Ohio Aerospace Institute

Graphene Polymer Nanocomposites

Mitra Yoonessi

mitra.yoonessi@nasa.gov

Thermal, Mechanical Properties, and Fracture Toughness of Surface Modified Graphene Epoxy Nanocomposites

Eileen Boyd, Derek J. Quade, Daniel Scheiman

Ohio Aerospace Institute, Cleveland, OH
NASA Glenn Research Center, Cleveland, OH

National Aeronautics and Space Administration

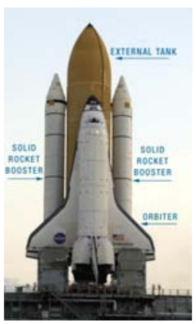
Ohio Aerospace Institute

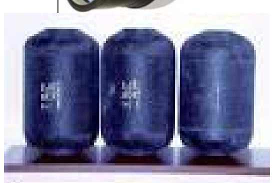
Polymer Nano-Composites for Aerospace Applications

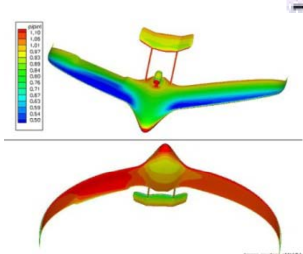
Multi-Functional Materials

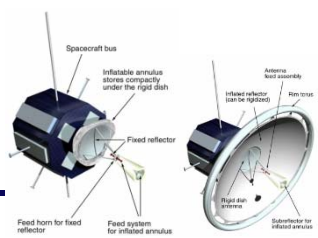
Reinforcements, Mechanical strength in a wide temperature range- Barrier - Toughness

- Graphene
- Layered Silicates
- Carbon NT
- Expanded Graphite
- Carbon nanofibers
- Magnetic nanoparticles
- Organometallic physical crosslink



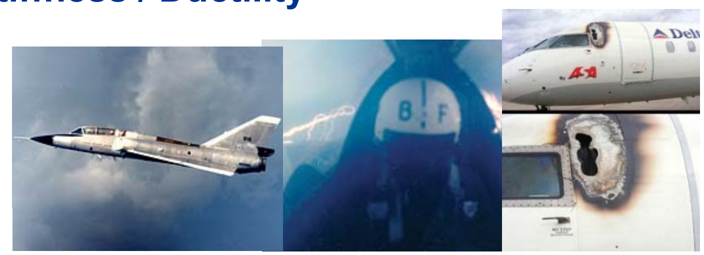






Conductive Polymers

DC & AC Electrical - Permittivity – Stiffness / Ductility



A two-seat F106B jet made 1,496 thunderstorm penetrations and got struck by lightning 714 times during NASA's eight-year Storm Hazards Research Program. Credit: NASA

Smart Adaptive Materials

Actuation– Thermal, Magnetic, Electrical

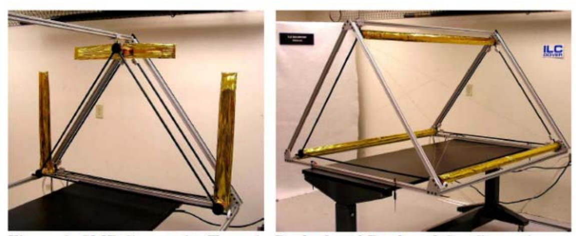
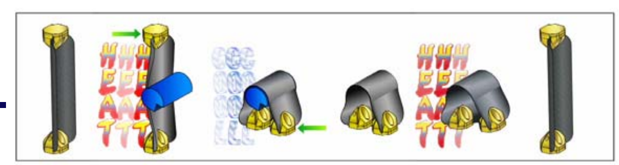


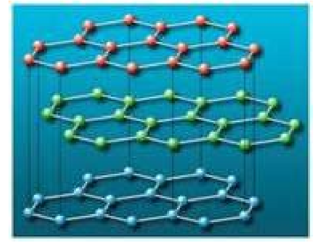
Figure 2. SMP Composite Truss in Packed and Deployed Configurations

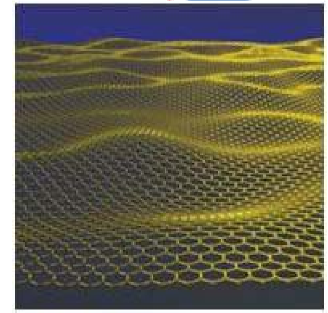
Morphing fan casing
Blended wing body inlet
Flex. packaging
Space deployable structures

Sensors
Static discharge
Lightening strike
Actuators



Graphite and Graphene



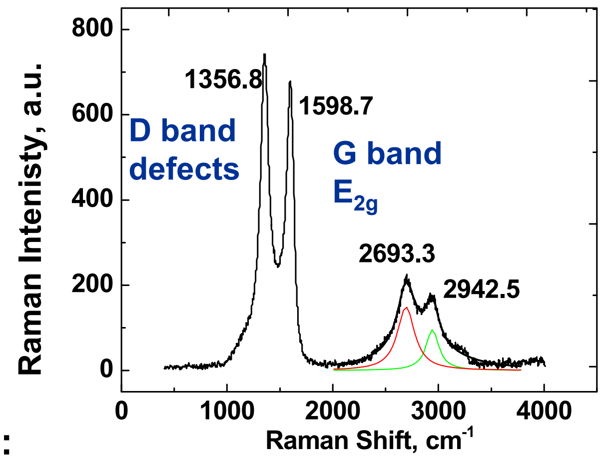


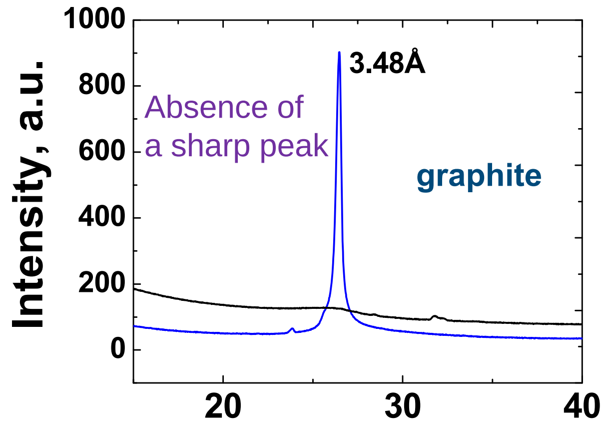
Graphite:

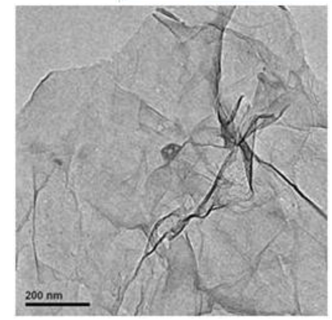
Advantages: Naturally abundant material, Low cost

Graphene

- **Mechanical peeling**
- **CVD**
- **Acid intercalation, thermal shock, sonication**
- **Acid intercalation followed by high pressure, high temperature treatments**







~ 9.2x 15.1 micron

700nm- 15 mic.
Average of 3 mic.

