



Interfacial engineering for low-density graphene nanocomposites

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Final Report

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14. ABSTRACT Over the course of this award, the PI and his group developed a variety of novel techniques for the dispersion of pristine graphene in both aqueous and polar organic solvents. These advances focused on the use of polymeric (polyvinylpyrrolidone) and polyaromatic hydrocarbon (pyrene) dispersants which non-covalently bind to graphene and prevent graphene aggregation. Increases in thermal conductivity were observed for these fluids. Such dispersions were also stable against drying, indicating that graphene-graphene stacking was impeded by the dispersants. Building on this foundation, the PI and group investigated several new platforms for graphene-based materials. They examined the use of graphene in polymer nanocomposites, including epoxy films and poly vinyl alcohol films and electrospun fibers. The addition of pristine graphene showed substantial increases in strength and modulus at low graphene loading; similarly, the excellent degree of dispersion was reflected by both microscopy and a low					
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FINAL PROGRESS REPORT

Subject: Final Progress Report to Dr. Joycelyn Harrison

Contract/Grant Title: (YIP 11) - Interfacial Engineering For Low-Density Graphene Nanocomposites and Fluids

Contract/Grant #: FA9550-11-1-0027

Reporting Period: 15 Apr 2011 - 14 Apr 2014

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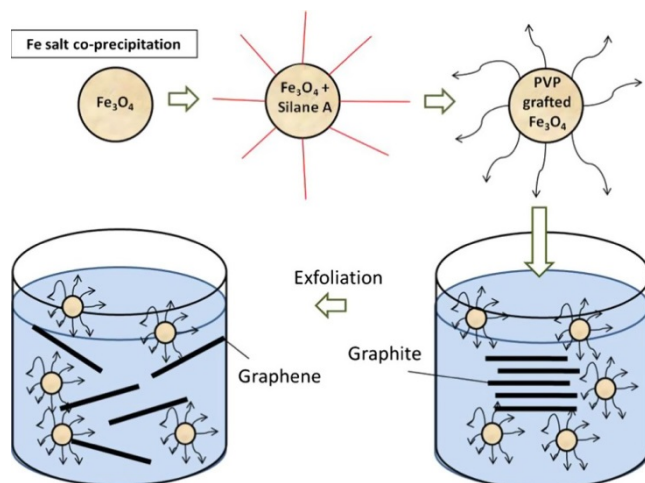
This document reports only the final year of the award (15 Apr 2013 – 14 April 2014); please refer to annual reports for years 1 and 2 for the work accomplished in those time periods.

In the final year of this work, we demonstrated that the graphene dispersants developed early in this award can serve as graphene-binding functional groups for a wide range of chemical species. Previously we had shown that polymers such as polyvinylpyrrolidone (PVP) and polyaromatic hydrocarbons such as functionalized pyrene will non-covalently physisorb onto the surface of exfoliated graphene in liquids such that the graphene will not reaggregate to form graphite.

