistry⁶⁻⁷. Our previous work demonstrated that care must be taken in choosing the proper solvent for reduced SWCNT, particularly in DMSO. Reduced SWCNT have increased nucleophilicity and are easily exfoliated in solution, thus allowing for versatile chemistries to be employed. However, reduced SWCNT can also act as initiators of radical reactions with radical scavengers such as DMSO. Our evidence has shown that DMSO *cannot* be used as a solvent with reduced SWCNT without first quenching their negative character⁸. Therefore, care must also be taken to maintain this negative character and its nucleophilic ability. In this work, covalent chemistry is applied to integrate reduced SWCNT into a single component epoxy resin (MY0510), which was used as test

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bed, as well as in an epoxy resin system commercially used in industrial scale processes. Preliminary impact, compression after impact and fracture toughness test results for the modified resin and carbon fibre composites are reported and discussed.

2. INTEGRATION OF SWCNT INTO EPOXY RESIN

2.1 Materials

A commercial trifunctional resin used in the aerospace industry, triglycidyl p-amino phenol (TGAP) with the trade name of Araldite MY0510, was used as the polymeric matrix precursor. Aradur HT976, 4,4'-diaminodiphenylsulfone (DDS), was chosen as the curing agent. Both were purchased from Huntsman Inc. The epoxy resin and curing agent were used without any further purification except that they were nitrogen-degassed before use.

The multi-part epoxy resin system was provided by Newport Adhesives Co. (NAC). This resin system is made of a mixture of epoxy resins with additives,

incorporated according to a proprietary recipe, and cured with a hardener and two catalysts using industrial standard 250 °F (121 °C) cure type⁹. To create a baseline with a neat resin system, a medium toughness, commercially available composite epoxy prepreg was used for this study.

SWCNT were produced in-house at NRC using a double-laser method as reported previously¹⁰. The produced pristine SWCNT were purified using in-house purification procedures, identified as WCPP in our recent publications¹¹⁻¹². The purity of tubes is greater than 90% by weight as shown in the SEM images in **Figure 1**.

2.2 Reduction of Neutral SWCNT by Sodium Naphthalene

The detailed procedure to reduce neutral SWCNT has been reported by Pénicaud *et al.* and in our previous publication^{5,8}. Briefly, a desired amount of dry SWCNT powder was ground in a small amount of tetrahydrofuran (THF) and then transferred into a Schlenk flask

with additional dry THF and sonicated until a well dispersed suspension formed. Then half-equivalent sodium with slightly excess naphthalene over sodium was applied. Note that it is preferable to prepare separately a stoichiometric amount of sodium-naphthalene THF solution rather than after the other constituents have been mixed together. The mixture was stirred at room temperature for roughly a day, then centrifuged at 5000 rpm for 30 minutes. The liquid phase was discarded, then the precipitate was washed twice with dry THF and suspended again in dry THF for the next processing steps.

2.3 Integration of Reduced SWCNT into a Single Epoxy Resin MY0510

In the usual procedure, the liquid epoxy resin MY0510 was heated to 50 °C and purged with nitrogen for 30 minutes, then poured under nitrogen into the reduced SWCNT suspension in THF. The amount of the resin used was calculated according to the desired SWCNT loading (e.g. from 0.1 to 0.6% of SWCNT by weight). The mixture was either mechanically shaken in a sealed plastic bottle or a vial or mechanically stirred in a Schlenk flask for about 2 hours. The well-mixed resin was then transferred into a beaker and sparged with nitrogen to slowly remove solvent, while stirring and heating up to 80 °C. After most of the solvent had evaporated, the resin was placed in a vacuum oven at 80 °C and the rest of the solvent was removed by vacuum at 1 torr.

