J Mater Sci (2011) 46:207–214
DOI 10.1007/s10853-010-4921-6

Nylon toughened epoxy/SWCNT composites

**Luyi Sun · G. L. Warren · D. Davis ·
H.-J. Sue**

Received: 28 July 2010 / Accepted: 10 September 2010 / Published online: 28 September 2010

Abstract Epoxy/single-walled carbon nanotube (SWCNT) composites toughened by nylon particles (epoxy/SWCNT/nylon) were prepared. The SWCNTs were functionalized by oxidation and subsequent grafting with sulfanilamide. It was found that surface functionalization can effectively improve the dispersion of SWCNTs in epoxy, thus improving composite mechanical properties. Meanwhile, preformed nylon particles were utilized to enhance the fracture toughness of the composites. The epoxy/SWCNT/nylon composites prepared exhibit simultaneously improved stiffness, strength, and toughness. B-staged (partially cured) epoxy/SWCNT/nylon composites were successfully cast into thin films by manipulating degree of cure and viscosity. These thin films can be seamlessly integrated into laminated composite systems upon heating for improving mechanical properties and compression after impact strength of the laminated composites.

Introduction

Carbon nanotubes (CNTs), especially single-walled carbon nanotubes (SWCNTs), have attracted significant attention due to their extraordinary properties [1–4]. In particular, high aspect ratio SWCNTs have been considered as an ideal reinforcing agent for composite applications because of their superior mechanical, electrical, and thermal properties [5–7]. While CNTs have been incorporated into a wide range of polymer matrices to explore different applications [5–8], epoxy/CNT composites are particularly attractive because of the widespread applications of epoxy in aerospace, military, and sporting goods fields [6, 7, 9]. Various epoxy composites containing nanoparticles [10–12], nanotubes/nanofibers [6, 7, 9, 13–18], and nanoplatelets [19–34] have been explored to further improve its mechanical properties and introduce additional functionalities so as to better match the demanding requirements from the above application fields, and lead to new applications where lightweight and high strength are of primary interest.

A vast majority of studies on epoxy/CNT composites focus on stiffness and strength improvement [5–7]. Although it has been reported that CNTs can toughen epoxy, typically owing to the crack bridging effect of CNTs [35, 36], the level of toughening is usually insignificant [37–39] compared to the well-established traditional epoxy toughening approaches [40–42]. For example, preformed core–shell rubber (CSR) particles have long been used to toughen brittle epoxy [43, 44]. With the incorporation of a small amount of CSR particles in epoxy, the fracture toughness will usually be improved significantly; however, the strength and stiffness of the epoxy will exhibit a noticeable reduction [43, 44]. Nylon, typically in the form of micrometer-scale preformed particles, has also been frequently used to toughen epoxy, and its toughening

---

L. Sun
Department of Chemistry and Biochemistry & Materials Science and Engineering Program, Texas State University—San Marcos, San Marcos, TX 78666, USA

G. L. Warren · H.-J. Sue (✉)
Department of Mechanical Engineering, Polymer Technology Center, Texas A&M University, College Station, TX 77843, USA
e-mail: hjsue@tamu.edu

D. Davis
Composite Engineering and Application Center, University of Houston, Houston, TX 77004, USA

mechanisms in epoxy composites have been extensively studied [45–48]. In brittle matrix systems, where matrix plastic deformation ahead of the crack tip is limited, the nylon particles toughen thermosets by introducing particle bridging and matrix dilatation bands under mode-I fracture [47, 49]. Under mode-II fracture, where it has been shown to strongly correlate with compression after impact (CAI) strength of the composites, thermoplastic particles are considered most effective in improving mode-II toughness and CAI strength of the composites, mainly due to negligible reduction in matrix modulus as well as effectiveness in promoting localized shear deformation around the rigid particles [45–48, 50, 51].

In this article, we propose to introduce both SWCNTs and nylon particles into epoxy resin to prepare nylon toughened epoxy/SWCNT composites with balanced stiffness and toughness. In addition to regular composite panels for mechanical property testing, nylon toughened epoxy/SWCNT composite thin films were also fabricated. These thin films are expected to find wide structural and functional applications, such as interleaves for enhancing interlaminar strength, fracture toughness, and CAI strength of laminated composites [52]. Laminated carbon fiber reinforced epoxy composites have been widely used in many structural integrity demanding fields [53, 54]. While they exhibit outstanding stiffness and strength, the interlaminar strength and toughness of the laminated composites are typically weak, which limits their applications [53–55]. The main reason that laminated composites have low interlaminar toughness is because of the presence of brittle resin-rich pockets in the interlaminar region. Many approaches have been developed to address the low interlaminar toughness issues [50, 56], among which the incorporation of reinforcing agents [57] and/or toughening particles [45–47, 51] in the resin-rich interlaminar regions appears to be one of the most effective approaches to improve delamination strength of laminated composites. Thus, epoxy/SWCNT/nylon composite thin films with balanced stiffness and toughness could be an excellent candidate for laminated composites applications. Strategy for introducing composite thin films into laminated composites will be discussed.

