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# Structure-Property Relationships in Polycyanurate / Graphene Networks

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# Outline

- Background / Motivation
- Sequentially Prepared Graphene Types
- Polycyanurate / GO Composite Preparation
- Composite Morphology
- Composite Mechanical and

  Physical Property Characterization

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- National Research Council (NRC) Research Associateship Program (RAP)
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# Potential Applications for Cyanate Ester Resins and Composites

Image courtesy US Navy (public domain)

- Ship structures

Image courtesy NASA (public domain)

- Heat shields

Image by Antonio Pedreira (public domain))

- Microchip housing

U.S. Navy photo by Photographer's Mate Airman Marvin E. Thompson Jr. (RELEASED

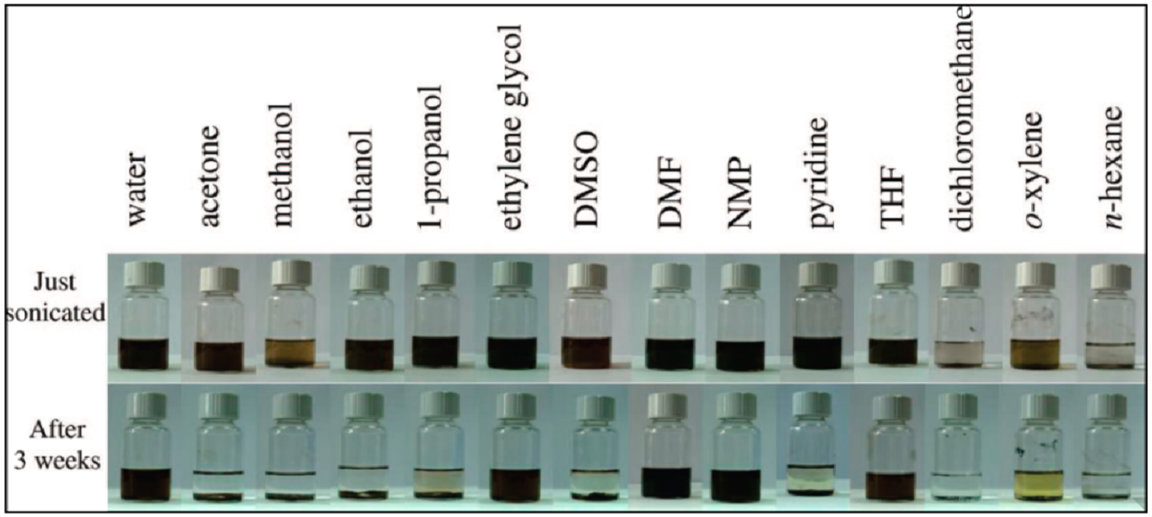
- Missile Fins, Radomes

Image courtesy NASA (public domain)

- Spacecraft antennas

- A better understanding of the physical properties, including water uptake, of cyanate ester resins will lead to improved performance in the example applications shown above.

# GO and TRGO



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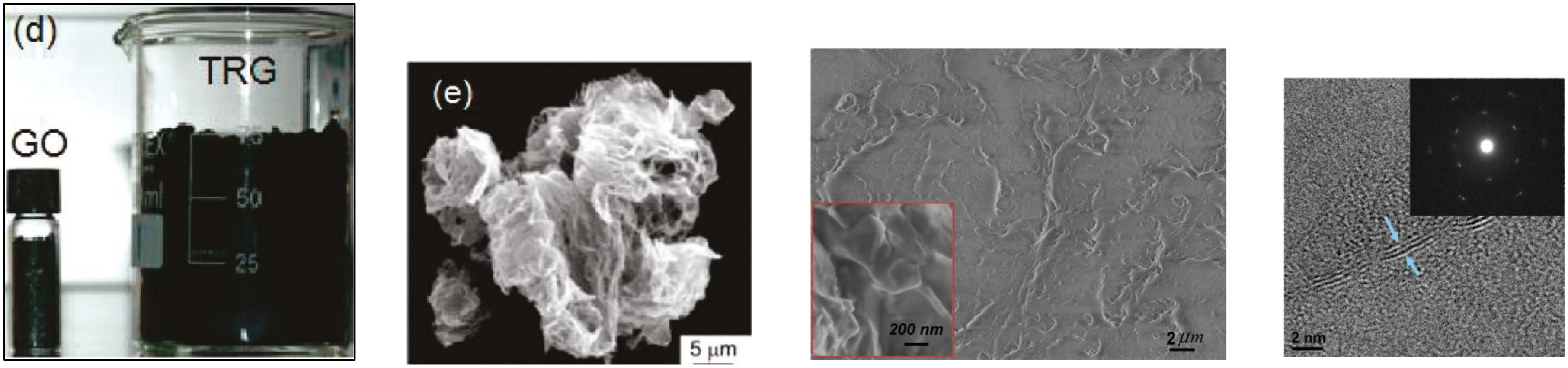

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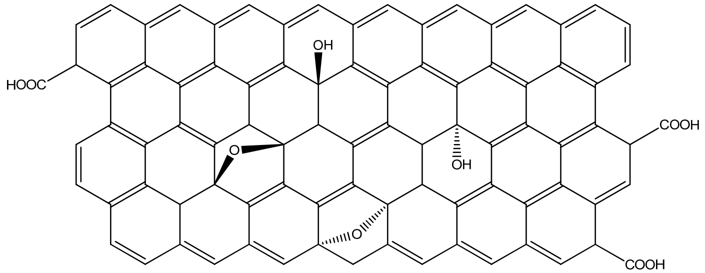
# Sequential Preparation of GO and TRGO

- Graphene oxide (GO) prepared by Hummers method of oxidation of XG Sciences® xGNP-M-25

Hummers, W. S., Jr.; Offeman, R. E. *J. Am. Chem. Soc.* 1958, 80,1339.