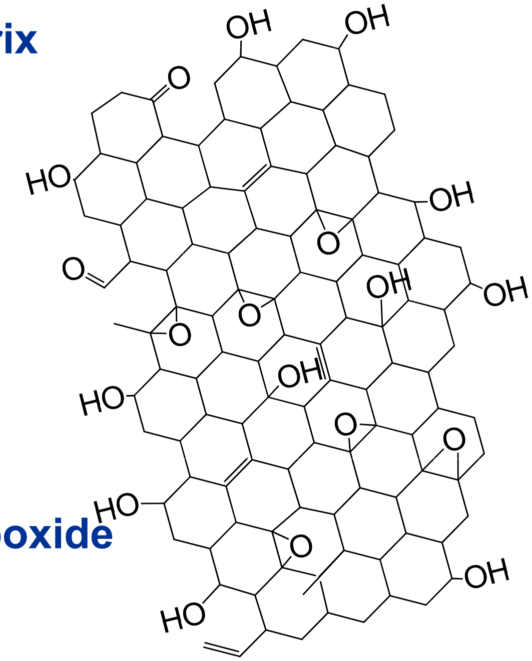
Graphene:

- **In-plane stiffness of 1,060 GPa**
- **resistivity in the range of 50μΩ cm**
- **98.7% transmission normal to the incident beam for the first layer, 2.3% reduction for the next layers in vacuum**
- **Thermal conductivity: ~ 3000 W/mK**
- Field effect mobility of 200 000 cm^2/Vs1

Polymer nanocomposites, optoelectronic applications; transparent conductors, field emission displays, supercapacitors, devices, emissive displays, micromechanical sensors.

Novoselov, K.S., Geim, A.K., et al. Science Oct 22 (2004)
McAllister, M. J.; Prud'homme, R. K.; Aksay I. A. *et al*. *Chem. Mater.* 2007, *19,* 4396- 4404.
Schniepp, H. C.; Kudin, K. N.; Li J.-L.; Prud'homme, R. K.; Car, R.; Saville, D. A.; Aksay, I. A. *ACS Nano* 2008, *2*, 2577-2584.
Schniepp, H.C.; Aksay, I. A. *et al*. *J. Phys. Chem. B*, 2006, *110*, 8535-8539.

Graphene Surface and Interface



Tailored Interface

- Compatibility with the polymer matrix
- Improving dispersion
- Load/stress transfer
- Electron transfer
- Thermal energy transport

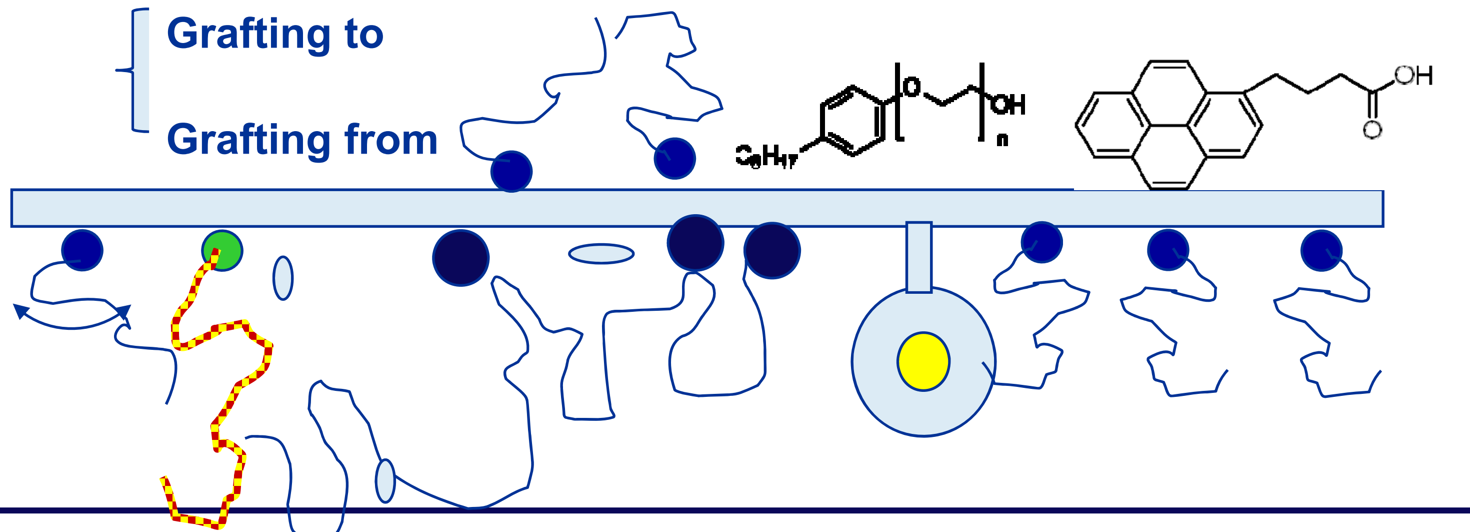
Surface Characteritics:

- SP^2 hybridization for electron transport
  van der Waal Interaction (aromatic structures)
- Combination of sp^3 and sp^2 hybridization
  Covalent bonding; -OH, -COOH, -phenolic-OH, -epoxide

Covalent bonding

Grafting to

Grafting from



Epoxy Graphene Nanocomposites-Reinforcement

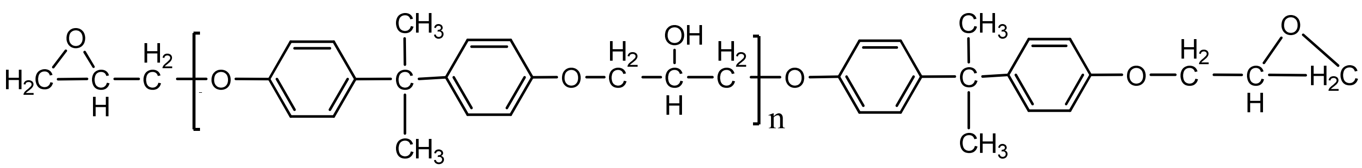
Objectives:

- To determine the effects of graphene addition and surface modification on the thermal and dynamic modulus, fracture toughness of the low content graphene nanocomposites.

