

Nanocomposite optimization using polymer-wrapped carbon nanofibers

M. R. Papantonakis¹, V. Nguyen², E. P. Gorzkowski², M. Barbano³, W. Ou³ and R. Andrew McGill²

¹U.S. Naval Research Laboratory, Washington, DC, USA, michael.papantonakis@nrl.navy.mil

²U.S. Naval Research Laboratory, Washington, DC, USA

³ ASEE participant in the Science and Engineering Apprentice Program tenured at the NRL 2014

ABSTRACT

The primary challenges of maximizing the contribution of additives in composites, homogeneous dispersion throughout the matrix and promoting a strong interfacial contact between the additive and host, has been studied using non-covalent modification of carbon nanofibers by polymer wrapping. A series of polymers with the same backbone and a range of pendant groups was selected to study the effect of different nanofiber surface chemistries on the dispersion and mechanical properties of the composites. In this paper we present data showing the confirmation of polymer wrapping by several polymers at a few percent by mass relative to the carbon nanofiber.

Keywords: nanocomposites, carbon nanofiber, inverse gas chromatography, polymer wrapping, non-covalent modification

1 INTRODUCTION

The surface modification of nanomaterials to improve their compatibility with polymer hosts can be accomplished by a range of methods. Covalent modification of nanomaterial surfaces to improve compatibility with a host polymer is one avenue. However, in order to achieve significant surface chemistry effects, covalent modification must be balanced by the potential for deleterious effects, which may vitiate the desired properties intended from the nanomaterials. Another approach is to use non-covalent chemistries or physisorption to modify the surfaces of nanomaterials. While physisorption involves inherently weaker interactions than covalent bonding or chemisorption, when larger molecules are physisorbed to a surface the total interaction strength can be quite significant. Additionally, it is known that simple dispersion of the nanomaterial in a polymer host without good interfacial adhesion between the two will not realize the full benefit of improved composite properties, for example in improving mechanical strength.

Carbon nanofibers (CNFs) are hollow, cylindrical materials that in terms of dimensionality, cost, and mechanical properties lie in between single walled carbon nanotubes and carbon fibers. The CNFs used in this study were grown by the floating catalyst method, where a solution of catalyst metals (e.g., Fe, Co, or Ni) is injected into a furnace in the presence of a hydrocarbon [1]. Fiber growth proceeds by dehydrogenation of the hydrocarbons

resulting fibers with diameters dependent on the length of the growth time in the heated zone. Typically the collected product contains fiber diameters ranging from 50-200 nm with lengths in excess of 50 μm . The fibers are believed to initially have a cone-helix structure with an outer layer of amorphous carbon, but upon post-processing heat treatment both the structure and the crystallinity of the CNFs can be modified [2]. The CNFs used in this study were heat treated to remove any aromatic hydrocarbons from the outer surface and to convert it to graphitic carbon. Given the range in the type and sizes of the CNFs, it should come as no surprise that there is a range in the reports of the mechanical properties. One study reported values for the elastic modulus ranging from 25 to 200 GPa [3]. Carbon nanofibers have been reported to improve the compressive strength of laminates and carbon fiber composites [4].

The polymers used in this study (Figure 1) were selected for several reasons. 1) They incorporate a flexible backbone, to better conform to the surface of the carbon nanofibers, maximizing their interaction to the SP₂ bonded carbon surface. 2) The pendant groups provide a range of solubility properties including nonpolar/pi base, hydrogen-bond base, and amphi-hydrogen-bonding structures, allowing comparison to a range of potential host polymers.

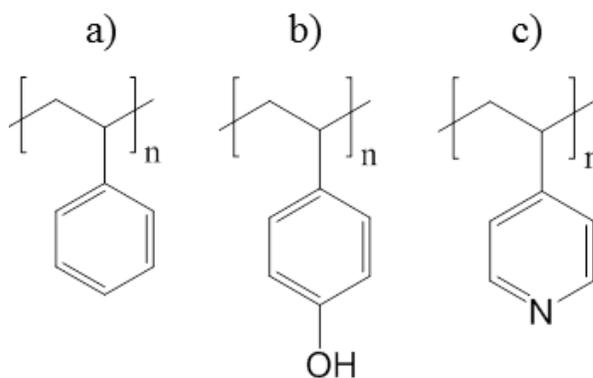


Figure 1. Repeat units of the three polymers chosen to non-covalently modify the carbon nanofiber surface. a) polystyrene, b) poly(vinylphenol) and c) poly(vinylpyridine). This set shares an identical backbone but have pendant groups with different chemical properties.