2.4 Curing of Reduced SWCNT Integrated Epoxy Resin MY0510

After solvent removal, the SWCNT integrated epoxy resin MY0510 was mixed again with a high-shear mixer (Ultra-TURRAX, T 25 basic, IKA-WERKE) for 10 minutes before adding the 4,4-DDS hardener. The curing agent was added in a 100:60 (w:w) mixing ratio. The cure cycle used was similar

Figure 1. (a) Pristine SWCNT as produced; (b) WCPP purified SWCNT

to that used in industrial practice within Huntsman and Hexcel Corporation. For comparison neat resin samples were also prepared in the same processing conditions as SWCNT-integrated samples.

2.5 Integration of Reduced SWCNT into the Epoxy Resin System (Provided by NAC)

A multiple component epoxy resin system with one plasticizer and additional additives was prepared in the following two ways: One method (Method 1) standard NAC procedures, putting all constituents into one pot, then mixed at 80 °C until a uniform liquid was obtained. The second method (Method 2) was to dissolve each epoxy resin component in a hot THF solution, one after another using a mechanical stirrer.

To prepare roughly 2.50 kg of resin system with 0.1 wt.% loading of SWCNT, 2.52 g of purified SWCNT, 2.42 g of sodium, 16.2 g of naphthalene, and 2.50 kg of epoxy resin system were used. The details of preparation of reduced SWCNT are as described in reference⁸. The reduced SWCNT was washed with dry THF to remove any excess sodium naphthalene residue and re-dispersed in dry THF as a thick suspension for further use.

A solution obtained through Method 1 or Method 2 was heated to 65 °C in a 4 L beaker and sparged with nitrogen for half an hour with strong mechanical stirring. Under continuous nitrogen flow and at constant temperature, the suspension of reduced SWCNT in THF was poured into the hot resin solution. After the addition of all SWCNT suspensions, the mixture was strongly stirred for an additional two hours in a nitrogen atmosphere above the surface of the mixture at 65 °C. Afterward, the nitrogen glass tubes were carefully moved into the resin mixture with gentle sparging while heating continued, until most of the THF solvent evaporated. By then, the

total volume was reduced to about 2.5 L. The nitrogen gas was replaced with compressed air and sparging continued for another 2 hours. The remaining resin mixture was finally placed in a vacuum oven at 100-120 °C at about 1 torr until solvent could no longer be detected by smell. This procedure was repeated until 20 kg of SWCNT-modified epoxy resin system had been successfully manufactured as shown in **Figure 2**.

This SWCNT-integrated epoxy resin system was then used to manufacture SWCNT-integrated epoxy resin/carbon fibre pre-impregnated sheets (unidirectional prepreg) using a standard NAC process.

3. MECHANICAL TESTING

3.1 Specimen Preparation

Two quasi-isotropic composite laminates (one based on the neat epoxy system and the other based on SWCNT-modified epoxy system) were fabricated from the prepreg. **Figure 3** shows composite panels with a nominal dimension of 152 mm x 102 mm x 5 mm. These specimens were later used for the impact and compression-after-impact (CAI) tests. Composite specimens for other mechanical tests were similarly fabricated using the prepreg.

Plane-strain fracture toughness (K_{IC}) was measured on samples of neat resin,

Figure 2. 20 kg of reduced SWCNT-integrated industrial epoxy resin system

Figure 3. 152 x 102 mm composite panels fabricated using the prepreps from the 20 kg reduced SWCNT integrated epoxy resin system with unidirectional carbon fibres

and SWCNT-integrated resin and resin system. Single-edge-notch bending (SENB) specimens as per ASTM D 5045 were used for this testing¹³.

Cast neat resin and SWCNT reinforced resin blocks were machined to 5 mm thickness. The resin blocks were cut to a width (W) slightly larger than 10 mm using a diamond saw blade as shown in **Figure 4**. The specimens were lightly sanded with 400-grit sandpaper to achieve 10 mm in width and improve the surface finish. A sharp notch was machined into the specimen using a milling machine with a Dremel rotary disk that would generate a flat bottom notch or a V-shaped notch.