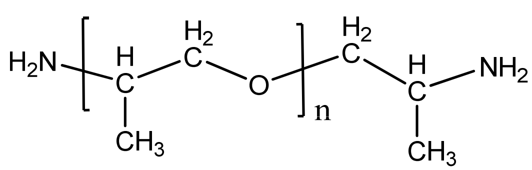
Epoxy: Epon 826

Chemical and heat resistance
Good to excellent mechanical properties
Low viscosity resin
Transparent
Excellent adhesion

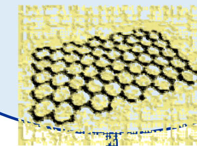
Durability - long-term,
High-temperature service
Brittleness



Jeffamine D230: a polyetheramine, (an amine terminated PPG)
MW 230, X~ 2.5



Polymer+



Dispersion via sonication

Reinforcement, toughness and thermal properties

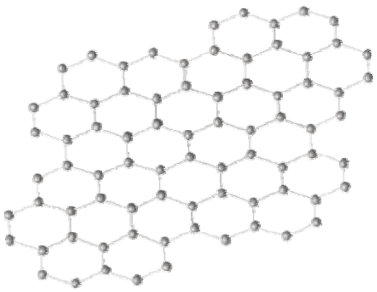
Epoxy

- Solution mixing
- Sonication
- High shear mixing

- Dynamic mechanical analyzer, modulus, T_g
- Fracture toughness
- TGA
- Morphology; electron microscopy

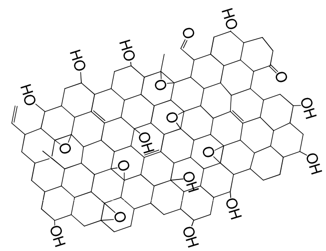
Epoxy Graphene Nanocomposites-Surface Modifications

Reduced graphene

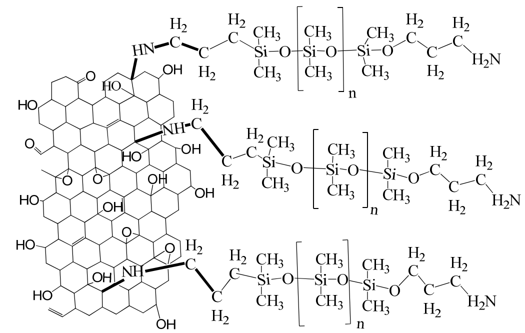


Reduced graphene
sp² hybridized

O- graphene

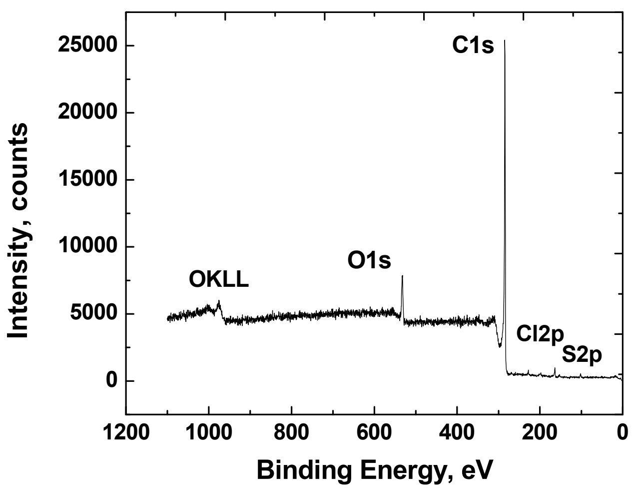


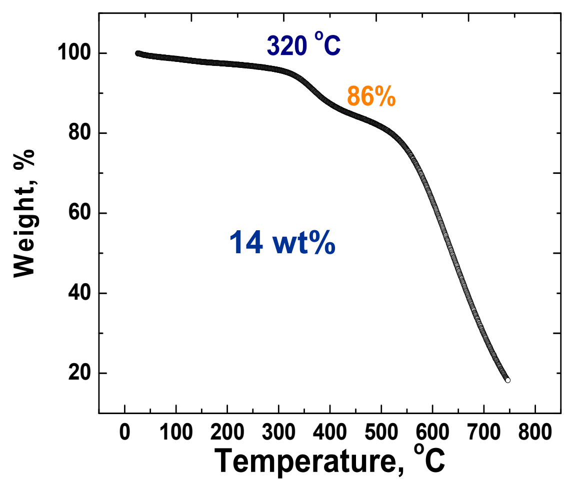
Highly oxygenated graphene, sp², and sp³

