

Morphology of Single-wall Carbon Nanotubes in Epoxy

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Introduction

Single-wall carbon nanotubes (SWNTs) show great promise as nanofillers or perhaps even as nanoreinforcements for composites. Adding SWNTs to a thermosetting or thermoplastic resin increases its strength and/or modulus by about 50% over the neat resin. This increase is much less than the reinforcement offered by off-the-shelf intermediate-modulus carbon fibers [1]. This reinforcement is also well below the order-of-magnitude improvement one might hope to see from SWNT reinforcement. This lackluster performance has been attributed to a number of factors, most of which are related to poor dispersion of the carbon in the matrix [2-6].

Since performance is dependent on many factors, it is important to have some measure of the degree of SWNT exfoliation other than composite mechanical properties. Here we use ultras-small-angle x-ray scattering (USAXS) to characterize the morphology of SWNT-reinforced epoxy, from which we infer the degree of dispersion.

Since SWNTs, exfoliated or not, rapidly increase the viscosity of resins, SWNT-loaded epoxies are difficult to process. In typical thermosetting formulations, a polymeric toughener would be dissolved in a compatible solvent that is later removed. Alternatively, the toughener could be dissolved in a liquid monomer, eliminating the need for solvent removal. Unfortunately, unmodified SWNTs are unwilling to disperse into solvents like acetone or ethanol or into the epoxy itself.

Fullerenes reportedly react with amines. By analogy, one would expect interesting interactions between SWNTs and amines. SWNTs reportedly disperse in boiling aniline [7]. SWNTs with amines have also been reported to form charge-transfer complexes that change the electrical properties of SWNTs [8].

While aniline is not a desirable curing agent, the interaction between SWNTs and amines suggests one might disperse the SWNTs into a liquid diamine curing agent at elevated temperatures and/or by sonication. We investigated this question by using USAXS to assess the dispersion of both SWNTs and their multiwalled "big brothers": vapor-grown carbon nanofibers (VGCNFs).

Methods and Materials

SWNTs manufactured by the HiPco™ process [9] were supplied by Rice University and cleaned [10] by a mild

treatment that removes most of the iron catalyst. The SWNTs were suspended in both aliphatic and aromatic amine curing agents at a power of 10 W at sonication times of up to 240 minutes. Jeffamine D2000 is a liquid, aliphatic polyoxypropylene diamine with a nominal degree of polymerization of 33. EpiCure-W is an aromatic amine. The SWNT-D2000 suspensions were then added to Epon 828, a thermoset based on diglycidylether of bis-phenol-A (DGEBA). The SWNT-EpiCure-W mixture was added to the Epon 862, a similar epoxy monomer made from bis-phenol F. Visually, the D2000 prepolymer mixtures were better dispersed than the Cure-W prepolymer mixtures.

The uncured prepolymer mixture was maintained at 75°C by using a water bath for an additional 60-minute sonication period. The samples were then placed into a heated 75°C mold and cured for a total of 2 hours at 75°C, followed by 2 hours at 125°C. The conventional mixture was stirred and cast without the second 60-minute sonication.

Except for one data set (SWNTs in Cure W) in Fig. 3, all scattering in this paper refers to cured epoxy-diamine-SWNT nanocomposites.

Combined light and x-ray scattering data were interpreted by using a unified fractal methodology [11-13], discussed previously by Schaefer [14] with regard to SWNTs. For all samples, a background of the same material without SWNTs was subtracted.

Results

Unfortunately, all the SWNT samples gave weak scattering signals due to the low concentration of carbon and poor contrast. Nevertheless, the data show that the SWNTs do not disperse down to the tube level.

Figure 1, for example, shows data as a function of the sonication time of the D2000-SWNT mixture. These data are rather featureless but show slopes of about -3, much larger than the slope of -1 expected for rodlike scatterers. Presumably, the scattering results from aggregated clumps of carbon.

