A Review of Nanoscale Carbon as a Filler in Polymer-Matrix Composites

For Tribomechanical Systems

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Outline

Introduction

- Development and testing of composite materials is a longstanding research area in tribology
- Properties of composites:
  - Light weight
  - High strength
  - Low cost
  - Good triboproperties
    - Friction
    - Wear
    - Lubricant wetting

Introduction

- Many tribosystems operate in the boundary lubrication regime because of unfriendly conditions
  - Temperature extremes
  - Chemical interactions
  - Severe geometric constraints
- No hydrodynamic lubrication possible under these conditions

Introduction

Composite surfaces are common in many industries:

- Electronics
- Aerospace
- Power generation
- Automotive

Outline

Background

What are composites?

- A light matrix material, which dominates composition by volume.
  - PTFE
  - Thermosetting polymer aka epoxies
  - Others
- A high-strength filler material, which is dispersed in the matrix
  - Graphene
  - CNT's
  - Nanodiamonds
  - Others

Examples of well-known composites

- Fibreglass
- Carbon fiber
- Reinforced concrete
- Oriented strand board

In the old days: Microscale fillers

- Microscale fillers in polymer matrices have been shown to reduce wear rates by one or two orders of magnitude. [17, 37]
- Polymer tribology is dominated by viscoelasticity and transfer films [2, 23, 14]
- Possible mechanisms of wear supression:
  - Wear rate limited by strength of composite's transfer film onto counterface [7, 39]
  - Presence of fillers reduces average size of wear debris to inhibit wear [1, 6, 31]

Transfer-film evolution in a PTFE composite

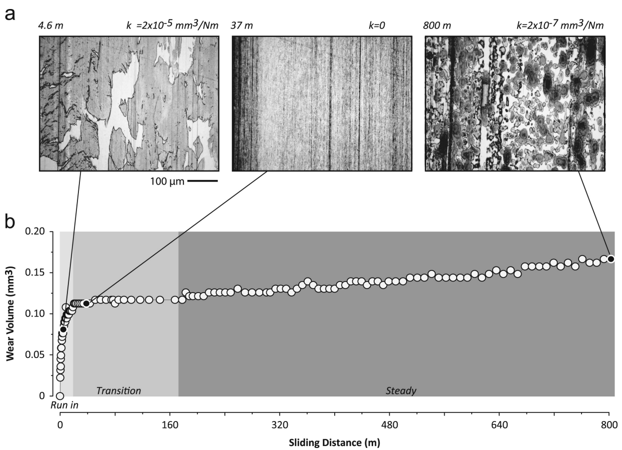

Figure: A representative time-map of transfer film evolution through the running in, transition, and steady-state wear regimes in linear-sliding PTFE-matrix wear against a steel counterface.

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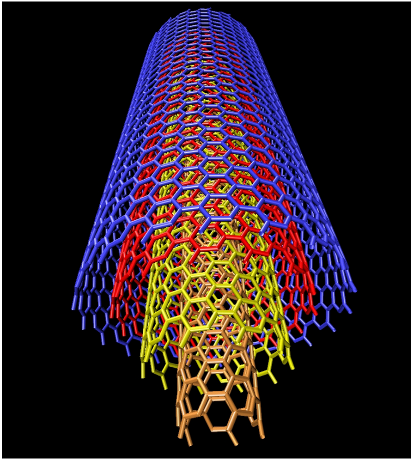
Nanofillers background



- Logical continuation of microfiller work from past decades
- Possibility of improved material properties and performance
- Carbon nanofillers are particularly promising
  - Graphene
  - CNT's
  - Nanodiamonds
  - Novel fullerenes

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PTFE matrix composites

- Plenty of research on PTFE matrix composites [25, 9, 10, 11]
- PTFE has low friction but high wear
- Many efforts to reduce wear via composite loading
  - Carbon fillers
  - Aluminum fillers
  - Nano-silicas and others
- Wear reductions as high as one or two orders of magnitude [8, 16, 5, 33]