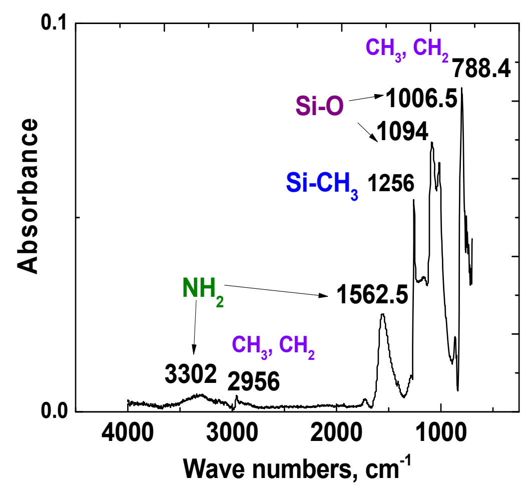


Amino propyl polydimethyl siloxane graphene, sp², and sp³

2500 – 27000 g/mol



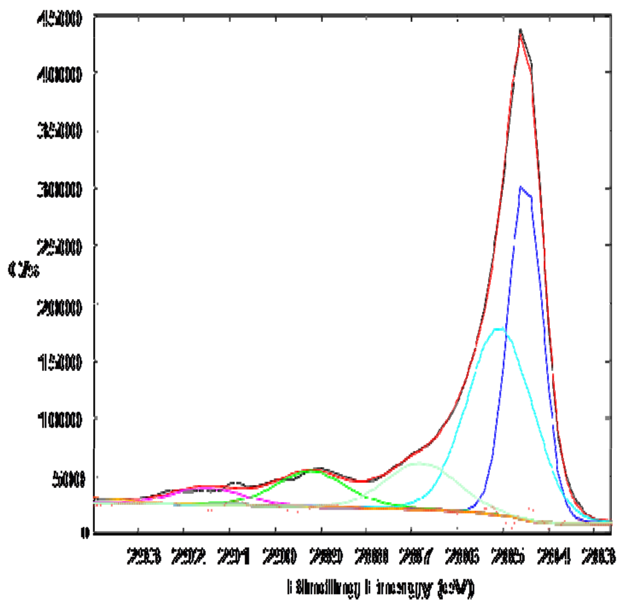


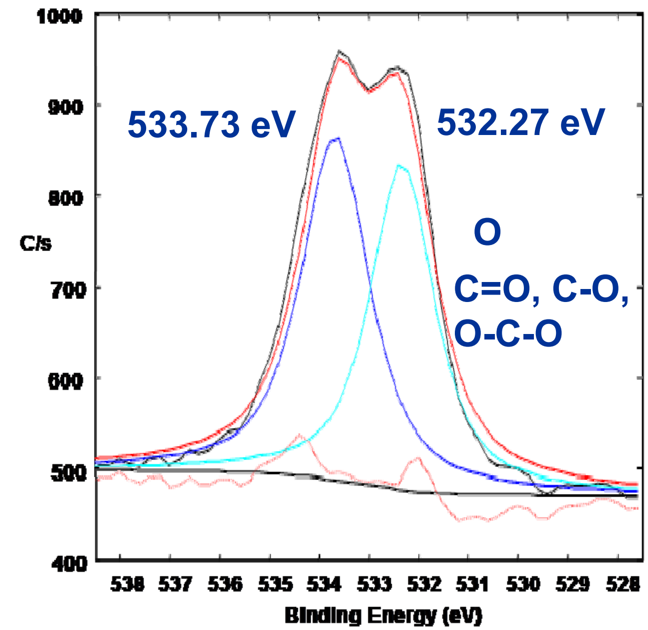


XPS, O- Graphene Surface

XPS

A range of carbon oxygen moieties with 7% atomic oxygen (high resolution survey scans).





C1s: 285.07, 286.78, 289.2, 291.48, 294.19 eV

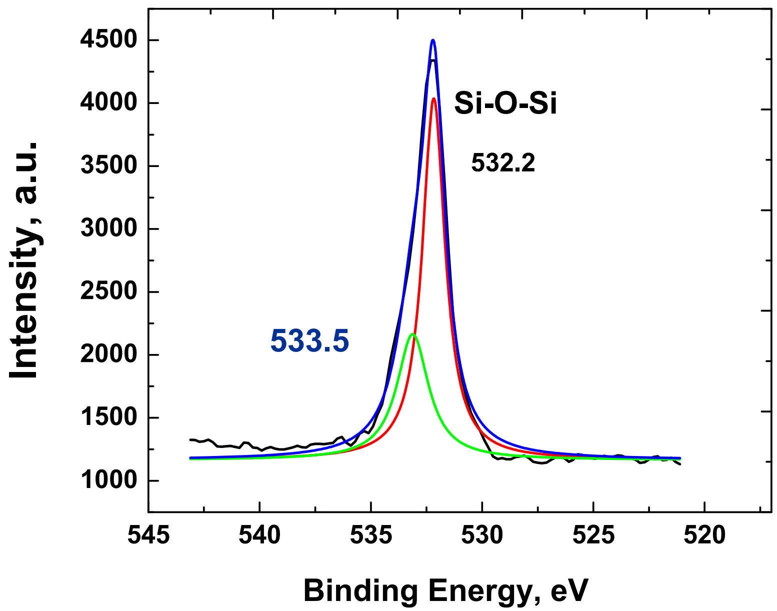
Bonding energies: ester, carboxylic, ether cabon, hydroxyl carbon, phenolic hydroxyl, carbonate, ..

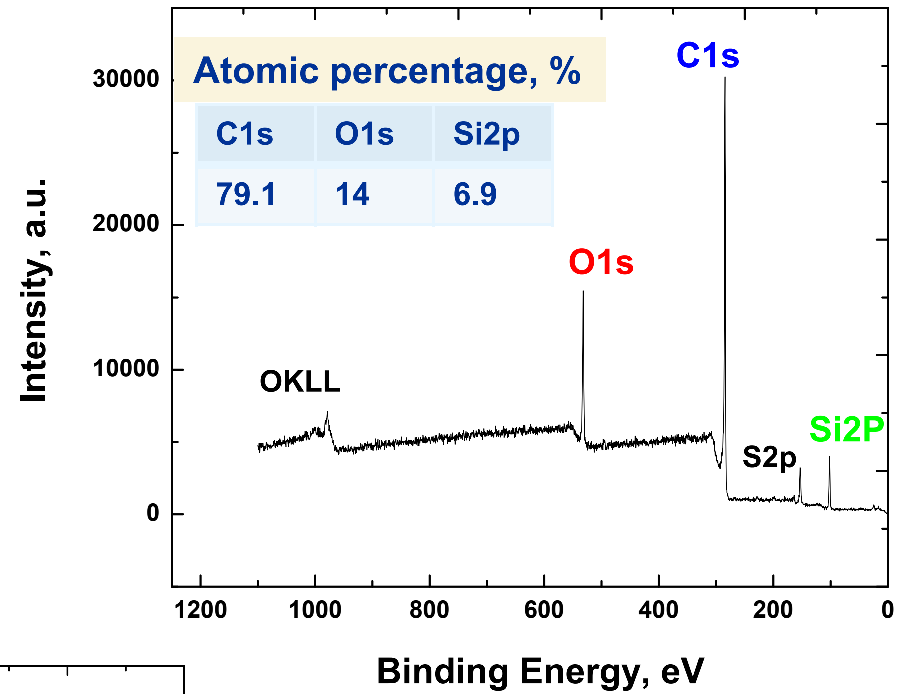
O1s binding energy: 532. 3 eV ketone, ester, or acetate
O1s binding energy: 533.73 eV adsorbed CO

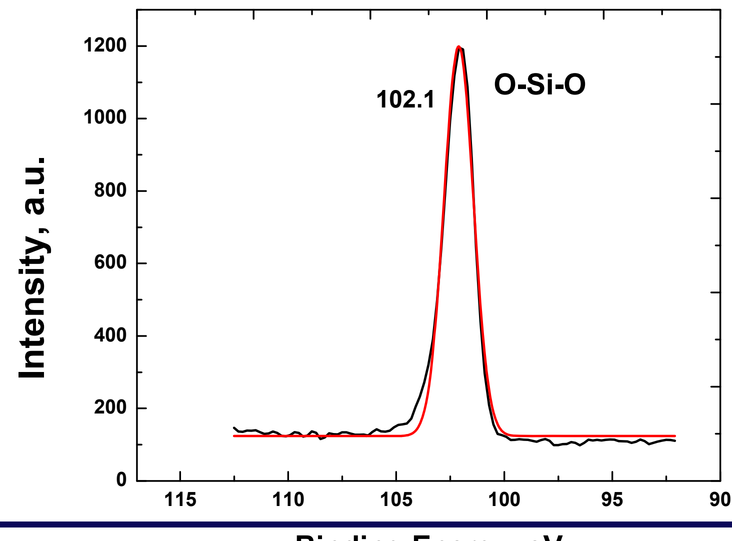
Beamson G., Briggs D. *High Res. XPS of Org. Polym.: the Sci. ESCA300 Database* **1992**

