Nanostructuring in Epoxy Thermosets: An SCFT Study

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What are Epoxy Thermosets?

+ Good adhesion, chemical and heat resistance, electrical insulating properties

Applications: powder coatings, adhesives, …

Highly crosslinked

diglycidyl ether of bisphenol A (DGEBA)

+ 4,4’-methylene bis(3-chloro-2,6-diethylaniline) (MCDEA)

The Problem: Epoxy thermosets are very brittle!

Goal: Toughening Epoxy without adversely affecting other properties (e.g. Tg and optical properties)
Design of High Impact Epoxy Thermosets

Standard Technique:
Introduction of rubbery additives e.g. reactive liquid rubbers (CTBN) and core shell particles

Drawbacks
- Limitation in size of particles (d < 200 nm)
- Miscibility decreases in growing thermoset - macrophase separation
- Difficult to process (high viscosity)
The PMMA block is soluble in DGEBA.

The PS and PB blocks are less soluble.

SBM Microstructure in DGEBA:

- Good dispersion of nanodomains
- Control over nanodomain size and geometry
- Robustness – incorporation of “living” SB diblock precursors of triblock (up to 40%) due to incomplete MMA polymerization
- Ease of processing (by varying temperature)
Effect of Block Composition on Morphology

SBM ⇄ Tailored morphologies: Adjusting the ratio S/B (long PMMA block)

$S_{12}B_{18}M_{70} + SB (10\%)$  $S_{22}B_{9}M_{69} + SB (21\%)$  Girard-Reydet et al, 2003

“Onion”

“Raspberry”
Effect Copolymer Concentration on Morphology

Ritzenhaller et al, 2003

$S_{12}B_{18}M_{70} + SB (10\%)$

Figure 6. Transmission electron micrographs (i, ii) and schematic description (iii) of the structure obtained for DGEBA—MCDEA epoxy systems containing 10 (a), 30 (b), and 50 (c) wt % $S_{12}B_{18}M_{70}−SB10$ copolymer (OsO4 staining).
**SBM & Epoxy**

<table>
<thead>
<tr>
<th>Additive</th>
<th>$K_{IC}$ (MPa√m)</th>
<th>Tg (°C)</th>
<th>Transparency</th>
</tr>
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<tbody>
<tr>
<td>Ref</td>
<td>0.65</td>
<td>187</td>
<td>Yes</td>
</tr>
<tr>
<td>10% SBM 1</td>
<td>0.95</td>
<td>183</td>
<td>Yes</td>
</tr>
<tr>
<td>10% SBM 2</td>
<td>1.15</td>
<td>184</td>
<td>Yes</td>
</tr>
<tr>
<td>30% SBM 1</td>
<td>1.53</td>
<td>171</td>
<td>Yes</td>
</tr>
<tr>
<td>15% CTBN 1</td>
<td>1.15</td>
<td>161</td>
<td>No</td>
</tr>
<tr>
<td>15% CTBN 2</td>
<td>1.23</td>
<td>149</td>
<td>No</td>
</tr>
</tbody>
</table>

Note: SBM 1 – Rasberry and SBM 2 - Onion

**SBM**: Significant impact modification without adversely affecting the Tg maintaining transparency.
Design Challenges

• Effect of composition, concentration, temperature and solvent selectivity on resulting morphology
• Inhibition of macrophase separation between the block copolymers and reactive solvent
• Huge design parameter space!
• Trial and error experimentation very expensive
• Can Theory/Simulation help?
Computational Model

• Ternary system: Triblock + Diblock + Solvent

• Monomer-monomer and monomer-solvent interactions described via Flory-Huggins pairwise form:

\[ \beta U_{\text{int}} = \rho_0^{-1} \sum_{i \neq j} \chi_{ij} \int d\vec{r} \hat{\rho}_i(\vec{r}) \hat{\rho}_j(\vec{r}) \]

