Predicting the Fraction of Mixing Between Latex Particles

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• Latex:
  - Stable dispersion of polymer particles in an aqueous solution

• Applications:
  - Products: gloves and tires
  - Additives: adhesives and paper coatings
  - Films: paints and coatings
The minimum film formation temperature (MFT) must be reached before polymer chains can interdiffuse (MFT \( \approx T_g \))^1

Interparticle polymer diffusion (IPD) during the coalescence of latex particles produces a homogeneous film

Mechanical properties are highly dependent on the extent of IPD^2

Quantification of IPD

Small Angle Neutron Scattering (SANS)

- Deuterated polymers are expensive
- Requires a neutron source
- Small particles only

Fluorescence Resonance Energy Transfer (FRET)

- Both latexes must be labeled with dyes
- Requires time-resolved fluorescence
Probing IPD: Pyrene Excimer Fluorescence (PEF)

• A simpler method to probe the degree of interparticle polymer diffusion (IPD) in latex films

• Using a fluorescently-labeled latex with an emission that changes depending on the degree of IPD

• A single fluorophore pyrene (Py) can be used
  • Only one fluorescently-labeled latex is required

• Steady-state fluorescence can be used

Pyrene Fluorescence

Py + Py $\rightarrow^{hv}$ Py* + Py $\rightarrow (PyPy)^*$ $\leftarrow^{hv}$ (PyPy)

$\frac{I_E}{I_M}$ – a measure of the amount of excimer formed
Interparticle Polymer Diffusion using PEF

$t=0$

- High $C_{py}$
- Lots of excimer formation
- High $I_E/I_M$ ratio

$t>0$

- Low $C_{py}$
- Little excimer formation
- Low $I_E/I_M$ ratio
Pyrene Labeled Latex

- Hydrophobicity of the monomer was controlled by varying the length of the oligo(ethylene glycol) unit

- Semi-batch emulsion process

- Copolymerized with \( n \)-butyl methacrylate (BMA) to yield a poly(\( n \)-butyl methacrylate) randomly labeled with pyrene (Py-PBMA)
## GPC: Py-PBMA-Latex-1

<table>
<thead>
<tr>
<th>Sample</th>
<th>PyLM</th>
<th>PyLM Incorporated (mol%)</th>
<th>Particle Size (nm)</th>
<th>PSD</th>
<th>$M_w$ (kg/mol)</th>
<th>$\bar{D}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Py-PBMA-Latex-1</td>
<td>PyEG₃MA</td>
<td>1.9</td>
<td>118</td>
<td>1.04</td>
<td>820</td>
<td>1.9</td>
</tr>
<tr>
<td>Py-PBMA-Latex-2</td>
<td>PyEG₃MA</td>
<td>1.8</td>
<td>120</td>
<td>1.04</td>
<td>360</td>
<td>1.8</td>
</tr>
</tbody>
</table>

![Graph](image.png)

**Retention Volume (mL)**

**DRI (a.u.)**

**Absorbance**
Film Preparation and Annealing

- A film was prepared from a mixture of 5 wt% Py-PBMA-latex in 95 wt% PBMA-latex

<table>
<thead>
<tr>
<th>Film</th>
<th>Latex</th>
<th>Latex Pyrene Content (mol%)</th>
<th>Particle Size (nm)</th>
<th>PSD</th>
<th>$M_w$ (kg/mol)</th>
<th>$D$</th>
<th>Weight Fraction</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Py-PBMA-Latex-1</td>
<td>1.9</td>
<td>118</td>
<td>1.04</td>
<td>820</td>
<td>1.9</td>
<td>0.05</td>
</tr>
<tr>
<td></td>
<td>PBMA-Latex-1</td>
<td>0</td>
<td>95</td>
<td>1.04</td>
<td>1,000</td>
<td>2.0</td>
<td>0.95</td>
</tr>
<tr>
<td>2</td>
<td>Py-PBMA-Latex-2</td>
<td>1.8</td>
<td>120</td>
<td>1.04</td>
<td>360</td>
<td>1.8</td>
<td>0.05</td>
</tr>
<tr>
<td></td>
<td>PBMA-Latex-2</td>
<td>0</td>
<td>119</td>
<td>1.04</td>
<td>320</td>
<td>1.7</td>
<td>0.95</td>
</tr>
</tbody>
</table>

Fluorescence Measurements
Steady-State Fluorescence: Film 1

Fluorescence Intensity (a.u.)