Experimental

Materials

EPIKOTE™ 862 resin and EPIKURE™ W curing agent were used for this study, both of which were obtained from Hexion Specialty Chemicals, Inc. The SWCNTs (XD Grade) having a reported aspect ratio of >1,000 were provided by Carbon Nanotechnologies, Inc., Houston, TX (now known as Unidym). Sulfanilamide (99%) was purchased from Sigma-Aldrich. The nylon 12 particles with a reported particle size of ca. 10 μm and a melting point of 165 °C were donated by Toray Industries. The thin film coater was purchased from Elcometer Inc. (Rochester Hills, Michigan) where a temperature control system was custom-built for controlling the processing temperature. The release paper was donated by Hexcel Corporation (Salt Lake City, UT). An ultrasonic cleaning bath (Branson 1510R, 70 W-42 kHz) was used for all the ultrasonication treatments in this study. All chemicals were used as-received.

Preparation of nylon toughened epoxy/SWCNT composites and thin films

Pristine SWCNTs (P-SWCNTs) were first acid-treated to produce oxidized SWCNTs (O-SWCNTs) via procedures reported elsewhere [13]. O-SWCNTs were further exposed to sulfanilamide in acetone dispersion to form functionalized SWCNTs (F-SWCNTs) at a weight ratio of 1:1. The acetone dispersion system was ultrasonicated for 10 min to ensure good mixing and interaction.

The nylon particles were first dispersed in acetone. The pre-dispersed F-SWCNTs in acetone were then mixed with nylon acetone dispersion followed by an additional 5 min of ultrasonication to further promote dispersion. A predetermined amount of epoxy monomer was added to the solution and ultrasonicated for 15 min to achieve a SWCNT loading of 0.5 wt% in the final composite. Multiple samples were prepared in conjunction with the various states of SWCNT treatment. Samples with nylon loadings of 5 and 10 wt% were prepared for evaluation. After removal of acetone with a rotary evaporator in a water bath at 70 °C, EPIKURE™ W curing agent (26.4 phr) was then added.

Epoxy composite panels (ca. 3 mm in thickness) were prepared for mechanical property tests. The epoxy composite panels were fully cured in an oven at 121 °C for 2 h, followed by 2 h of post-cure at 177 °C.

Composite thin films were fabricated using a thin film coater. The samples were first B-stage cured (partially cured) at 121 °C for 70 min in an oven [14]. Prior to the removal of the epoxy/SWCNT samples from the oven, the thin film coater was preheated to 90 °C. The B-staged epoxy/SWCNT samples were quickly transferred from the oven and immediately cast into thin films with a thickness of 50 μm on top of release paper. The thin films can be further cured, or remain to be partially cured depending on their intended usage.

Characterizations

A Mettler Toledo (Model DSC821e) differential scanning calorimeter (DSC) was used to obtain DSC thermograms at a heating rate of 10 °C/min under nitrogen purge (80 mL/min). Viscosity profiles of epoxy/SWCNT/nylon dispersions were recorded on an Anton Paar Physica MCR 300 Rheometer using a 25-mm diameter parallel plate setup.

The optical microscopy (OM) investigation was carried out using an Olympus BX60 optical microscope. Scanning electron microscopy (SEM) study on the fracture surfaces of the composites were performed using a JEOL-6400 SEM. The fracture surface was coated with a thin layer (ca. 3 nm) of Au/Pd prior to SEM imaging.

Tensile properties of epoxy/SWCNT composites were tested following ASTM D638-98. Dynamic mechanical analysis (DMA) was conducted using a Q800 dynamic mechanical analyzer (TA Instruments) under three-point-bending mode at a fixed frequency of 1 Hz, and with a temperature increment of 5 °C/step. The single-edge-notch three-point-bending (SEN-3PB) test, based on ASTM D5045, was performed to obtain the mode-I critical stress intensity factor (K_{IC}) of the neat epoxy and epoxy composites, which was detailed in a previous report [13]. At least five specimens were tested for tensile, DMA, and K_{IC} measurements, and average values are reported.

Results and discussion

In order to fully impart the unique properties of SWCNTs into a polymer composite, it is necessary to achieve good SWCNT dispersion and strong adhesion between SWCNTs and the matrix [5–7]. A vast amount of research has been carried out to address the above issues, among which surface functionalization of SWCNTs has been demonstrated to be most effective because it can address both the dispersion and the adhesion requirements [58]. In this study, SWCNT was first oxidized and then functionalized by sulfanilamide via the interaction between the carboxylic acid groups on the surface of O-SWCNTs and the amino groups of sulfanilamide. Since nylon particles can be easily dispersed and form strong bonding in epoxy, they were used as-received without any pre-treatment.

