National Aeronautics and Space Administration

Graphene Polymer Nanocomposites for Aerospace Applications

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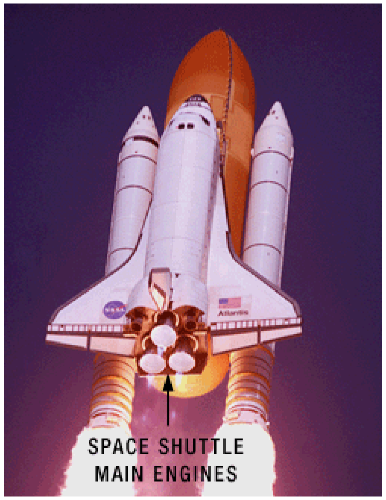
FACSS – Oct. 4th, Reno, NV



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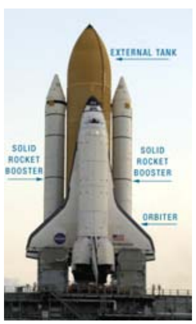
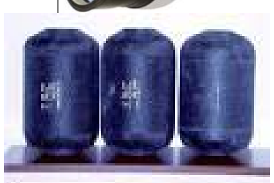
Polymer Nano-Composites for Aerospace Applications

Multi-Functional Materials

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

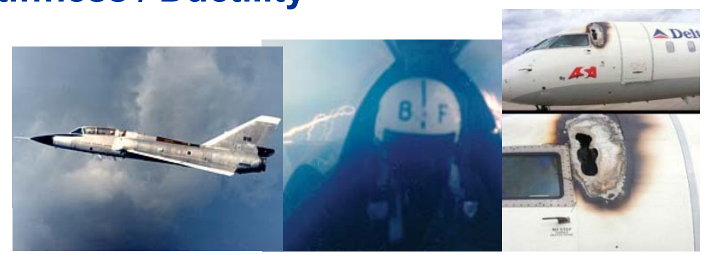




- Graphene
- Layered Silicates
- Carbon NT
- Expanded Graphite
- Carbon nanofibers
- Magnetic nanoparticles
- Organometallic physical crosslink

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

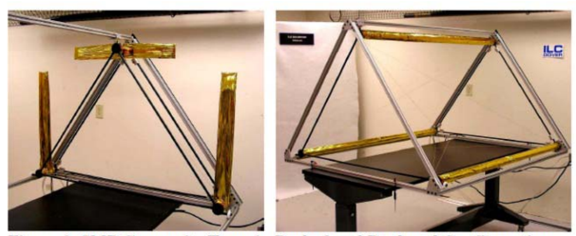


Figure 2. SMP Composite Truss in Packed and Deployed Configurations

Sensors
Static discharge
Lightening strike
Actuators

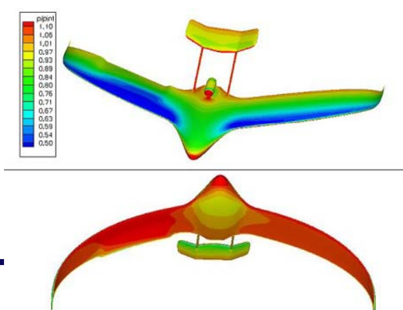
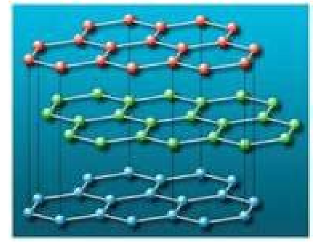


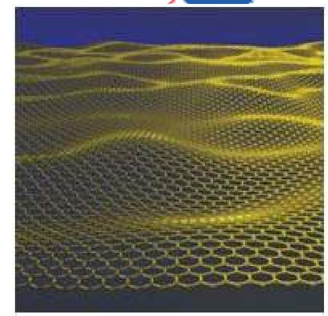
Image courtesy of NASA

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

Figure 4. 0.5-m Diameter SMP Reflector in Both Deployed and Packed Configurations

Graphite and Graphene



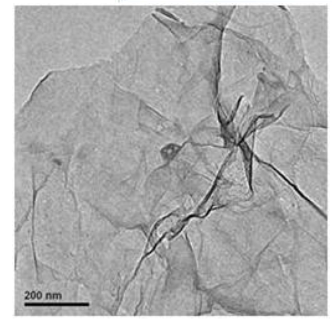


Graphite:

Advantages: Naturally abundant material, Low cost

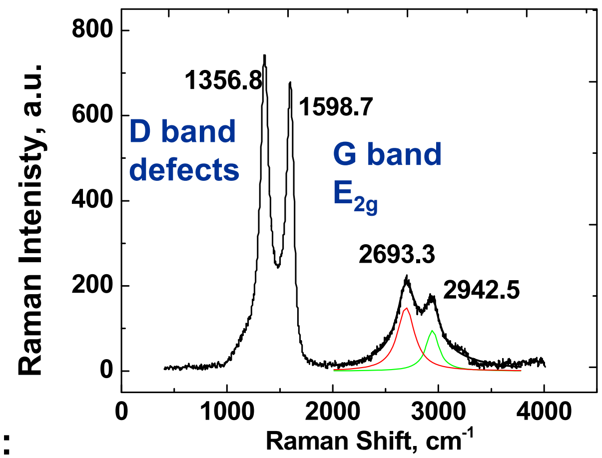
Graphene

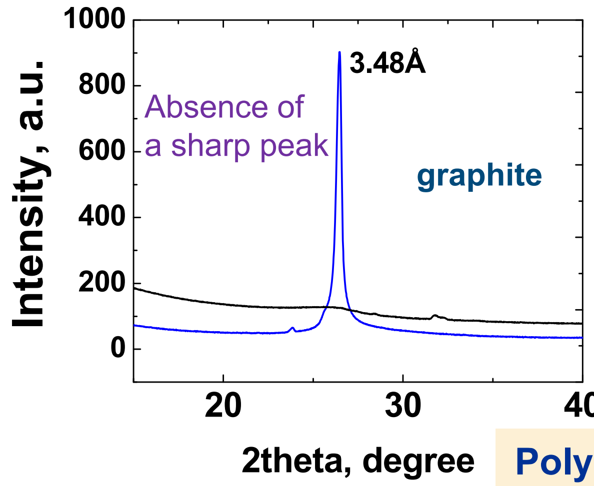
- **Mechanical peeling**
- **Acid intercalation, thermal shock, sonication**
- **Acid intercalation followed by high pressure, high temperature treatments**



~ 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

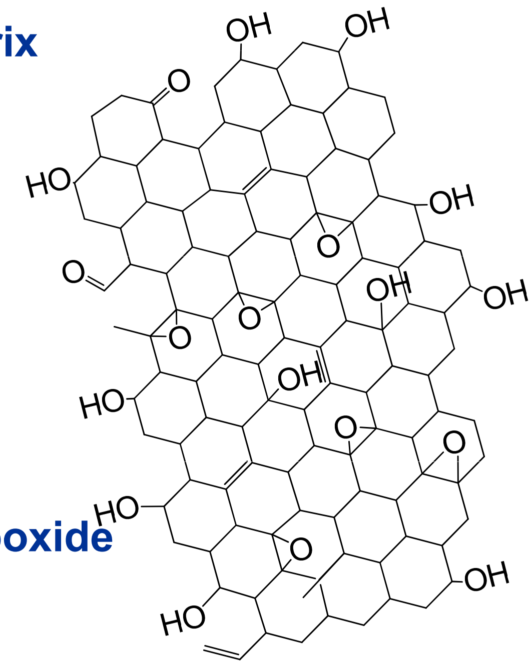
Polymer nanocomposites, optoelectronic applications; transparent conductors, field emission displays, supercapacitors, devices, emissive displays, micromechanical sensors.

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)

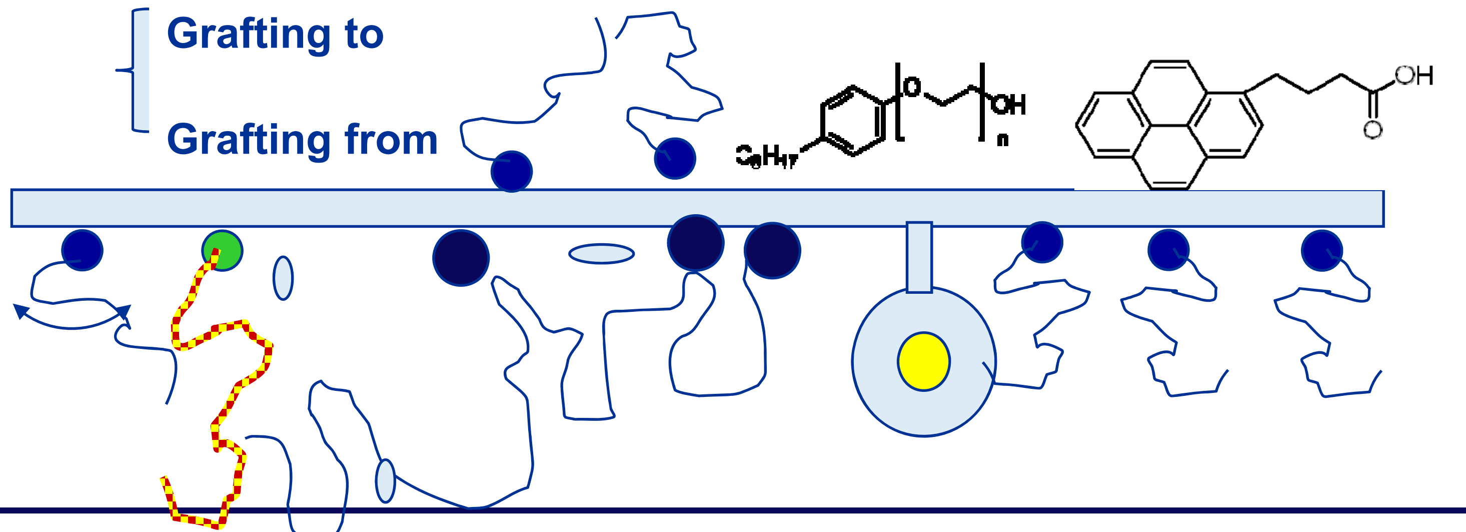
- Combination of sp^3 and sp^2 hybridization

