Supporting Information

Cure dependent morphology of acrylic/alkyd hybrid latex films via nanomechanical mapping

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1. Particle morphology of the hybrid acrylic/alkyd particles latex

![TEM images of the acrylic / alkyd hybrid particles. Dark regions correspond to the alkyd rich phase](image)

**Figure S1**: TEM images of the acrylic / alkyd hybrid particles. Dark regions correspond to the alkyd rich phase

2. Synthesis of the all acrylic dispersion by miniemulsion polymerization

A 25 wt % solids content miniemulsion was prepared as follows. First, the organic phase was prepared by dissolution of the SA (4 wbm%) into the monomer mixture (MMA/BA/AA, 49.5/49.5/1 wt %). Then, the organic phase was poured into an aqueous solution of Dowfax (2.7 % weight based on organic phase, wbop, of active surfactant) and NaHCO₃ (0.015M) under magnetic stirring at 700 rpm to create an emulsion. The resulting emulsion was sonicated with a Branson 450W sonifier for 10 minutes at an amplitude of 70% and a duty cycle of 80%. During sonication, the flask was immersed in an ice bath to avoid overheating. Polymerization was carried out in batch in a 500-mL glass reactor equipped with a reflux condenser, stirrer, sampling device, and nitrogen inlet. When the reaction mixture reached 70°C a shot of initiator (KPS, 1.3 wbm% in 7 wt% of the total amount of water) was added and the reaction was let to react for 7 hours. The formulation for the reaction is given in Table S1
Table S1: Formulation for the synthesis of the acrylic particles latex

<table>
<thead>
<tr>
<th>Compounds</th>
<th>Weight (g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Water</td>
<td>268.5</td>
</tr>
<tr>
<td>Dowfax 2A-1*</td>
<td>1.1</td>
</tr>
<tr>
<td>BA</td>
<td>37.1</td>
</tr>
<tr>
<td>MMA</td>
<td>37.1</td>
</tr>
<tr>
<td>AA</td>
<td>0.75</td>
</tr>
<tr>
<td>NaHCO₃</td>
<td>0.32</td>
</tr>
<tr>
<td>SA</td>
<td>4.5</td>
</tr>
<tr>
<td>KPS</td>
<td>1</td>
</tr>
</tbody>
</table>

3. Mechanical maps of pure acrylic and pure alkyd films

In order to get an idea of the expected distribution of the moduli of the two polymer phases, before analysis of the hybrids we performed PF-QNM measurements on films cast from acrylic and alkyd phases separately. Figure S2 shows a PF-QNM mechanical modulus map of a bare MMA/BA film cast on a PET sheet dried for 8 days at 23 ºC and 55% relative humidity. It should be noted that this image correspond to the “top” of a film, i.e., without cross sectioning. We present three different probed areas of the film, measured on different days. The mean adhesion force was 5 ± 2 nN. The image showed a mean mechanical modulus of 70 MPa, with a broad distribution (see histogram). The modulus distribution broadness could be probably related to the batch process used to synthesis the polymer that, because of the different reactivity ratios of the monomers, led to a broad polymer composition distribution. From the results in Figure S2, we can expect that the MMA/BA areas in the PF-QNM modulus maps of hybrid samples would appear in colors ranging from green to black, indicating a modulus distribution in the range $30 \leq E \text{ (MPa)} \leq 100$.

Figure S3 shows the elastic modulus map of a pure alkyd resin film, with a Co-based catalyst, dried at 65 ºC for two weeks. We found a mean elastic modulus of 35 MPa, with a narrow distribution (light green monocolor image). The mean adhesion force was 6 ± 2 nN. We consider this to be the best possible scenario of a fully dried alkyd sample. In other words, uncured alkyd areas in the PF-QNM modulus maps are expected to have a modulus below 35 MPa. Thus, we expect that the hybrid film will contain regions...
with widely different moduli. As discussed in the Experimental Part, this is a long-standing challenge in AFM-based mechanical measurements. In this work, the challenge was overcome by using different conditions for the two objectives of this article. To study the curing process attention should be paid to the increase of the modulus of the soft areas of the hybrid films (alkyd regions). In this case, the reference was a PDMS sample of known modulus (E= 3.5 MPa) and this allowed to get accurate measurements in the range \(2 \leq E(MPa) \leq 30\). On the other hand, when the evolution of the morphology was studied an acrylic sample with a modulus of 70 MPa was used as a reference and this allowed us to have accurate measurements in a range of \(30 \leq E(MPa) \leq 150\). In this case, the modulus of the alkyd regions cannot be accurately detected and therefore in the PF-QNM mechanical maps used to investigate the evolution of the film morphology the (not completely cured) alkyd regions (\(\leq 30\) MPa) appear red and the acrylic areas (40-100 MPa) in green to black.

![Image](image_url)

Figure S2: a) Mechanical map and b) histogram of the modulus distribution of the surface of pure acrylic polymer films. c) Representative force-separation PF-QNM curve for a point on the surface of pure acrylic polymer film.
Figure S3: a) Mechanical map and b) histogram of the modulus distribution of the surface of a pure alkyd film with Co-based catalyst dried at 65 °C for two weeks. c) Representative force-separation curve for a point on the surface of the film.