Morphology characterization

It was observed that the addition of both O-SWCNTs and F-SWCNTs into the epoxy led to a dramatic increase in viscosity and significant shear thinning behavior, as shown in Fig. 1. Both the significant build-up in viscosity and pronounced shear thinning characteristics indicate that O-SWCNTs and F-SWCNTs have been well dispersed in epoxy matrix [30]. The higher viscosity and more significant shear thinning behavior of epoxy/F-SWCNT dispersion compared to epoxy/O-SWCNT suggest that sulfanilamide did help further improve the dispersion of SWCNTs in epoxy. In contrast, the addition of the same concentration of P-SWCNTs only increased the viscosity slightly, most likely due to the low level of dispersion of P-SWCNT in epoxy. The addition of 10 wt% nylon particles to the epoxy/SWCNT dispersions exhibited only marginal effect on the overall rheological behavior of the systems (Fig. 1). Probably because of its spherical shape, the addition of nylon particles did not lead to shear thinning, and only increased the viscosity slightly [59]. Meanwhile, the significantly increased viscosity of epoxy/F-SWCNT/nylon dispersion suggests that the addition of nylon particles did not negatively affect the dispersion of F-SWCNTs in epoxy.

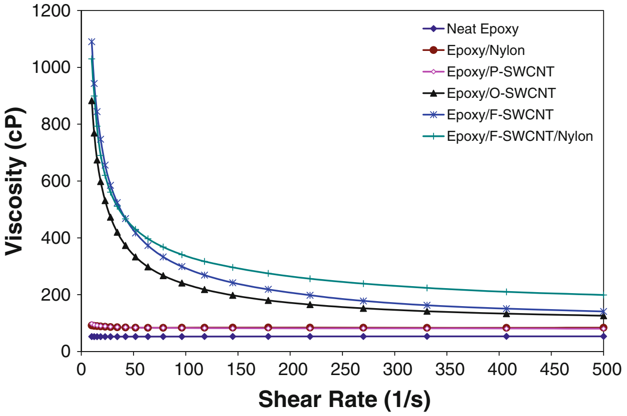


Fig. 1 Viscosity versus shear rate of epoxy, epoxy/SWCNT, and epoxy/SWCNT/nylon dispersions. The concentrations of SWCNTs and nylon particles in epoxy dispersions are 0.5 and 10 wt%, respectively (please note that epoxy/nylon and epoxy/P-SWCNT viscosity curves almost overlap with each other)

To confirm the above conjecture, OM was performed to directly observe the dispersion of SWCNT in epoxy matrix and compared with another functionalization agent, polyamidoamine generation 0 (PAMAM-G0) dendrimer, which yielded good dispersion and adhesion of SWCNT with epoxy and improved mechanical properties in our previous report [14]. The OM images presented in Fig. 2 show that sulfanilamide gives a slightly higher degree of dispersion when compared to PAMAM-G0 dendrimer. Considering its lower cost and better dispersion than PAMAM G0 dendrimer, sulfanilamide appears to be a better candidate for the functionalization and dispersion of SWCNTs in epoxy.

Fracture surface of epoxy/P-SWCNTs and epoxy/F-SWCNTs composite samples were further examined. It shows that, without any surface treatment, P-SWCNTs form aggregates and their adhesion with epoxy matrix is generally poor (Fig. 3a). Many tube bundles were pulled out of the epoxy matrix. In contrast, sulfanilamide functionalized SWCNTs are better dispersed. Broken F-SWCNT tube bundles on the fracture surface were observed (see arrows in Fig. 3b), which is indicative of excellent bonding between epoxy matrix and SWCNT. The above results demonstrate that similar to PAMAM G0 dendrimer, sulfanilamide can

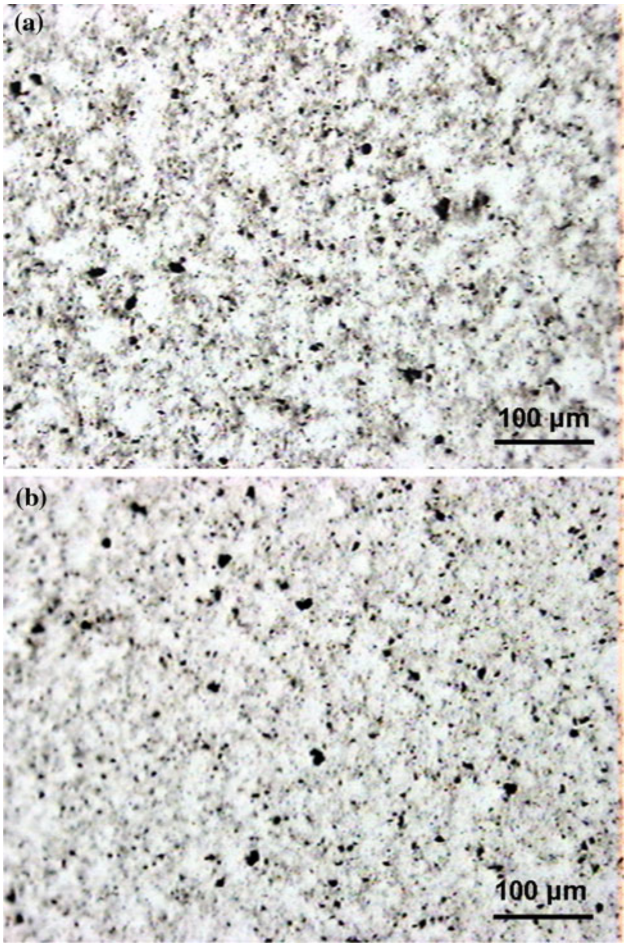


Fig. 2 OM images showing the dispersion of **a** PAMAM G0 and **b** sulfanilamide functionalized SWCNTs (0.5 wt%) in epoxy matrix

also help improve both dispersion and adhesion between SWCNTs and epoxy matrix.