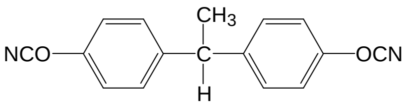


  - $H_2SO_4$, $KMnO_4$, $NaNO_3$
  - $H_2O$ wash
  - Filtration
- Forms stable dispersions in water and polar organic solvents
- Thermally reduced graphene oxide (TRGO) prepared by thermally treating GO at 800°C for 5 minutes
- Large volume expansion upon thermal treatment

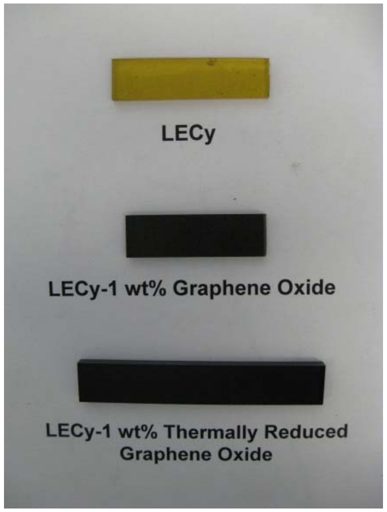
# GO and TRGO LECy Composite Fabrication

LECy dicyanate (matrix) purchased from Lonza

- Liquid at room temperature
- Low viscosity



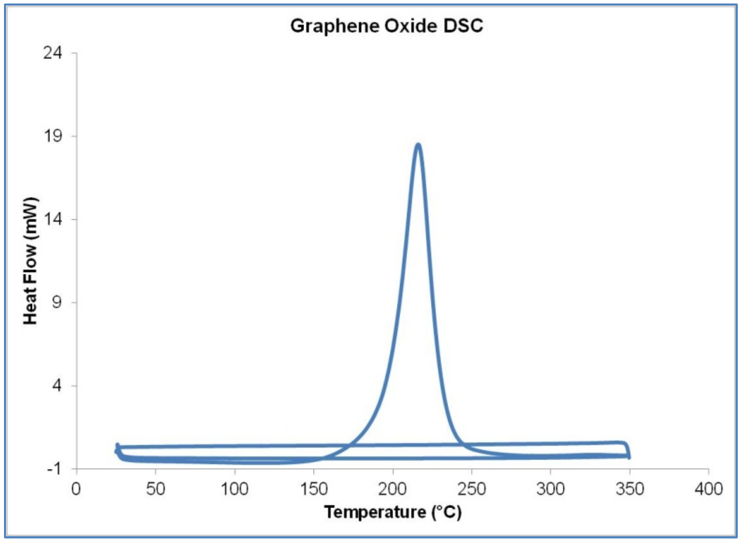
LECy



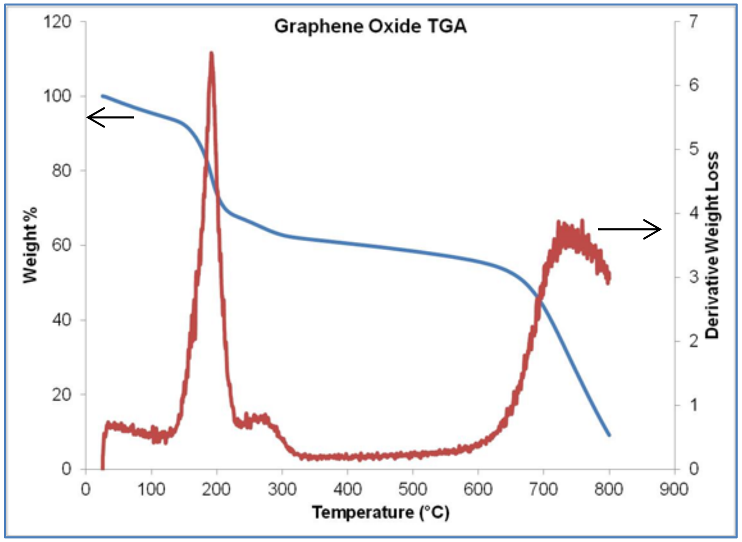
| Filler Type and Amount | Dispersed in Monomer | Dispersed in Cured Resin |
|---|---|---|
| 1 wt% xGNP-M-25 | N | N |
| 1 wt% GO | Y | Y |
| 2 wt% GO | Y | Y |
| 5 wt% GO | Y | N |
| 1 wt% TRGO | Y | Y |