2 METHODS AND MATERIALS

The carbon nanofibers were from Applied Sciences (PR-24-XT_LHT) and polymers were from Sigma-Aldrich. Three polymers with 4-vinyl backbones were used; poly(4-vinylbenzene) or polystyrene, poly(4-vinylphenol), and poly(4-vinylpyridine) (Figure 1). As received, the CNFs are a low-density powder of tangled bundles of fibers. Sonication (Branson Digital Sonifer) was used to disentangle the bundles. Typically, 300 mg of CNFs in 300 mL of solvent (appropriate for the intended wrapping polymer) were sonicated for 60 minutes at about 100 W of power in an ice bath that kept the mixture from overheating at about 35 °C. A solution of wrapping polymer, in the same or compatible solvent, was then added to the dispersion of CNFs and stirred for 2-48 hours. Polymer wrapping was typically allowed to proceed at ambient laboratory temperatures but some lower and higher temperatures have been examined. After stirring, centrifugation was used to separate the wrapped CNFs from any reagglomerated CNF material. The supernatant was then decanted and filtered with a Buchner funnel on a PTFE filter. The filtrate was then refluxed by Soxhlet extraction to rinse any loose polymer from the CNFs. Refluxing was continued until samples taken from the filtrate showed no evidence of the polymer, as measured by UV-Visible spectrophotometry (Agilent 8453).

Three techniques were used to confirm the presence of wrapping polymer on the CNFs. A Netzsch STA F1 Jupiter instrument was used to measure the weight loss of wrapped and neat materials by thermal gravimetric analysis (TGA) while simultaneously recording the mass spectra of the decomposition products. Approximately 50 mg of sample was placed in a crucible under argon, and the temperature ramped to 500 °C at 20K/min and then held at that temperature for one hour. A quadrupole mass spectrometer was used to monitor the decomposition products as a function of temperature. X-ray photoelectron spectroscopy

(XPS) (K-Alpha XPS System) was used to measure the spectra of the C1s, N1s, and O1s signals peaks for both neat and polymer-wrapped CNFs. Inverse Gas Chromatography (IGC-2000, Surface Measurement Systems) was used to measure the London dispersive and polar surface energies of the modified CNFs. Solvents used were all spectroscopic grade. For IGC measurements, typically 50 mg of rinsed polymer-wrapped CNFs was ground with a mortar and pestle and then packed into a glass column (30 cm length, 4 mm inner diameter) with glass wool plugs as a retainer. The packed column was first heated to 100°C for several hours to remove any physisorbed volatile species. The temperature was then reduced to 60°C, and a sequence of solutes with known physicochemical properties were injected into the packed IGC column. From their elution times, the dispersive and specific surface energies were obtained [5].

3 RESULTS AND DISCUSSION

The effect of sonicating the CNFs had a profound effect on their bundling as observed by scanning electron microscopy (SEM). After adequate sonication, very little of the CNF material was observed as bundled fibers. When CNFs were sonicated without adding a wrapping polymer, centrifugation quickly resulted in all of the fibers settling at the bottom of the centrifuge tube, showing the tendency of these high surface area materials to agglomerate. However, with wrapping polymer added and stirred for a sufficient time, the solution turned black and opaque, and remained so without settling even when observed for several months.

TGA of the neat and thoroughly rinsed polymer-wrapped CNFs provided the following polymer wrapping results: 2.0% w/w for polystyrene, 3.3% w/w for polyvinylphenol, and 5.0% w/w for polyvinylpyridine (Figure 2). This is consistent with calculations of the maximum coverage of a single layer of polystyrene on the surface of a 100 nm diameter carbon nanofiber, which suggests that a monolayer of polymer will constitute approximately 1.5% of the total mass. Significant variations in the CNF diameters make it difficult to predict a precise coverage value, but together these suggest that the CNF surfaces is largely covered by polymer. The decomposition products of a polymer-wrapped CNF sample were compared to the products of the neat polymer. While there were few species generated during heating of unwrapped CNFs over the temperature range studied, the products from the polymer-wrapped CNFs were well correlated to the products from the neat polymer at their respective decomposition temperatures.