Dynamic mechanical behavior

The DMA test results are shown in Fig. 4. As expected, the incorporation of F-SWCNT increased the storage modulus of epoxy. The T_g of the epoxy composites is reduced slightly after the addition of F-SWCNTs and nylon particles. The slight decrease of T_g of the composites is probably due to the presence of SWCNT and nylon particles that caused under-curing of the epoxy matrix. Similar results were reported earlier [60, 61].

Tensile behavior

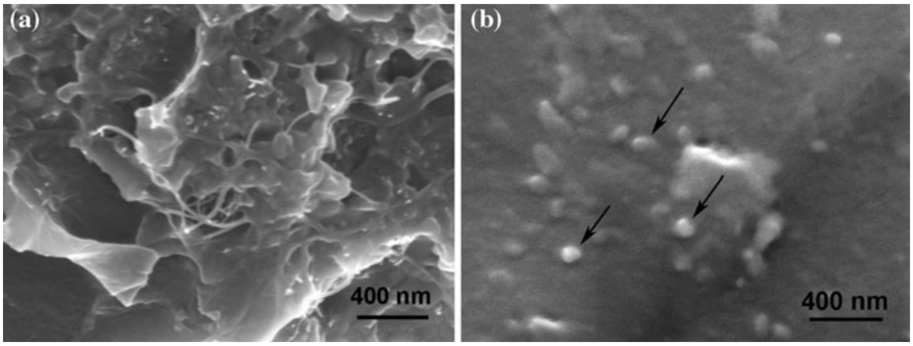
Tensile test was performed to evaluate the effect of the SWCNT surface functionalization and the addition of nylon particles on the mechanical properties of epoxy. The key tensile properties of bulk epoxy/SWCNT and epoxy/SWCNT/nylon composites are listed in Table 1. The results show that the incorporation of P-SWCNT can only slightly improve the Young's modulus of the composite. The marginal property improvement is due to the fact that most P-SWCNTs were poorly dispersed and still highly bundled, which was also corroborated by the limited viscosity increase as shown in Fig. 1. Oxidation of SWCNTs leads to a better dispersion, thus better improvements in mechanical properties. The incorporation of F-SWCNTs leads to the best overall reinforcement effect. The tensile properties of the epoxy composites exhibit a good correlation with the dispersion level of SWCNTs in epoxy matrix.

The addition of nylon particles in neat epoxy and epoxy/SWCNT samples slightly reduced their Young's modulus, and a higher nylon loading led to a larger drop in Young's modulus. This is believed to be due to the lower modulus nature of the nylon particles. As a result, the reinforcement effect is slightly compromised. It should be noted that if higher Young's modulus is of concern, higher modulus polymers, such as polyphenylene ether or polyetherimide, instead of nylon particles, can be incorporated to maintain or further increase the modulus of epoxy matrix [49].

Fracture behavior

The K_{IC} values of the composite samples are also shown in Table 1. There are only slight differences in K_{IC} values among the neat epoxy and the three epoxy/SWCNT

Fig. 3 SEM images of the fracture surface showing the dispersion of **a** pristine SWCNT bundles and **b** sulfanilamide functionalized SWCNT bundles in epoxy matrix



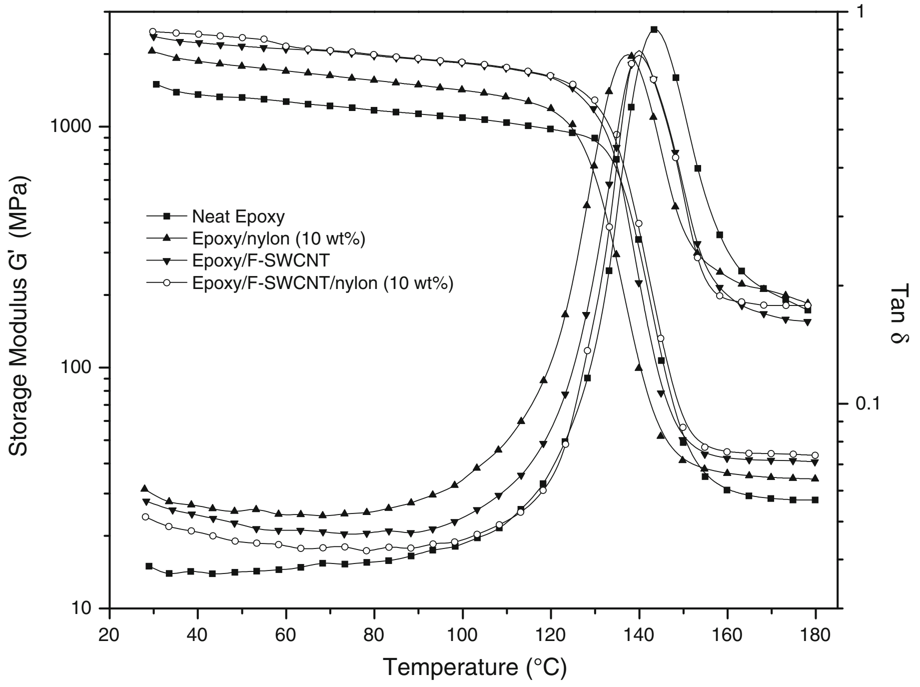


Fig. 4 DMA results of epoxy composites (0.5 wt% SWCNT)

