Analysis of Flocculated Latex Particles using Multi-Detector Hydrodynamic Chromatography

Amandaa K. Brewer
ARKEMA Inc., Analytical and Systems Research, King of Prussia, PA, USA
Latex Particles

Colloids or polymers with a molar mass > $10^6$ g/mol.

Particle size and shape play a role in:

- Development of new materials
- Shelf-life of materials
- Control of material processing
- Quality control of colloids
- End-use properties

Latex Particles

- Colloids or polymers with a molar mass $> 10^6$ g/mol.

- Particle size and shape play a role in:
  - Development of new materials
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  - Control of material processing
  - Quality control of colloids
  - End-use properties

- Methodology
  - Sieving
  - Sedimentation
  - Microscopy
  - Laser Diffraction

- Limitations
  - Cost, speed, complexity, accuracy, resolution, etc.

Flocculated Latex Particles

System of interests:

• A fluoropolymer/acrylic hybrid latex particle with surfactant package

Properties of interest:

• Particle size/particle size distribution is speculated to effect the end-use properties of the latex such as thickening response.

• Morphology of the fluoropolymer/acrylic hybrid latex particle may influence the end-use properties of the particle.

• Effects of pH and heat aging on the particle size/shape and their distributions (latex flocculation).

• Shelf-life of the fluoropolymer/acrylic hybrid latex particle (time frame for flocculation.)
Hydrodynamic Chromatography

- A solution-based separation method
  - Open tube
  - Packed (Non-porous beads)

- Separation is due to parabolic (Poiseuille) flow profile in an open tube channel.
Hydrodynamic Chromatography

- Analytes are sampled in a size-dependent manner
Hydrodynamic Chromatography

- Analytes are sampled in a size-dependent manner.
- Small particles sample region close to the walls, where the flow is stagnant.
- Large particles remain nearer to center where the flow is faster.
Multi-Detector Hydrodynamic Chromatography

HDC Columns

Multi-Angle Light Scattering (MALS)
Multi-Detector Hydrodynamic Chromatography

HDC Columns

Multi-Angle Light Scattering (MALS)

Quasi-Elastic Light Scattering (QELS)
Multi-Detector Hydrodynamic Chromatography

- HDC Columns
- Quasi-Elastic Light Scattering (QELS)
- Multi-Angle Light Scattering (MALS)
- Differential Refractometry (DRI)
Multi-Detector Hydrodynamic Chromatography

HDC Columns

Multi-Angle Light Scattering (MALS)

Quasi-Elastic Light Scattering (QELS)

Differential Refractometry (DRI)

MALS → $R_G$

QELS → $R_H$

DRI + MALS → $M$
## Non-Flocculated Latex Particle

<table>
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<tr>
<th>Polymer</th>
<th>$M_n$ ($\times 10^9$ g/mol)</th>
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![Graph showing retention time vs. 90°SLS(V) and Molar Mass](image-url)
Polymeric Radii

**MALS $\rightarrow R_G$**
Root mean square distance of an array of atoms from their common center of mass

$$R_G = \left[ \left( \frac{1}{n+1} \right) \sum_i (r_i - R_{cm})^2 \right]^{1/2}$$

- $n =$ number of bond in polymer backbone
- $r_i =$ location of an individual atom or group of atoms
- $R_{cm} =$ the location of the center of mass
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![Graph of retention time vs. radius](image)
**Polymeric Radii**

**MALS → \( R_G \)**
Root mean square distance of an array of atoms from their common center of mass

\[
R_G = \left( \frac{1}{n+1} \sum_{i} (r_i - R_{cm})^2 \right)^{1/2}
\]

- \( n \) = number of bond in polymer backbone
- \( r_i \) = location of an individual atom or group of atoms
- \( R_{cm} \) = the location of the center of mass

**QELS → \( R_H \)**
Radius of an equivalent hard sphere that has the same translational diffusion coefficient \( (D_T) \) as a macromolecule.

\[
R_H = \frac{k_B T}{6 \pi \eta_s D_T}
\]

- \( k_B \) = Boltzman's Constant
- \( \eta_s \) = Viscosity of the solvent
- \( D_T \) = Translational Diffusion Coefficient
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[Graph showing retention time vs. radius for Original Fluoropolymer/Acrylic Particle]
Non-Flocculated Latex Particle

Particle Morphology

MALS/QELS: \( \rho \equiv \frac{R_{G,z}}{R_{H,z}} \)
**Non-Flocculated Latex Particle**

**Particle Morphology**

MALS/QELS: $\rho \equiv \frac{R_{G,z}}{R_{H,z}}$

<table>
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<td>1.36-2.24</td>
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### Particle Morphology

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<tr>
<td>1.36-2.24</td>
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<tr>
<td>~2.7-4.0</td>
<td>Sample</td>
</tr>
<tr>
<td>2.0-3.5</td>
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![Retention time vs. \( \rho \)](image)
Heat-Aging Latex Particles

\[
\text{Retention time (minutes)}
\]

\[
90^\circ \ \text{SLS (V)}
\]

- Original Particle
Heat-Aging Latex Particles

Retention time (minutes)

90° SLS (V)

- Original Particle
- Original Particle Heat Aged at 40°C
Heat-Aging Latex Particles

Retention time (minutes) vs. 90° SLS (V)

- Original Particle
- Original Particle Heat Aged at 40°C
- Original Particle Heat Aged at 50°C
Heat-Aging Latex Particles

Retention time (minutes)

$90^\circ$ SLS (V)
pH Manipulated Latex Particles

Retention time (minutes)

pH 8
pH Manipulated Latex Particles

Retention time (minutes)
## pH Manipulated Latex Particles

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<td>pH 7.5</td>
<td>88 ± 1</td>
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<td>170 ± 1</td>
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<td>pH 7</td>
<td>71 ± 1</td>
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<td>76 ± 1</td>
<td>25 ± 1</td>
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![Graph showing retention time vs. (v)SLS 0.06 for pH 8, pH 7.5, and pH 7.](image-url)
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The graph shows the retention time (minutes) vs. the absorbance (A) at 506 nm for different pH conditions: pH 8, pH 7.5, and pH 7.
AFM and HDC both show that the particles at pH=7 are more monodisperse and uniform than those at the other pHs.

pH appears to play a role in particle flocculation of the fluoropolymer/acrylic hybrid particle.
Time Aged Latex Particles

Retention time (minutes)
**Time Aged Latex Particles**

Retention time (minutes)

<table>
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<th>Time (months)</th>
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<tr>
<td>0</td>
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</tr>
<tr>
<td>2</td>
<td>2 month old original particle</td>
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$g_{0^0}$SLS (V) vs Retention time (minutes)
Time Aged Latex Particles

Retention time (minutes)

Flocculation
Size

90° SLS (V)

Retention time (minutes)
A decrease in viscosity was observed by rheology as the fluoropolymer/acrylic latex particle ages, indicating an increase in flocculation.

Both HDC and rheology show an increase in flocculated particles as the fluoropolymer/acrylic particle ages.
Multi-detector hydrodynamic chromatography (HDC) was successfully used to analyze the particle size, shape, and their distributions of a fluoropolymer/ acrylic hybrid latex particle.

HDC provided a tool for monitoring the flocculation of a fluoropolymer/ acrylic hybrid latex particle as a function of pH, heat aging and time aging.

HDC results were consistent with those observed by microscopy (particle size/ shape as a function of pH) and rheology (increase of flocculation with latex age.)
Acknowledgements

- Sara Reynaud (Arkema Inc. Rheology)
- Gunter Moeller (Arkema Inc. Microscopy)

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# Heat-Aging Latex Particles

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