Evolution of Carbon Fibre Morphology: Considerations of PAN Copolymer Precursor Design

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Carbon Fibres Future Conference
Carbon Nexus 2017
34 Australian Polymer Symposium

Darwin Mindil Beach Beer Can Boat Races
THAMES POLYMER SCIENCE RESEARCH CENTER

2015-16 Statistics:
> 16,000 Students @ USM
> $80M Funded Research
72 Ph.D. Students in Polymer Science & Engineering
110 B.Sc. Students in Polymer Science & Engineering
106,000 ft.² Research Center
13 Faculty in Polymer Science
> $14M Annual Research Funding
USM-Deakin Carbon Fibre Milestones

- Oct 2010 Met Deakin Administration in Salt Lake City
- Feb 2011 Carbon Fibre Future Directions Conference
- Sept 2011 Deakin/USM/UK/Oak Ridge/Cytec/Boeing Team Formed
- Apr 2012 University of Kentucky Meeting
- Nov 2012 Despatch Kit Review Minneapolis
- Feb 2013 Carbon Fibre Future Directions Conference
- May 2013 Deakin / Oak Ridge “Queen Mary Summit” Long Beach
- Jun 2013 Deakin University “Thinker In Residence”
  - CSIRO / White-Fiber Strategy Discussions
- Sept 2014 Deakin/USM/UK/Cytec Fibre Made
Progress in Geelong

June 2012

September 2012

June 2013
July 2013
WHERE IS STEVE CHRISTENSEN?
SC1: Think in Terms of “First Principles” Multi-Scale

- Building Block approach in place for decades
- New materials development a separated activity
- Connection across the discrete-continuum border

The atoms to airplanes model – Requires a “Physics” based approach
SC2: Think About Computational Methods for Next Generation Materials Development

- Quantum
- Molecular Dynamics
- Mesoscale
- Statistical Methods

Computational Simulations used for virtual properties development
SC3: Think about Bonded vs. Non-Bonded Forces

\[ v_f = \frac{2\pi r_f^2}{a^2} \]

\[ R = \frac{a}{\sqrt{2}} - 2r_f = r_f \left[ \left( \frac{\pi}{v_f} \right)^{\frac{1}{2}} - 2 \right] \]
SC4: Develop Matrices in Terms of Irreversible Deformation in Strain Space

Onset Theory:
- Strain rather than stress based method for continuum level analysis of composites
- Quantifies the strain environment within a composite using invariants
- Invariants of strain can be used as scalar descriptors of a critical event

\[ J_1 = \varepsilon_1 + \varepsilon_2 + \varepsilon_3 \]
\[ J_2 = \varepsilon_1 \varepsilon_2 + \varepsilon_1 \varepsilon_3 + \varepsilon_2 \varepsilon_3 \]
\[ J_3 = \varepsilon_1 \varepsilon_2 \varepsilon_3 \]
\[ \varepsilon_{volumetric} = J_1 + J_2 + J_3 - J_1 \]
\[ \varepsilon_{von Mises} = \sqrt{0.5[(\varepsilon_1 - \varepsilon_2)^2 + (\varepsilon_1 - \varepsilon_3)^2 + (\varepsilon_2 - \varepsilon_3)^2]}} \]
“Critical strain” for yield –related to phenyl ring rotation and buckling of glycidyl unit

Drop in stresses due to Torsional rearrangement

Steve Christensen – Boeing (Unpublished)

Work preformed at Univ. of Michigan, PI: Prof. Veera Sundararaghavan
Glassy Polymer Matrix Molecular Design

• Select monomers for torsional conformations – increased distortional deformation
• Consider pendant groups and ring links
• Understand nano-particle contributions
• Isomer influences on torsions
• Reactivity, kinetics and processability
• Stoichiometric considerations
• Cure influence on architecture and morphology
• Primary properties of interest:
  • Compression Strain
  • Tg
  • Modulus
  • Fluid / Environmental stability
• Other properties:
  • Heat of reaction / exotherm / out-time
  • CTE
  • density
Hybrid AEK Networks

5RA/DDS Blended Networks (20, 10, 5 mol %)

4RA/DDS Blended Networks (20, 10, 5 mol %)

Baseline Chemistry

AEK Chemistries

5RA

4RA

2/27/2017 DEAKIN FIBRE HUB
AEK Mechanical Properties

- AEK networks have overall improved mechanical properties
  - 4RA-TGDDM has 20% increase in modulus, 19% increase in strength, 40% increase in strain
  - 5RA-TGDDM has 23% increase in modulus, 18% increase in strength, 37% increase in strain
  - Low concentrations of both AEKs provide improved strain and modulus