composite samples, which is likely because of the inherent brittleness of epoxy resin. The addition of SWCNTs in epoxy cannot promote effective toughening mechanisms, such as shear banding. However, the addition of nylon particles to the epoxy/SWCNT composites is found to significantly improve the fracture toughness by promoting effective particle bridging mechanism. As expected, a higher concentration of nylon particles in epoxy led to a more significant fracture toughness improvement. The epoxy/F-SWCNT/nylon (10 wt%) composite exhibits the highest fracture toughness improvement, where over 40% increase in K_{IC} is observed.

SEM investigation on the fracture surfaces of the epoxy/SWCNT/nylon composites clearly shows evidence of fracture toughness improvement with the addition of nylon particles. The crack tip regions of the fracture surfaces are shown in Figs. 5 and 6. The neat epoxy shows a nearly featureless fracture surface without any deviation in crack growth, which is indicative of the brittleness of the sample. With an addition of 10 wt% of nylon particles, the crack propagation is accompanied by numerous crack steps, which are indicative of the localized crack deflection and crack bifurcation (Fig. 5). In addition, it is shown that the nylon particles are drawn on the fracture surface, which implies that particle bridging mechanism has also taken place. The above toughening mechanisms account for the increased fracture toughness for the epoxy/SWCNT/nylon composite systems.

The crack tip regions of the fracture surfaces of epoxy/F-SWCNT and epoxy/F-SWCNT/nylon (10 wt%) are shown in Fig. 6. Rough crack steps that move toward the SWCNTs and nylon particles are observed. The presence of SWCNT and nylon particles has promoted crack deflection, crack bifurcation, and microcracking. The nylon particles can further promote crack bridging. Therefore, the fracture toughness of the epoxy/F-SWCNT/nylon is greatly improved.

Overall, the addition of F-SWCNTs and nylon particles in epoxy leads to simultaneous improvements in modulus, strength, and fracture toughness, without noticeable compromise in processability.

Thin film fabrication and applications

The epoxy/F-SWCNT/nylon composite thin films were successfully prepared by manipulating the sample viscosity via processing temperature and degree of cure. This effective approach involves partial curing of the epoxy samples in an oven at 121 °C for 70 min, leading to ca. 50% of cure [14]. The B-staged epoxy/SWCNT/nylon samples were quickly transferred from the oven and immediately cast into thin films at a thickness of 50 µm on a thin film coater, which was preheated to 90 °C. As discussed above, probably because of their spherical shape, the addition of nylon particles did not lead to shear thinning, and only increased the viscosity slightly (Fig. 1) [59]. Therefore, the processability of the epoxy/SWCNT/nylon samples is similar to the epoxy/SWCNT samples reported earlier [14]. They maintain good processability even with up to 10 wt% addition of nylon particles.

The choice of sulfanilamide as functionalization agent for SWCNTs also helps to manipulate the viscosity of

Table 1 Mechanical properties of epoxy/SWCNT and epoxy/SWCNT/nylon composites (0.5 wt% SWCNT)

Property	Neat epoxy	Neat epoxy/nylon (10 wt%)	Epoxy/P-SWCNT	Epoxy/P-SWCNT/nylon (10 wt%)	Epoxy/O-SWCNT	Epoxy/O-SWCNT/nylon (5 wt%)	Epoxy/O-SWCNT/nylon (10 wt%)	Epoxy/F-SWCNT	Epoxy/F-SWCNT/nylon (5 wt%)	Epoxy/F-SWCNT/nylon (10 wt%)
Young's Modulus (GPa)	2.77 ± 0.01	2.61 ± 0.13	2.84 ± 0.05	2.73 ± 0.16	3.17 ± 0.01	2.88 ± 0.06	2.79 ± 0.10	3.21 ± 0.16	3.05 ± 0.08	2.98 ± 0.09
Tensile Strength (MPa)	60.1 ± 5.6	78.3 ± 1.4	74.2 ± 0.5	80.4 ± 1.4	76.5 ± 3.9	79.8 ± 0.5	84.0 ± 1.7	88.3 ± 0.6	87.0 ± 1.4	77.3 ± 0.4
Elongation (%)	1.98 ± 0.22	4.26 ± 0.76	2.57 ± 0.18	1.51 ± 0.50	2.97 ± 0.40	3.26 ± 0.31	3.30 ± 1.02	3.05 ± 0.30	5.56 ± 0.43	3.33 ± 0.84
K_{IC} (MPa $m^{1/2}$)	0.78 ± 0.01	0.95 ± 0.09	0.76 ± 0.03	0.99 ± 0.07	0.83 ± 0.05	0.94 ± 0.05	1.02 ± 0.10	0.86 ± 0.08	1.02 ± 0.07	1.12 ± 0.09

