Plasma Treatment of Nanofillers for Polymer Nanocomposites

Andrew C. Ritts[1], Qingsong Yu[1,2], Hao Li[2]

[1] Center for Surface Science and Plasma Technology, Department of Chemical Engineering,
University of Missouri, Columbia, MO 65211, USA, yuq@missouri.edu
[2] Department of Mechanical and Aerospace Engineering,
University of Missouri, Columbia, MO 65211, USA, liha@missouri.edu

ABSTRACT

Plasma nanocoatings can create a variety of desirable surface functionalities and thus to tailor the surface characteristics of multiwalled carbon nanotubes (MWNTs) and silicon carbide nanofibers (SiCNFs) for improved dispersion capability in polymer matrices. Ultrasonication was used to disperse MWNTs and SiCNFs into epoxy Epon 815c resin. The amine groups on the coating surface are believed to strengthen the interfacial interactions through chemical bond formation between the fillers and matrix. Plasma nanocoated MWNTs and SiCNFs were characterized using SEM, XRD, FTIR, surface contact angle and pH value measurements. Mechanical testing results showed that all SiCNF reinforced nanocomposites were found to be stronger than the MWNT reinforced nanocomposites. Plasma coated (PC) MWNTs better dispersed in the Epon 815C resin than the uncoated nanotubes and enhanced the mechanical properties significantly. Plasma treated SiCNFs increased the tensile strength of the epoxy by 40% with only 1.0wt% loading.

Keywords: low-temperature plasma nanocoatings, amine, interface, polymer nanocomposite, and SiC nanofibers

1 INTRODUCTION

Because of their lightweight and significantly improved properties, polymer nanocomposites reinforced with nanosize fillers make up a new class of materials. Polymer nanocomposites have low percolation thresholds (~0.1 to 2vol%) requiring only minute quantities of nanofillers to significantly enhance the properties of the composites.[1] Nanotubes and nanofibers are excellent choices for the reinforcement of polymer nanocomposites due to their high aspect ratio, and outstanding mechanical, thermal, and electrical properties.[2] The comparative experimental strengths of carbon nanotubes (CNTs) and SiCNFs are reported to be 100 GPa[3] and 50 GPa[4] respectively, much higher than their microscale counterparts. Controlling the strength transfer of these nanofillers can form a new class of high-strength polymeric materials never before seen. To date, two major challenges exist in developing novel polymer nanocomposites. First, a homogeneous dispersion of nanofillers in their host polymer matrices must be achieved.[5] Second, an enhanced interfacial adhesion must be attained in order to provide effective load transfer between polymer matrices and the reinforcing nanofillers.[3]

Previous work has applied various techniques to functionalize CNTs, however this requires defects in the CNTs lowering the theoretical strength of the tubes significantly.[2] SiCNFs are stable compounds which can be functionalized without producing defects making SiCNFs a better candidate as a filler in polymer nanocomposites. Plasma technologies have been utilized as an environmentally friendly way to enhance the surface properties of fibrous materials for composite materials since the 1960's.[6] However plasma coating of nanopowders introduces unique challenges due to increased surface energies at the nano-level which produces agglomerations. Powder-plasma coating reactors must be designed to prevent agglomerations during its operation and allow the plasma coating to prevent agglomerations when introduced to the polymer matrix.
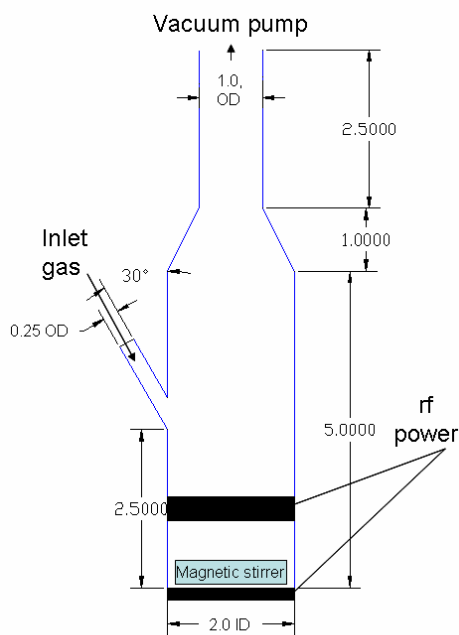
In this proceeding, a low-temperature nanocoating process is proposed for treating nanosized fillers for use in composite material applications. Specifically amine rich surface functionalities are deposited on MWNTs and SiCNFs which are used in epoxy nanocomposites and are compared to their non-coated counterparts. The amine functional groups on the nanofiller are believed to chemically bond the filler to the epoxy matrix enhancing the interfacial tension.

