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

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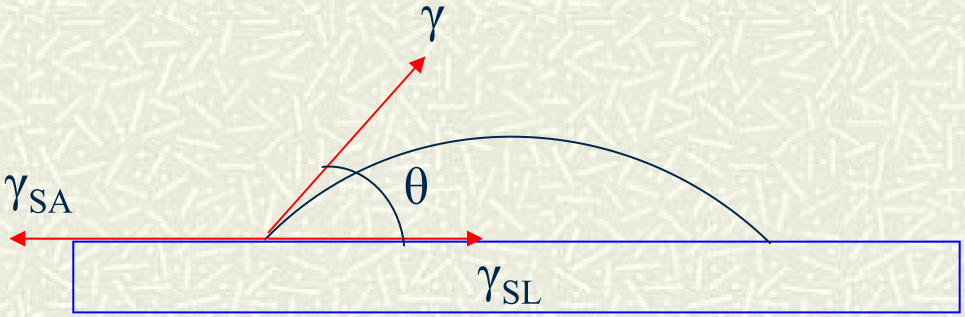
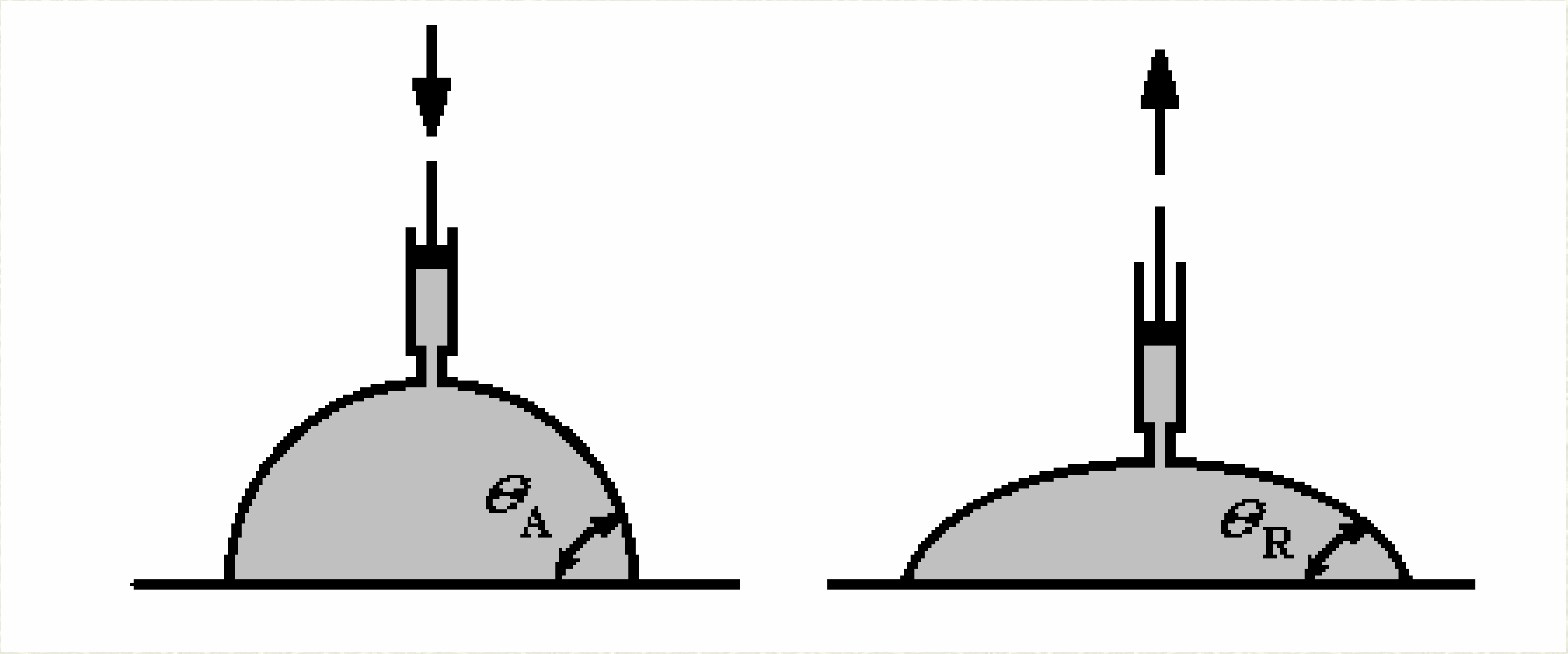
Wetting of the flat substrates