  Covalent bonding; -OH, -COOH, -phenolic-OH, -epoxide

Covalent bonding

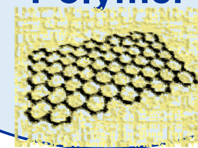
Grafting to

Grafting from



Graphene Polymer Nanocomposites

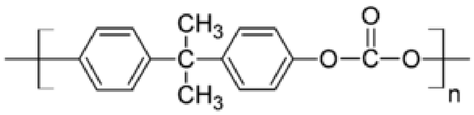
Polymer+



Conductive Nanocomposites

Electrical Performance

Polycarbonate



- Solution mixing
- Emulsion mixing

- DC electrical conductivity
- AC electrical conductivity
- Dynamic mechanical analyzer, modulus, Tg
- Morphology:
  - electron microscopy
  - SANS

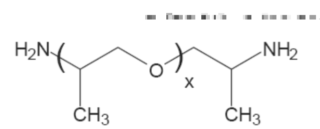
Dispersion via sonication

Reinforcement, toughness and thermal properties

Epoxy

Epon 826

D 230



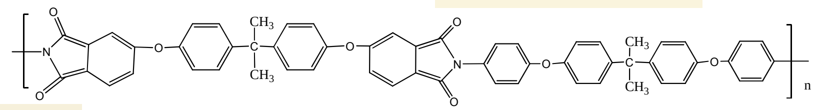
- Solution mixing

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

Multifunctional actuators

Electrical, thermal, mechanical And actuation performance

Polyimide



- Solution mixing

- DC electrical properties
- Mechanical properties, modulus, Tg
- Morphology: electron microscopy

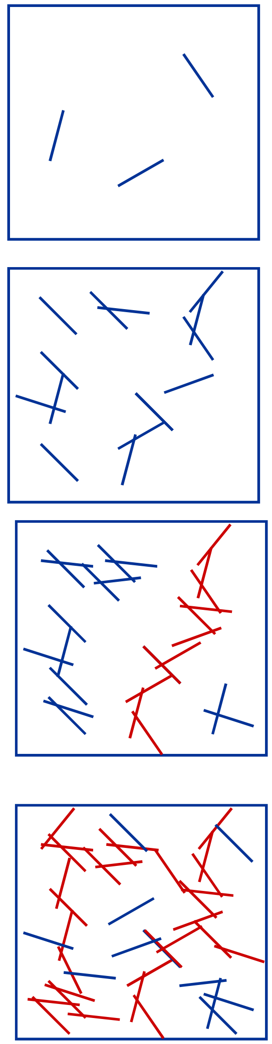
Electrical Percolation

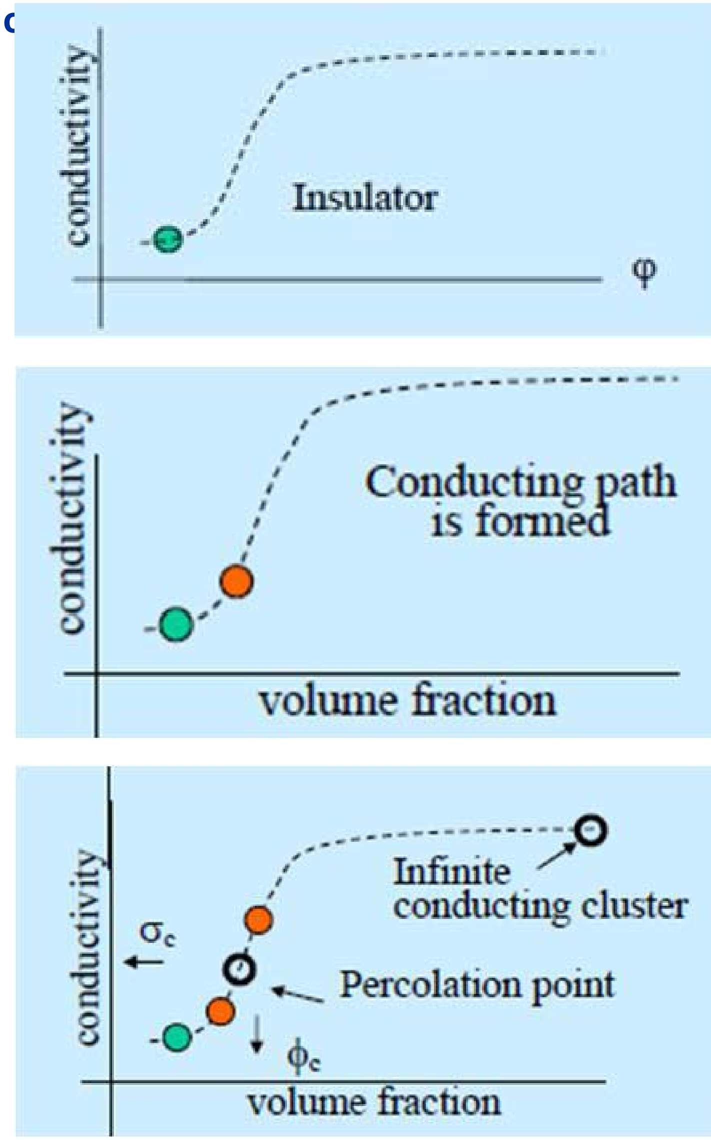
Low conductive nanoparticle c

Percolating the conductors

- Inherent conductivity of nanoparticle
- Concentration
- Aspect ratio
- Dispersion
- Orientation

Increasing C-nanoparticle concentration





Conductive path

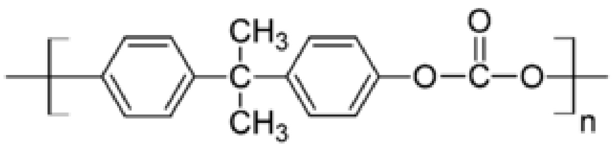
Aggregation and Dispersion of nanoparticles

Type of Nanoparticle	van der Waals Interaction Energies
Two spheres (radii, R_1 and R_2) separated by distance D	$W = -\frac{A}{6D}\left(\frac{R_1R_2}{R_1+R_2}\right)$
Two parallel cylinders (radii, R_1 and R_2) separated by a distance D and of length L	$W = -\frac{AL}{12\sqrt{2}D^{3/2}}\left(\frac{R_1R_2}{R_1+R_2}\right)^{1/2}$
Two crossed cylinders (radii, R_1 and R_2) separated by a distance D	$W = -\frac{A}{6D}(R_1R_2)^{1/2}$
Two parallel plates separated by a distance D	$W = -\frac{A}{12\pi D^2}$

Notes: A (Hamaker constant) $= \pi^2 C\rho_1\rho_2$, where C is the coefficient in the atom–atom pair potential, and ρ_1 and ρ_2 are the number of atoms per unit volume.

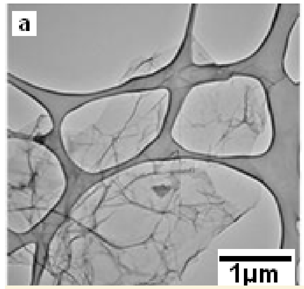
Israelachvili *Intermolecular Surface Forces, Academic Press, San Diego, Ed. 3, 2006*

Graphene Polycarbonate



Lexan 121, Mw = 26,301 g/mol, PDI=1.72

- Excellent thermal properties
- Good mechanical properties
- High impact strength and toughness
- Good processability