2 EXPERIMENTAL

MWNTs with 10-30nm in diameter, 20-40μm in length, and 95% purity were purchased from Helix Material Solutions. SiCNFs produced from various carbon sources were made and characterized in lab as previously reported.[7] The following abbreviations will be used to compare different types of SiC nanofibers: SMG is 99.9% submicron scale graphite with average particle size of 500nm purchased from Nanostructured and Amorphous Materials, MG is 99.995% micron scale graphite with 2-10μm purchased from Alfa Aesar, and LG is 99.99% 44μm average particle size graphite purchased from Sigma Aldrich. MWNTs were also used to synthesize SiC NFs.

2.1 Amine Plasma Treatment of MWNTs and SiCNFs

Plasma conditions were chosen by determining deposition rates of the amine coating on Si wafers prior to the filler treatment. One gram of nanofiller was plasma treated with 50% Ar, 50% allylamine at 100mtorr with 6 or 10 watts of power, and 40 or 60 minutes of treatment. Figure 1 shows

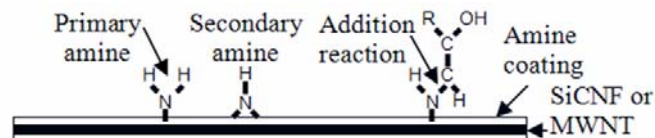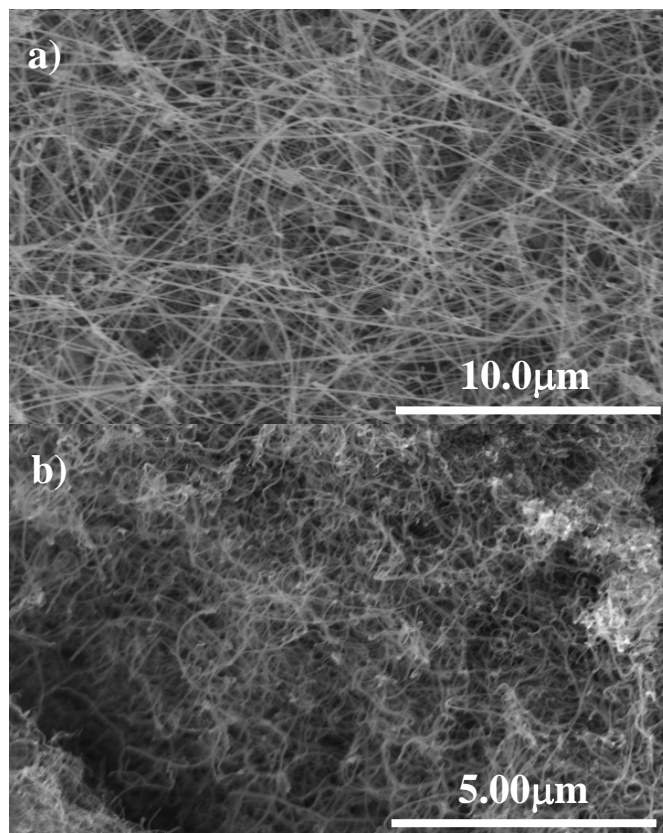**Figure 1.** Low-temperature plasma powder reactor (dimensions in inches)

Figure 2. Depiction of an epoxide reaction with a primary amine functionality on the surface of a nanofiller.

figure 2. Epoxides react with amines by adding each individual part into a single molecule. Primary amines have a higher probability to react compared to secondary amines, but secondary amines can also react in this manner.