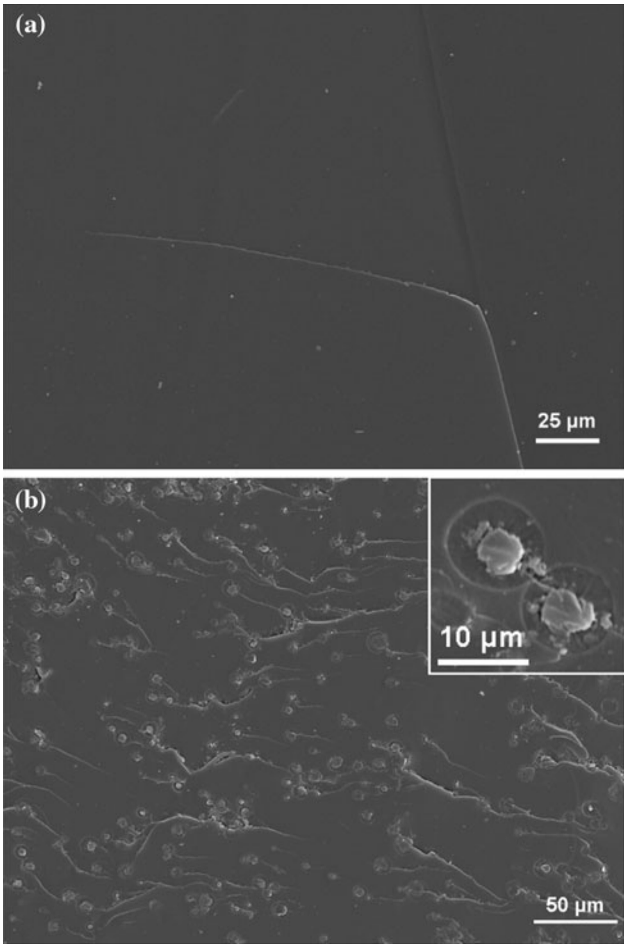


Fig. 5 SEM images of the fracture surface of **a** neat epoxy and **b** epoxy/nylon (10 wt%) composite. The *inset* shows nylon particles are drawn on the fracture surface, which typifies the crack bridging phenomenon

epoxy/SWCNT/nylon dispersions. Sulfanilamide contains two amino groups with two distinctly different reactivities: the aniline end of the molecule is more reactive than the sulfonamide end. Thus, the SWCNT surfaces are likely to react with the amino groups from the aniline side of sulfanilamide first during the functionalization step. This leaves the SWCNTs grafted with short chains terminated with sulfonamide groups. Since such sulfonamide groups are less reactive when compared to the curing agent, the functionalized SWCNTs will not be integrated into the epoxy network until a later stage when curing temperature is raised [62–64]. Therefore, the viscosity build-up is less likely to occur during the mixing and B-stage curing step, which facilitates the film casting process.

The B-staged thin films themselves can find a multitude of applications, such as micro-devices, electronic packaging [65–67], and coatings for corrosion protection [68] after they are cured. But they can also remain B-staged, and subsequently be co-cured with fresh epoxy monomers. This

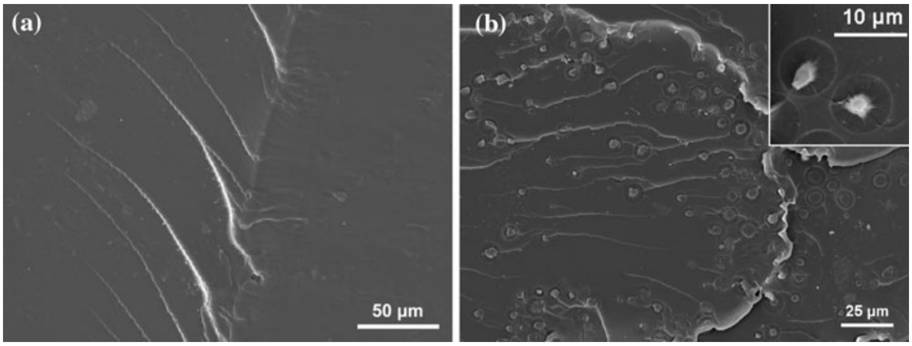


Fig. 6 SEM images of the fracture surfaces of **a** epoxy/F-SWCNT and **b** epoxy/F-SWCNT/nylon (10 wt%) composites. The *inset* shows nylon particles are drawn on the fracture surface, which indicates the occurrence of crack bridging. The concentration of F-SWCNT is 0.5 wt% in both samples

allows the thin films to be integrated into the newly infused epoxy system. A unique approach to introduce SWCNTs into epoxy matrix only at locations of interest has been developed by inserting epoxy/SWCNT B-staged thin films into epoxy matrix followed by complete curing [16]. In this way, expensive SWCNT can be used only at the designated locations of interest, and thus lowering cost. Meanwhile, the handling issue due to the high viscosity of epoxy/SWCNT dispersion can be minimized.

The B-staged epoxy/F-SWCNT/nylon thin films prepared in this study have been successfully utilized as interleaves by vacuum-assisted resin-transfer-molding (VARTM) to prepare high-performance laminated composites. Good-quality composite panels with improved mechanical performance have been prepared [69]. Their effect on the mechanical performance of carbon fiber reinforced composites, including interlaminar strength, fracture toughness, and CAI strength, will be reported in the near future.