- GO and TRGO dispersed in LECy / catalyst by high shear mixing (1 hour) followed by sonication (1 hour)
- Catalyst (2phr): 1:30 by weight Cu(II) acetylacetonate : nonylphenol
- Mixture degassed at 300 mm/Hg 30 minutes at 90 °C and prior to pouring into silicone molds
- Cure schedule: 150°C 1hour, 210 °C 24 hours (5 °C/min ramp rate)
- Dispersion had little noticeable effect on monomer viscosity

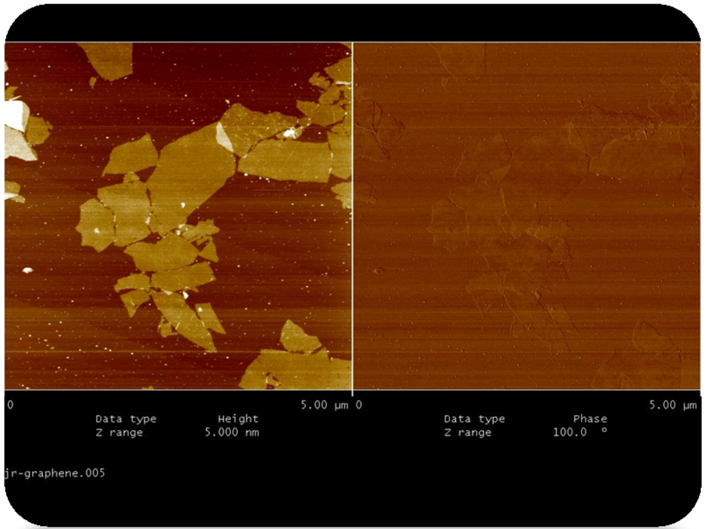
# Characterization of Graphene Oxide

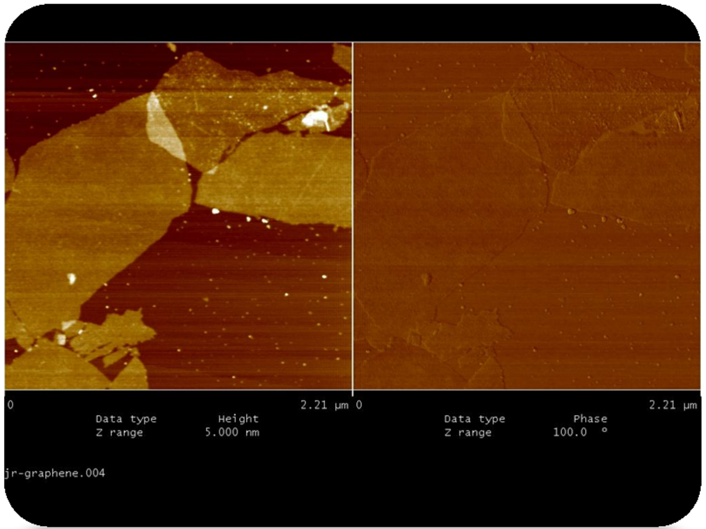


- GO does have stability issues during cure of polycyanurates



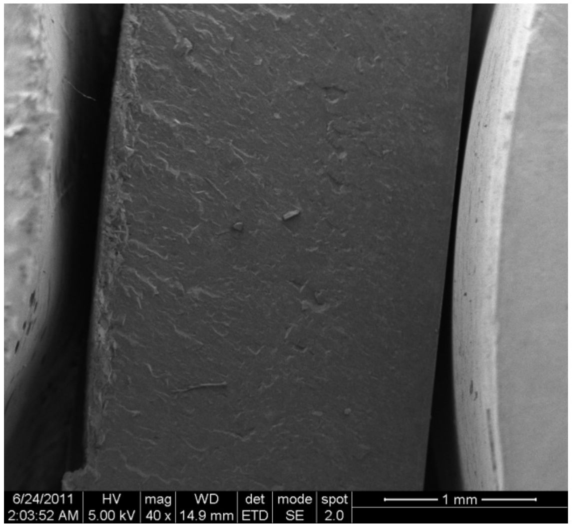
AFM image (5 µm x 5 µm) of graphene oxide





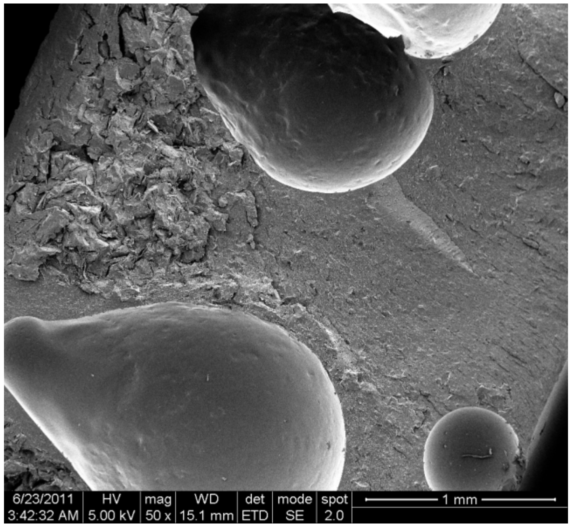
AFM image (2.2 µm x 2.2 µm) of graphene oxide