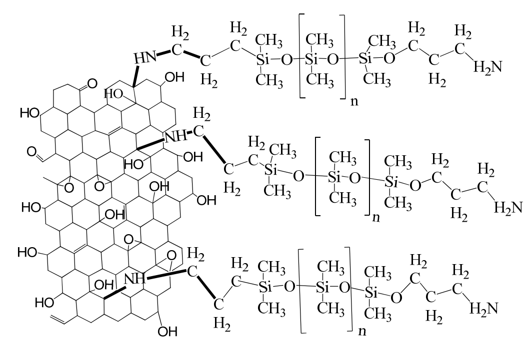
Wu, M.C.; Dong, S.Z.; Zhu, A.R. *Surf. Sci.* **1989**, 216, 420

XPS – Surface Modified





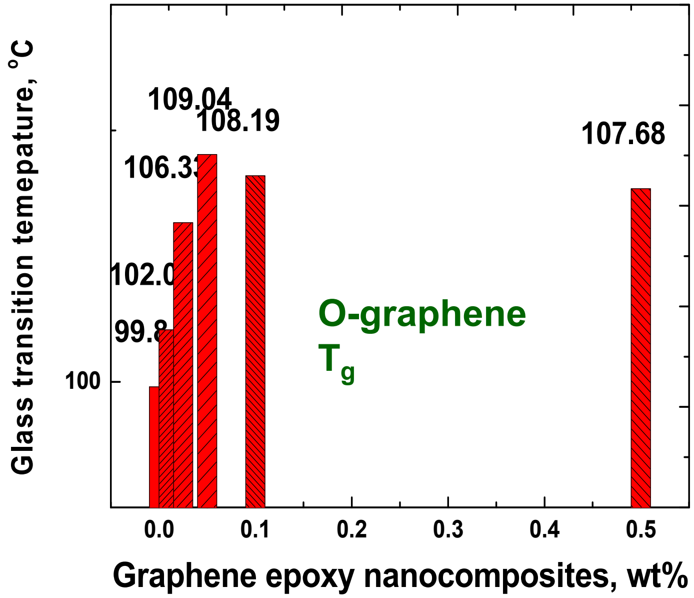


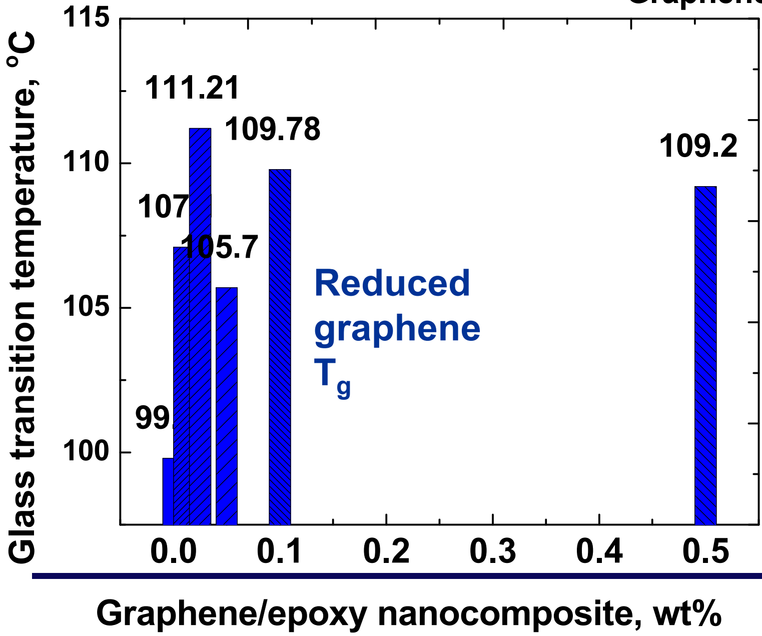


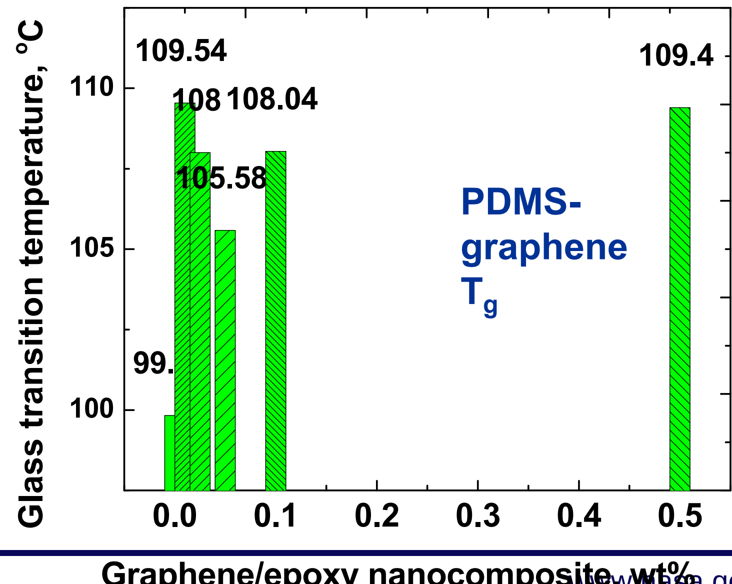
Patel N. M., Dwight D. W., Hedrick J. L., Webster D. C., McGrath J. E. Macromolecules 21, 2689 (1988)