~ 9.2x 15.1 micron

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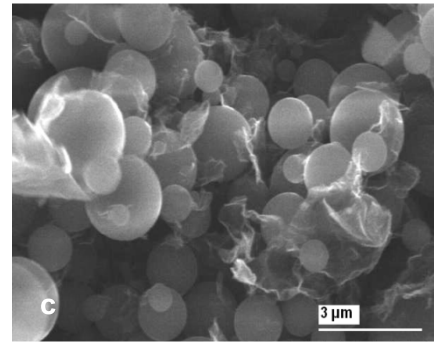
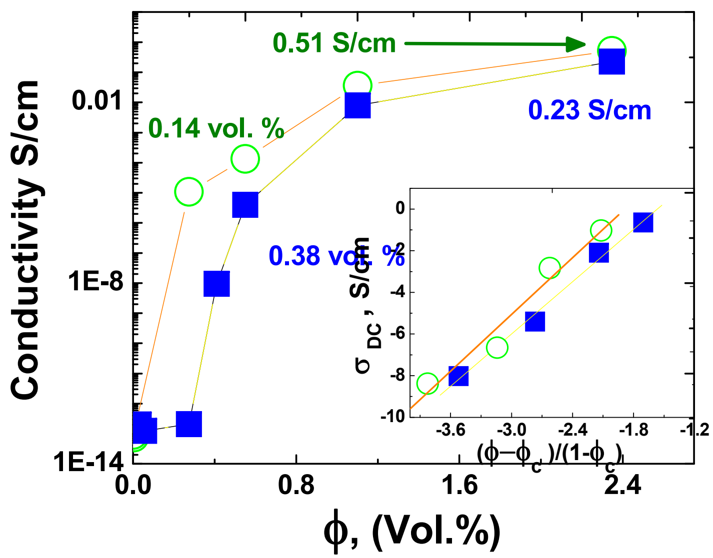
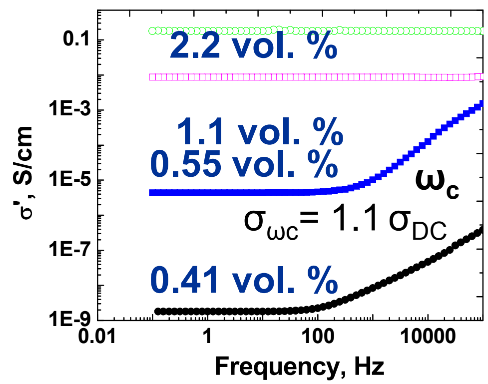
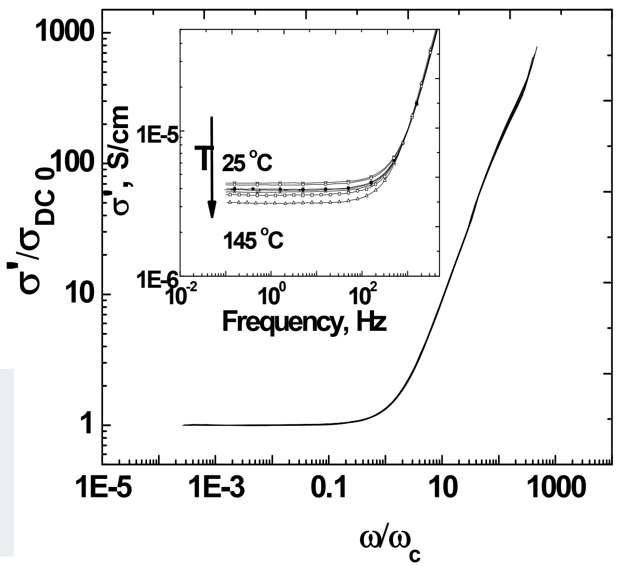


Extended pair approximation model

$$\sigma_{DC} = \sigma_f [(\phi - \phi_C)/(1-\phi_C)]^t \qquad \sigma(\omega)/\sigma_{DC0} = 1 + k(\omega/\omega_c)^s$$







S-G PC series $t = 4.18 \pm 0.26$
σ_f, $=106.55 \pm 0.69$ S/cm
E-G PC series $t = 4.04 \pm 0.58$
$\sigma_f = 106.39 \pm 1.32$ S/cm

Chemically modified graphene PS nanocomposites 0.1 vol. %
Conductivity of 0.001 S/cm at 1 vol.%

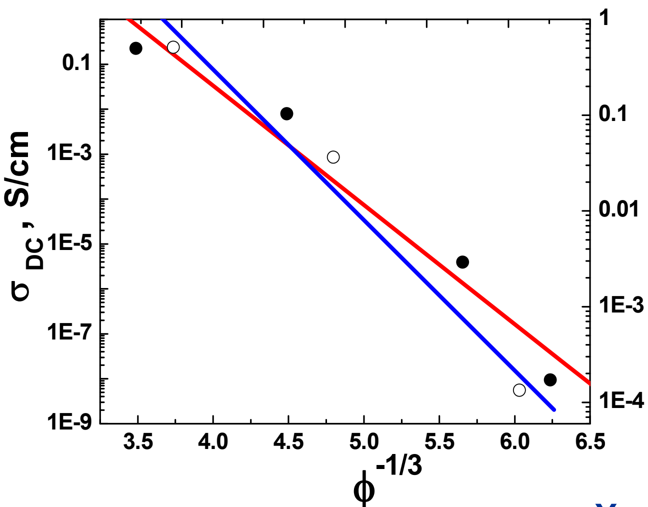
•Stankovich, S.; Ruoff, R.S. *et al.* Graphene-Based Composite Materials. *Nature* 2006, *442*, 282- 286.

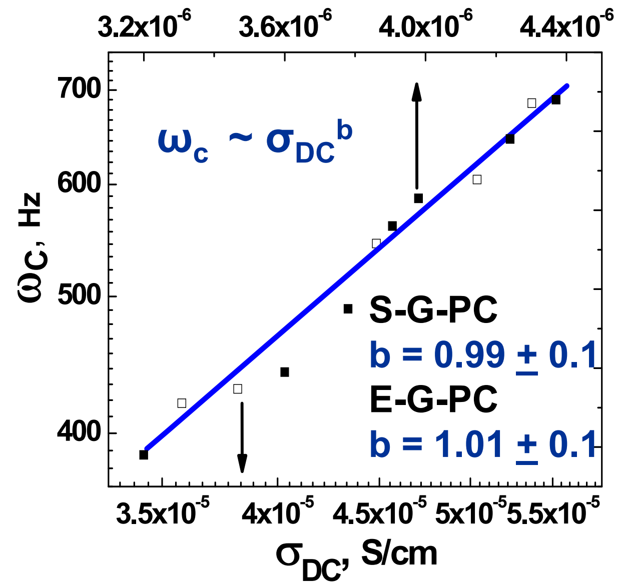
Kilbride, B. E.; *et al*. *J. Appl. Phy.* 2002, *92*, 4024-4030.

Graphene Polycarbonate

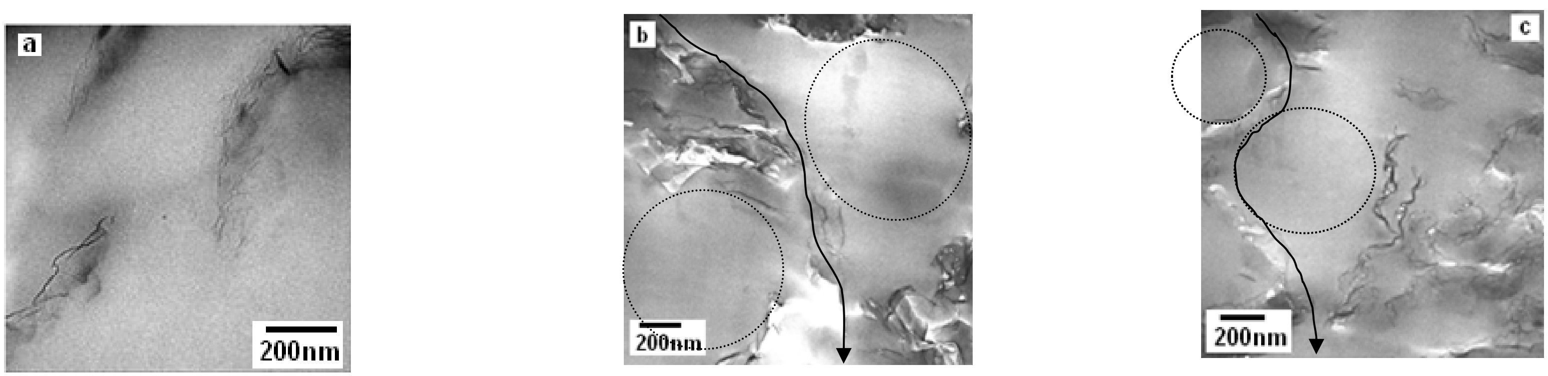
Tunneling

Charge carrier can travel through the barrier insulating polymer gap, a distance longer than the nanoparticle length





Yoonessi, M.; Gaier, J. R. *ACS Nano*, 2010



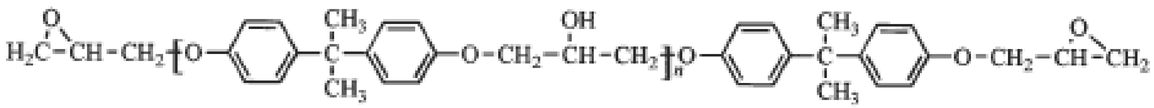
Kilbride, B. E.; *et al*. *J. Appl. Phy.* 2002, *92*, 4024-4030.

Epoxy Graphene Nanocomposites- Reinforcement

Objectives:

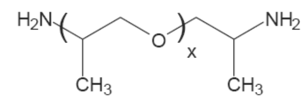
- To determine the effects of graphene addition and surface modification on the thermal and dynamic modulus, fracture toughness of the low content graphene nanocomposites.

Epoxy: Epon 826

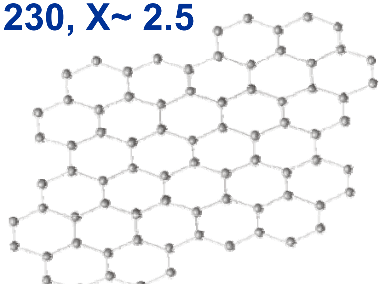


$n = 0$ (90 %), 1 (10 %)

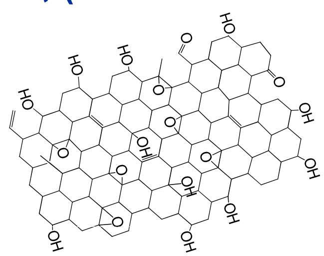
Low viscosity resin
Transparent



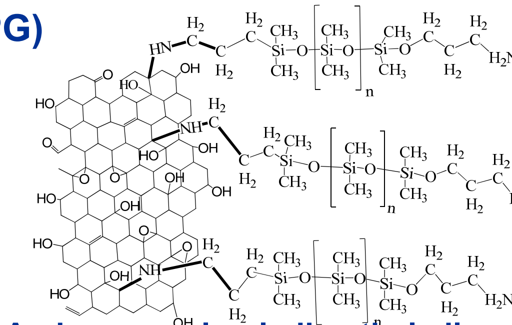
Jeffamine D230: a polyetheramine, (an amine terminated PPG)
MW 230, X~ 2.5