# Graphene Oxide Composites: Platelet Dispersion



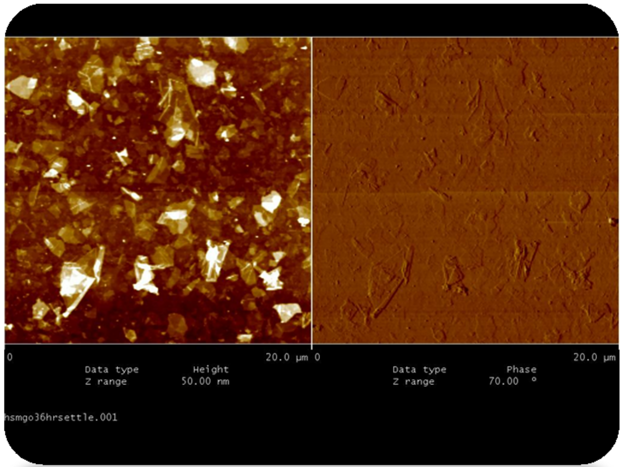
LECY 1wt% GO
1mm scale bar

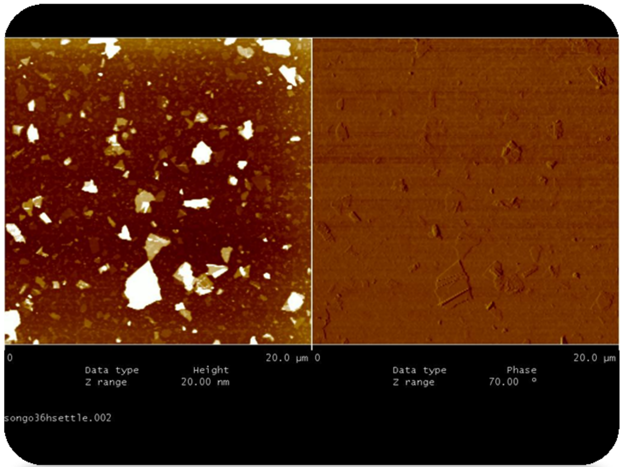
LECY 5wt% GO
1mm scale bar



- **Void content and settling was low in the LECy 1 wt% GO composite and much greater in the 5 wt% GO sample**
- **Lateral dimensions of GO sheets were approximately the same for both high shear mixed and sonicated GO**

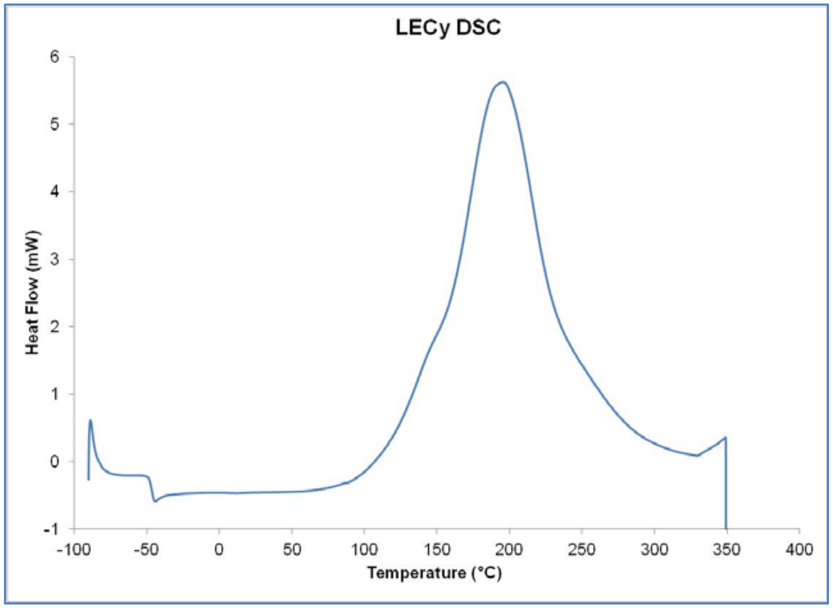
AFM image
(20 µm x 20 µm)
high shear mixed
graphene oxide





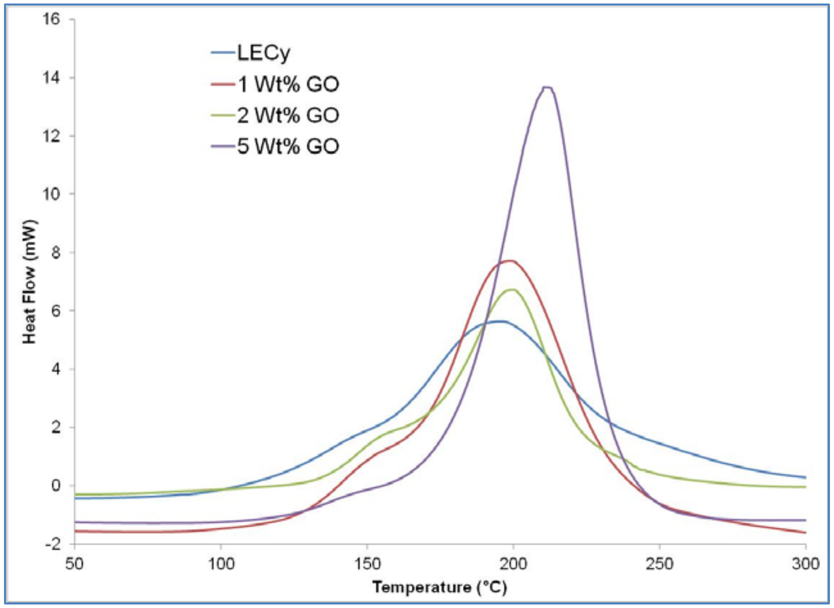
AFM image
(20 µm x 20 µm)
sonicated
graphene oxide