Conclusion

Epoxy/SWCNT/nylon composites with a high degree of dispersion of SWCNTs and nylon particles throughout the matrix have been prepared. The high degree of SWCNTs dispersion in epoxy was achieved by the functionalization of oxidized SWCNTs with sulfanilamide, which improves epoxy modulus and strength. Sulfanilamide is inexpensive but effective as a functionalization agent to improve dispersion of SWCNT and does not compromise processability. The addition of nylon particles to epoxy/SWCNT composites improves fracture toughness, with only negligible effect on modulus, T_g, and processability. B-staged epoxy/SWCNT/nylon composite thin films were successfully fabricated by manipulating degree of cure and viscosity. These thin films can be seamlessly integrated into laminated composite systems and are expected to serve as effective interleaves for improving mechanical properties and CAI strength of the laminated composites.

Acknowledgements The authors acknowledge partial financial support of the U.S. Air Force AFRL Contract # FA8650-05-D-1912, the Minority Leaders Program. The authors would also like to thank Dr. Victor M. Ugaz and Hugo Y. Acosta from the Chemical Engineering Department, Texas A&M University for their help with the viscosity measurements, and Ms. Xi Zhang for her help on SEM imaging. Acknowledgement is also extended to Dr. Tony Golato of Hexcel for providing release paper for this study.

References

1. Ebbesen TW (1994) Annu Rev Mater Sci 24:235
2. Bernholc J, Brenner D, Buongiorno Nardelli M, Meunier V, Roland C (2002) Annu Rev Mater Res 32:347
3. Terrones M (2003) Annu Rev Mater Res 33:419
4. Dresselhaus MS, Dresselhaus G, Jorio A (2004) Annu Rev Mater Res 34:247
5. Xie X-L, Mai Y-W, Zhou X-P (2005) Mater Sci Eng R 49:89
6. Moniruzzaman M, Winey KI (2006) Macromolecules 39:5194
7. Thostenson ET, Ren Z, Chou T-W (2001) Compos Sci Technol 61:1899
8. Suhr J, Koratkar N (2008) J Mater Sci 43:4370. doi:10.1007/s10853-007-2440-x
9. Sun L, Sue H-J (2010) In: Pascault J-P, Williams RJJ (eds) Epoxy polymers: new materials and innovations. Wiley-VCH, Weinheim, p 185
10. Sreekala MS, Eger C (2005) In: Friedrich K, Fakirov S, Zhang Z (eds) Polymer composites. Springer, New York, p 91
11. Jiao J, Sun X, Pinnavaia TJ (2009) Polymer 50:983
12. Zhu J, Wei S, Ryu J, Sun L, Luo Z, Guo Z (2010) ACS Appl Mater Interfaces 2:2100
13. Sun L, Warren GL, O'Reilly JY, Everett WN, Lee SM, Davis D, Lagoudas D, Sue HJ (2008) Carbon 46:320
14. Warren GL, Sun L, Hadjiev VG, Davis D, Lagoudas D, Sue H-J (2009) J Appl Polym Sci 112:290
15. Hadjiev VG, Warren GL, Sun LY, Davis DC, Lagoudas DC, Sue HJ (2010) Carbon 48:1750
16. Sun LY, Warren GL, Sue HJ (2010) Carbon 48:2364
17. Zhu JH, Wei SY, Ryu J, Budhathoki M, Liang G, Guo ZH (2010) J Mater Chem 20:4937
18. Chang L, Friedrich K, Ye L, Toro P (2009) J Mater Sci 44:4003. doi:10.1007/s10853-009-3551-3
19. Lan T, Pinnavaia TJ (1994) Chem Mater 6:2216
20. Wang MS, Pinnavaia TJ (1994) Chem Mater 6:468
21. Wang K, Chen L, Wu J, Toh ML, He C, Yee AF (2005) Macromolecules 38:788
22. Sue H-J, Gam KT, Bestaoui N, Spurr N, Clearfield A (2004) Chem Mater 16:242

