Monitoring nanostructural transformations during film formation in waterborne coatings using variable angle X-ray scattering

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Features outlining coating quality

“Barrier property” of coatings

- Solvents can unavoidably penetrate through structural defects in applied materials.
- Optimal coatings needed to prevent solvent penetration

https://www.shutterstock.com/de
Keddie J. et al., ACS Appl. Mater. Interfaces, 2018, 8 (50)
Structural heterogeneities in coatings

Coffee-stain effect = “in-plane” inhomogeneities


Stratification = “out-of-plane” heterogeneities

Keddie J. et al., *ACS Appl. Mater. Interfaces*, 2016, 8 (50)

https://i.ytimg.com
Waterborne coatings and latex film formation

- **Latex** = aqueous dispersion of polymer colloids
- Challenging to realize uniform films (polymer incompatibility)
- Defects reported down to micron-sized range (not in nanoscale)

Grazing Incidence SAXS (GISAXS)

Can probe **buried nanoscopic objects** at interfaces

- **Surface sensitive** for structures at interfaces (minimum penetration depth, $\xi_p \approx 10$ nm)
- **High scattering intensity** ideal for in-situ study
- **2-D detectors** probe at once lateral & normal order

http://www.gisaxs.de/theory2.html  (Andreas Meyer, Uni Hamburg)
Depth ($\xi_p$)-resolution of GISAXS

Calculations of $\xi_p (\alpha_i)$ vs. $\alpha_i$, for polyacrylates ($\alpha_c \sim 0.1^\circ$)

$k_i$ (= incident X-ray wavevector)

$k_f$ (= scattered X-ray wavevector)

Substrate (glass)

Polymer Film

$\alpha_c$ (critical angle of the polymer)
## Materials (from DSM)

Three different polyacrylic (PA) samples investigated

<table>
<thead>
<tr>
<th>Type</th>
<th>PA-662</th>
<th>PA-661</th>
<th>PA-660</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hardness</td>
<td>hard</td>
<td>soft</td>
<td>2 phases: 70 % (wt) soft / 30 % (wt) hard</td>
</tr>
<tr>
<td>(T&lt;sub&gt;g&lt;/sub&gt; ~80 °C)</td>
<td>soft (T&lt;sub&gt;g&lt;/sub&gt; ~4 °C)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Solids (%)</td>
<td>39.1</td>
<td>39.1</td>
<td>39.0</td>
</tr>
<tr>
<td>pH</td>
<td>8.1</td>
<td>6.8</td>
<td>7.0</td>
</tr>
<tr>
<td>Particle size (nm), DLS</td>
<td>100 ±3</td>
<td>107 ±1</td>
<td>106±3</td>
</tr>
</tbody>
</table>

Non- film forming coating (T<sub>FFT</sub> < T<sub>g</sub>)

Film forming coating (T<sub>FFT</sub> > T<sub>g</sub>)
Coating preparation and beamlines

**MINA**: Multipurpose X-ray Instrument for Nanostructure Analysis (University of Groningen)

**Synchrotron X-rays**

**Dutch-Belgian Beam Line DUBBLE BM26B** (ESRF, Grenoble)
GISAXS data analysis

Intensity cuts $I(q_y)$ vs. $q_y$ at $q_z$ = constant

$T$: Transmission
$R$: Refraction
$S$: Reflection

$q_y^* = 2\cdot\pi/d^* (=0.08 \text{ nm}^{-1})$

$d^*$ (~80 nm): heterogeneity spacing
Depth-resolved GISAXS (PA-660)

- (Strong) Scattering is lost at $\xi_p \sim 15$ μm
- Crossover transition at $\xi_p \sim 10$ μm ($\alpha_i = 0.15^\circ$) from structure (heterogeneities) to structure-less region

Depth-resolved GISAXS patterns

- (Strong) Scattering lost at $\xi_p \sim 10-15 \mu m$
- Top film layer with heterogeneities
- Lower film layer: no heterogeneities
- PA-662: Control case with strong contrast (non-film-forming)

Vagias A. et al. submitted to ACS Applied Polymer Materials (under review)
GISAXS $I(q_y)$ vs. $q_y$ cuts: proposed nanostructures

Sideview

PA-660 (multiphase)

PA-661 (soft)

PA-662 (hard)
Quantifying GISAXS analysis: nanostructural heterogeneities

Topview:
- $d_\text{domain} \approx 20 \text{ nm}$
- $d^* \approx 80 \text{ nm}$
- $d_\text{domain} \approx 5-10 \text{ nm}$
- $d_\text{domain} \approx 60 \text{ nm}$

Sideview:
- PA-660 (multiphase)
- PA-661 (soft)
- PA-662 (hard)