The XPS data of the as-received CNF show a small signal for the O1s peak but no signal for the N1s peak. The polystyrene-wrapped CNF showed no additional signal in either region. However, the poly(vinylphenol)-wrapped CNF showed a stronger signal for the O1s peak while the poly(vinylpyridine)-wrapped CNF showed a stronger signal

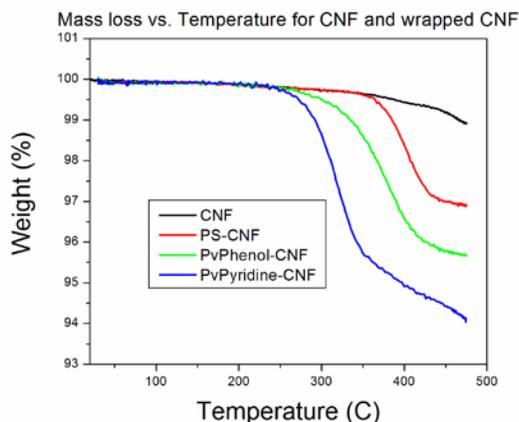


Figure 2. Weight loss for neat and polymer-wrapped CNFs. Wrapped CNFs showed a weight loss ranging from 2-5% weight loss relative to the neat material

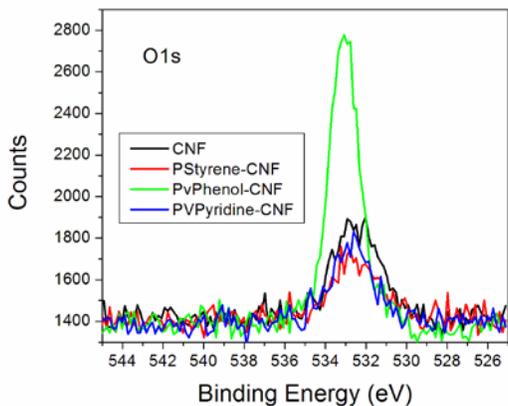


Figure 3. XPS of the O1s peak for the neat and polymer-wrapped CNFs. The small peak seen on the as-received CNF does not increase when coated with polystyrene or poly(vinylphenol), but the O1s signal increases significantly when poly(vinylphenol) is used to modify the CNF surface.

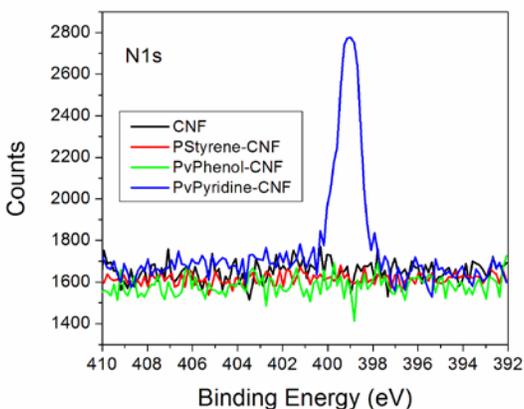


Figure 4. XPS of the N1s region for the neat and polymer-wrapped CNFs. No peak is present in the as-received CNF or when poly(vinylphenol) or polystyrene is present, but the poly(vinylpyridine) is clearly indicated by the strong peak.

for the N1s peak. These results are expected based on the elements making up the three polymers.

Inverse gas chromatography was also used to confirm the modification of the CNF surface. The London dispersive surface energy of the as-received CNF was high, as has been shown for other carbon nanomaterials [6]. Coating the CNFs resulted in a significant decrease in the London dispersive surface energy. Poly(vinylpyridine), which was found by TGA to effect the highest amount of polymer wrapped coating, provided the largest decrease in the dispersive surface energy.

The specific surface energy for a number of solute probes was measured for both as-received and polymer-wrapped CNFs. The largest changes were seen for poly(vinylphenol)-wrapped CNFs, where the phenol group

interacted strongly with the polar probes (methanol, ethyl acetate, and methyl ethyl ketone) but showed no change for the cyclohexane and toluene. The insensitivity of the polystyrene-wrapped CNFs to the polar probes is logical, but the lack of an effect by the poly(vinylpyridine)-wrapped CNFs is at present inexplicable.