PTFE matrix composites

- The following images show representative micrographs of graphene's morphology in and out of a PTFE matrix.
- Other approaches have also borne fruit, including nanolayered metal-graphene composites
  - Strengths as high as 4.0 GPa
  - Demonstrating graphene's unusually high ability to impede dislocation progagation. [13]

Graphene Composites in pictures

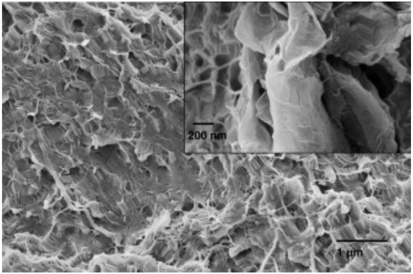

Figure: A high-resolution SEM image showing the microstructure of a graphene-loaded PTFE composite (2% by mass load fraction.) The inset image shows the rippling edges of graphene platelets.

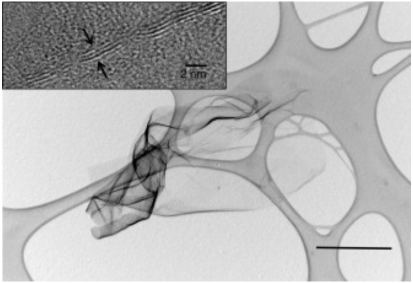

Figure: A graphene platelet deposited on an ordinary TEM grid. Note the low opacity of the platelet, even in the non-monolayer regions. The unlabeled scale bar is $.5\mu$m.

Outline

Thermosetting Polymer Matrices

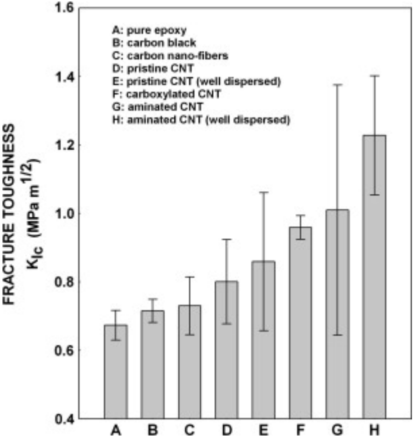

Figure: Fracture toughness improvements in several composites.

- In epoxy composites, nanoscale fillers including graphene, CNT's, and layered silicates have been shown to improve properties significantly: [4, 32, 38]
  - Toughness
  - Elastic modulus
  - Hardness
- Fracture toughness in particular is commonly improved by the introduction of CNT fillers. [15]

Possible Mechanism of Toughness Improvement

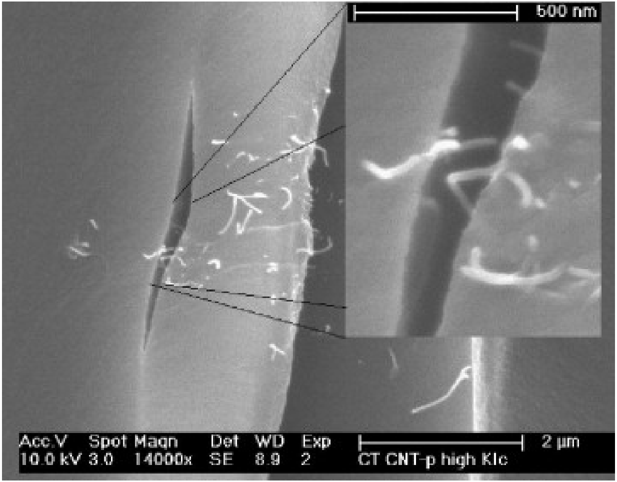

Figure: An SEM micrograph showing a CNT bridging a developing subsurface microcrack in a thermosetting polymer matrix.

Outline

Other Matrices

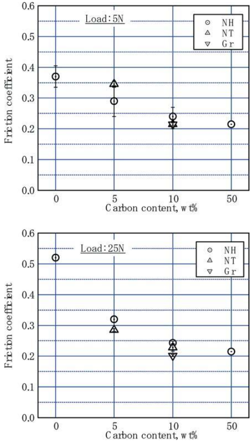

Figure: Friction is often reduced with increasing filler load.