Wavelength (nm)

Annealing Time (min.) | $I_E/I_M$
---|---
0 | 0.13
25 | 0.10
110 | 0.08
560 | 0.07
$\infty$ | 0.04

$T_{an} = 102 \, ^\circ C$
Fraction of Mixing

Film 1: $M_w = 820$ kg/mol

Film 2: $M_w = 360$ kg/mol

\[
f_m(t) = \frac{\left(\frac{I_E}{I_M}\right)_{(t)} - \left(\frac{I_E}{I_M}\right)_{(t=0)}}{\left(\frac{I_E}{I_M}\right)_{(t=\infty)} - \left(\frac{I_E}{I_M}\right)_{(t=0)}}
\]
**Fraction of Mixing: Linear Trend**

*Film 1: $M_w = 820$ kg/mol*

*Film 2: $M_w = 360$ kg/mol*

\[
f_m(T, t_{an}) = A(T) \cdot \ln(t_{an}) + B(T)
\]
\[ f_m(T, t_{an}) = A(T) \ln(t_{an}) + B(T) \]

Film 1:  
\[ f_m(T, t_{an}) = (6.71 \times 10^{-4} T - 0.184) \ln(t_{an}) + (7.74 \times 10^{-3} T - 2.65) \]

Film 2:  
\[ f_m(T, t_{an}) = (-0.172 \times 10^{-4} T + 0.144) \ln(t_{an}) + (1.16 \times 10^{-2} T - 4.05) \]
Predicting $f_m$: Time and Temperature

**Film 1:** $M_w = 820 \text{ kg/mol}$

$$f_m(T, t_{an}) = \left(6.71 \times 10^{-4} T - 0.184\right) \ln(t_{an}) + \left(7.74 \times 10^{-3} T - 2.65\right)$$

**Film 2:** $M_w = 360 \text{ kg/mol}$

$$f_m(T, t_{an}) = \left(-0.172 \times 10^{-4} T + 0.144\right) \ln(t_{an}) + \left(1.16 \times 10^{-2} T - 4.05\right)$$
Applications

• The properties of a film are directly related to the extent of coalescence

\[ f_m(T, t_{an}) = A(T) \ln(t_{an}) + B(T) \]

\[ t_{an} = \exp \left( \frac{f_m^{\text{desired}} - B(T)}{A(T)} \right) \]

• Predict the coalescence time required to reach a specific \( f_m \).

Example:

• Abrasion resistance
  • Mechanically robust
  • Low \( f_m \approx 0.4 \)
    • Film 1 (102 °C) \( t_{an} = 34 \) min.

• Corrosion resistance
  • Void-free
  • High \( f_m \approx 0.95 \)
    • Film 1 (102 °C) \( t_{an} = 3 \) months

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Onset Time for Diffusion

Film 1 ($M_w = 820$ kg/mol): $E_a = 109 \pm 13$ kJ/mol

Film 2 ($M_w = 360$ kg/mol): $E_a = 169 \pm 21$ kJ/mol

Why do the chains in Film 1 flow sooner?
Future Work

Probe the diffusion between asymmetric latex nanoparticles:

- Particle size
- Molecular weight
- Polymer Type
- Plasticizer Content

Increase pyrene monomer incorporation to enhance excimer formation
Acknowledgements

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Prof. Mario Gauthier

All members of the Duhamel and Gauthier groups.

Thank you for your attention!
## Why Use Pyrene Excimer Formation?

<table>
<thead>
<tr>
<th>Requirement</th>
<th>FRET</th>
<th>Pyrene Excimer Formation</th>
</tr>
</thead>
<tbody>
<tr>
<td>Instrumentation</td>
<td>Time-resolved fluorometer (complex and expensive)</td>
<td>Steady-state fluorometer (simple and inexpensive)</td>
</tr>
<tr>
<td>Data Acquisition</td>
<td>~ 10 minutes per decay</td>
<td>~ 30 seconds per spectrum</td>
</tr>
<tr>
<td>Fluorescence Analysis</td>
<td>Decay must be modeled, fitted, and then integrated</td>
<td>$I_E/I_M$ ratio</td>
</tr>
<tr>
<td>Fluorescently-Labeled Latex</td>
<td>2 (donor labeled, acceptor labeled)</td>
<td>1 (pyrene labeled)</td>
</tr>
<tr>
<td>Film Composition</td>
<td>100 wt% labeled-latex</td>
<td>≤ 5 wt% labeled-latex</td>
</tr>
<tr>
<td></td>
<td></td>
<td>≥ 95 wt% native-latex</td>
</tr>
<tr>
<td>Latex Nanoparticles</td>
<td>Symmetrical</td>
<td>Symmetrical or Asymmetrical</td>
</tr>
</tbody>
</table>