Reduced graphene
sp^2 hybridized

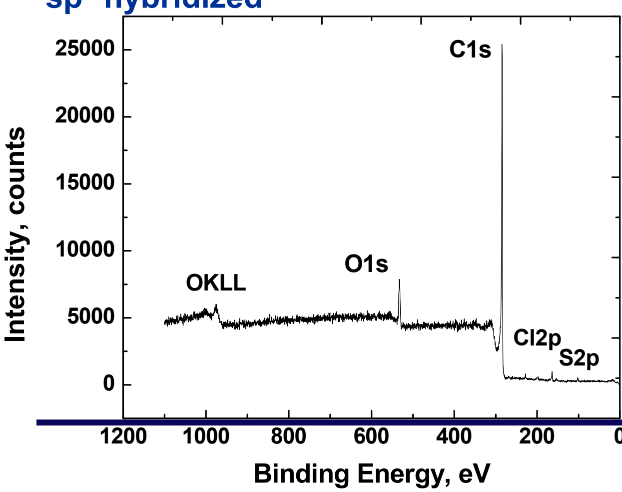


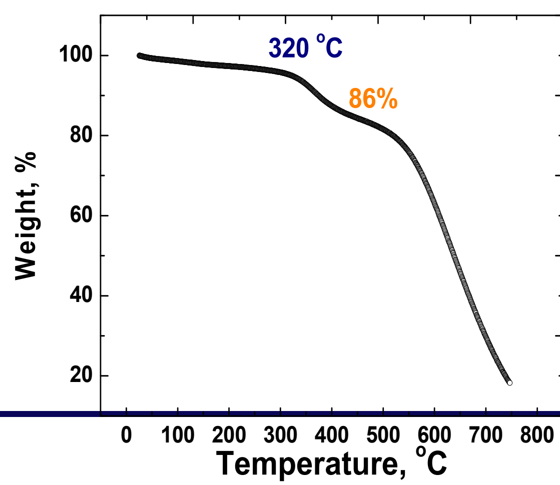
Highly oxygenated graphene, sp^2, and sp^3

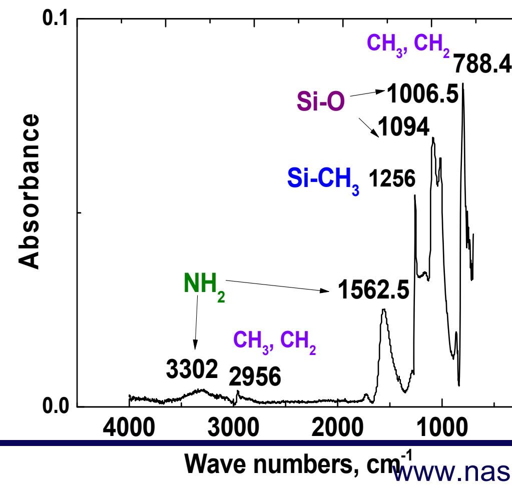


2500 – 27000 g/mol

Amino propyl polydimethyl siloxane graphene, sp^2, and sp^3





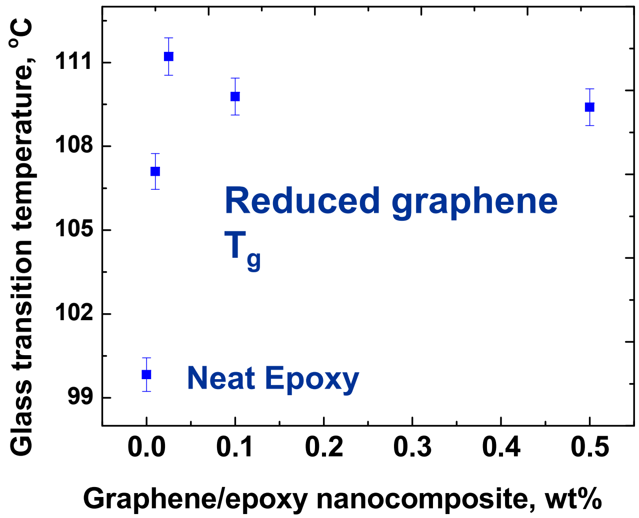


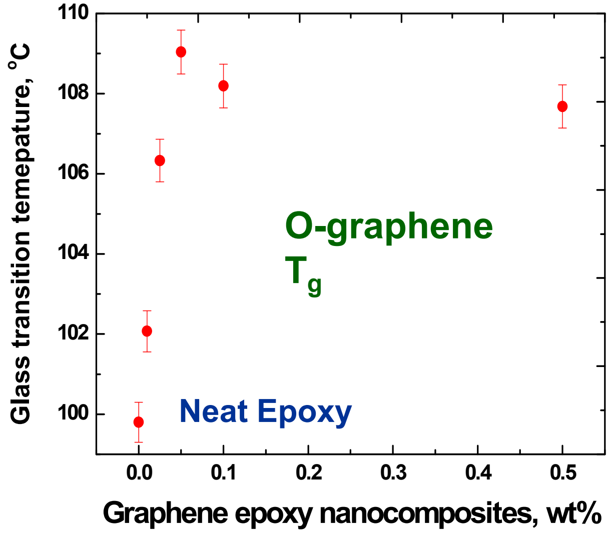
National Aeronautics and Space Administration