Epoxy Graphene Nanocomposites Glass Transition Temperature

Graphene loading 0.05 - 0.5 wt%



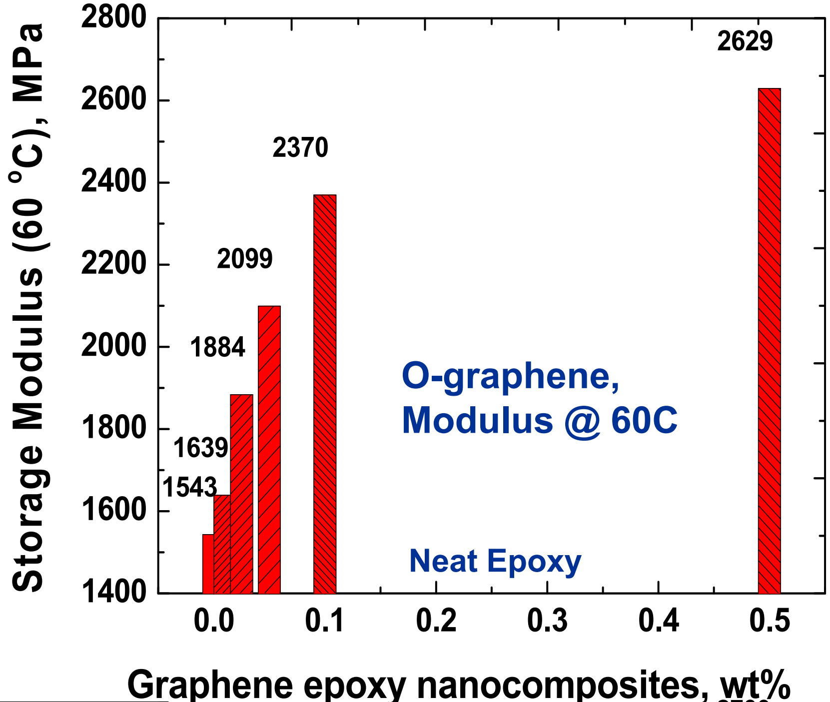


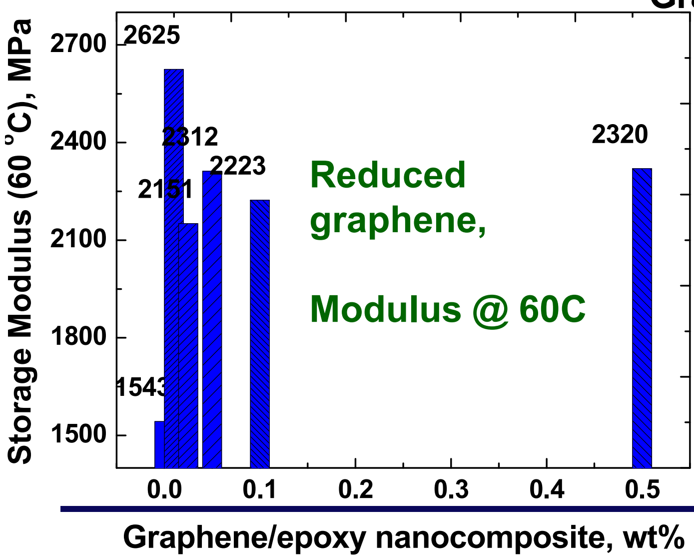


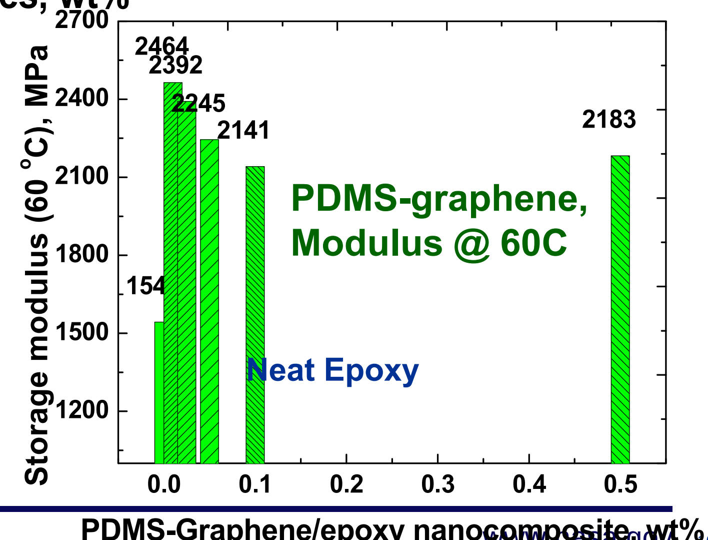
Ohio Aerospace Institute

Epoxy Graphene Nanocomposites-Reinforcements

Graphene loading
0.05 - 0.5 wt%





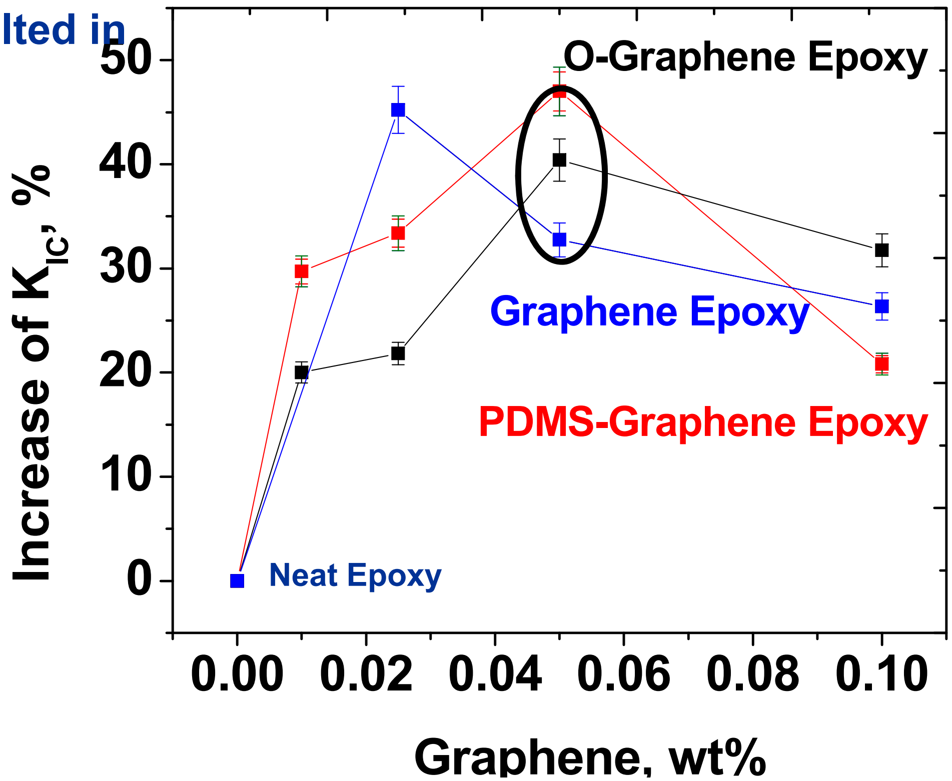


Epoxy Graphene Nanocomposites Fracture Toughness

Mode I Fracture Toughness

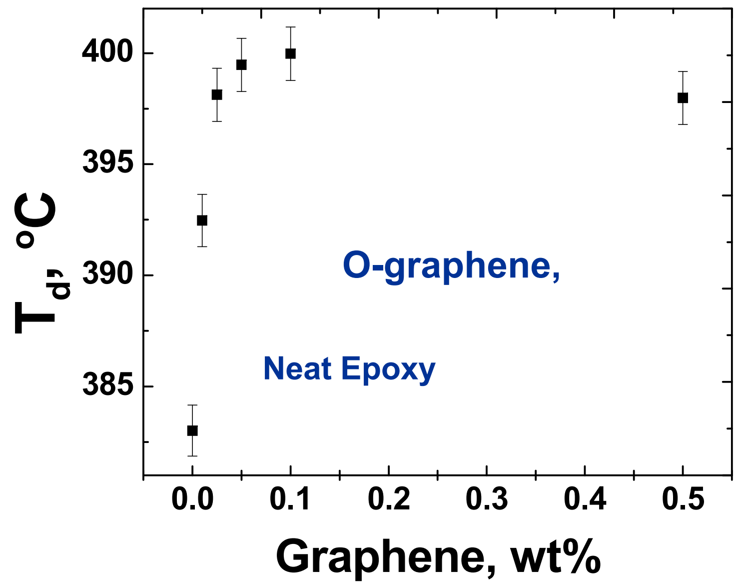
The fracture toughness improved with Low graphene content, where further addition of graphene resulted in K_{IC} deterioration.