# Graphene Oxide Composite Cure

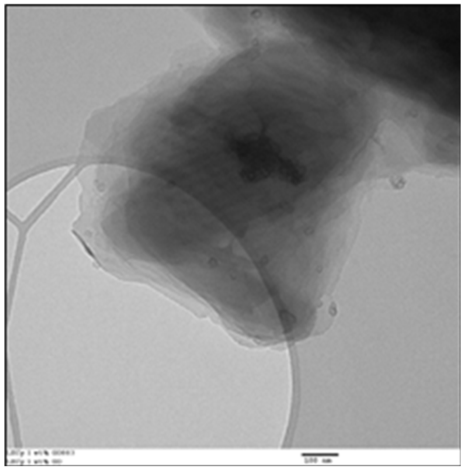


Impurities, such as aryl phenols and transition metals, catalyze cyclotrimerization and lowers the peak of the cure exotherm temperature thereby narrowing the processing "window."

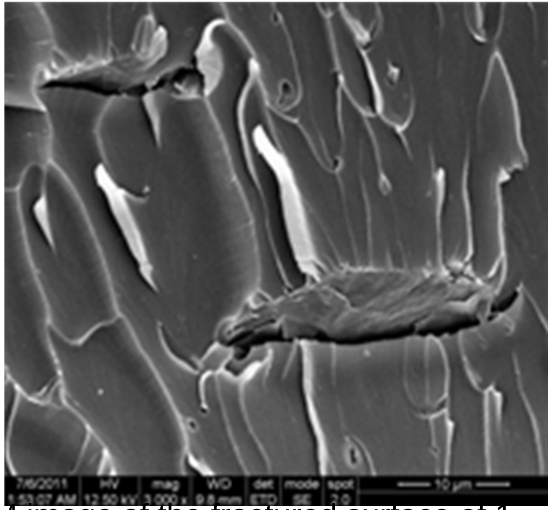
Dispersion of graphene oxide in LECy dicyanate did not significantly change the cure kinetics of the monomer. Therefore, the attractive processing characteristics of LECy are retained in graphene oxide / LECy mixtures.



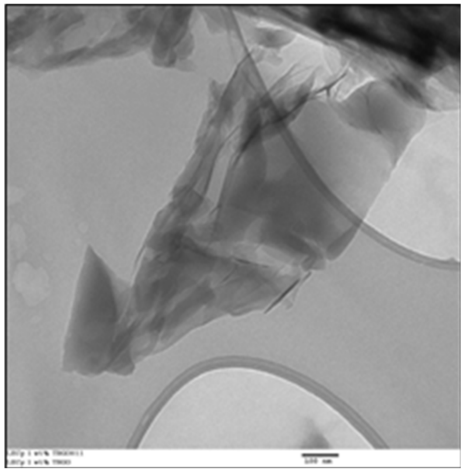
# Morphology of LECy / Graphene Composites



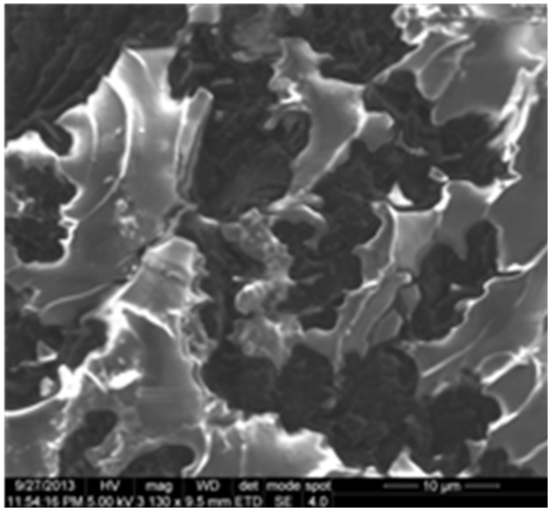
TEM of 1 wt% graphene oxide LECy polycyanurate