4. Film of cured pure alkyd

Figure S4: Photo of an alkyd film with 1% of Mn-based catalyst after one week of curing.
5. Mechanical maps for 1 day of curing with different concentrations of the Mn-based catalyst

Figure S5: Mechanical maps for the films with 1% of Mn-based catalyst abc) and 2% Mn-based catalyst def) after 1 day of curing at 23 °C and 55% relative humidity. For each system, the left image was performed close to air-film interface, the second in the center of the film and the right image close to the film-substrate interface.
6. Alkyd cluster size distributions for different concentrations of the Mn-based catalyst

Figure S6: Number size distributions of the alkyd clusters for the films with 0.25% of Mn-based catalyst abc), 1% of Mn-based catalyst def) and 2% of Mn-based catalyst ghi) after 3 days of curing at 23 °C and 55% relative humidity. For each system, the left image was performed close to air-film interface, the second in the center of the film and the right image close to the film-substrate interface.
Figure S7: Number size distributions of the alkyd clusters for the films with 0.25% of Mn-based catalyst abc), 1% of Mn-based catalyst def) and 2% of Mn-based catalyst ghi) after 8 days of curing at 23 °C and 55% relative humidity. For each system, the left image was performed close to air-film interface, the second in the center of the film and the right image close to the film-substrate interface.
7. Mechanical maps after 1 day of curing with 1% Mn-based catalyst and the Zr secondary catalyst

Figure S8: Mechanical maps for the films with 1% Mn-based catalyst solely (a-c) and Zr-based catalyst (d-f) after 1 day of curing at 23 ºC and 55% relative humidity. For each system, the left image was performed close to air-film interface, the second in the center of the film and the right image close to the film-substrate interface.
8. Alkyd cluster size distributions after 8 days of curing for 1%Mn-based catalyst and the Zr secondary catalyst

Figure S9: Number size distributions of the alkyd clusters for the films with 1% Mn-based catalyst solely (abc), and Zr-based catalyst (def) after 8 days of curing at 23 ºC and 55% relative humidity. For each system, the left image was performed close to air-film interface, the second in the center of the film and the right image close to the film-substrate interface.
9. Tensile tests

**Figure S10:** Stress-strain curves of dried films from acrylic/alkyd resin hybrid particles latex with different concentration of Mn-based catalyst after 8 days of curing

**Table S2:** Tensile test results of dried films from acrylic/alkyd resin hybrid particles latex with different concentration of Mn-based catalyst after 8 days of curing

<table>
<thead>
<tr>
<th></th>
<th>Young’s modulus (MPa)</th>
<th>Elongation at break</th>
<th>Stress at break (MPa)</th>
<th>Toughness x $10^6$ (J/m$^3$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0% Mn – 8 days</td>
<td>0.512 ± 0.2</td>
<td>1.16 ± 0.19</td>
<td>0.123 ± 0.004</td>
<td>0.127 ± 0.036</td>
</tr>
<tr>
<td>0.25% Mn - 8 days</td>
<td>6.5 ± 0.8</td>
<td>0.81 ± 0.03</td>
<td>2.93 ± 0.56</td>
<td>1.25 ± 0.26</td>
</tr>
<tr>
<td>1% Mn - 8 days</td>
<td>6.4 ± 0.5</td>
<td>0.94 ± 0.1</td>
<td>3.68 ± 0.44</td>
<td>1.72 ± 0.34</td>
</tr>
<tr>
<td>2% Mn - 8 days</td>
<td>6.7 ± 1.5</td>
<td>1.08 ± 0.11</td>
<td>4.74 ± 0.51</td>
<td>2.48 ± 0.42</td>
</tr>
<tr>
<td>Pure acrylic</td>
<td>54 ± 9.8</td>
<td>3.4 ± 0.17</td>
<td>7.3 ± 0.65</td>
<td>17 ± 2.11</td>
</tr>
</tbody>
</table>
Figure S11: Stress-strain curves of dried films from acrylic/alkyd resin hybrid particles latex with 1 wt% of Mn-based catalyst and with the Zr secondary catalyst after 8 days of curing

Table S3: Tensile test results of dried films from acrylic/alkyd resin hybrid particles latex with 1 wt% of Mn-based catalyst and with the Zr secondary catalyst after 8 days of curing

<table>
<thead>
<tr>
<th></th>
<th>Young’s modulus (MPa)</th>
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</tr>
</thead>
<tbody>
<tr>
<td>1% Mn - 8 days</td>
<td>6.4 ± 0.5</td>
<td>0.94 ± 0.1</td>
<td>3.68 ± 0.44</td>
<td>1.72 ± 0.34</td>
</tr>
<tr>
<td>1% Mn + Zr - 8 days</td>
<td>9.0 ± 1.6</td>
<td>0.88 ± 0.01</td>
<td>4.10 ± 0.11</td>
<td>1.86 ± 0.06</td>
</tr>
</tbody>
</table>