3.1 Characterization of PC MWNTs and PC SiCNFs

Nanofillers characterized by SEM seen in figure 3 compare strait SiCNFs (40-100nm diameter) with tortuous MWNTs (10-30nm in diameter). Tortuous nanotubes should affect the composite more as whiskers than fibers due to their relative aspect ratio in a single direction; in contrast the straight SiCNFs should give better load transfer to the epoxy matrix due to their significantly larger relative aspect ratio. However, the 50-70% yield of SiCNFs is significantly lower than the 95% yield of MWNTs. When 1wt% of SiC is added to the epoxy only 0.5-0.7wt% of the SiC is nanofibers. CNTs also have significantly higher strengths than SiCNFs, however these strengths may be misleading when looking at

the plasma reactor setup where the electrodes were placed one inch apart. The powder was stirred at a rate of 300 rotations per minute, pushing the powder into a direct contact with the amine plasma. Approximately 700mg of plasma treated nanofiller was used in the epoxy composite, and the excess was characterized by SEM, XRD, FTIR, surface contact angle, and pH value measurements.

2.2 Epoxy Nanocomposite Fabrication

Fillers were incorporated into the Epon 815c epoxy resin (Miller-Stephenson) via Ultra Sonic horn (Branson Ultrasonics Corporation) for 4 minutes with 8 microtip limit and 50% duty cycle (~40W). The Epon 815c resin was cured using 12 parts of Epicure 3223 (Miller-Stephenson) for 100 parts of epoxy resin by weight. Resin, filler, and curing agent were mixed with a magnetic stirrer for 5 minutes at 300 rotations per minute. Five samples were cast in an aluminum dog bone shaped mold and cured for 1 hour at 100°C. Dog bone samples were tested in a tensile testing machine (MTS).

3 RESULTS AND DISCUSSION

Before manufacturing the composite, a thorough characterization of the filler and matrix material should help determine the treatment method of the filler. Epon 815c resin contains 86.4% bisphenol-A-(epichlorhydrin) and 13.6% N-butyl glycidyl ether, both of which contain at least one epoxide group. Epicure 3223 curing agent mainly consists of diethylenetriamine, which allows the matrix to crosslink. Coating the nanofiller with amine groups can allow the filler to be chemically incorporated into the matrix as seen in

Figure 3. SEM images of SiCNFs synthesized in our lab (a) and MWNTs purchased (b)

Table1. ΔpH from plasma treated and untreated nanofillers

Material	mass (mg)	ΔpH
PC SiCNF from MWNT	100	0.40
SiCNF from MWNT	100	-0.55
PC SiCNF from SMG	300	0.86
SiCNF from SMG	300	-0.77
PC MWNT	100	0.68
MWNT	100	0.1

Table 2. Tensile testing results of epoxy and untreated MWNTs and SiCNFs nanocomposites.

Filler	Tensile Strength (MPa)	STD (MPa)
None	34.32	1.31
MWNTs	22.70	8.23
SiCNFs1*	31.12	3.26
SiCNFs2**	32.97	2.65
SiCNFs3***	31.40	5.48

*SiCNFs synthesized from MWNT
**SiCNFs synthesized from MG
***SiCNFs synthesized from LG

these materials as fillers for composite materials as mentioned previously. XRD determined that SiCNFs are β-SiC with some stacking faults. Previous TEM analysis has shown a thin amorphous SiO_x and C coatings on the surface of the fibers.

After plasma treatment approximately ~100 mg of PC SiCNFs from MWNT precursor was able to increase the pH of 50 mL of distilled water by ~0.40 where ~100 mg of untreated SiCNFs lowered the pH by ~0.55 as seen in table 1. The PC nanofillers were extremely hydrophobic so they were dispersed into distilled water using the ultra sonic horn. All PC nanofillers increased the pH of distilled water significantly due to the amine groups that can be found on the surface. Amines become protonated in water producing hydroxyl groups in solution, thus increasing the pH. Untreated MWNTs have little effect on the pH; however SiCNFs decrease the pH of the significantly. This is believed to be due to the SiOH groups produced insitu during the nanofiber fabrication. These SiOH will deprotonate in water producing H^+ which in turn decreases the pH. It is very difficult to determine amine plasma coatings on nanopowders with FTIR, but small NH peaks on PC SiCNF from 2560 to 2700 can be seen when compared with untreated SiCNFs. When a silicon wafer is PC under the same amine plasma conditions for 10 minutes, contact angle measurements can show a change in surface energy. At different heights in the reactor there are different deposition rates of amine coating which has an effect on the surface energy, however there is a significant change between the coated and plain wafers. When Epon 815c resin droplets came in contact with amine plasma coatings they spread across the wafer until reaching the edge, where untreated samples had contact angles around 30°.