• Explicit treatment of solvent (incompressibility enforced)

• Mean Field Approximation (SCFT)
Application to Epoxy Thermosets

• Determination of Chi Parameter
  – Polymer-Polymer
  – Polymer-Solvent

• SBM+SB Blend
  – Demixing transition, i.e. maximum concentration of SB “impurities”

• SBM+SB+Solvent
  – Morphology as a function of solvent concentration
Chi Parameters

Polymer-Polymer: \[ \chi = A + \frac{B}{T} \]

<table>
<thead>
<tr>
<th>Blend</th>
<th>A</th>
<th>B (K)</th>
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<tbody>
<tr>
<td>PS/PB</td>
<td>-0.0157</td>
<td>18.7</td>
</tr>
<tr>
<td>PS/PMMA</td>
<td>0.0129</td>
<td>1.96</td>
</tr>
</tbody>
</table>

\[ V_{ref} = 100 \text{Å}^3 \]

No references for PB/PMMA?

Source: Thermodynamics of Polymer Blends, N. Balsara

Determined PB/PMMA and polymer/solvent \( \chi \) - parameters using Solubility Parameter
### $\chi$-Parameter Summary

<table>
<thead>
<tr>
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<th>$\chi$</th>
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<tbody>
<tr>
<td>PS/PB</td>
<td>0.045</td>
</tr>
<tr>
<td>PS/PMMA</td>
<td>0.02</td>
</tr>
<tr>
<td>PB/PMMA</td>
<td>0.07</td>
</tr>
<tr>
<td>PS/DGEBA</td>
<td>0.017</td>
</tr>
<tr>
<td>PB/DGEBA</td>
<td>0.083</td>
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<tr>
<td>PMMA/DGEBA</td>
<td>0.00053</td>
</tr>
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</table>

**Assumption:**
Equal volume of segments and solvent molecules, $V_{ref}$

$$V_{ref} = 100 \text{Å}^3$$

$$T = 308.1K$$
Test of $\chi$ parameters I

$S_{12}B_{18}M_{70} + SB$ (10% vol. frac.)

<table>
<thead>
<tr>
<th></th>
<th>SBM</th>
<th></th>
<th></th>
<th>SB</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>$f_S$</td>
<td>0.13</td>
<td>$f_B$</td>
<td>0.2</td>
<td>$f_S$</td>
<td>0.39</td>
</tr>
<tr>
<td>$f_M$</td>
<td>0.67</td>
<td></td>
<td></td>
<td>$f_B$</td>
<td>0.61</td>
</tr>
</tbody>
</table>

**Expt:** Core-Shell Cylinder Morphology (Ritzenhaler et al. Macro. 2002, 35, 6245)

SCFT (Unit Cell) 64 x 64 Spectral elements

**S blocks at B/M interface?**
Test of $\chi$ parameters II

$S_{22}B_9M_{69} + SB$ (21% vol. frac.)

<table>
<thead>
<tr>
<th></th>
<th>SBM</th>
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<th>SB</th>
</tr>
</thead>
<tbody>
<tr>
<td>$f_S$</td>
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<td>$f_B$</td>
<td>0.1</td>
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<tr>
<td>$f_M$</td>
<td>0.66</td>
<td></td>
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</tr>
<tr>
<td>$f_S$</td>
<td>0.71</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$f_B$</td>
<td>0.29</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

**Expt:** Lamellar-Cylinder Morphology (Ritzenhaler et al. Macro. 2002, 35, 6245)

SCFT (Unit Cell) 64 x 64 Spectral elements
Demixing Transition Studies

Goal: Determine maximum volume fraction of SB diblock (“impurities”)

- Large Cell Calculation
- $S_{12}B_{18}M_{70}$ + SB Blend (No Solvent!)
- 128 x 128 spectral elements
- Simulation Box Length = 32 $R_g$