In-situ GISAXS ($\alpha_i = 0.15^\circ$): PA-660

Insets: time after slot die coating ($t_{\text{drying}}$)

At $t_{\text{drying}} = 4'$: “colloidal suspension”-like (4')
At $t_{\text{drying}} > 9'$: partially coalesced particles

Vagias A. et al. (in preparation)
Nanostructural transformations during drying

- \((d^*)\) decreases with \(t_{\text{drying}}\) more strongly for PA-660

- Nanostructural evolution during drying can be quantified

Vagias A. et al. (in preparation)
Conclusions

GISAXS is an optimal technique to probe:

- Rich unexplored nanostructural transformations during film drying
- The quality of (dry) waterborne coatings at the nanoscale (submicrometric heterogeneities)
- Depth-dependent stratification in the films
Perspectives

To expand the successful ex-situ/ in-situ options:

- couple with laser speckle imaging (structure-dynamics) (Prof. J. Sprakel, WUR) / environmental effects (airflow, humidity, aging)

- different chemistries (also polyurethanes, blends) / substrates (metal, wood) successfully assessed

- Biomedicine: polyhydroxyurethane (PHU-QAS) dental coatings (UMCG, P. Sharma group)
Acknowledgements

• DPI for funding INCOAT (914ft16)
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• D. Hermida-Merino (DUBBLE BM26B@ESRF)
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• ALL OF YOU for your attention!
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SAXS in suspensions: NP shape/size
SAXS modeling

\[ I(q) = \Delta \rho^2 V \int_{R_1}^{R_2} S(q) P(q, R) D(R) dR \]

- Polydisperse ensemble of spheres
- \( S(q) \): local monodisperse approximation
SAXS structure factor \( (S(q)) \)

\[ I(q) = \frac{N}{V} V_{\text{part}}^2 P(q) S(q) \]

S(q) simulations for liquid-like systems at different volume fractions \( \phi \)

The peak \( (q^* = 2 \cdot \pi / d^*) \) accounts for spatial correlation between particles (=spacing \( d^* \))
SAXS in aqueous PA-660 suspensions

- PA-660: ($d_{SAXS} \approx 96 \text{ nm}, d_{DLS} \approx 106 \text{ nm}$)
Modeling of SAXS curves in suspension

PA-661, PA-662: Polydisperse particle model
PA-660: (Polydisperse) Core-shell particle model
Monodisperse model
Particle radii: PA661 (45nm) > PA662 (41nm) > PA660 (40nm)

Very different nanostructure morphology in films vs. suspensions for PA660 and PA661. PA662 shows absence of deformability!
Appendix- Features on GISAXS patterns
Depth-resolved GISAXS (PA systems)

- Peak intensity: PA-662 > PA-660 > PA-661
- Different form factor and nature of scattering in hard PA-662 coating
Depth-resolved GISAXS (PA-660)

- (Strong) Scattering is lost at $\xi_p \sim 10-15$ μm
- Top layer with heterogeneities
Cross-sectional AFM (at DSM)

Cross-sectional AFM corroborates stratification!
GISAXS simulations

<table>
<thead>
<tr>
<th>Object shape</th>
<th>I(0)</th>
<th>D, (nm)</th>
<th>d,</th>
<th>h</th>
</tr>
</thead>
<tbody>
<tr>
<td>PA662 (hard)</td>
<td>Sphere</td>
<td>1.1 x 10^{-4}</td>
<td>60</td>
<td>70</td>
</tr>
<tr>
<td>PA661 (soft)</td>
<td>Cylinder</td>
<td>3.0 x 10^{-5}</td>
<td>8</td>
<td>72</td>
</tr>
<tr>
<td>PA660 (multiphase)</td>
<td>Cylinder</td>
<td>1.0 x 10^{-7}</td>
<td>15</td>
<td>70</td>
</tr>
</tbody>
</table>

The local monodisperse approximation was used to take into account for the object size polydispersity described by a log-normal distribution function. The structure factor was in all cases a Percus-Yevick function. The fits were achieved using the FitGISAXS program.

Randomly packed hard sphere model

Randomly packed cylinder model

Randomly packed cylinder model
Aging effects ($\alpha_i = 0.1^\circ$)

- $T_{\text{annealing}} (= 150 \, ^\circ\text{C}) > T_{g,\text{DMTA, hard}} (~105 \, ^\circ\text{C})$

- Annealing smears out nanostructural heterogeneities
Edge effects ($\alpha_i = 0.2^\circ$)

- Annealing at $150^\circ C > T_g, \text{DMTA, hard}$ (~105 °C)
- Annealing smears out the nanostructure (heterogeneities evidenced by GISAXS)