Our results indicated that PC MWNTs and PC SiCNFs had better dispersed in the Epon 815C resin than the uncoated fillers which should increase the tensile strength of their composites significantly. When uncoated samples were tested the nanofiller would accumulate at the bottom of the beaker, even after sonication. Therefore the epoxy composites formed with out PC had less filler than recorded, and the probability of aggregates in the samples increased significantly.

3.2 Mechanical Testing of Epoxy Nanocomposites

Mechanical testing results showed that all SiCNF reinforced nanocomposites were found to be stronger than the MWNT reinforced nanocomposites. The SiO_x coatings found

on the SiC are believed to enhance the interface better than the MWNT surface. The slight polarity of the SiOH groups should also enhance the dispersion of the SiCNFs in the epoxy resin. The SiCNFs samples made from larger carbon precursors had lower strengths than their smaller analogues. SiCNFs made from MWNTs had the highest strengths, closely followed by SiCNFs from MG. This is believed to be due to the size of the SiC by-products produced and their role as defects in the composite. However, it was found that all nanocomposites prepared from untreated MWNTs and SiCNFs had inferior mechanical strength as compared with the controls of the pure epoxy samples as seen in table 2. SiCNF epoxy nanocomposites made from MG and MWNT have statistically the same strengths, which are very close to pure epoxy. When the SiCNFs are plasma coated the improved dispersion and interfacial tension should increase the strengths significantly.

PC nanofillers in contrast showed vast improvement compared to their untreated counterparts. Table 3 shows tensile strength tests with PC and pure epoxy. PC SiCNFs from SMG precursor out perform all other samples with a tensile strength of 54.95 MPa, with more than a 40% increase from the highest plain epoxy sample. The Young's Modulus of a majority of the samples were close to 21.5 GPa; in contrast PC MWNTs increased the Young's Modulus by 12.8%. Stress strain curves of PC fillers compared with the best plain epoxy samples are found in Figure 4. Certain PC MWNT and PC SiCNF samples failed at the clamp during testing, which implies that the test section is stronger than the recorded values. Both PC nanofillers had the largest strain measurements around 1.0029, but MWNTs also have the

Table 3. Tensile testing results epoxy and PC MWNTs and PC SiCNFs nanocomposites.

| Filler	Tensile Strength (MPa)	STD (MPa)	Young's Modulus (GPa)	Max Strain
plain1	38.84	3.85	21.47	1.0018
plain2	34.23	5.71	21.41	1.0016
MWN1	52.64	16.29	24.24	1.0029
SiC1*	54.95	8.60	21.56	1.0028

*SiCNFs synthesized from SMG
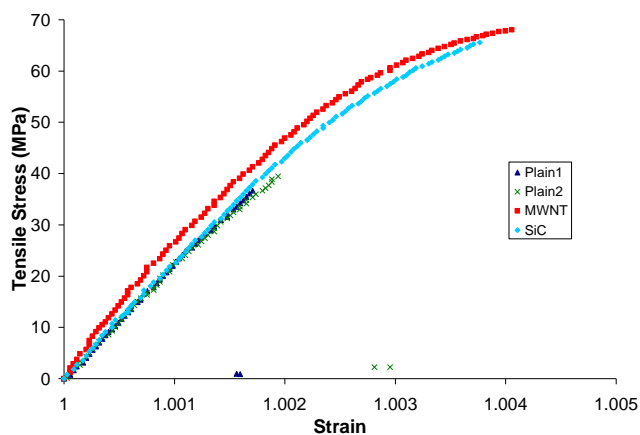
Figure 4. Tensile stress strain curves of epoxy composites with PC MWNTs, PC SiCNFs, and plain epoxy.

largest standard deviation.