SEM image of the fractured surface of 1 wt% graphene oxide LECy polycyanurate



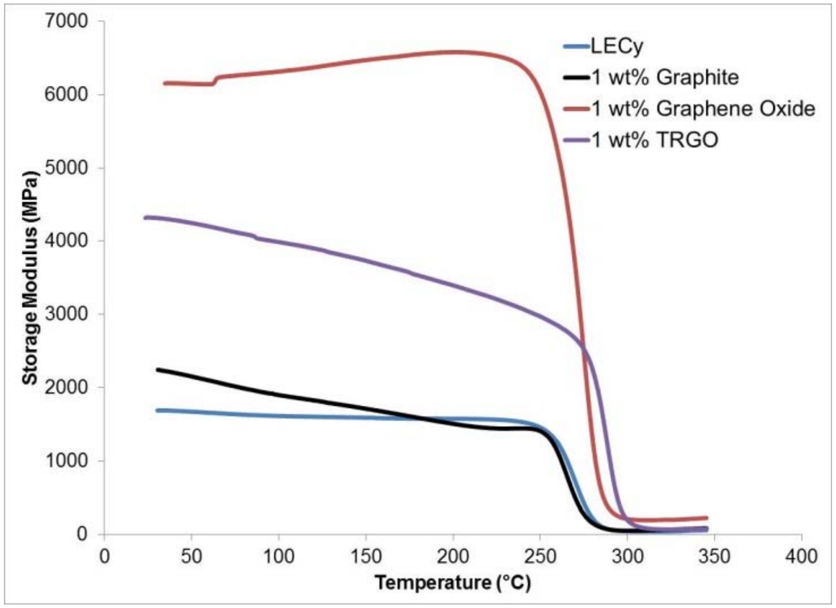
TEM of 1 wt% thermally reduced graphene oxide LECy polycyanurate



SEM image of the fractured surface of 1 wt% thermally reduced graphene oxide LECy polycyanurate

- GO tends to form “sloppy stacks” of well-separated micron-sized aggregates, these aggregates show little or no adhesion to the polycyanurate matrix.
- TRGO, in contrast, forms interconnected aggregates of “shredded stacks”, with non-planar sheets, internal tearing, and mechanical interlocking apparent. Percolation networks are evident in SEM charging effects.

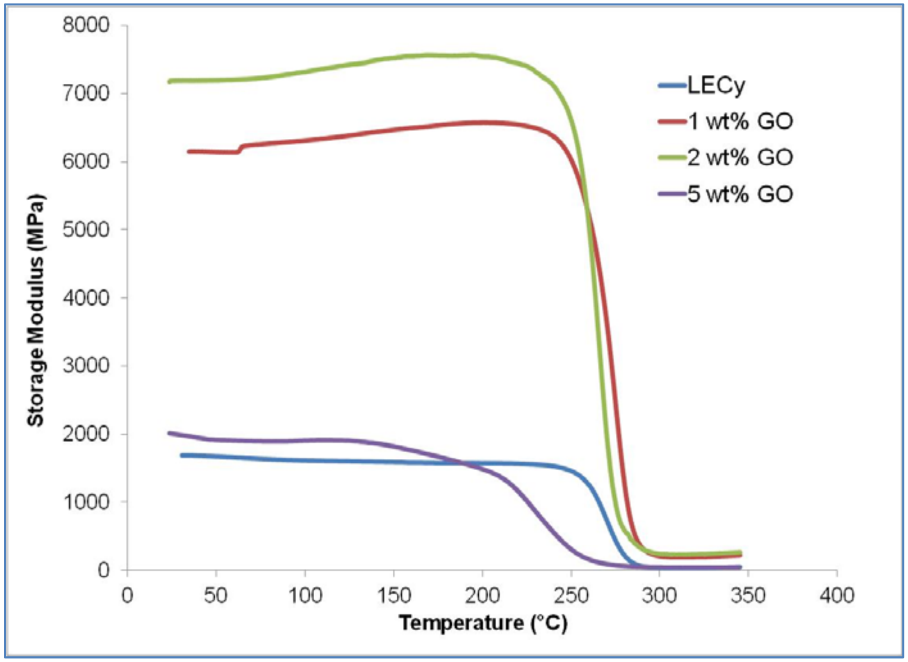
# Mechanical and Fracture Analysis of Graphene / LECy Composites