4 SUMMARY

A non-destructive physisorption approach to modifying carbon nanofibers for use in composite materials has been demonstrated. Sonication was effective for dispersing the as-received CNF bundles and polymer wrapping in keeping them from reagglomerating. The presence of the polymers was confirmed and loadings were found between 2-5% w/w, and the presence of the polymers was verified and characterized by XPS and IGC.

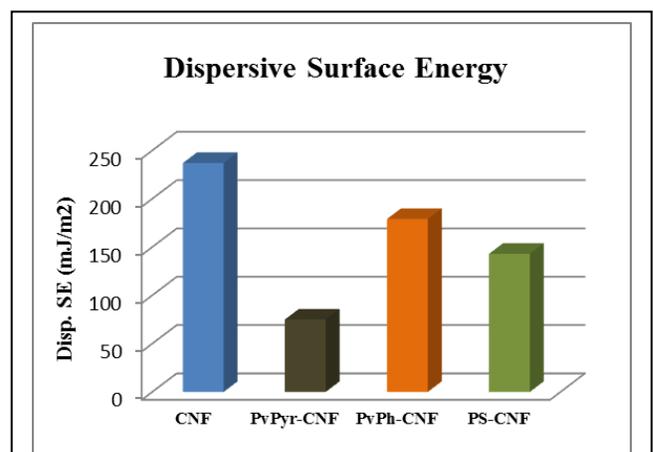


Figure 5. The dispersive surface energy of as-received CNFs. Coating the fiber surface

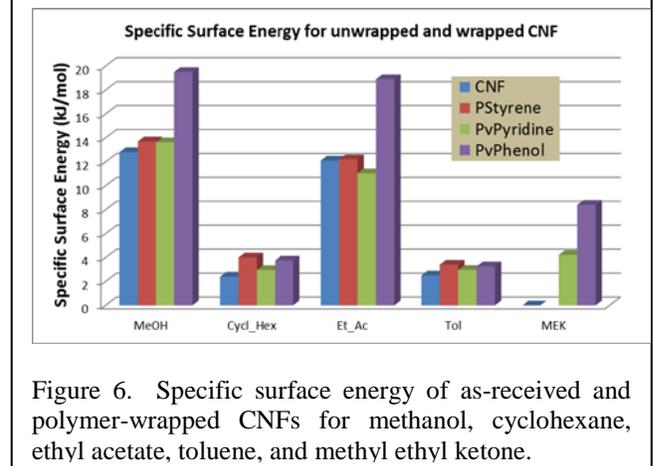


Figure 6. Specific surface energy of as-received and polymer-wrapped CNFs for methanol, cyclohexane, ethyl acetate, toluene, and methyl ethyl ketone.

5 ACKNOWLEDGMENTS

This work was sponsored by core NRL basic research with funds administered by ONR. M.B. and W.O. were supported at NRL by ASEE through the SEAP program.

6 REFERENCES

- [1] Tibbetts, G.G., et al., Physical properties of vapor-grown carbon-fibers *Carbon*, 1993. **31**(7): p. 1039-1047.
- [2] Lawrence, J.G., L.M. Berhan, and A. Nadarajah, Structural transformation of vapor grown carbon nanofibers studied by HRTEM. *Journal of Nanoparticle Research*, 2008. **10**(7): p. 1155-1167.
- [3] Lawrence, J.G., L.M. Berhan, and A. Nadarajah, Elastic properties and morphology of individual carbon nanofibers. *Acs Nano*, 2008. **2**(6): p. 1230-1236.
- [4] Peponi, L., et al., Processing of nanostructured polymers and advanced polymeric based nanocomposites. *Materials Science & Engineering R-Reports*, 2014. **85**: p. 1-46.
- [5] Thielmann, F., Introduction into the characterisation of porous materials by inverse gas chromatography. *Journal of Chromatography A*, 2004. **1037**(1-2): p. 115-123.
- [6] Menzel, R., et al., Inverse Gas Chromatography of As-Received and Modified Carbon Nanotubes. *Langmuir*, 2009. **25**(14): p. 8340-8348.