- Other polymeric matrices have also been loaded with nanoscale carbon fillers [36, 21]
- Significant tribological and mechanical improvements have been reported
  - Coefficient-of-friction reductions of more than 90% at high loading fractions
  - Reductions in specific wear coefficient of up to an order of magnitude [3, 27, 30]

Performance Limits

- However, friction in monolayer graphene has been shown to depend upon the degree mechanical confinement to the substrate in the system. [20]
- Graphene's frictional behavior has also been shown to depend upon number of layers. [19]

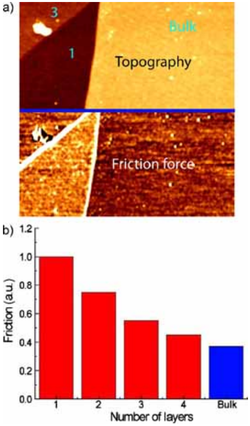

Figure: Layer-dependence in graphene CoF.

AFM Images of Graphene

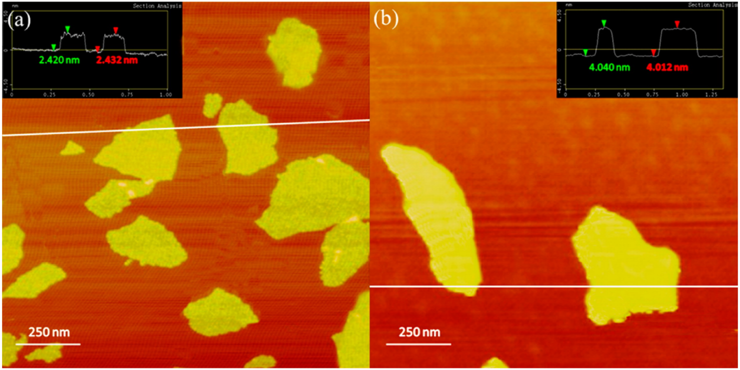

Figure: Atomic force microscope images showing a plan-view of functionalized graphene. (a) is ordinary functionalized graphene, (b) is a proprietary (somewhat thicker) modified graphene. The inset images show cross-sectional height changes.

Dispersion Dependence

- As dispersion quality rises, property improvements are magnified.
- However, present dispersion techniques rely on expensive, loud ultrasonication processes
- Impractical in an industrial setting
  - Cost
  - Operating volume (very loud)
  - Cooling requirements
  - Exotic solvents, bioincompatible chemistry
- Further research required to develop new dispersion techniques. Aim for:
  - Same property improvements
  - Reduced processing requirements

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Graphene Fillers in Detail

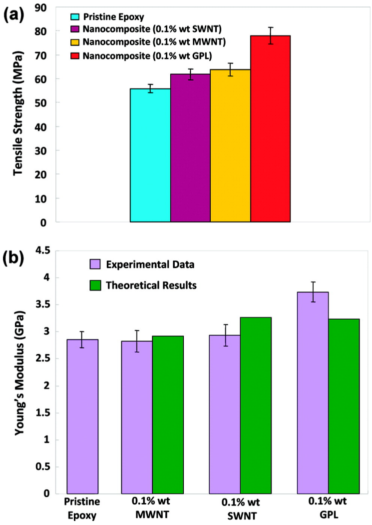

Figure: Tensile tests and theory

- Significant current research interest in graphene fillers
- May outperform existing nanocomposites
- Processing costs similar or perhaps reduced