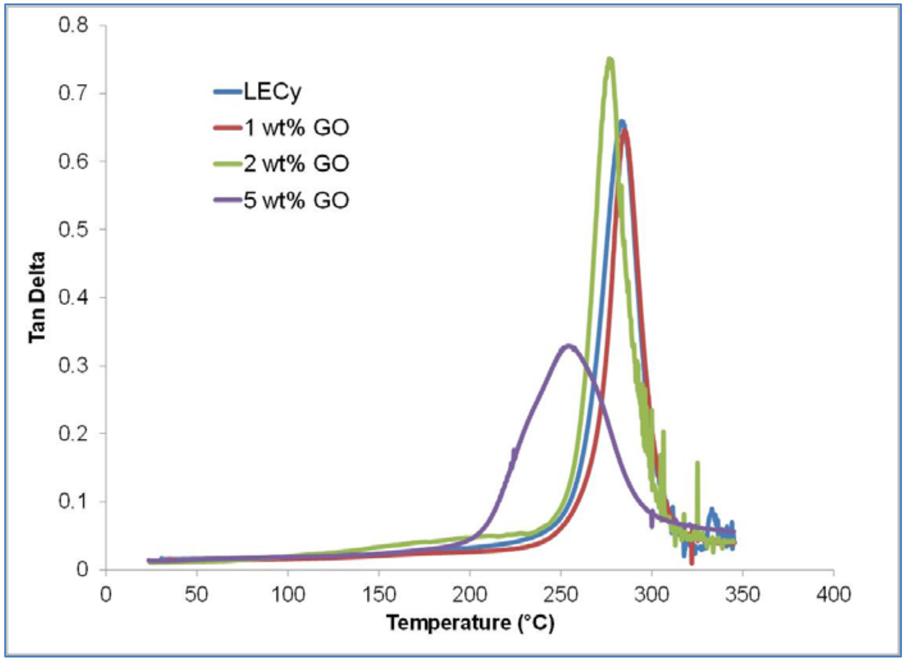


| Sample | $K_q$ ($K_{IC}$) (psi·in$^{1/2}$) |
|---|---|
| LECy | 988 ± 311 |
| 1 wt% GO | 1353 ± 75 |
| 1 wt% TRGO | 1270 ± 208 |

- The extent of reinforcement does appear to correlate with dispersion in terms of stiffness, and more modestly, in terms of toughness.
- Glass transition temperatures (which may reflect extent of cure) are increased with GO and TRGO incorporation.

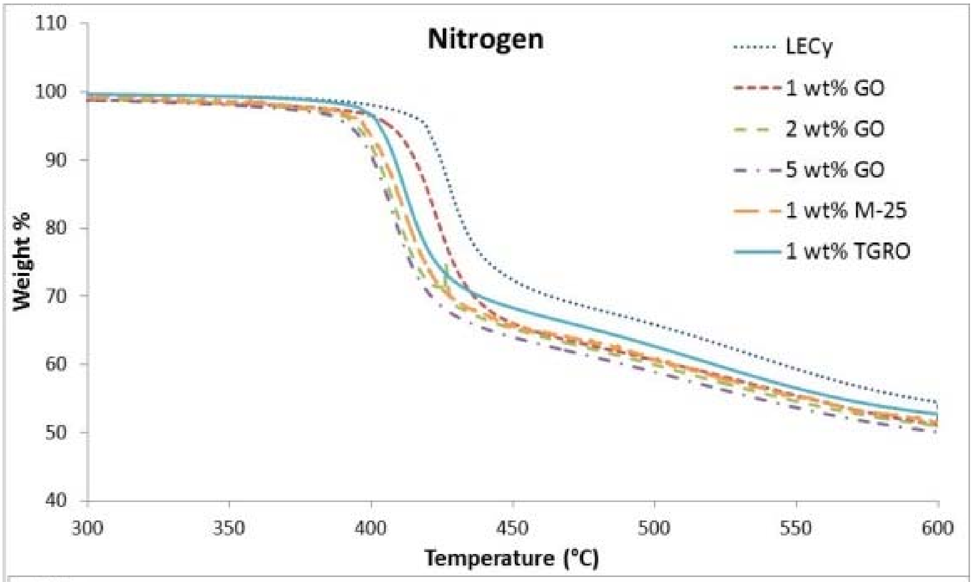
# Effect of GO Loading on Dynamic Mechanical Properties

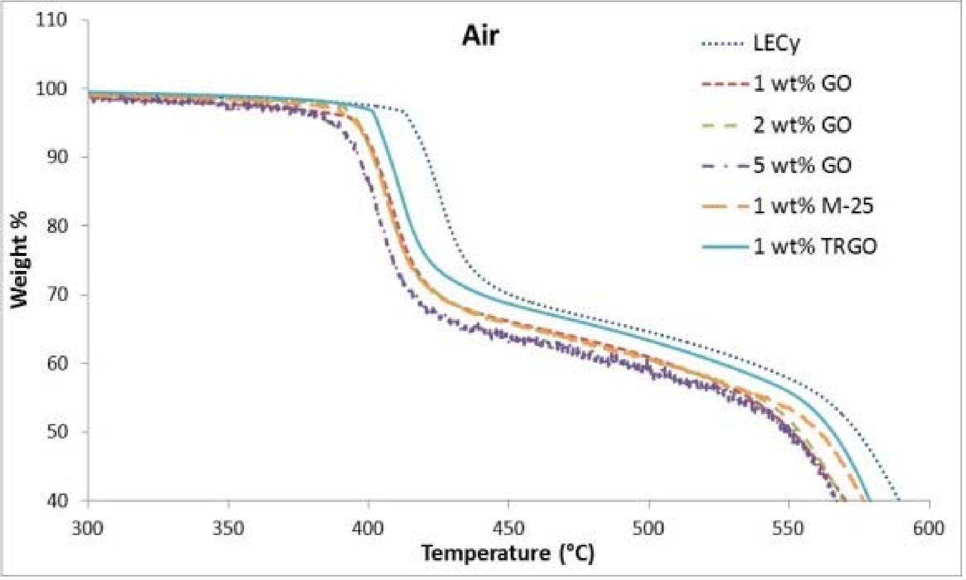




- As expected, there is a large increase in stiffness and minimal change in glass transition temperature with addition of 1 wt% GO.
- Addition of another 1 wt% only modestly increases stiffness and decreases glass transition temperature, indicating the onset of significant aggregation.