- Improved properties attributed to a number of factors:
  - Increased molecular weight between crosslinks (conformational degrees of freedom)
  - Increased secondary interactions (intermolecular cohesion)
Novel Low-Energy Processing Reactor Science

**Batch Reactor**
- Increased matrix viscosity
- Long reaction time
- Substantial energy consumption

**Continuous Reactor**
- Solvent free
- Excellent heat transfer & mixing ability
- Reduces reaction time
- Reduces cost

DEAKIN FIBRE HUB
Benzoxazine Matrix Composites

Poly(benzoxazines)

Near-zero shrinkage

High thermal stability

Excellent flame resistance

Low water absorption

Shortcoming of benzoxazines in aerospace composites result from unfavorable processability

MWCNT/Epoxy Prepolymers Continuous Reactor

- Not efficient MWCNT dispersion using twin screw extruder
- Unstable MWCNT dispersion due to re-agglomeration

Hot Zone (160~220°C)          Cold Zone (RT~100°C)
Next Generation Matrix Prepreg
Final Tensioning / Alignment
New Polymer Matrix Carbon Fiber Prepreg

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>Spindle Speed (RPM)</th>
<th>Viscosity (Poise)</th>
</tr>
</thead>
<tbody>
<tr>
<td>70</td>
<td>5</td>
<td>8000</td>
</tr>
<tr>
<td>70</td>
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<td>900</td>
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<td>400</td>
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<tr>
<td>90</td>
<td>20</td>
<td>200</td>
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</tbody>
</table>

2/27/2017
New Toughened Matrix Carbon Fiber Prepreg
Multi-Functional Carbon Fiber Composites
Benzoxazine Matrix Carbon Fiber Composites
Carbon Fiber Tow-Preg
MECHANICAL ANALYSIS
Scalable Nano Processing Platform Developed

- Continuous Nano Matrix Reactor Developed
- Nano Matrix Lamination Films Developed
- Nano Matrix Prepreg Developed
- Nano Matrix Test Panels Developed
Motivation: Precursor Science

To understand the fundamental polyacrylonitrile properties that drive morphological defects in carbon fiber development

![Chemical structure](image)

**Graphite Fiber Matrix Composite**

*Theoretical is based on perfect graphite fiber*

Chand, S. *Journal of Materials Science* 2000, 5, 1303–1313

To understand the fundamental polyacrylonitrile properties that drive morphological defects in carbon fiber development.

Fiber

Composite

Matrix

**Tensile Modulus (GPa)**

- Theoretical: 1000 GPa
- HexTow IM10: 800 GPa
- Torayca T1000G: 750 GPa
- Thorol T650: 600 GPa
- Panex 35: 200 GPa

*Graphical representation of stress-strain behavior and tensile modulus for different types of carbon fibers.*

*Theoretical is based on perfect graphite fiber*
International Collaboration

- The University of Southern Mississippi
- University of Kentucky
- Deakin University

- Controlled Precursor Chemistry
- Oak Ridge National Laboratory
- Fiber Spinning
- Carbonized and Sized Carbon Fibers

DEAKIN FIBRE HUB
Carbon Fiber Strength v. Modulus

![Graph showing carbon fiber strength vs. modulus]

- T300
- T650/35
- Panex 35
- M65J
- M60J
- M55J
- M50J
- M46J
- M40J
- PV42/850
- MR60H
- IM9
- IM10
- T1000G
- IMS
- UMS

Tensile Modulus (GPa) vs. Tensile Strength (GPa)

2/27/2017
DEAKIN FIBRE HUB
Conversion of PAN into Carbon Fiber

Goal: Understand fundamental polyacrylonitrile properties that drive morphological defects in carbon fiber development

Polyacrylonitrile

250 to 400 °C

400 to 1200 °C

1200 to 2000 °C

Carbonized Fiber
Precursor Chemistry Parameters

- Comonomers
- Comonomer sequencing
- Molecular weight
- Polydispersity
- Tacticity
- End groups
- Crystallinity
- Solubility

\[ \text{PAN-co-acrylic acid (AA)} \]

\[ \text{PAN-co-N-isopropylacrylamide (NIPAM)} \]
Cyclization of Polyacrylonitrile Copolymers

Free radical cyclization (homopolymer)

Ionic cyclization (copolymer)

Homopolymer

Heat Flow (W/g)

Temperature (°C)
Cyclization of Polyacrylonitrile

Polymer dissolved in DMSO solution cast onto KBr salt plate 200 °C for 300 min in N₂

- C=N– peaks (ca. 1595 cm⁻¹) increase with Temp
- C≡N peaks (ca. 2240 cm⁻¹) decrease with Temp
Cyclization of Polyacrylonitrile

CN Fraction = \frac{A_{(-C≡N)}}{A_{(-C≡N)} + f \times A_{(-C=N-)}}

f = 0.29 = ratio of absorptivity constants
The crystalline structure of atactic PAN is mostly planar zigzag.