AFM Images of Graphene

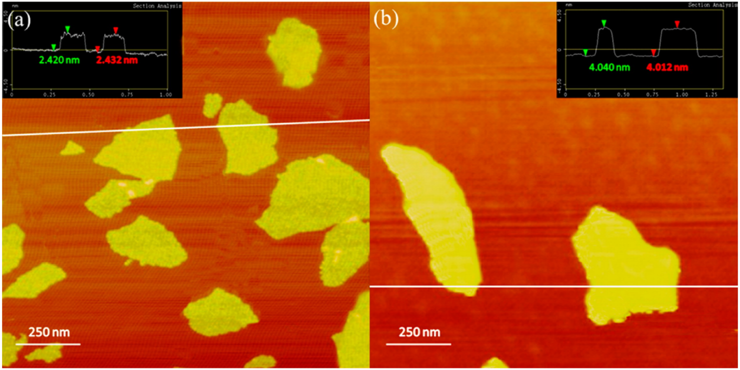

Figure: Atomic force microscope images showing a plan-view of functionalized graphene. (a) is ordinary functionalized graphene, (b) is a proprietary (somewhat thicker) modified graphene. The inset images show cross-sectional height changes.

Graphene Fillers in Detail

- Graphene's strength and stiffness were characterized by nanoindentation of suspended graphene membranes in 2008
  - Elastic modulus of defect-free samples = 1 TPa
  - Ultimate strength was determined to be 130 GPa at an ultimate strain of nearly 25% [18]
  - Corresponding to the intrinsic stress-strain behavior of the carbon-carbon bonds
  - Strongest material ever measured by man

Early Graphene Experiments

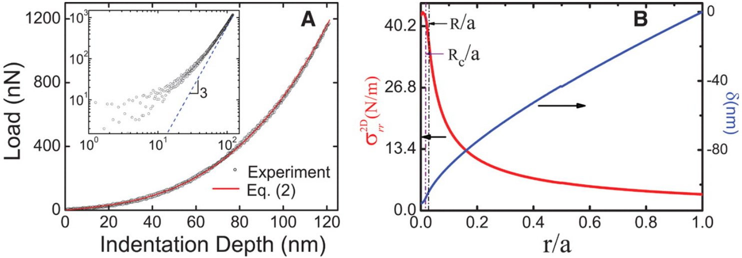

Figure: (A) shows force-displacement curves for graphene. (B) shows stress and deflection against dimensionless distance

Graphene vs. Other Fullerenes

- Graphene fillers have been shown to outperform carbon nanotube fillers for fracture resistance and other mechanical property improvements by 20-30% at weight fractions as low as .1% [26, 28, 29]
- Gains attributed to graphene's high specific surface area.
- Wear reductions of an order of magnitude have been shown in graphene-loaded composites [12, 35]
- Wear reductions accompanied by:
  - Fine wear debris
  - Improved transfer films from highly-loaded samples

Graphene fillers for other property improvements

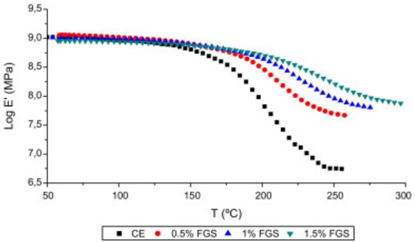

Figure: Viscoelastic onset temperature can be altered by graphene loading and cure parameters

- Exotic methods have been found to improve unusual properties of graphene loaded composites
- Can alter viscoelastic limit onset temperature via UV exposure cure. [24]

- Significant mechanical improvements have been shown in graphene composites
- Graphene-oxide fillers at low weight percentages reduce specific wear rates of epoxy materials by around 90% when compared to neat epoxies [34, 22]
- Wear behavior of unfunctionalized graphene nanocomposites is not well understood
- Interference of graphene with debris generation in the epoxy system?

Outline

Conclusions

- Microscale fillers have long been known to cause measureable triboperformance increases
  - Friction
  - Wear
  - Mechanical Properties
- Recent research has demonstrated that nanoscale fillers can improve properties further still
- Polymer tribology is dominated by transfer films and viscoelastic effects.
- Fullerene composite fillers may improve triboproperties by transfer film promotion and interference with debris generation
- Graphene often outperforms other forms of nanoscale carbon as a filler

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