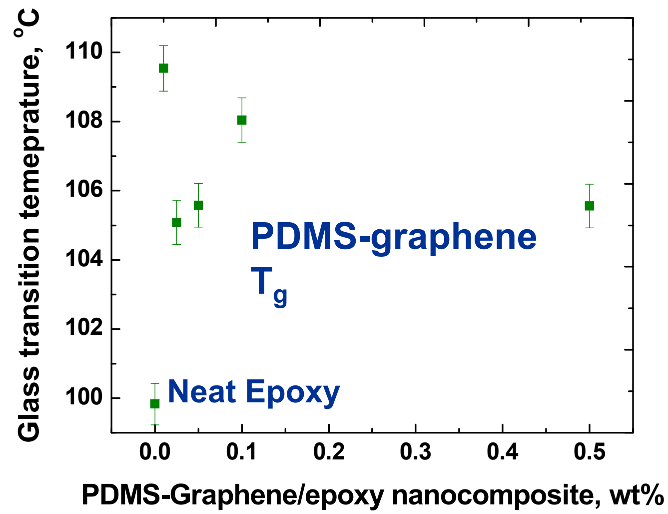
Ohio Aerospace Institute

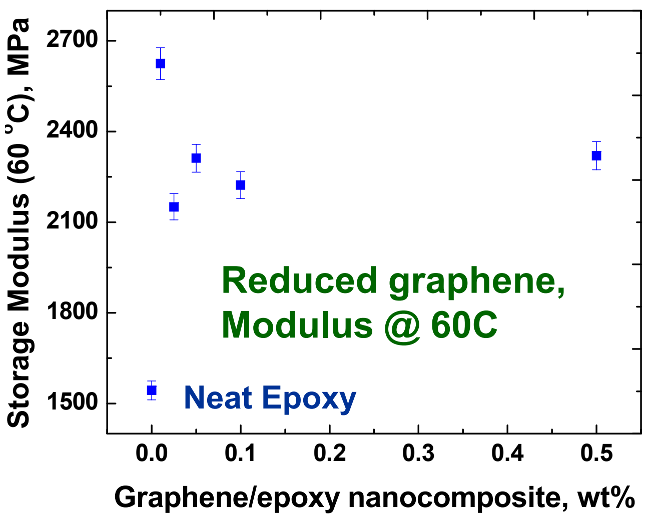
Epoxy Graphene Nanocomposites

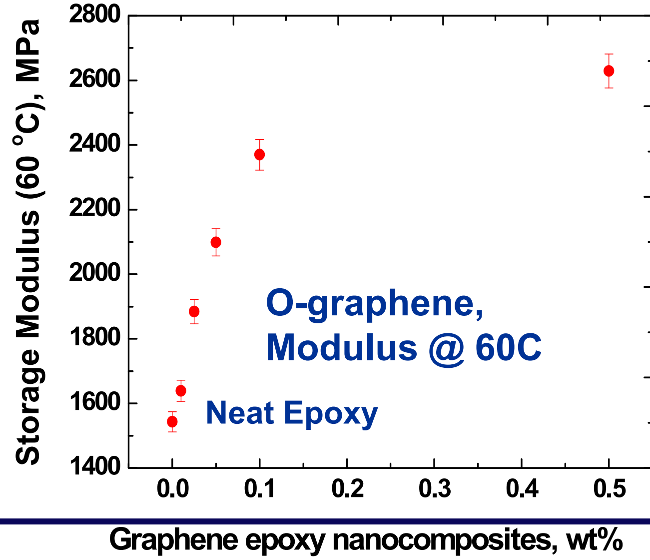
Graphene loading 0.05 - 0.5 wt%

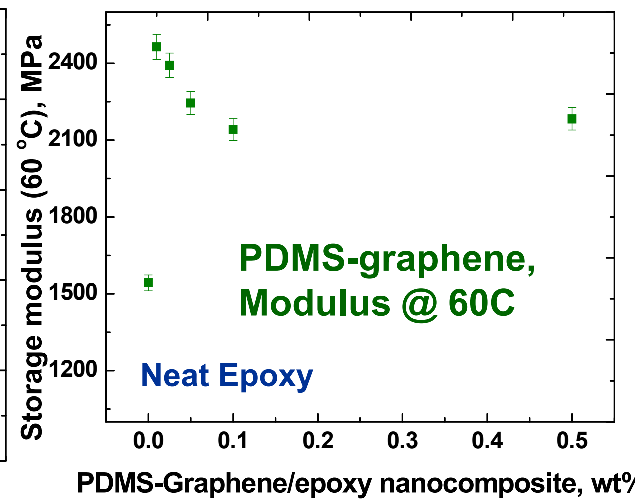










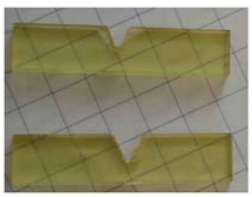


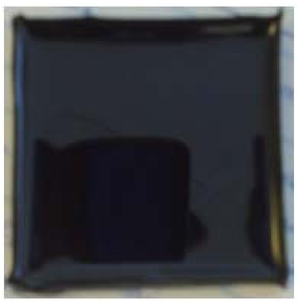
Epoxy Graphene Nanocomposites

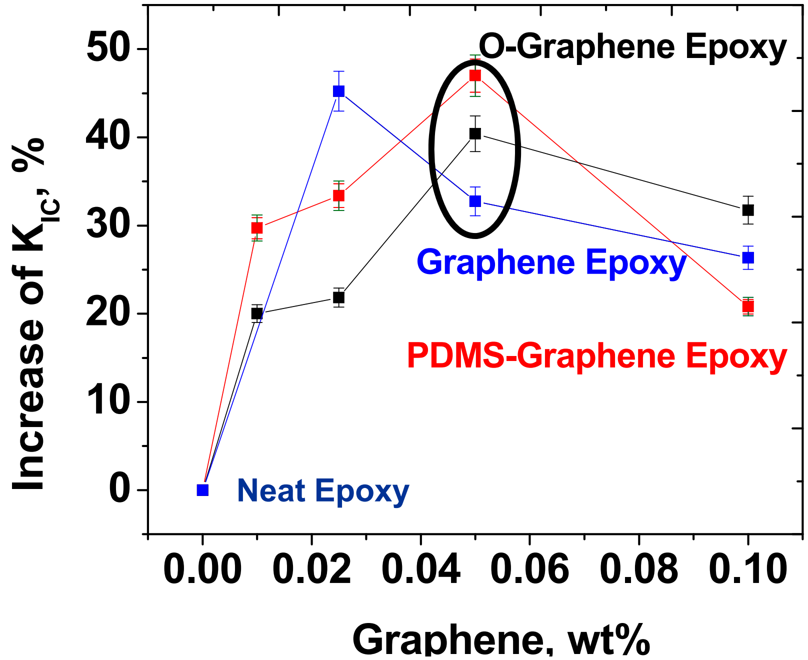
$$K_{IC} = \frac{P_{max}}{B\sqrt{W}} f(x)$$

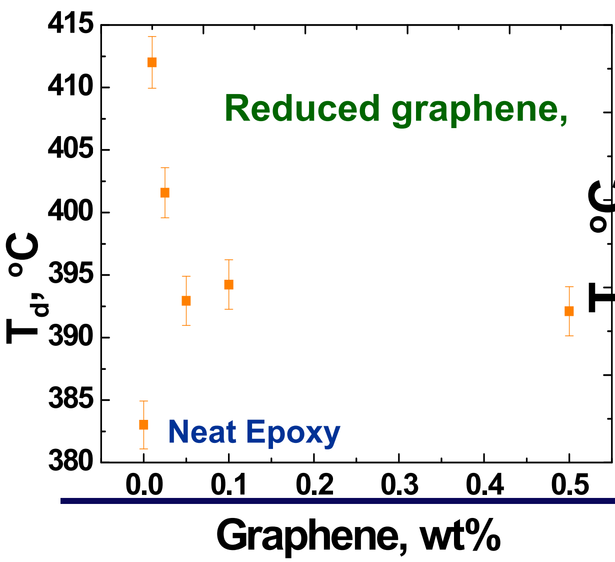
$$G_{IC} = \frac{(1-\nu^2)K_{ic}^{\,2}}{E}$$

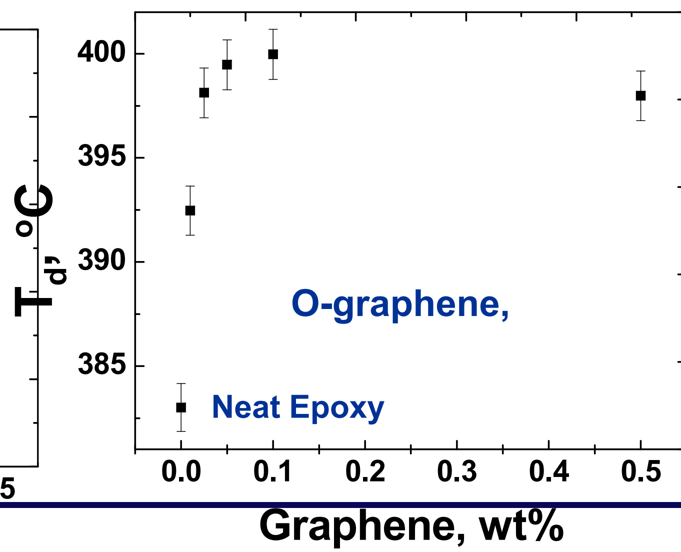
$$f(x) = 6x^{1/2}\frac{\left[1.99 - x(1-x)(2.15 - 3.93x + 2.7x^2)\right]}{(1+2x)(1-x)^{3/2}}$$