Increased sonication time has some effect on the size of the aggregates. At short sonication times, no Guinier region is observed in the range of the USAXS instrument. At longer times, a Guinier radius is observed in a range of 500 to 2000 Å, but there is no consistent trend with sonication time.

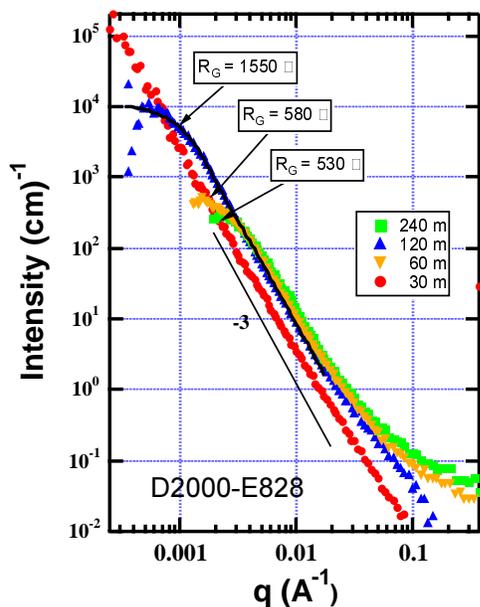


FIG. 1. USAXS profile for D2000-Epon 828-SWNT composite as a function of sonication time of the D2000-SWNT mixtures. The R_G values come from a Guinier fit in the small- q region.

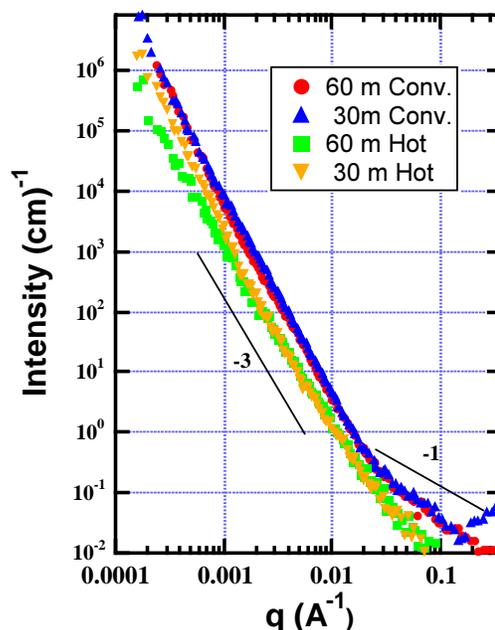


FIG. 2. USAXS data for Epon 828 epoxy cured with SWNT-containing EpiCure-W as a function of sonication time and cure protocol (conventional versus hot cure).

In the case of Cure-W, no Guinier region was observed (Fig. 2) for any of the data. The data are also featureless with a slope near -3 .

Figure 3 compares the scattering for SWNTs in Cure W and in the final composite. The slope for the amine-SWNT mixture approaches -4 , indicating a more compact morphology with smoother interfaces for the aggregates than the aggregates in the final epoxy.

Discussion

Except for the high q region of Fig. 2, we find no evidence of dispersion of SWNTs to the tube level, either in cured epoxy or in the Cure-W curing agent. These results indicate that SWNTs remain aggregated in robust ropes or other structures, in spite of sonication.

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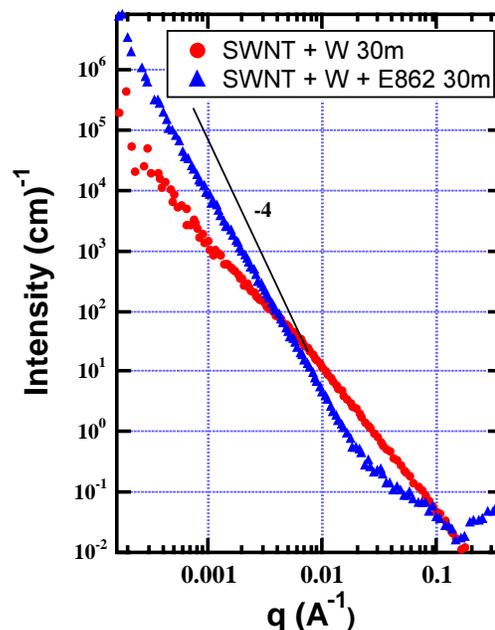


