Supporting Information

‘The Good, the Bad and the Slippery’: A Tale of Three Solvents in Polymer Film Dewetting

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Solvent mixture vapor fractions

The plot of mole fraction of each solvent in the vapour phase in binary solvent mixtures of ethanol, acetone and water is provided in Figure S1. Furthermore, tabulated data for the mole fraction of each solvent in the ternary mixture composed of the three solvents mentioned is provided in Table S1.

Figure S1: Mole fractions of the liquid and vapour phases for binary mixtures at 25 °C1-3 of (a) ethanol - water (b) ethanol – acetone, and (c) acetone - water.
Table S1: Conversion between composition in the liquid phase to vapor phase for a ternary mixture of ethanol - acetone - water at 25°C calculated by the UNIFAC method.\textsuperscript{43}

<table>
<thead>
<tr>
<th>Liquid phase (water mass fraction)\textsuperscript{a}</th>
<th>Liquid phase (mole fraction)</th>
<th>Vapour phase (mole fraction)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Acetone</td>
<td>Ethanol</td>
</tr>
<tr>
<td>0.0</td>
<td>0.44</td>
<td>0.56</td>
</tr>
<tr>
<td>0.1</td>
<td>0.34</td>
<td>0.42</td>
</tr>
<tr>
<td>0.2</td>
<td>0.26</td>
<td>0.33</td>
</tr>
<tr>
<td>0.3</td>
<td>0.20</td>
<td>0.25</td>
</tr>
<tr>
<td>0.4</td>
<td>0.15</td>
<td>0.19</td>
</tr>
<tr>
<td>0.5</td>
<td>0.11</td>
<td>0.14</td>
</tr>
<tr>
<td>0.6</td>
<td>0.08</td>
<td>0.11</td>
</tr>
<tr>
<td>0.7</td>
<td>0.06</td>
<td>0.07</td>
</tr>
<tr>
<td>0.8</td>
<td>0.04</td>
<td>0.04</td>
</tr>
<tr>
<td>0.9</td>
<td>0.02</td>
<td>0.02</td>
</tr>
</tbody>
</table>

\textsuperscript{a}Mass fraction of water added to a 1:1 (w/w) liquid mixture of ethanol and acetone. A 1:1 (w/w) ethanol-acetone mixture without water corresponds to the first row of data in the table.

**Rim and droplet profiles**

Representative cross sectional profiles of the rim morphology surrounding a dewetting hole in the P4VP film during solvent and thermal annealing were obtained by AFM for holes approximately 100 µm in diameter (Figure S2(a)). AFM was also used to obtain the cross sectional profiles of isolated P4VP droplets on the PS substrate at the conclusion of film dewetting (Figure S2(b)). The droplet profile provides evidence of layer inversion during thermal annealing, seen in the distortion of the contact line between the P4VP droplet and the substrate, leading to a contact angle value lower than expected for P4VP on PS. A summary of the contact angles for P4VP on PS in the different annealing conditions used in this paper is provided in Table 2.
Figure S2: (a) AFM cross section of the rim surrounding holes approximately 100 μm in diameter in a dewetting P4VP (107 ± 4 nm) film from a PS (98 ± 4 nm) substrate when annealed in a solvent vapor mixture (mol/mol) at 23° ± 1°C composed of acetone–water (90:10) (blue solid line), ethanol-water (51:49) (red dotted line), ethanol-acetone(15:85) (black dashed line) and upon thermal annealing at 180°C (green dashed-dotted line). (b) AFM cross section profiles of droplet for P4VP fully dewetted from the underlying PS. The line styles and colour denote the annealing conditions as they are indicated in (a).

**Three solvent mixture annealing**

Time-lapse image series of dewetting P4VP from PS in the saturated vapours of a ternary ethanol – acetone – water solvent mixture (Figure S3). The ethanol – acetone mixture was maintained at a 1:1 wt. ratio while the amount of water was increased. The mass ratios have been converted to mole ratios in the liquid phase and the mole ratio in the vapour phase calculated using the UNIFAC method and presented in Table S1. The vapour phase mole fractions are reported in the Results section and Figure S3.
Conversion of Hansen to Hildebrand solubility parameters

Hansen identified the individual contributions of the dispersion $\delta_D$, polar $\delta_P$ and hydrogen-bond $\delta_H$ energy towards the cohesive energy density described by the Hildebrand solubility parameter, $\delta$:  \(^6\)

$$\delta^2 = \delta_D^2 + \delta_P^2 + \delta_H^2$$  \(\text{(S1)}\)

As an example, in the case of ethanol the Hansen solubility parameters are $\delta_D = 15.8$ MPa\(^{1/2}\), $\delta_P = 8.8$ MPa\(^{1/2}\) and $\delta_H = 19.4$ MPa\(^{1/2}\), the Hildebrand solubility parameter can be calculated from

$$\delta_{\text{etoh}} = \sqrt{\delta_D^2 + \delta_P^2 + \delta_H^2} \approx 26.5 \text{ MPa}^{1/2}$$  \(\text{(S2)}\)

Empirical data for PS and P4VP surface tension

A model was developed by Sauer and Dee to convert pressure – volume – temperature (PVT) data for a polymer into the cohesive energy density (CED) from which it is possible to calculate the surface tension.
Table 2: Cohesive energy density (CED) data and surface tension information used for spreading parameter, interaction parameter and surface tension calculations obtained from experimental work by Sauer and Dee.²

<table>
<thead>
<tr>
<th>Polymer</th>
<th>CED (temp) (MPa °C)</th>
<th>Polynomial Fits of Surface Tension Data</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>$A_0$ (mN m$^{-1}$) $^a$</td>
</tr>
<tr>
<td>PS</td>
<td>230 (200)</td>
<td>41.5</td>
</tr>
<tr>
<td>P4VP</td>
<td>600 (250)</td>
<td>74.1</td>
</tr>
</tbody>
</table>

$^a \gamma = A_0 + \text{slope} \times T$, where temperature is in °C.

References