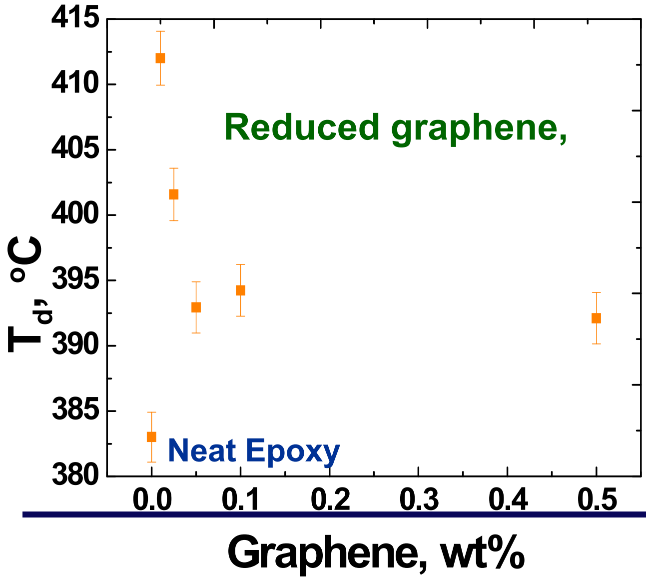
$$K_{IC} = \frac{P_{max}}{B\sqrt{W}} f(x)$$

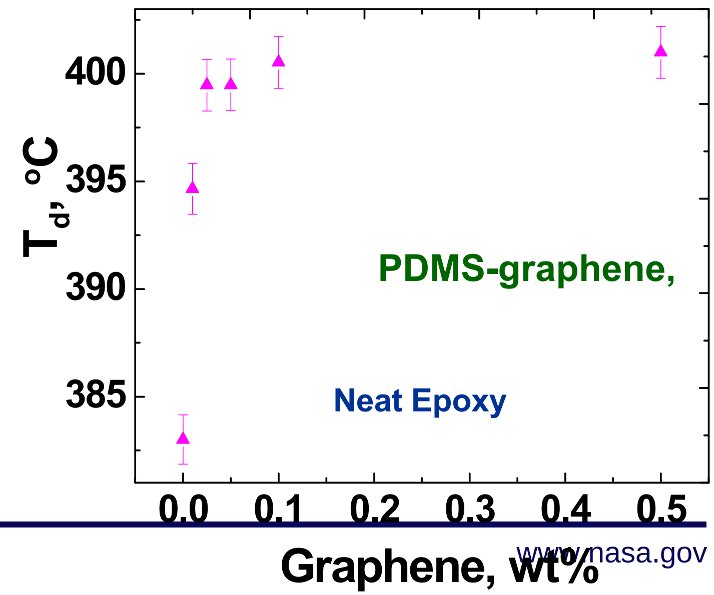


$$f(x) = 6x^{1/2} \frac{\left[1.99 - x(1-x)(2.15 - 3.93x + 2.7x^2)\right]}{(1+2x)(1-x)^{3/2}}$$

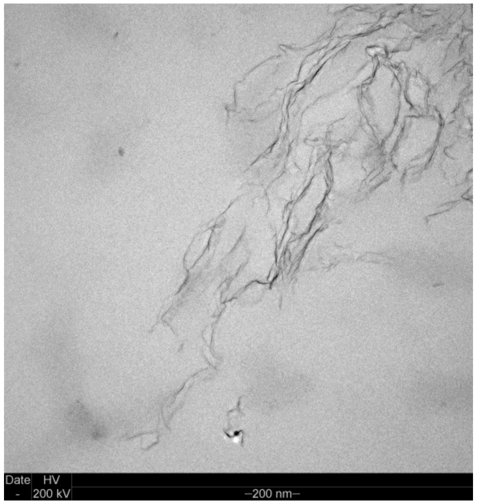
Epoxy Graphene Nanocomposites Thermal Stability