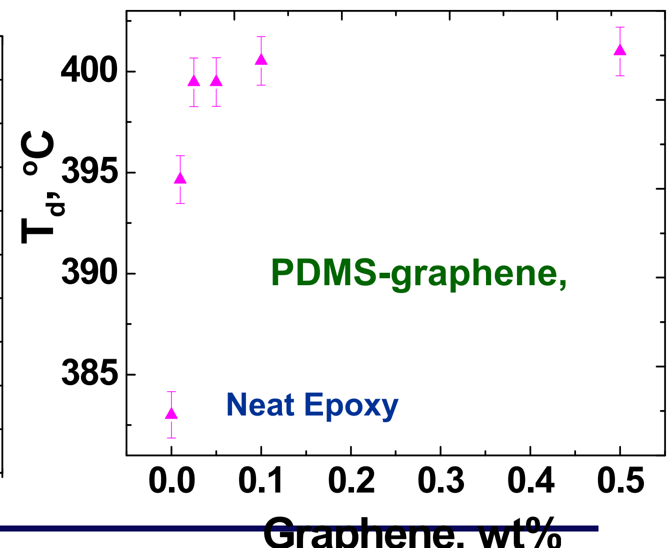




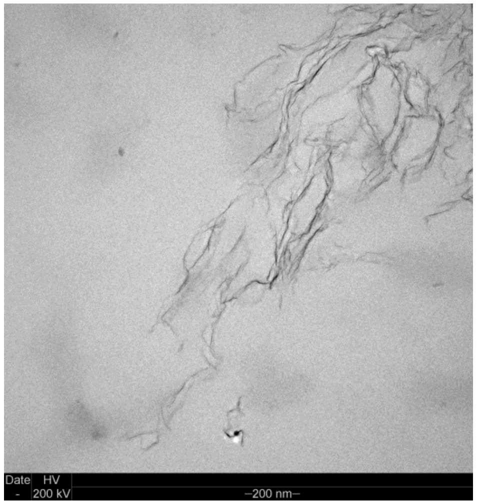


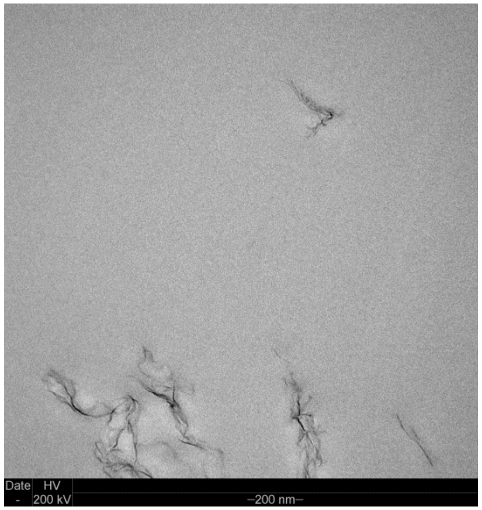


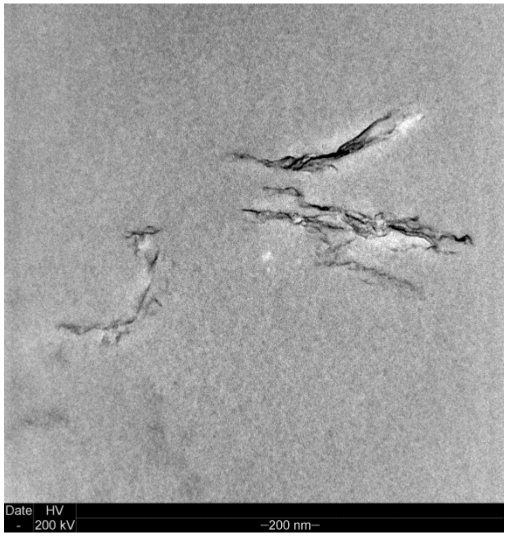


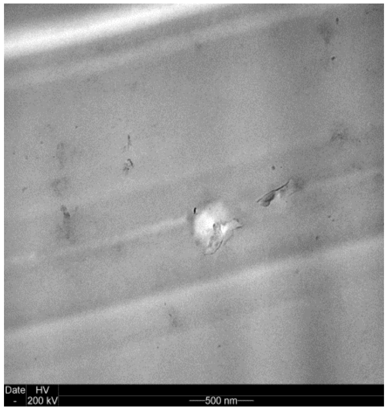


Epoxy Graphene Nanocomposites-Dispersion

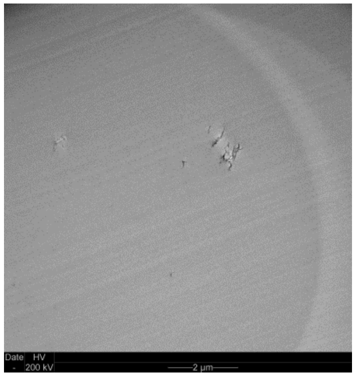




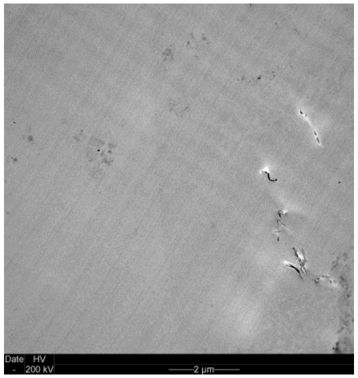




Reduced graphene in epoxy



O-graphene in epoxy



PDMS modified graphene in epoxy 0.05wt%

Good dispersion was obtained in all nanocomposites

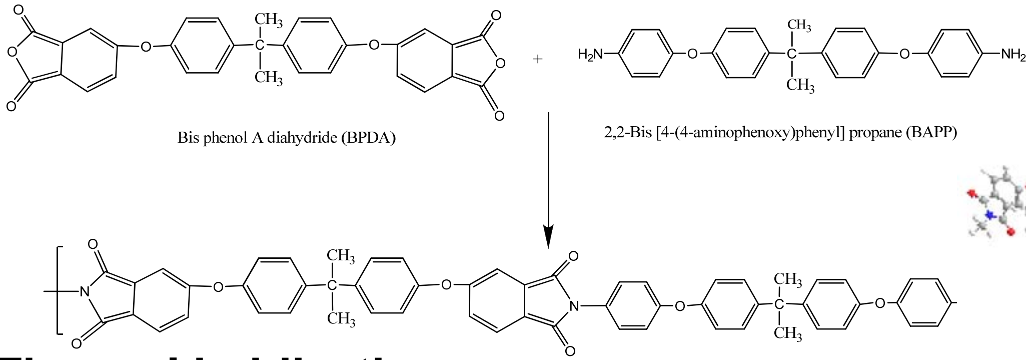
Spacecraft launched from Space Shuttle

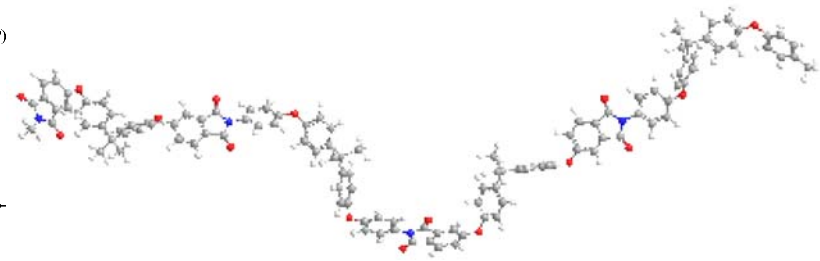
Polyimide Graphene Nanocomposites

PMR-15
GRC
After burner

Aromatic polyimide: low color, flexibility, high T_g, high thermal stability, and radiation resistance.[1]

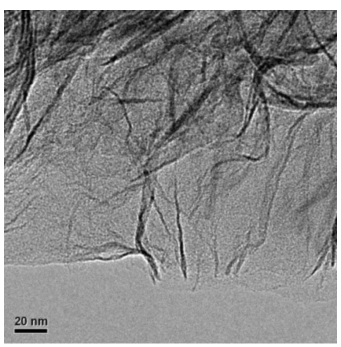
[2] Polyimide, thermal stability >500 °C, T_g > 200 °C, flexible and semi-transparent.





Thermal imidization:

- **Mixing and dissolving equi-molar ratio diamine in anhydrous-NMP under dry N_2 followed by addition of dry anhydride and stirring for 24h in flame dried vessels.**
- **Then, increasing the temperature ~230 °C (NMP reflux) for 3h and precipitating in methanol and drying**



+ Polyimide solution

sonication

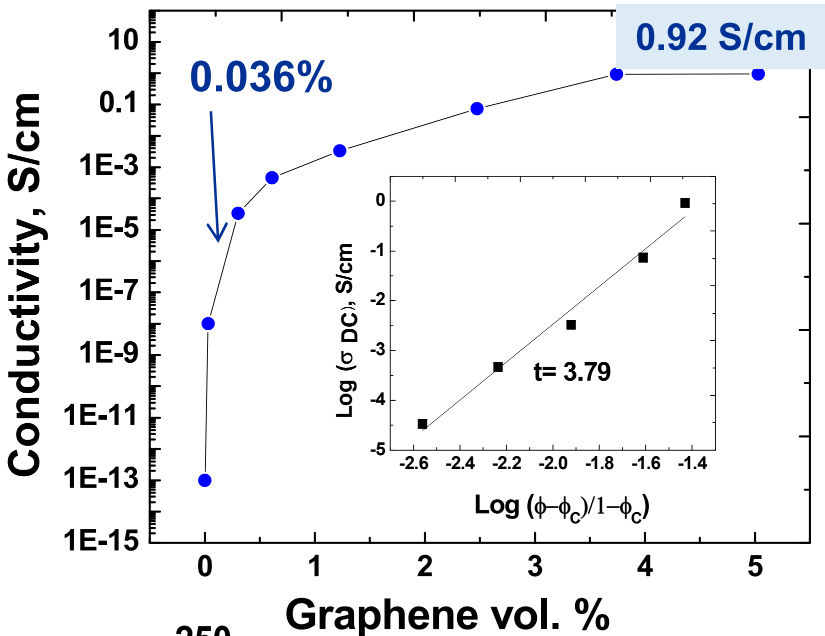
Solvent casting →

[1]Qu,L., Connell, J.W., Sun, Y.-P., Macromolecules, 2004, 37, 6055-6060.
[2]Lebron-Colon, M. Meador, M. A., Gaier, J. R., Sola, F., Scheiman, D.A., McCorkle, L.S. ACS Applied Materials and Interfaces, 2010, 2 ,3 , 669–676 .

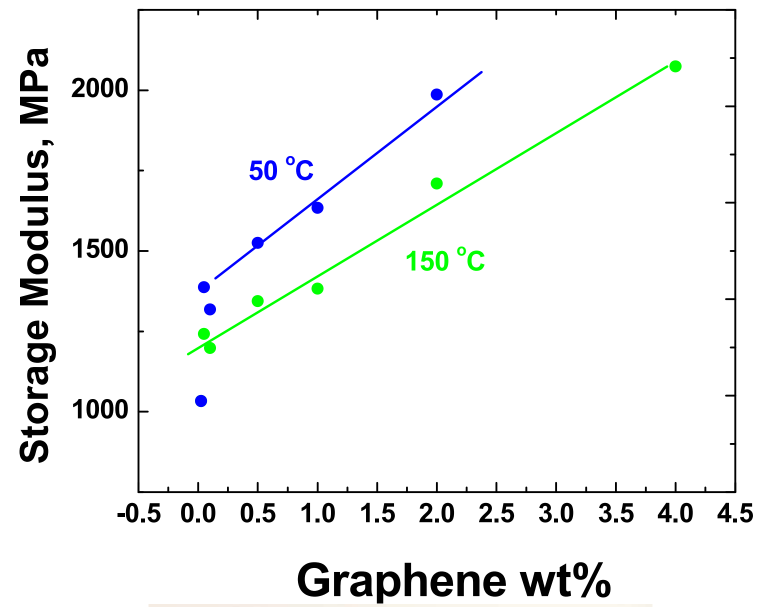
Ohio Aerospace Institute

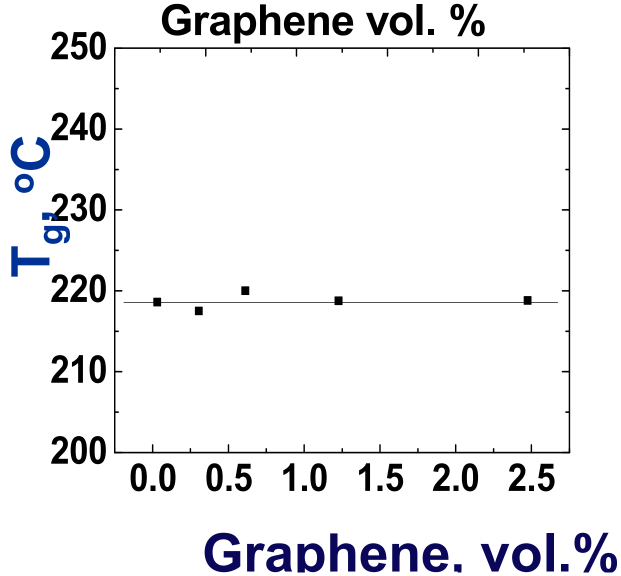
Polyimide Graphene Nanocomposites

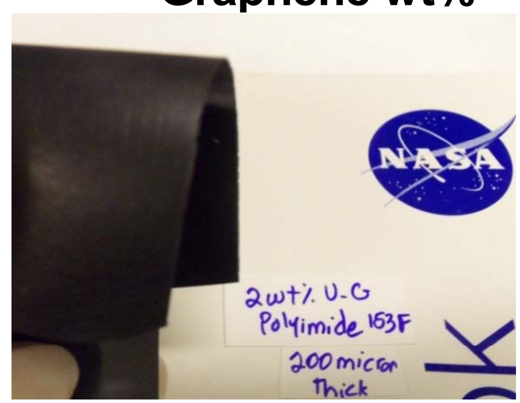
$$\sigma_{DC} = \sigma_f [(\phi - \phi_C)/(1-\phi_C)]^t$$



Addition of graphene resulted in composite reinforcement without adverse effect on the T_g