A sharp natural crack was generated by sliding a razor blade across the root notch to ensure the total crack length (a) was such that $0.45 < a/W < 0.55$. It was observed that all the specimens with a V-notch had the natural crack in the centre of the notch whereas the location of the natural crack in the flat bottom notch varied for each specimen. The coupon was then assembled on a compact loading test system as shown in **Figure 5**.

The test system in **Figure 5** was comprised of an Omega Digital Force Gauge and Displacement Transducer mounted to an Omega Manual Lever Test Stand. The test system was set up in a 3-point bending configuration such that when the lever is pulled down, the specimen is loaded between two stationary rollers and the indenter. The

ASTM standard requires that the crack length be measured after specimen fracture. The crack length was also checked prior to testing, in order to ensure the validity of the test.

Impact and compression after impact (CAI) tests were performed on two carbon fibre composite systems: The carbon/SWCNT epoxy system described in Section 2.5 and the similar NAC carbon/epoxy without SWCNT modification. In this paper, these two composite material systems are designated NCT4400 (SWCNT) and NCT4400, respectively. The specimens were fabricated according to the ASTM D7136/D7137 standards^{14,15}. For each material system, six specimens 152 mm x 102 mm x 5 mm were tested

as shown in **Figure 3**. The stacking sequence was $[45/0/-45/90]_4s$, which is a quasi-isotropic, midplane symmetric, 32-ply thick layup. The 0° lamina is in the 152 mm direction according to the guidance from the ASTM standard. The 12 specimens were fabricated by NAC and labelled as: 1) 7070-1 to 7070-6 for the six specimens of NCT4400 and 2) 7071-1 to 7071-6 for the six specimens of NCT4400 (SWCNT).

Specimens were first impacted according to the ASTM standard¹⁵. The residual compressive strength of impact-damaged specimens was then determined by loading them to failure in compression. The CAI specimen fixture shown in **Figure 6** was used for the compression testing. The fixture

Figure 5. Specimen installed in the compact load test system

Figure 4. Diamond saw cutting resin blocks and specimens with flat-bottom or V-notch

provides simple support to the vertical edges of the specimen to prevent global buckling, and clamped support to the top and bottom edges to suppress edge delamination. Compressive load was applied under displacement control at a rate of 1.27 mm/min using an MTS 880 load frame and data acquisition system. The load frame had a 440000 Newton load capacity and was hydraulically driven.

4. RESULTS AND DISCUSSION

As the reduced SWCNT are charged negatively, they ex-foliate as a result of electrostatic repulsion and solvent association with their cationic counterparts. In addition, reduced SWCNT have higher nucleophilic character than neutral SWCNT, exhibiting higher reactivity towards various reagents.¹⁶ They can readily react with the resin epoxide groups, directly anchoring to the resin backbone as represented in **Figure 7**.

The ring opening of the epoxide group supports propagation of the nucleophilic reaction to the next epoxy resin molecules by alkoxide groups. This crosslinking will continue until all free-standing epoxide groups are consumed, so that the entire resin will be completely reacted without the addition of any curing agent. This result with the epoxy resin MY0510 has been observed repeatedly but only if its nucleophilic character was protected under inert atmosphere. In this case, the fully crosslinked resin

solidified and cannot be processed any further (**Figure 8**). Hence, controlling the degree of covalent connection of reduced SWCNT to the epoxy resin became a major issue. Although the

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

Figure 6. Upper: Load frame and Lower: specimen fixture

Figure 7. Schematic of the reaction of reduced SWCNT with a single epoxy resin MY0510 monomer and secondary crosslink propagation