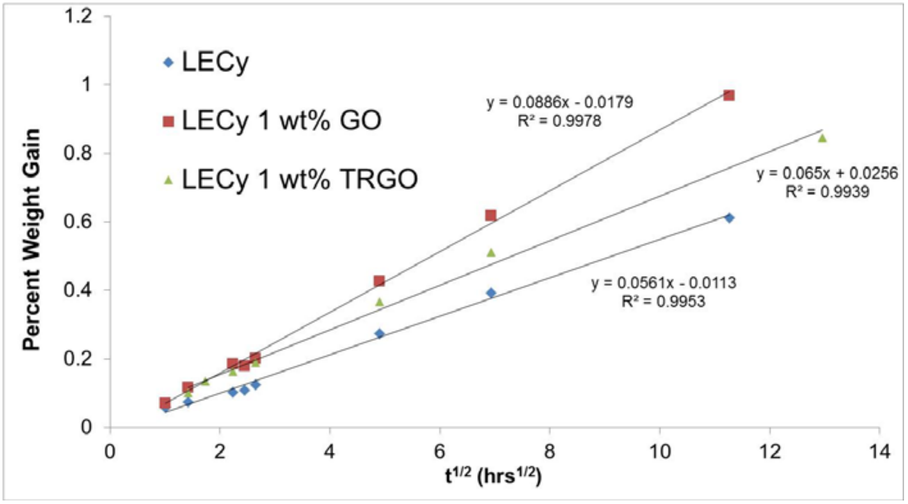
# Thermochemical Stability of LECy / Graphene Composites





- In all cases, there is a stability penalty associated with incorporation of some form of graphene
- Both lower char yield and earlier onset of degradation result from incorporation of graphene, regardless of which form is used
- In air, the penalty is mitigated by use of thermally-reduced graphene oxide
- The overall mechanism of polycyanurate degradation does not appear to change

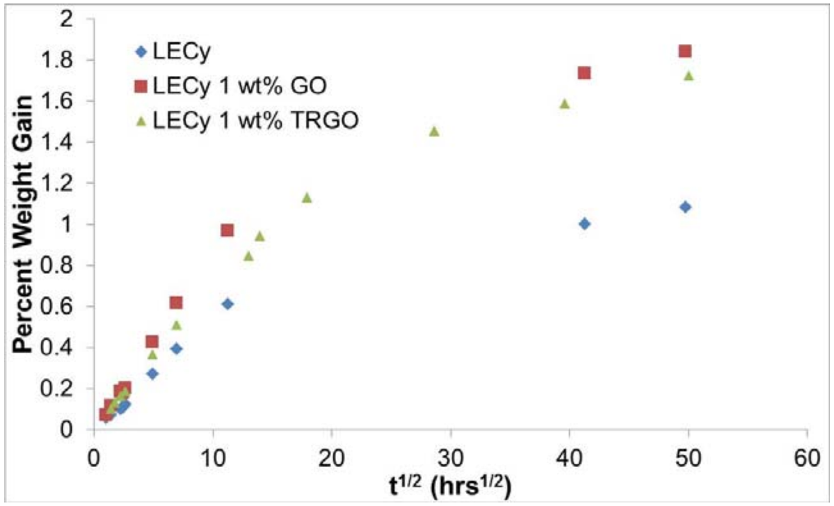
# Graphene Oxide Composites: Ambient Temperature Water Uptake



- Rectangular samples with dimensions of approximately 31 mm X 12 mm X 3 mm were immersed in deionized water at ambient temperature
- Addition of graphene did not significantly change diffusion coefficient
- Equilibrium water uptake was greater for GO and TRGO composites than for LECy

$$D = \frac{\pi}{t}\left(\frac{lM_t}{4M_m}\right)^2 = \pi\left(\frac{l\Theta}{4M_m}\right)^2$$

| Sample | $M_m$ (%) | $D\cdot10^{-8}$ ($cm^2/s$) |
|---|---|---|
| LECy | 1.1 | 1.2 |
| 1 wt% GO | 1.8 | 1.1 |
| 1 wt% TRGO | 1.7 | 1.2 |



# Summary

- Different forms of graphene in polycyanurate networks showed markedly different dispersion behavior. Graphene oxide dispersed well, but retained the form of stacked aggregates. Thermally-reduced graphene oxide formed mechanically interlocked “shredded stacks”. Edge-functionalized graphene showed little or no dispersion.
- Dispersion processes for graphene oxide generally did not affect aggregate morphology. Instead, the chemical processes employed were primarily responsible for the differences in composite morphology.
- Trends in mechanical property data generally followed expectations for non-bonded aggregates, with increased stiffness and toughness correlated to the quality of dispersion.
- Incorporation of graphene in all forms led to decreases in the onset temperature of thermochemical degradation and char yields.
- Incorporation of graphene oxide and thermally-reduced graphene oxide led to increased water uptake, and no measureable change in diffusion rates. The hydrophilic nature of graphene oxide aggregates, and the interconnected nature of thermally-reduced graphene oxide aggregates, prevent the expected reduction in permeation.

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