Block Composition

<table>
<thead>
<tr>
<th>SBM</th>
<th>SB</th>
</tr>
</thead>
<tbody>
<tr>
<td>$f_S$</td>
<td>$f_B$</td>
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<tr>
<td>$f_M$</td>
<td>$f_S$</td>
</tr>
<tr>
<td>0.13</td>
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</tr>
<tr>
<td>0.67</td>
<td>0.39</td>
</tr>
<tr>
<td>0.61</td>
<td>0.61</td>
</tr>
</tbody>
</table>
Lamella Phase (Large Cell)

(diblock = 10%)

volume fraction of SB diblock = 0.1

PS block still at PB/PMMA Interface

Diblocks well incorporated into Triblock
Lamella Phase (Continued)
(diblock = 30%)

Emergence of diblock-rich phase regions
Diblock Volume Fraction = 0.38

Multiple diblock-rich phase regions visible as concentration is further increased
Demixing Transition in 2D

Labeled PS blocks

\[ \Phi_{SB} = 0.3 \]

PS (Diblock)  

PS (Triblock)
\[ \Phi_{SB} = 0.4 \]

PS (Diblock)  

PS (Triblock)
\[ \Phi_{SB} = 0.5 \]

PS (Diblock)       PS (Triblock)
SBM+SB+Solvent

Goal: Variation of Morphology with Copolymer Concentration

- 2D Unit Cell and Large Cell Calculations
- $S_{12}B_{18}M_{70} + SB + DGEBA$
- 64 x 64 spectral elements
- SB Diblock Volume fraction (dry) = 0.1
- $N_{\text{Triblock}} = 2000$
- $N_{\text{Diblock}} = 660$
- solvent volume = monomer volume
Copolymer Volume Fraction = 0.16

Minimum concentration for occurrence of mixed PS+PB micelle in PMMA/DGEBA

\[ D_{\text{micelle}} \approx 3.8 R_g \]

PS and PB Indistinguishable
Copolymer Volume Fraction = 0.29

Minimum concentration for appearance of a core-shell structure

**PS Density Profile**

**PB Density Profile**

\[ D_{\text{core}} \approx 3 \, R_g \]

\[ D_{\text{shell}} \approx 5 \, R_g \]
Copolymer Volume Fraction = 0.4

\[ D_{\text{core}} \approx 2.7 \, R_g \]

\[ D_{\text{shell}} \approx 6 \, R_g \]
Copolymer Volume Fraction = 0.15

Two Step “Annealing”

\[ N_{SBM} = 2000, \ N_{SB} = 660 \]

PS Density Profile  
PB Density Profile
Copolymer Volume Fraction = 0.2

\[ N_{SBM} = 2000, \ N_{SB} = 660 \]
Copolymer Volume Fraction = 0.3

\[ N_{SBM} = 2000, \ N_{SB} = 660 \]

PS Density Profile

PB Density Profile
Copolymer Volume Fraction = 0.4

\[ N_{SBM} = 2000, \ N_{SB} = 660 \]

PS Density Profile

PB Density Profile
Copolymer Volume Fraction = 0.5

\[ N_{SBM} = 2000, \ N_{SB} = 660 \]

PS Density Profile  
PB Density Profile
$S_{22}B_9M_{69} + \text{SB} + \text{DGEBA}$

50% Copolymer concentration

"Sphere-on-sphere" Morphology

PB Core (orange) surrounded by PS Shell (Blue) in PMMA/DGEBA Matrix

PB "bead" at Interface
Summary

• SCFT studies of nanostructuring of SBM and SB in Epoxy developed
• Theoretical prediction of macrophase separation of SB diblocks in ternary blend in good agreement with experiments
• Good agreement is also found for the variation of the morphology with copolymer concentration
• SCFT prediction S blocks at the B/M due to unfavorable B and M contacts remains to experimentally verify
Acknowledgment

• Arkema for Financial Support
• Prof. Eric Cochran, Iowa State University
• Erin Lennon