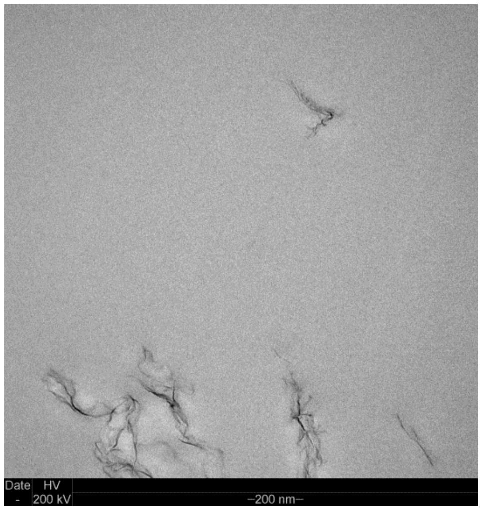


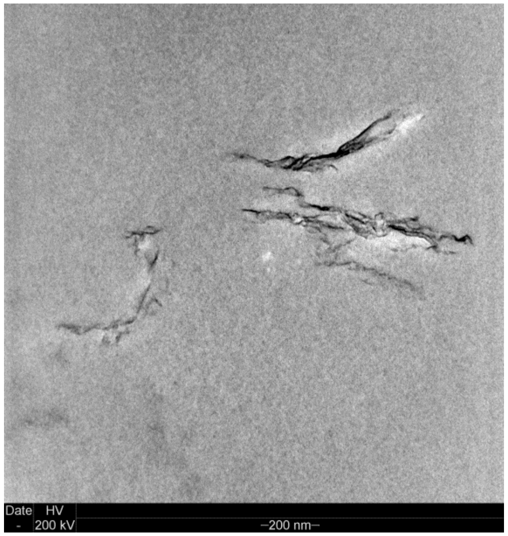


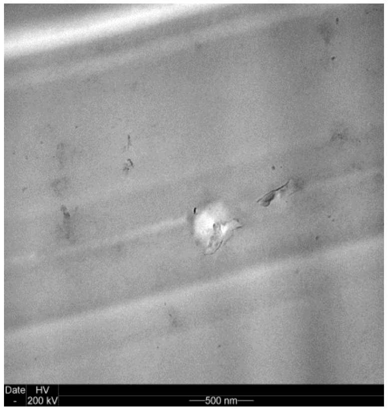


Epoxy Graphene Nanocomposites-Dispersion

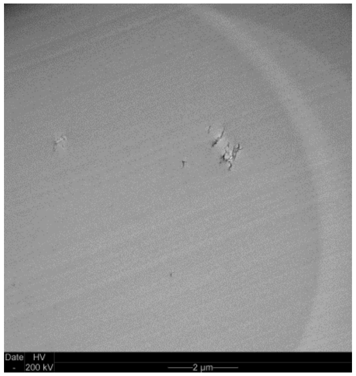




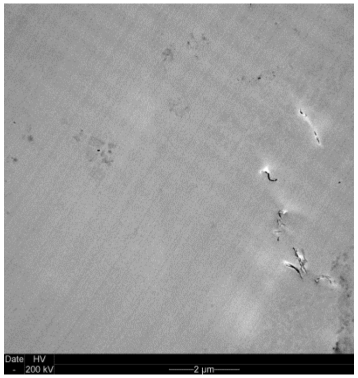




Reduced graphene in epoxy



O-graphene in epoxy

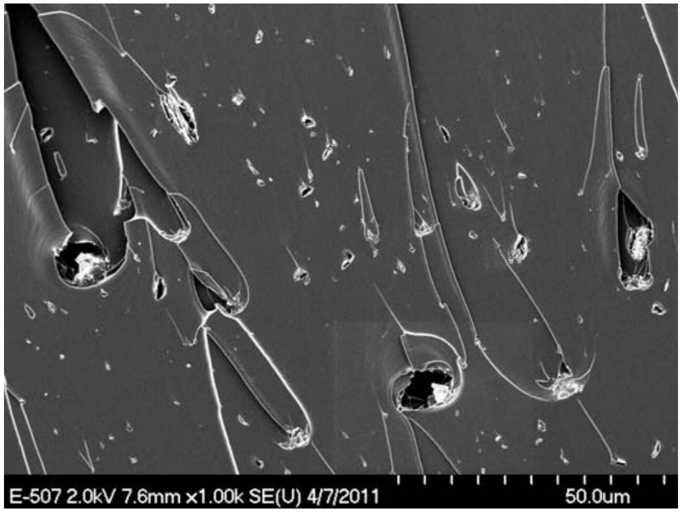


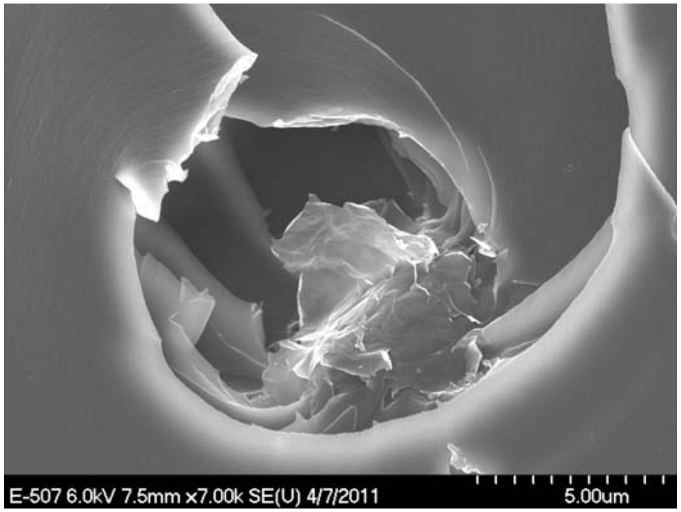
PDMS modified graphene in epoxy 0.05wt%

Good dispersion was obtained in all nanocomposites

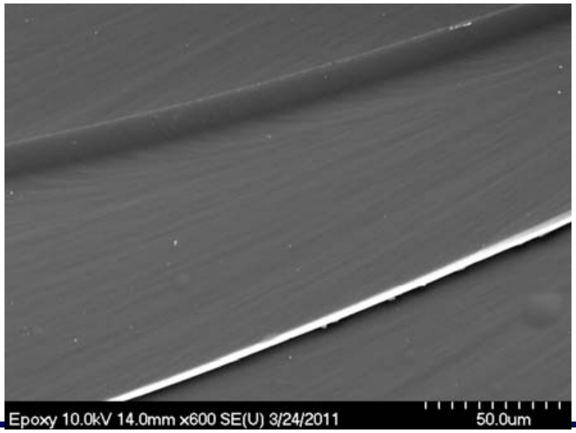
SEM

Fractured, O_2 plasma treated surface of PDMS-Graphene epoxy nanocomposites





0.5 wt% PDMS-graphene Nanocomposites



Concluding Remarks

- Low graphene content (0.05-0.5 wt%) graphene epoxy nanocomposites using reduced graphene, O-graphene, and surface modified graphene were prepared by solution mixing.
- All nanocomposites exhibited improvements in glass transition temperature, modulus, thermal stability, and fracture toughness.
- TEM studies showed good dispersion of graphene in the epoxy resin matrix.
- SEM micrographs indicated crack generation and energy dissipative phenomena in the graphene nanocomposites compared to neat epoxy.

Acknowledgements

•The NASA Aeronautics-Subsonic Fixed Wing Program: Contract NNC07BA13B

• Dr. Michael A. Meador, Agency Nanotechnology Lead, Polymer Branch Chief, NASA GRC
• Dr. Dave Kankam, NASA USRP program, NASA GRC
• Dr. Rick Rogers, Dave Hull,Terry McCue, NASA/GRC
• Professor Aksay, Princeton University,
• Vorbeck Materials Inc., John Lettow

NASA-University Programs

GRC ⟹ Lead for the agency nanotechnology

- **NRA – Aeronautics**
  - **NASA inspire web site**

- **NASA Graduate Student Researchers Program (GSRP)**
  - **http://fellowships.hq.nasa.gov/gsrp/nav/**

- **NASA Undergraduate Student Research Program (USRP)**
  - **http://usrp.usra.edu/**
- **NASA Experimental Program to Simulate Competitive Research (EPSC**

- **NASA Glenn Faculty Fellowship Program (NGFFP)**
  - **http://nbpo.grc.nasa.gov/university-affairs/ngffp/**

- **LERCIP Higher Education (College) – Undergraduate program**

- **Space Grant Consortium**