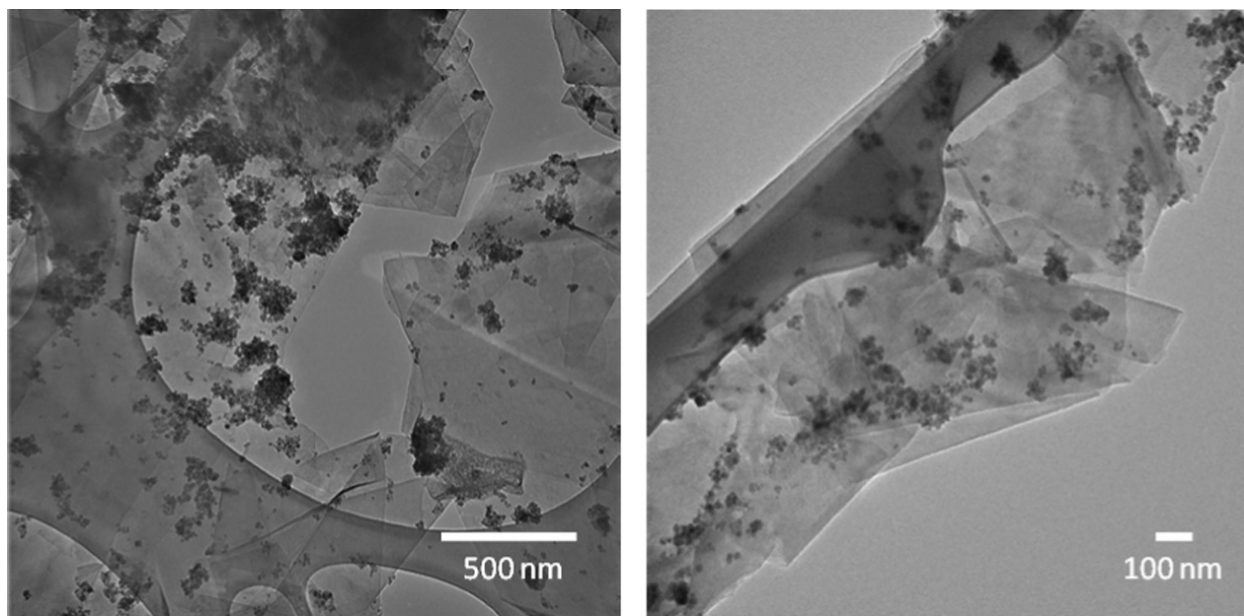
This same logic applies even when these dispersants are used as functional or pendant groups on other species. One of the chief goals of our AFOSR-funded work was the creation of multifunctional composites with both electrical conductivity and enhanced mechanical properties. Developments in novel dispersants that are tailored to the composite can allow this to occur.

Iron oxide / graphene work

For instance, we demonstrated that iron oxide nanoparticles can be grafted with PVP pendant groups; such a Fe_3O_4 /PVP hybrid will still bind to graphene, allowing for a graphene dispersant with magnetic functionality.



Extensive characterization (Vibrating Sample Magnetometer (VSM), TEM, XRD, TGA) was used to characterize both the iron oxide (magnetite) nanoparticles and their hybrid with PVP. The final dispersant on graphene surfaces can be observed using TEM:



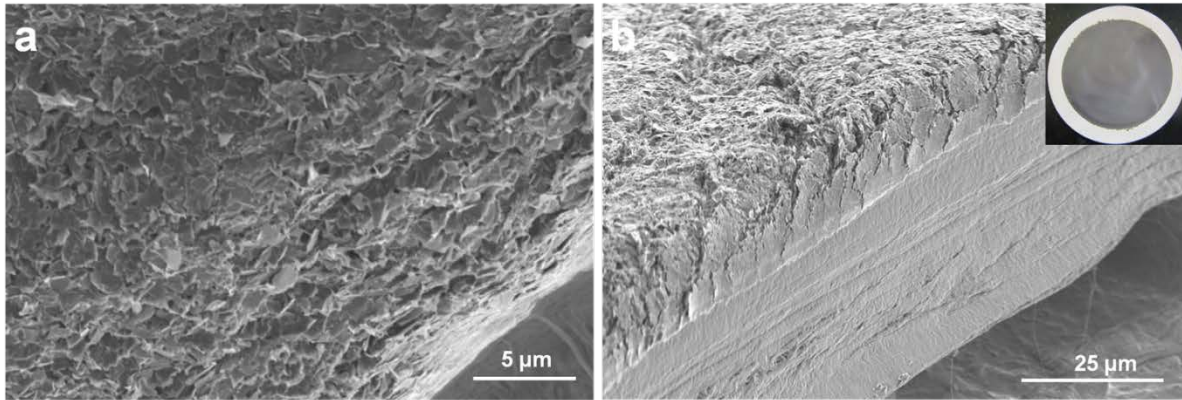
Such dispersions can be easily manipulated using an external magnetic field:



Such work allows for magnetically patternable graphene composites. Simple vacuum-filtered composite films displayed an excellent conductivity of 30 S/m.