The fractured interface was examined using HR-SEM to study the fracture mechanisms. Figure 5 shows SEM images at various magnifications showing PC MWNT pullout in the epoxy nanocomposite fracture surface. MWNT loading in the epoxy was relatively small and provided for infrequent pullout. The average diameter of the MWNTs found on the surface was around 50nm; much larger than the original 10-30nm implying the MWNTs were strongly bonded with the epoxy. Similar fiber pullout was seen on the PC SiCNF epoxy fracture surface. All non PC epoxy nanocomposites fracture surfaces had similar topologies and no fiber pullout
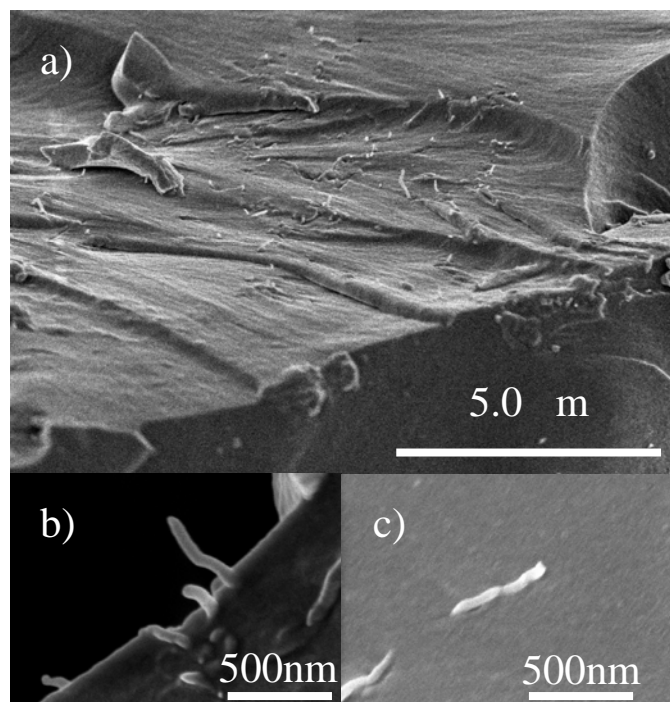
Figure 5. SEM images of PC MWNT pullout of epoxy nanocomposite fracture surface

was found using HR-SEM. A few agglomerations could be found in MWNT composites that were not PC.

4 CONCLUSIONS

Low-temperature plasma coatings for nanopowder applications have promise in improving the mechanical properties of polymer nanocomposites by enhancing dispersion of the nano-filler and interfacial tension between the matrix and composite. PC SiCNFs in particular have increased the tensile strength of epoxy nanocomposites by 40% with only 1wt% loading. PC MWNTs have increased the Young's modulus of the composite by 12.8%. Future work involves enhancing the properties of other polymer composite materials with plasma coating technologies.

REFERENCES

[1] Vaia, R.A. and H.D. Wagner, *Framework for nanocomposites.* Materials Today, 2004. **7**(11): p. 32-37.
[2] Breuer, O. and U. Sundararaj, *Big Returns From Small Fibers: A Review of Polymer/Carbon Nanotube Composites.* Polymer Composites, 2004. **25**(6): p. 630-645.
[3] Wagner, H.D. and R.A. Vaia, *Nanocomposites: issues at the interface.* Materials Today, 2004. **7**(11): p. 38-42.
[4] Wong, E.W. and P.E. Sheehan, *Nanobeam mechanics: Elasticity, strength, and toughness of nanorods and nonotubes.* Science, 1997. **277**(5334): p. 1971.
[5] Graff, R.A., et al., *Achieving Individual-Nanotube Dispersion at High Loading in Single-Walled Carbon Nanotube Composites.* Advanced Materials, 2005. **17**(8): p. 980-984.
[6] Tatoulian, M., et al., *Plasma Deposition of Allylamine on Polymer Powders in a Fluidized Bed Reactor.* Plasma Processes and Polymers, 2005. **2**(1): p. 38-44.
[7] Ritts, A.C., H. Li, and Q. Yu, *Synthesis of SiC Nanofibers with Graphite Powders.* Proceedings Coco Beach J. Am. Ceramics Soc., 2007.