23. Sue H-J, Gam KT, Bestaoui N, Clearfield A, Miyamoto M, Miyatake N (2004) Acta Mater 52:2239
24. Sun L, Boo WJ, Sun D, Clearfield A, Sue H-J (2007) Chem Mater 19:1749
25. Boo WJ, Sun L, Liu J, Clearfield A, Sue H-J (2007) J Phys Chem C 111:10377
26. Boo WJ, Sun L, Liu J, Clearfield A, Sue H-J, Mullins MJ, Pham H (2007) Compos Sci Technol 67:262
27. Boo WJ, Sun L, Liu J, Moghbelli E, Clearfield A, Sue H-J, Pham H, Verghese N (2007) J Polym Sci B 45:1459
28. Boo WJ, Sun L, Warren GL, Moghbelli E, Pham H, Clearfield A, Sue H-J (2007) Polymer 48:1075
29. Sun L, Boo WJ, Clearfield A, Sue H-J, Pham HQ (2008) J Membr Sci 318:129
30. Sun L, Boo W-J, Liu J, Clearfield A, Sue H-J, Verghese NE, Pham HQ, Bicerano J (2009) Macromol Mater Eng 294:103
31. Moghbelli E, Sun L, Jiang H, Boo WJ, Sue H-J (2009) Polym Eng Sci 49:483
32. Sun L, Liu J, Kirumakki SR, Schwerdtfeger ED, Howell RJ, Al-Bahily K, Miller SA, Clearfield A, Sue H-J (2009) Chem Mater 21:1154
33. Sun L, Sue H-J (2010) In: Mittal V (ed) Barrier properties of polymer clay nanocomposites. Nova Science Publishers, New York, p 73
34. Sun L, Boo WJ, Liu J, Tien C-W, Sue H-J, Marks MJ, Pham H (2007) Polym Eng Sci 47:1708
35. Ritchie RO (1999) Int J Fract 100:55
36. Geng Y, Liu MY, Li J, Shi XM, Kim JK (2008) Composites A 39:1876
37. Salinas-Ruiz MdM, Skordos AA, Partridge IK (2010) J Mater Sci 45:2633. doi:10.1007/s10853-010-4241-x
38. Ma P-C, Liu M-Y, Zhang H, Wang S-Q, Wang R, Wang K, Wong Y-K, Tang B-Z, Hong S-H, Paik K-W, Kim J-K (2009) ACS Appl Mater Interfaces 1:1090
39. Ma PC, Kim J-K, Tang BZ (2007) Compos Sci Technol 67:2965
40. Bagheri R, Marouf BT, Pearson RA (2009) Polym Rev 49:201
41. Hodgkin JH, Simon GP, Varley RJ (1998) Polym Adv Technol 9:3
42. Sue H-J, Garcia-Meitin EI, Pickelman DM (1996) Plast Eng 30:131
43. Sue H-J (1991) Polym Eng Sci 31:275
44. Sue H-J, Garcia-Meitin EI, Pickelman DM (1993) In: Cheremisinoff NP (ed) Elastomer technology handbook, Chap. 18. CRC Press, Boca Raton, p 661
45. Shi YB, Groleau MR, Yee AF, Yang PC, Sue HJ, Bertram JL (1993) Polym Mater Sci Eng 70:110
46. Sue HJ, Bertram JL, Garcia-Meitin EI, Puckett PM (1995) J Polym Sci B 33:2003
47. Groleau MR, Shi YB, Yee AF, Bertram JL, Sue HJ, Yang PC (1996) Compos Sci Technol 56:1223
48. Kishi H, Shi YB, Huang J, Yee AF (1998) J Mater Sci 33:3479. doi:10.1023/A:1013222421843
49. Wei G, Sue HJ (1999) J Appl Polym Sci 74:2539
50. Tsotsis TK (2009) Polym Compos 30:70
51. Derkowski BJ, Sue H-J (2003) Polym Compos 24:158
52. Dominy J, Rudd C (2006) In: Long AC (ed) Design and manufacture of textile composites. CRC Press, Boca Raton, p 476
53. Lee S-H, Noguchi H, Kim Y-B, Cheong S-K (2002) J Compos Mater 36:2153
54. Lee S-H, Noguchi H, Kim Y-B, Cheong S-K (2002) J Compos Mater 36:2169
55. Fan Z, Santare MH, Advani SG (2008) Composites A 39A:540
56. Sue HJ, Jones RE, Garcia-Meitin EI (1993) J Mater Sci 28:6381. doi:10.1007/BF01352201
57. Zhu J, Imam A, Crane R, Lozano K, Khabashesku VN, Barrera EV (2007) Compos Sci Technol 67:1509
58. Liu P (2005) Eur Polym J 41:2693
59. Nguyen-Thuc BH, Maazouz A (2002) Polym Eng Sci 42:120
60. Bae J, Jang J, Yoon S-H (2002) Macromol Chem Phys 203:2196
61. Tao K, Yang S, Grunlan JC, Kim Y-S, Dang B, Deng Y, Thomas RL, Wilson BL, Wei X (2006) J Appl Polym Sci 102:5248
62. Fainleib A, Galy J, Pascault JP, Sue HJ (2001) Mater Res Innov 4:179
63. Fainleib A, Galy J, Pascault J-P, Sue H-J (2001) J Appl Polym Sci 80:580
64. Sue H-J, Puckett PM, Bertram JL, Walker LL, Garcia-Meitin EI (1999) J Polym Sci B 37:2137
65. Xu X, Thwe MM, Shearwood C, Liao K (2002) Appl Phys Lett 81:2833
66. Xu NS, Wu ZS, Deng SZ, Chen J (2001) J Vac Sci Technol B 19:1370
67. Cao Q, Xia M-G, Shim M, Rogers JA (2006) Adv Funct Mater 16:2355
68. Aglan A, Allie A, Ludwick A, Koons L (2007) Surf Coat Technol 202:370
69. Sager RJ, Klein PJ, Lagoudas DC, Warren GL, Sue H-J (2008) Fracture toughness of woven carbon fiber/epoxy laminates with carbon nanotube/epoxy thin films. In: 49th AIAA/ASME/ASCE/AHS/ASC structures, structural dynamics, and materials conference. AIAA, Schaumburg, p 2008