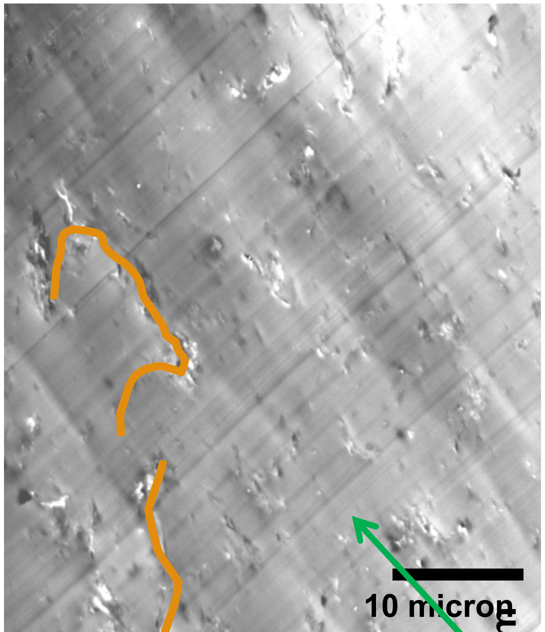




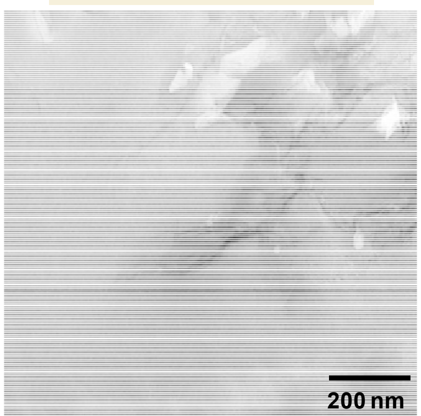


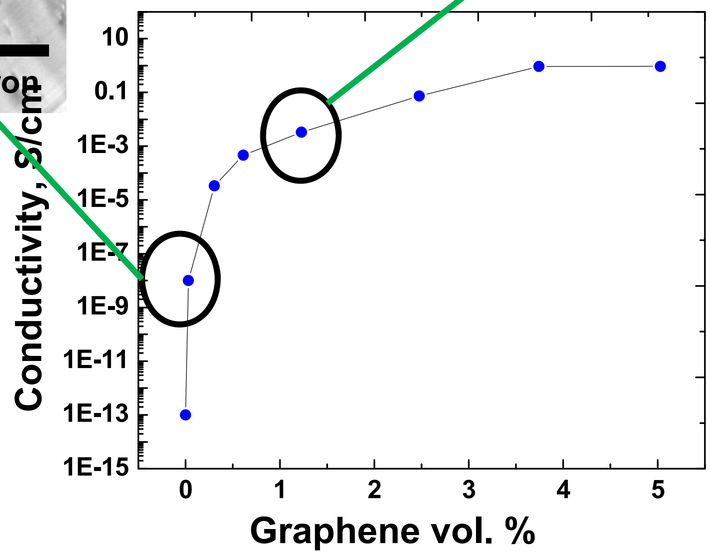
Flexible films at 2wt% with 200 micron thickness

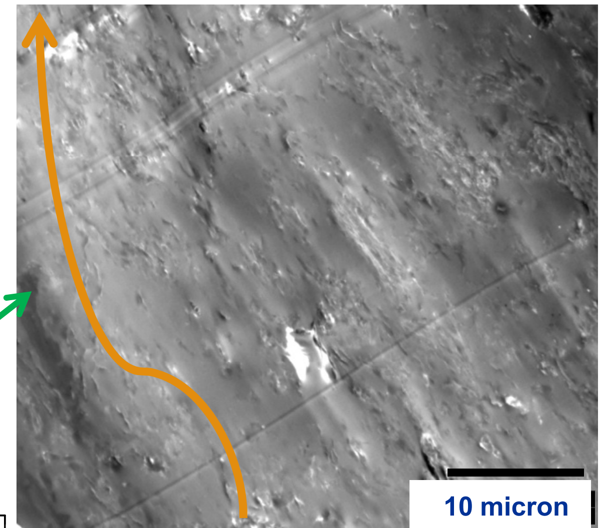
Dispersion of graphene in polyimide TEM



0.025 vol.%

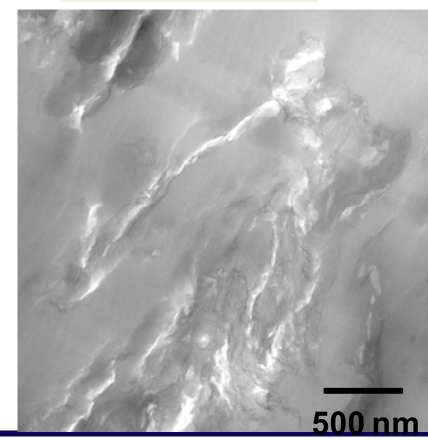






Conductive path

1.1 vol.%

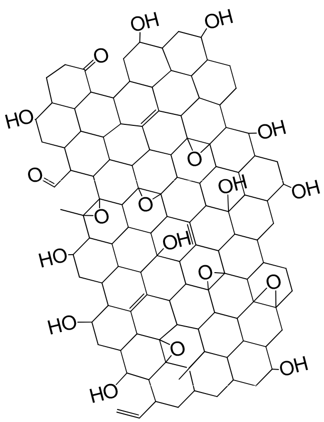


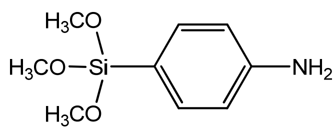
Reinforcement: O-Graphene Surface Modifications

-Covalent bonding of imide moieties using grafting to method

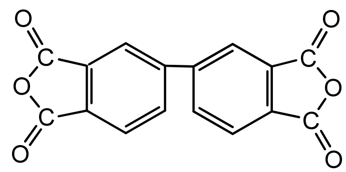
-Provide compatibility with the polyimide resin matrix

-Generate steric hindrance and promote dispersion

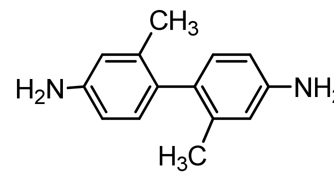




P-amino phenyl trimethoxy silane

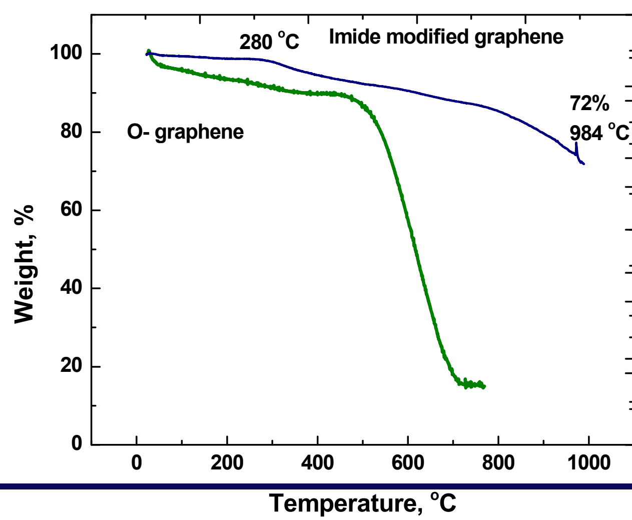


3,3',4,4'-Biphenyl tetracarboxylic dianhydride (s-BPDA)



2,2'-Dimethyl-4,4'-diaminobiphenyl (m-Tolidine)

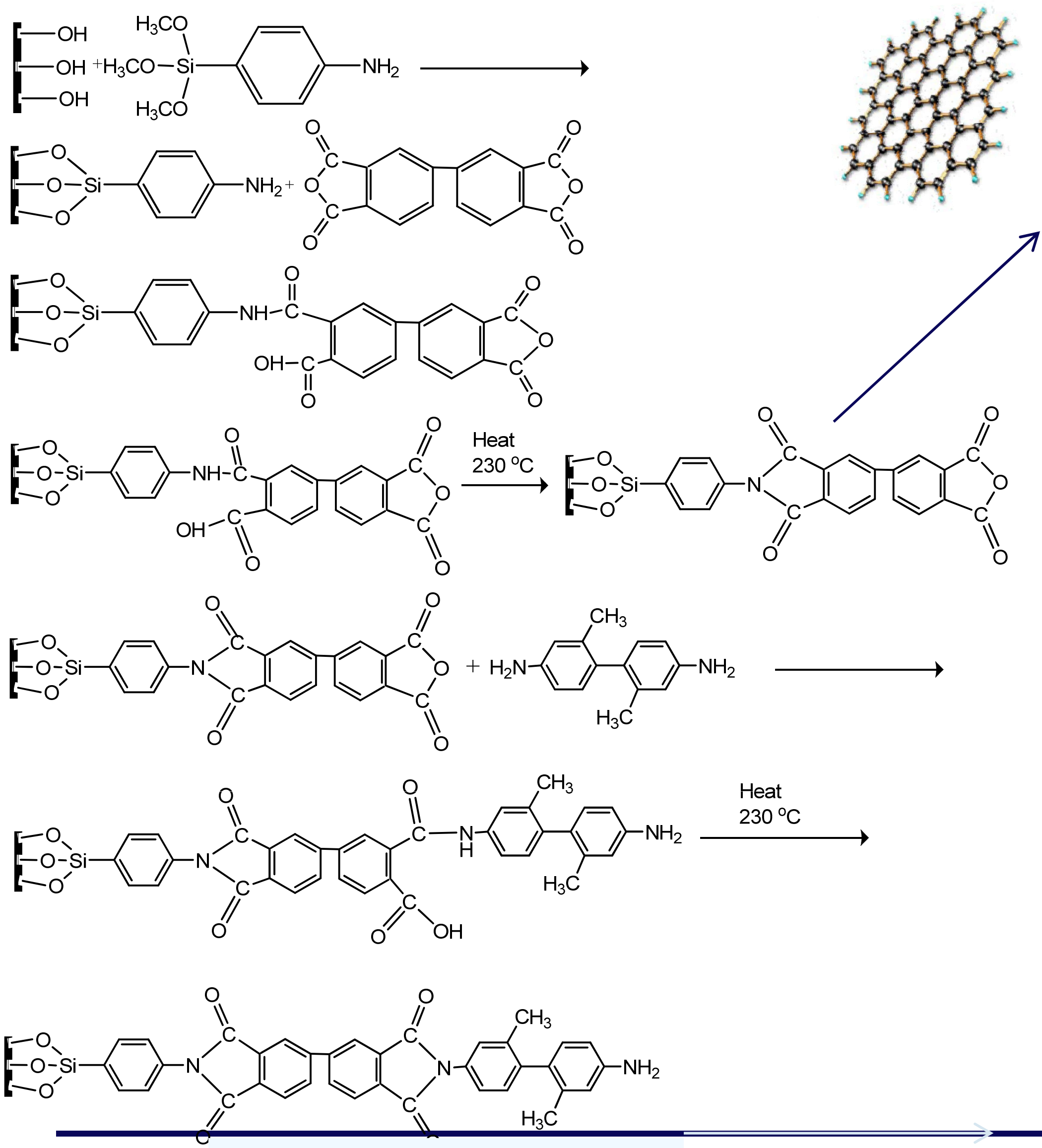
3 units were on the surface: 2 anhydride and 1 diamine