Figure 8. Reduced SWCNT curing MY0510 to different stages

Fracture toughness values G_{Ic} and K_{Ic} were measured according to ASTM D 5045 at Hexcel Composites Ltd. laboratories in Duxford, UK for MY0510 epoxy resin with 0.1 wt.% and 0.2 wt.% loading (before adding cure agent) of reduced SWCNT. The results indicated a consistent linear increase in fracture toughness with SWCNT loading as shown in **Figure 9**. For 0.1 wt.% loading, a 30% increase in K_{Ic} was observed while a 60% increase was measured for 0.2 wt.% loading. However, the samples showed a significant reduction in T_g from 250 °C for neat resin to 190 °C for the 0.2 wt.% loaded SWCNT. The modulus also dropped from 3.80 GPa to 3.56 GPa. The reasons for these decreases are still unclear, but one phenomenon has been repeatedly observed that different loadings of reduced SWCNT have different cure behaviours, which may affect the modulus and T_g performance, therefore, fine tweaking the cure cycle details for each individual loading may find out the solution of improving T_g and modulus. The critical energy release rate (G_{Ic}) was also plotted for comparison in **Figure 9**. The definition and calculation of K_{Ic} and G_{Ic} can be seen, e.g., in Ref.¹³.

The specimens labelled 7070 in **Figure 10** and SWCNT-integrated

specimens with 0.1 wt.% loading labelled 7071 in **Figure 11** were tested for drop-weight impact resistance and CAI. The detailed test results were reported elsewhere¹⁷. Here only a brief summary of the impact and CAI results are provided. From the impact force *versus* time curves and absorbed energy *versus* time curves obtained from the drop-weight impact test¹⁷, it was found that in terms of the maximum impact force and the absorbed energy, the damage resistance of the two composite systems [NCT4400(SWCNT) and NCT4400] are very close. Quantitative comparison of the internal damage detected by C-Scan approach has also been conducted. In terms of the measured damage length, width and the maximum damage diameter, the difference of the two material systems is very small (less than 3%)^{14,17}.

Images of failed specimens after CAI tests are shown in **Figure 10** for NCT4400 specimens (labelled 7070) and in **Figure 11** for NCT4400 specimens (labelled 7071). Damage occurs at the middle zone of the specimen as shown from the side view. The main fracture separates the fibres and progresses along a direction approximately $\pm 45^\circ$ to the longitudinal (loading) direction. The main fracture goes through the entire thickness and is accompanied by a certain extent of visible delamination, especially near the layers at the surfaces. However, as seen from the front views, the specimens are not completely separated. At the front face and the back face the specimens are wrinkled in the middle zone but not fractured. It is difficult to visually identify any difference between the two composite systems. Further fractographic analysis needs to be conducted with the aid of an optical microscope.

Although visual observations from both types of damaged specimens detected no significant difference, the residual compressive strength of impact-damaged specimens was still detectable. The average differences in

Figure 9. Fracture toughness tests - K_{Ic} and G_{Ic}

Figure 10. Specimens of NCT4400 after CAI tests

Figure 11. Specimens of NCT4400(SWCNT) after CAI tests

the failure load and the compression after impact strength of the two composite systems are 5.5% and 3.5%, respectively, with the composite enhanced by SWCNT having higher values. However, it has been observed that the coefficients of variations of the NCT4400 and NCT4400(SWCNT) specimens are 5.2% and 2.1%, respectively.¹⁷ Therefore, the results should be used with caution.

Furthermore, the two types of laminates were further tested for interlaminar fracture toughness using Mode I and Mode II tests. A 13% increase in propagation toughness and a 3% increase in initiation toughness were observed in Mode I, while a 28% increase in pre-cracked fracture toughness and a 13% increase in non pre-cracked specimens were observed in Mode II tests. Details of these tests and results will be reported elsewhere.

5. SUMMARY

We have successfully integrated reduced SWCNT into the single epoxy resin MY0510 as well as into an industrially relevant epoxy resin system. Significant improvements in fracture toughness with very small loading of SWCNT have been recorded. In particular, we have demonstrated that reduced SWCNT can be readily anchored to the resin backbone through covalent chemistry to produce well-dispersed composites with control. In addition, special care needs to be given to process the samples in order to obtain actual improvement in terms of mechanical properties.

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