Siloxane work

In a similar vein, we sought to alter the chemical structure of polydimethylsiloxane (PDMS) to contain pyrene pendant groups such that it would non-covalently bind to graphene. This would allow for high graphene loadings and conductive strain-sensitivity in PDMS. SEM images of these composites are shown here:

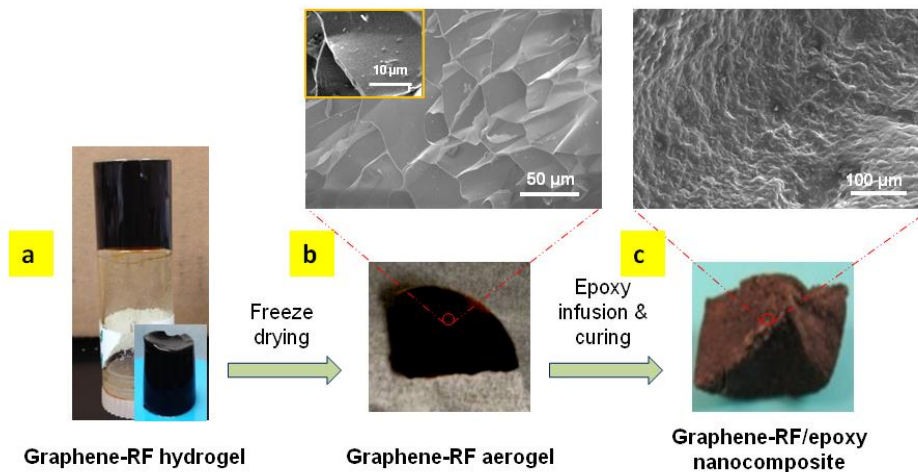


The high level of dispersion allowed for a pristine graphene composite conductivity of 220 S/m; this is after using a membrane to induce separation between graphene-bound PDMS and free PDMS to increase the graphene loading. This value is among the highest ever reported for pristine graphene composites.

(Note that this aspect of our AFOSR-funded work on conductive composites paralleled our recent NSF-funded work on scalable graphene exfoliation and production.)

Aerogel-templated percolation

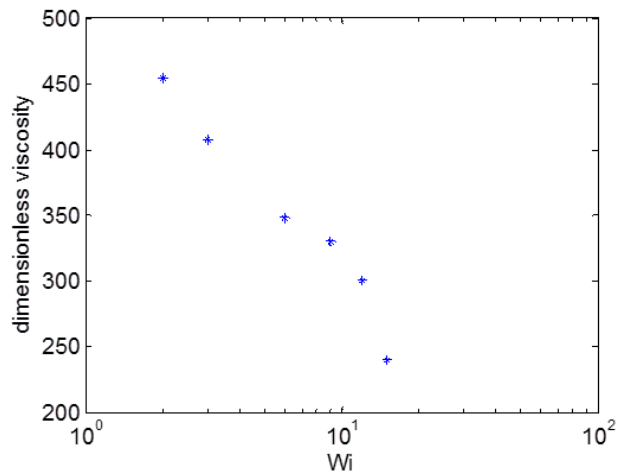
We also demonstrated that graphene in high-porosity solids such as aerogels will retain their conductivity, even after the porous space is backfilled with a thermosetting resin as shown in the following Figure:



This suggests a novel technique for creating composites with ultralow percolation threshold; such a technique is parallel to a similar concept used to localize conductive nanofillers in immiscible polymer blends.

Rheological properties

Finally, we used coarse-grained simulations to investigate the influence of graphene on the viscosity of graphene-loaded fluids. Preliminary studies were limited to viscosity enhancements of dilute graphene solutions in Newtonian solvents. Shear rate sweeps indicate a weak shear-thinning effect associated with graphene stretching out into a flat conformation.



This work is the first flow-conformation study of its kind and paves the way for further studies in the area of graphene-loaded polymer melts for composite processing. Such studies are critical for understanding how non-flat nanosheets affect composite properties.

See attached publication list for full list of publications that cite AFOSR support.