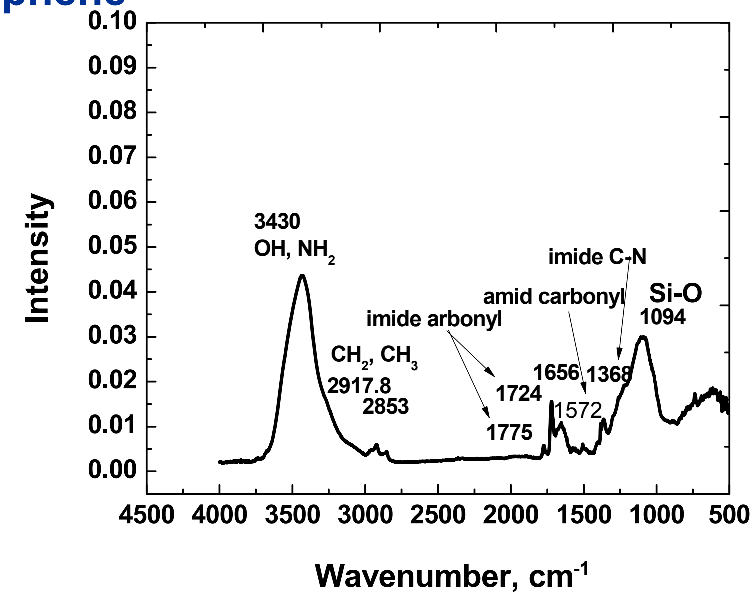


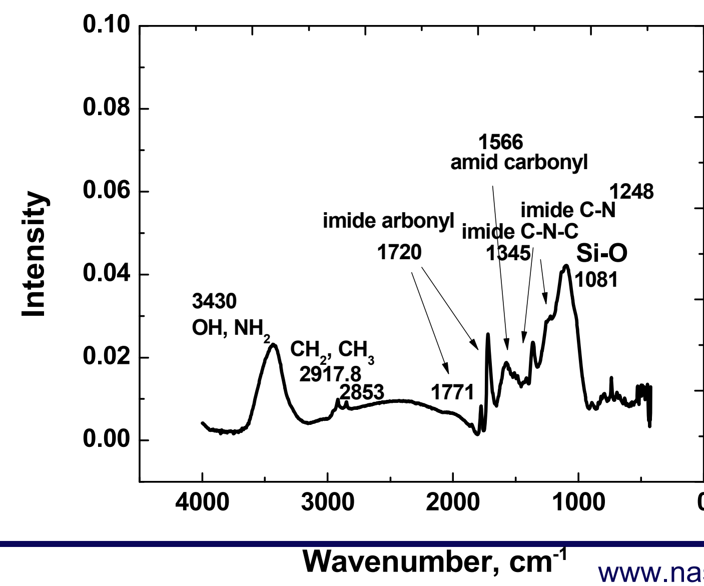
O-graphene
Graphene with rigid surface modifier
Graphene with flexible surface modiier

Surface Modification of Graphene with Rigid Imides

Covalent Functionalization of imide structure to Graphene



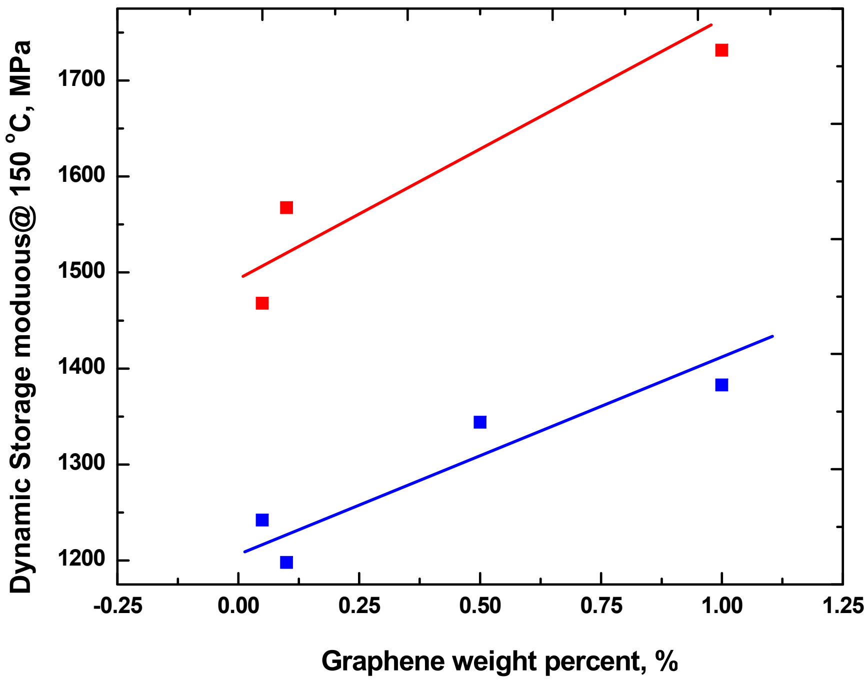


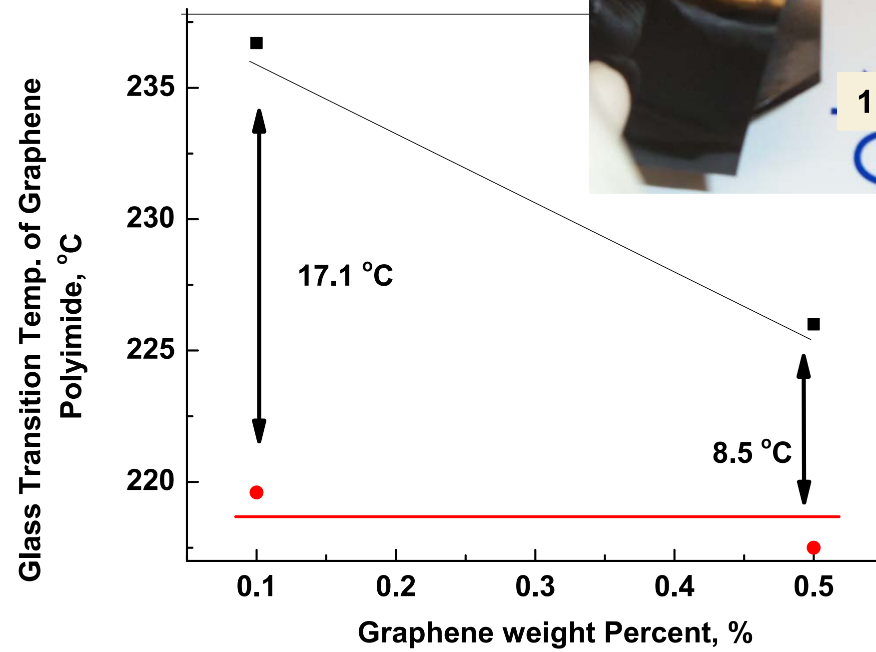


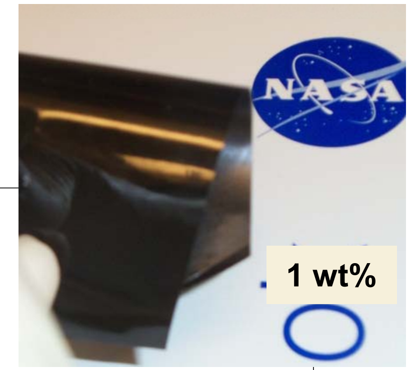
Mw 1058.28 g/mol: 3 unit

Surface Imidized Graphene Polyimide Nanocomposites

Addition of graphene with rigid surface imide moieties resulted in increase in modulus and T_g







Conclusions

- Incorporation of reduced graphene in the both polycarbonate and polyimide resulted in superior electrical conductivity along with reinforcement with none or insignificant adverse effect on the glass transition temperature.
- The plateau electrical conductivity of graphene polyimide nanocomposite reached to 0.92 S/cm with a critical percolation of 0.036 vol. fraction.
- Low graphene content (0.05-0.5 wt%) graphene epoxy nanocomposites exhibited improvements in glass transition temperature, modulus, thermal stability, and fracture toughness.
- Graphene surface characteristics is the key for the target property enhancement in all three resin matrices.

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- 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)
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