Contact Angle Hysteresis on the Polymer Substrates: Experimental Techniques and Calculation of CAH Energy

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Wetting of the flat substrates

$\theta$ – local (Young) contact angle

$$\cos \theta = \frac{\gamma_{SA} - \gamma_{SL}}{\gamma}$$
What is the contact angle hysteresis (CAH)
Motivation

Contact angle hysteresis is responsible for lots of wetting related phenomena.

Experimental data concerning contact angle hysteresis are contradictory and sensitive to the experimental technique.
Materials

Extruded polymer films of:

- low density polyethylene (PE),
- polypropylene (PP),
- polyethylene terephthalate (PET),
- polysulfone (PSU),
- polyvinylidene fluoride (PVDF unpoled),
- polyvinylidene fluoride (PVDF poled)
Experimental Techniques

- needle-syringe method
- evaporation of the drop
- deformation of the drop
The New Technique for CAH Measurement

- Precise micrometrical stage
- Teflon plate
- Water droplet
- Polymer film
- Horizontal plate

θ adv, θ rec
The New Technique for CAH Measurement

- Precise micrometrical stage
- Polymer film
- Teflon plate
- Water droplet
- Laser
- Screen

θ_{adv}  θ_{rec}
CAH established with the evaporation technique
Adv. and Rec. Angles Established with Various Techniques

<table>
<thead>
<tr>
<th>Polymer</th>
<th>$\theta_{1 \text{adv}}$</th>
<th>$\theta_{1 \text{rec}}$</th>
<th>$\theta_{2 \text{adv}}$</th>
<th>$\theta_{2 \text{rec}}$</th>
<th>$\theta_{3 \text{rec}}$</th>
<th>$\Delta \theta_2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>PE</td>
<td>103.5±1</td>
<td>70.5±2</td>
<td>105±2</td>
<td>54±3</td>
<td>78±1</td>
<td></td>
</tr>
<tr>
<td>PP</td>
<td>102.5±1.5</td>
<td>74±3</td>
<td>94±2</td>
<td>79±2</td>
<td>91±1</td>
<td>15</td>
</tr>
<tr>
<td>PET</td>
<td>84±2</td>
<td>40.5±2.5</td>
<td>83.5±2</td>
<td>53.5±2.5</td>
<td>56±1</td>
<td>30</td>
</tr>
<tr>
<td>PVDF Non-poled</td>
<td>86.5±1.5</td>
<td>48±4</td>
<td>92±2.5</td>
<td>52±2</td>
<td>74±1</td>
<td>40</td>
</tr>
<tr>
<td>PVDF poled</td>
<td>87±2</td>
<td>38±3</td>
<td>83.5±3</td>
<td>51±2.5</td>
<td>48±1</td>
<td>32.5</td>
</tr>
<tr>
<td>PSU</td>
<td>90.5±2</td>
<td>37.5±2</td>
<td>86.5±3</td>
<td>45±2</td>
<td>47±1</td>
<td>41.5</td>
</tr>
</tbody>
</table>

Hysteresis: The pressed drop method 51
Results of CAH Measurements

Advancing angle:

• excellent agreement of advancing angles measured with the needle-syringe method and pressing the drop for PE, PET and PSU substrates

• satisfactory agreement for poled and non-poled PVDF and PP

• Max. discrepancy for PP - 8°
Results of CAH Measurements

Receding angle

High discrepancy for all polymer substrates as high as 24° for PE substrates

Neumann and Chibowski:

Receding contact angles on a dry surface are experimentally conceptually inaccessible
Factors exerting an influence on the contact angle hysteresis

Chemical and physical heterogeneities of the surface

Roughness

Precursor film surrounding the drop
Fine structure of the triple line and the receding contact angle
Taking into account the precursor film

\[ E = E_{\text{drop}} + E_{\text{precursor}} \]

\[ E_{\text{drop}} = \pi R^2 (\gamma f(\theta) + \gamma_{SL} \sin^2 \theta) \]

\[ \Delta E_{\text{precursor}} = (\gamma + \gamma_{SL} + P(e))2\pi rH \]

\[ \Pi(h) = -\frac{dP}{de} \]

\[ R = 2H \frac{\gamma + \gamma_{SL} + P(e)}{\gamma f(\theta) + \gamma_{SL} \sin^2 \theta} \sin \theta \]
Quantitative characterization of hysteresis: calculation of CAH energy:

Approach developed by Extrand:

\[ dg = -\frac{1}{A} d \mu_s \]

\[ dg = -\frac{R_g T}{A} d \ln p \]

\[ g \text{ is the surface free energy of the solid and } \mu_s \text{ is its chemical potential} \]

\[ \Delta g = -\frac{R_g T}{A} \ln \frac{\sin \theta^{adv}}{\sin \theta^{rec}} \]

\[ A = \left( \frac{M_0}{\rho} \right)^{\frac{2}{3}} N_a^{\frac{1}{3}} \]

\[ A - \text{the molar surface area} \]

\[ \rho - \text{the density, } M_0 - \text{the monomer weight, } N_a - \text{the Avogadro number} \]
Quantitative characterization of hysteresis: calculation of CAH energy:

Our approach:

\[ \Delta g = g_r - g_a \]

\[
\Delta g = \frac{R_g T}{A} \ln \frac{\Delta p_{adv}}{\Delta p_{rec}} = \frac{R_g T}{A} \ln \frac{R_{rec}}{R_{adv}} = \frac{1}{3} \frac{R_g T}{A} \ln \frac{(1 - \cos \theta_{adv})^2 (2 + \cos \theta_{adv})}{(1 - \cos \theta_{rec})^2 (2 + \cos \theta_{rec})}
\]

\[
V = \frac{\pi R^3}{3} (1 - \cos \theta)^2 (2 + \cos \theta)
\]
Quantitative characterization of the pinning force

The critical force is attained when:

$$\theta = \theta^{adv}$$

$$\frac{d F}{d l} = \frac{R_{adv} p}{4 \sin \theta^{adv}} (2 \theta^{adv} - \sin 2 \theta^{adv})$$

$$p = \frac{2 \gamma}{R} + \rho gh$$

The Force per Unit Length of the Triple Line vs. Contact Angle
Quantitative characterization of hysteresis:

<table>
<thead>
<tr>
<th>Polymer</th>
<th>$\varepsilon$</th>
<th>$\Delta g_s$</th>
<th>$\frac{d F}{d l}(\Theta_{av})$</th>
</tr>
</thead>
<tbody>
<tr>
<td>PE</td>
<td>2.3</td>
<td>17.7</td>
<td>150</td>
</tr>
<tr>
<td>PP</td>
<td>2.2</td>
<td>3.3</td>
<td>150</td>
</tr>
<tr>
<td>PET</td>
<td>2.9-3.2</td>
<td>5.1</td>
<td>100</td>
</tr>
<tr>
<td>PVDF Non-poled</td>
<td>15.1</td>
<td>110</td>
<td></td>
</tr>
<tr>
<td>PVDF poled</td>
<td>13.6</td>
<td>110</td>
<td></td>
</tr>
<tr>
<td>PSU</td>
<td>3.14</td>
<td>4.1</td>
<td>110</td>
</tr>
</tbody>
</table>
The potential barrier to be surmounted by the triple line to jump:

$$\delta r \approx 0.1 - 1 \text{ nm}$$

$$\delta U = \frac{dF}{dl} (\theta^{adv}) \delta r \approx 10^{-10} - 10^{-11} \frac{J}{m}$$

The value coincides with the linear surface tension of water
Force per unit length of triple line vs. dielectric constant of substrate
Conclusions

New technique for advancing and receding angle measurement is presented

Advancing angles established with various techniques demonstrated satisfactory agreement

Receding angles demonstrated high discrepancy

The fine structure of triple line was studied with ESEM microscopy
Conclusions

The energy of hysteresis was calculated.

The force acting on the unit length of the triple line was calculated.

The pinning force correlates with dielectric constants of polymer substrates.
Publications:


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