Crystallinity is governed by copolymer composition this includes:
- Comonomer selection, distribution, and concentration

Systematically increasing the steric bulk of our comonomer will disrupt crystallinity in a controlled manner.

PRECURSOR SOLVATION

• PAN is only soluble in highly polar solvents (DMF, DMSO, DMAc and aqueous solutions of NaSCN or ZnCl$_2$) due to its strong dipole-dipole interactions
  • Wu et al. showed that PAN prefers solvent in the following order: DMSO$_2$ > DMSO > EC > PC > DMF > DMAc
  • Solvent choice can effect gelation, plasticization, morphology, and final mechanical properties

• During white fiber formation, PAN’s coagulation is effected by:
  • Polymer solvent concentration
  • Solvent bath contents and concentration
  • Coagulation bath temperature
  • Winder Rate

Solvent and Coagulation play a crucial role in fiber development

POLYACRYLONITRILE COPOLYMERS: EFFECTS OF **MOLECULAR WEIGHT, POLYDISPERSITY, COMPOSITION, AND SEQUENCING** ON THERMAL RING-CLOSING STABILIZATION

**Molecular Weight (Mₙ)**

- **Mₙ** ↑:
  - Higher mechanical properties
  - Lower processability
  - Target 100,000 g/mol

**Polydispersity Index (PDI)**

- **PDI** ↑:
  - Inhomogeneity during processing
  - Lower processability
  - Current fibers PDI ≈ 2–3

**Composition**

- Bulky comonomers assist processing
- Acidic comonomers facilitate stabilization
- Optimum concentration varies

**Sequencing**

- Distribution of comonomers along the PAN backbone
  - Gradient vs. uniform
RAFT Polymerization

I. Initiation

II. Addition to CTA

III. Chain Transfer Equilibrium

• Reversible Addition-Fragmentation chain Transfer (RAFT)
  • Control over molecular weight and polydispersity
  • Versatile and robust
  • No metal catalyst required
Semibatch RAFT Copolymerization

- Control the addition of the more reactive monomer
- RAFT slows down polymerization providing time to control structure
- Successfully applied to styrene and butyl acrylate

### The Dream

#### Isolated ANs

| SB-1 | 1.4 | 0.058 | 24 | 97.2 | 2.8 |
| SB-2 | 2.8 | 0.058 | 48 | 93.6 | 6.4 |
| Batch | - | - | - | 96.3 | 3.7 |

**SB = Semibatch**

#### Long AN sequence

- **Acrylonitrile**
- **N-isopropylacrylamide**

**Reality**

**Dream**
Semibatch Promotes Cyclization

<table>
<thead>
<tr>
<th>Entry</th>
<th>Injection Volume (mL)</th>
<th>Injection Rate (mL/h)</th>
<th>Duration of Injection (h)</th>
<th>$F_{\text{AN}}$ (%)</th>
<th>$F_{\text{NIPAM}}$ (%)</th>
</tr>
</thead>
<tbody>
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<td>SB-1</td>
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<td>0.058</td>
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<td>-</td>
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<td>96.3</td>
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Thermal Degradation of Semibatch

A greater extent of stabilization leads to a more thermally stable ladder structure
Scale-Up 2 mol% NIPAM FR

80 gram reaction (1 L flask) x 3

Fiber spinning by UKY-CAER. Carbonization and TEM by Deakin Univ.
Molecules to Materials
Australian Next Generation Carbon Fibre Strategy

Molecules to White Fibres
- Polymer Precursor Chemistry
- Polymer Precursor Analysis
- Polymer Precursor Solutions
- Polymer Precursor Spinning
- Polymer Precursor Orientation
- Polymer Precursor Surfaces
- Polymer Precursor Morphology
- 1K to 50K White Fibre

White Fibres to Carbon Fibres
- White Fibre Oxidation
- White Fibre Carbonization
- Stabilization Morphology
- Process Development
- Process Controls
- Controlled Pyrolysis
- Tensioning Fibre Orientation
- Carbon Fibre Morphology Analysis
- Carbon Fibre Surface Chemistry
- Carbon Fibre Surface Sizing
- 1K to 50K Tows

Carbon Fibres to Materials
- Polymer Matrix Science
- Prepreg Development
- Low-Cost Processing
- Quickstep Processing
- Infusion Processing
- Autoclave Processing
- Interface / Interphase
- Knitting / Weaving
- Fracture Mechanics
- FEA / Molecular Dynamics

AFFRIC (Deakin / VCAMM / CSIRO)

Students / Science / Research / Innovation