FIG. 3. Comparison of SWNTs sonicated for 30 minutes in EpiCure-W with the final epoxy composite consisting of SWNTs, EpiCure-W, and epoxy.

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References

- [1] B. Maruyama and H. Alam, "Carbon nanotubes and nanofibers in composite materials," *Sampe® Journal* **38**(3), 59-70 (2002).
- [2] M. Biercuk, M. Llaguno, M. Radosavljevic, J. Hyun, A. Johnson, and J. Fischer, "Carbon nanotube composites for thermal management," *Appl. Phys. Lett.* **80**(15), 2767-2769 (2000).
- [3] J. Salvétat, G.A. Briggs, J. Bonard, R. Basca, and A. Kulik, "Elastic and shear moduli of single-walled carbon nanotube ropes," *Phys. Rev. Lett.* **82**(5), 944-947 (1999).
- [4] S. Arepalli, P. Nikolaev, and W. Holmes, "Production and measurements of individual single-wall nanotubes and small ropes of carbon," *Appl. Phys. Lett.* **78**(11), 1610-1612 (2001).
- [5] D.W. Schaefer, J. Zhao, J. Brown, D. Anderson, and D. Tomlin, "Morphology of dispersed carbon single-walled nanotubes," *Chem. Phys. Lett.* **375**(3-4), 369-375 (2003).
- [6] S. Frankland, A. Caglar, D. Brenner, and M. Griebel, "Molecular simulation of the influence of chemical cross-links on the shear strength of carbon nanotube-polymer interfaces," *J. Phys. Chem. B* **106**(12), 3046-3048 (2002).
- [7] Y. Sun, R. Wilson, and D. Schuster, "High dissolution and strong light emission of carbon nanotubes in aromatic amine solvents," *J. Am. Chem. Soc.* **123**, 5348-5349 (2001).
- [8] J. Kong and H. Dai, "Full and modulated chemical gating of individual carbon nanotubes by organic amine compounds," *J. Phys. Chem. B* **105**(15), 2890-2893 (2001).
- [9] P. Nikolaev, M. Bronikowski, R.K. Bradley, F. Rohmund, D. Colbert, K.A. Smith, and R. Smalley, "Gas-phase catalytic growth of single-walled carbon nanotubes from carbon monoxide," *Chem. Phys. Lett.* **313**(1-2), 91-97 (1999).
- [10] K.L. Strong, D. Anderson, K. Lafdi, and J. Kuhn, "Purification process for single-wall carbon nanotubes," *Carbon* **41**(8), 1477-1488 (2003).
- [11] G. Beaucage and D.W. Schaefer, *Structural "Studies of Complex Systems Using Small-Angle Scattering — A Unified Guinier Power-Law Approach,"* *J. Non-Crystallogr. Solids* **172**, 797-805 (1994).
- [12] G. Beaucage, "Approximations leading to a unified exponential power-law approach to small-angle scattering," *J. Appl. Crystallogr.* **28**, 717-728 (1995).
- [13] G. Beaucage, "Small-angle scattering from polymeric mass fractals of arbitrary mass-fractal dimension," *J. Appl. Crystallogr.* **29**, 134-146 (1996).
- [14] D. Schaefer, J. Brown, D. Anderson, J. Zhao, K. Chokalingam, D. Tomlin, and J. Ilavsky, "Structure and dispersion of carbon nanotubes," *J. Appl. Crystallogr.* **36**, 553-557 (2003).