ACSNANO

# Nanodiamond-Polymer Composite Fibers and Coatings

Yury Gogotsi et al.

A.J. Drexel Nanotechnology Institute and Department of Materials Science and Engineering Drexel University, Philadelphia, Pennsylvania

ACS Nano, 2009, 3 (2), pp 363-369

Muhamed Shareef PH08D022

7<sup>th</sup> March 2009

- To manufacture composite polymer-nanodiamond fibers by electrospinning.
- These fibers can be used for producing thin and transparent diamond coatings with very high diamond contents
- Nanodiamond(ND) exhibit the properties of diamond on the nanoscale As a powder, ND could be introduced into fibers, coatings, or other shapes to utilize its useful properties.
- Traditional polymer processing techniques yield poor dispersion of ND due to agglomeration/reagglomeration of the nanodiamonds
- The electrospun polymer nanofibers can be act as a host for nanoparticles
- The confinement of the fiber diameter, polymer surface tension, and strong electrostatic force help in deagglomeration of nanoparticles

#### Initial Processing

- The ND powder was produced *via* a detonation synthesis(Commercially obtained)
- The ND powder has been thoroughly characterized using Raman spectroscopy, TEM and FTIR.
- ND has been purified by air oxidation (2 hrs at 425 °C) to remove nondiamond carbon
- Treated in conc HCl at 100 °C for 24 hrs to remove metals and metal oxides by transforming them into water-soluble salts.
- Finally the ND powder was rinsed with DI water until reaching neutral pH.
- Purified ND was dispersed in a solvent that was compatible with the particular polymer that is to be dissolved and then electrospun.



Fig 1. Low resolution TEM of oxidized ND powder containing both the individual particles (a) and loosely bound agglomerates (b). High resolution TEM (c) showing mostly pristine nanodiamond particles with little content of disordered carbon.

# Two similar methods were employed based on the matrix polymer

- For Polyacrylonitrile( PAN),6 wt% polymer in dimethylformamide (DMF) + 0-90% ND by wt
- For Polyamide 11(PA 11),1-10%wt polymer in formic acid(FA) and dichloromethane (DCM) in a 1:1 volume ratio +2.5-40% ND by wt

#### Electrospinning parameters

- The high voltage applied is 23 kV for the PAN solution and between 15 and 20 kV for the PA 11 solution.
- A spinning distance is maintained at 15 cm
- The flow rate is 0.015 cm/min in both cases.
- The fibers were collected on glass, aluminum foil, silicon, or TEM grids for subsequent studies

### Electrospinning of PAN -ND polymer matrix



#### Figure 2. SEM of pure PAN nanofibers electrospun from 8 wt % PAN in DMF



Fig 3. (Top row) SEM (a) and TEM (b,c) images of electrospun PAN nanofibers with 10 wt % ND incorporation. (Bottom row) SEM (d) and TEM (e,f) images of electrospun PAN nanofibers with 60 wt % ND incorporation. Nanodiamond particles, which have a higher density than PAN, appear as dark spots in TEM images in panels b and e. Inset in panel e shows a fracture surface of a polymer-bonded diamond fiber (60 wt % of ND in the polymer).

- PAN fiber mats spun for 10 and 20 min were white or light gray and translucent, independent of the diamond content. This is due to light scattering on nanofibers. The gaps between the fibers are comparable to the wavelength of visible light.
- Heating to 200 °C makes fiber mats transparent due to fibers fusing to the surface and material uniformly spreading over the surface (the softening temperature of PAN is 180 °C), leading to the formation of a continuous film
- These films can be further heated to completely remove the polymer and leave a pure nanodiamond coating, which can provide seeds for chemical vapor deposition (CVD) of polycrystalline diamond films

### Spectroscopic properties



- PAN-ND fiber mats are heated for 20 min at 200 °C.
- The transmission decreases as the ND content increases from 10 to 40 wt % and finally to 50 wt %, as expected.
- Some absorption in the visible range may be due to about 5% of sp2 carbon present on the surface of oxidized ND.
- There is a decrease of about 25% in the transmission from 10 to 40 wt % and a further decrease of 25% for the 40–50 wt % samples.
- The fact that all samples absorb in deep UV implies that even a small addition of nanodiamond can be used for UV protection.

### PA11 as polymer matrix

- PA11 has good wear resistance and chemical stability, important for coatings and may be further improved by diamond addition.
- The electrospun PA 11 fibers with various diamond is a milky film on the surface due to light scattering.
- The PA 11 fibers were then fused at 180 °C for 30 min which suppress reagglomeration of NDs.
- The average thickness of the films spun for 20 min was  $2.6 \pm 0.4 \mu m$
- The surface roughness of the PA 11 fibers increases with ND content due to viscosity rise
- The appearance of the fibers changes from smooth to rough to droplets with ND content



Fig 5. SEM images of PA 11 electrospun fibers with varying loads of nanodiamond: (a) 2.5 wt %, (b) 10 wt %, (c) 20 wt %, and (d) 40 wt %.

# **Optical properties**

- show absorption in the UV range due to ND incorporation
- optically transparent up to at least 40 wt % of diamond.
- Used as glass coating and protective layers on UV sensitive materials.



Fig 6. Optical images of electrospun PA 11 nanofibers with different loadings (wt %) of ND, on different substrates: (a) on steel, (b) on silicon, (c) on a computer chip, and (d) on a glass slide both (c,d) before (left) and after (right) heating that leads to fiber fusing to the surface and formation of a transparent film.



Load-displacement curves (a) and hardness and Young's modulus (b) of PA 11-ND films with different contents of nanodiamond. Inset in panel a shows a PA 11-ND film with 20 wt % of nanodiamond on a thin glass slide. Film thickness was  $2.6 \pm 0.4 \mu m$ 

### **Mechanical properties**

- The indentation was carried out to the depth of 300 nm (10% of the coating thickness) to minimize substrate effects on the measured properties
- The addition of nanodiamond raising their Young's modulus by a factor of 4
- Hardness doubled
- It can be seen that if a load of 1.3 mN is required to penetrate the pure PA 11 coating to the depth of 300 nm, a 3-times higher load is required to reach the same depth for a coating with 20 wt % ND
- The scratch under 5 mN load in pure PA 11 is 1.7 μm deep while for 10 wt % of ND it is 0.8 μm deep scratch.

# Applications

- ND powders, being biocompatible and having easily accessible surface, used as a filler of a polymer matrix in many applications
- Medical diagnostics, imaging and labeling as well as photovoltaics
- Biomedical applications such as wound dressings, cell growth scaffolds, sensing and drug delivery systems
- ND-polymer composites coatings effectively protect from UV rays on windows or prevent degradation of UV sensitive materials .

### Summary

- ND-containing composite nanofibers can be produced by electrospinning with ND content as high as 60–80 wt % in PAN and up to 40 wt % in PA 11 with minimum agglomeration
- At 50–60 wt % of ND, the density of the nanodiamonds inside the fibers is so high that the fibers may be well-considered as ND fibers with a polymer binder.
- These ND composite mats on heating results in the formation of a thin layer of ND on the surface which offer UV protection and improved scratch resistance to surfaces

#### Future plan

Electrospinning of nanowires, nanoparticles

Tellurium Nanowire is narrow band gap semiconductor with properties

Good photoconductivity
Photo electricity
Thermoelectricity
Catalytic
Non linear optical properties
High piezoelectricity

# Thank you