θ – 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

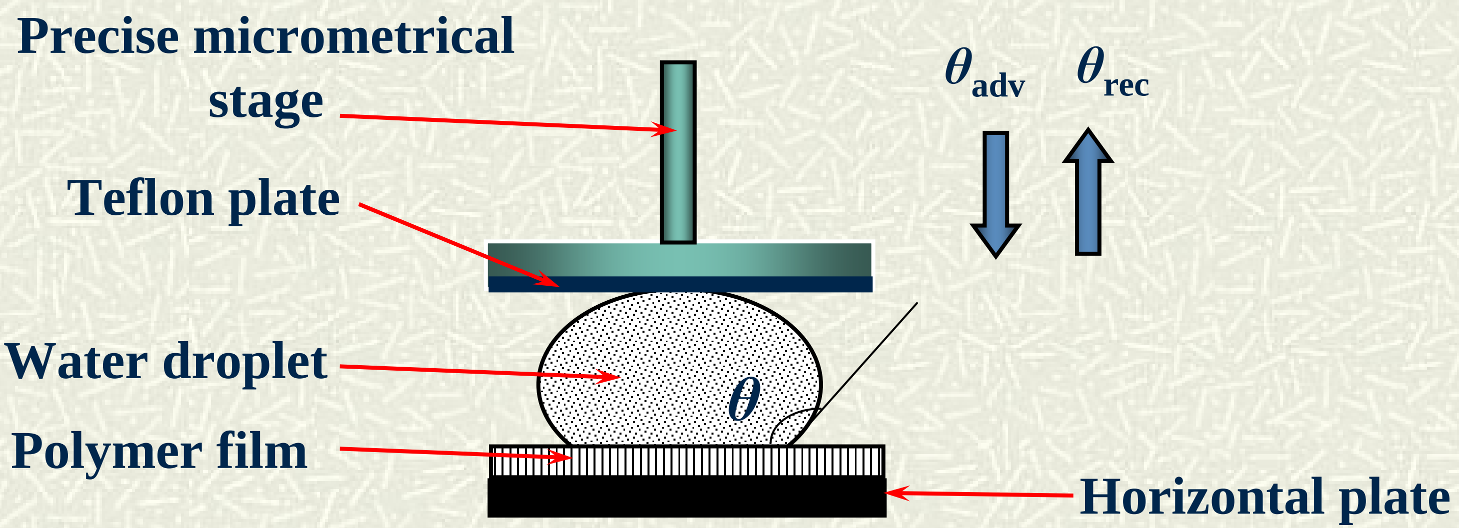
Extruded polymer films of:

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

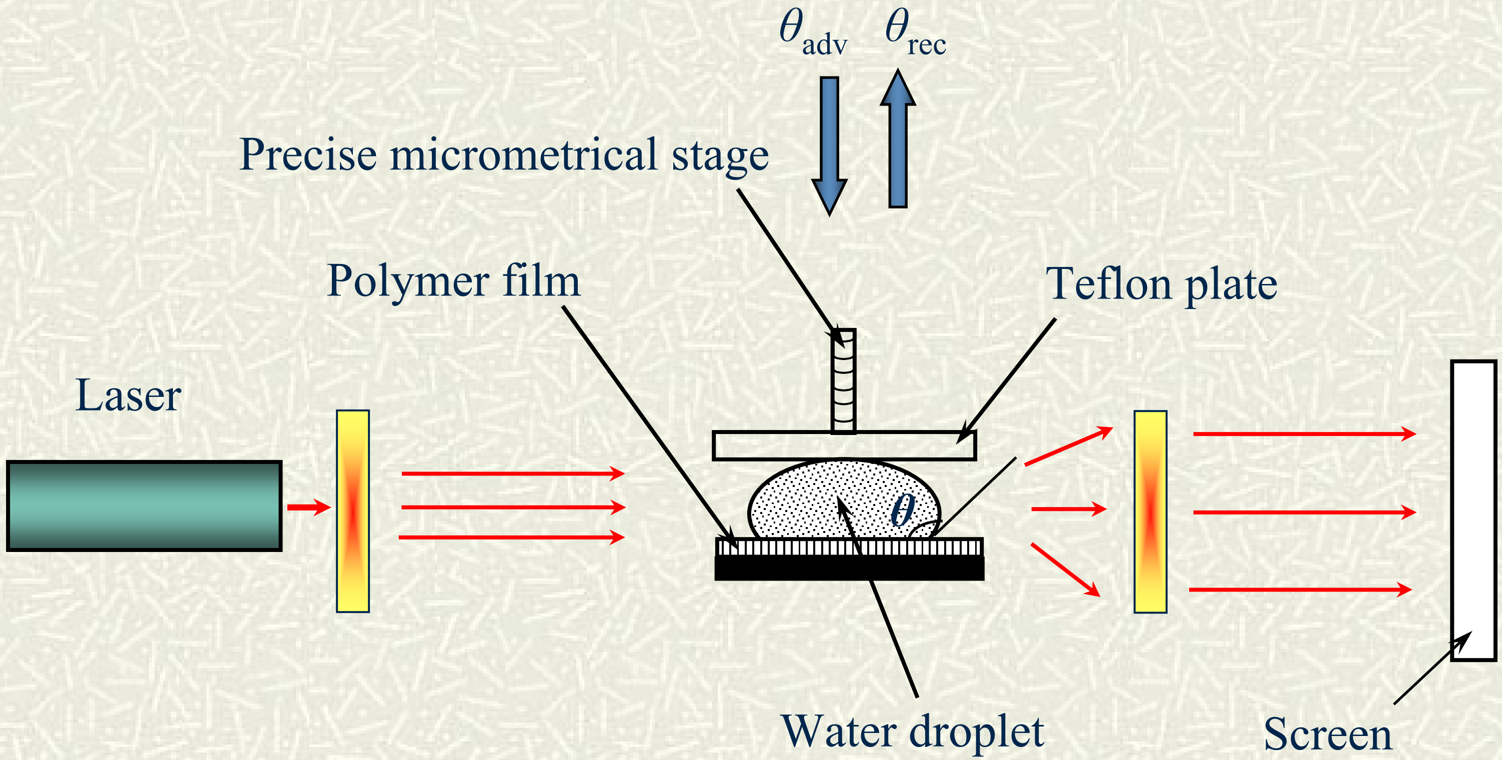
Experimental Techniques

- needle-syringe method
- evaporation of the drop
- deformation of the drop

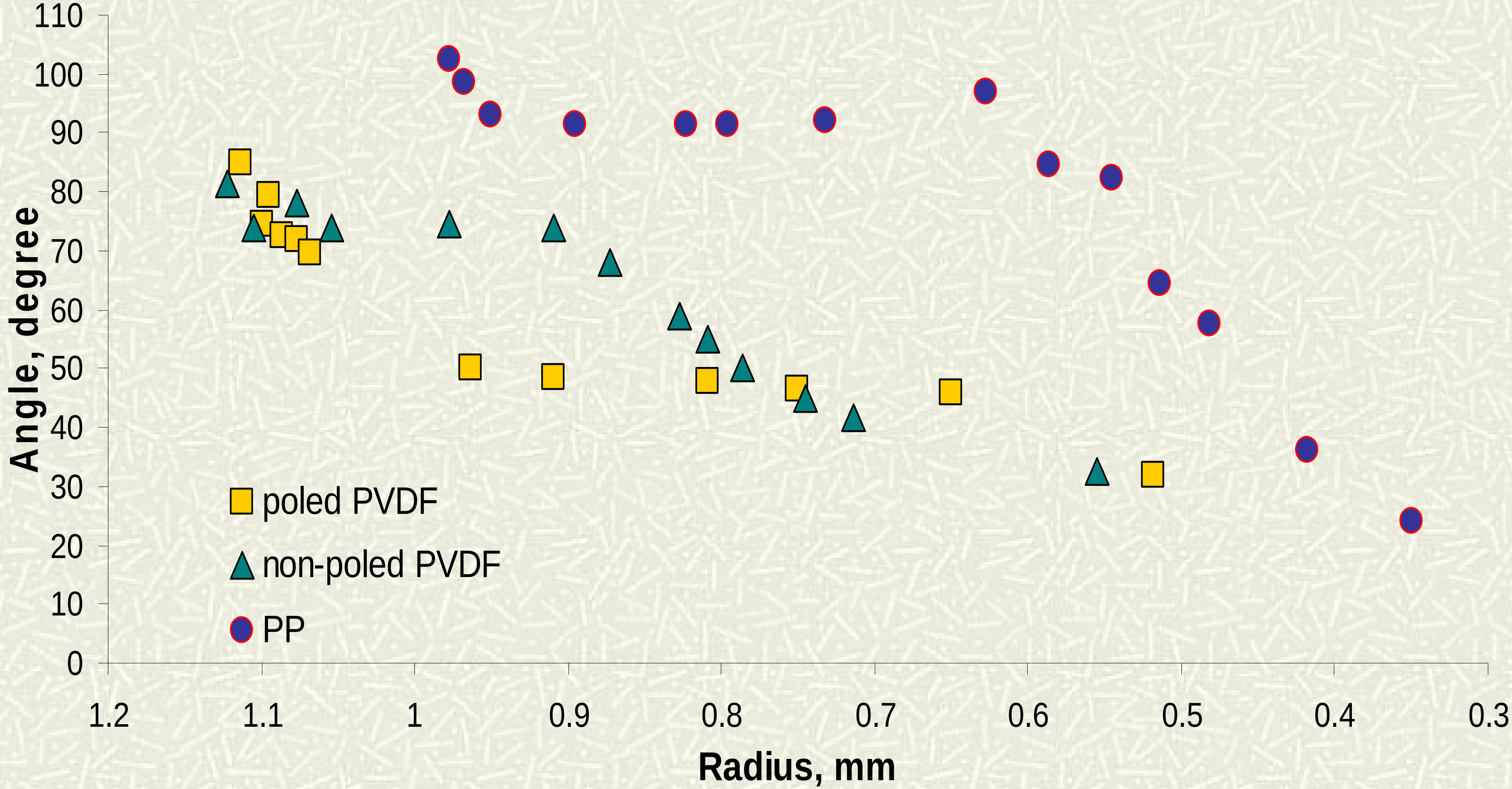
The New Technique for CAH Measurement



The New Technique for CAH Measurement



CAH established with the evaporation technique



Adv. and Rec. Angles Established with Various Techniques

Polymer	θ_1^{adv}, The needle-syringe method	θ_1^{rec}, The needle-syringe method	θ_2^{adv}, The pressed drop method	θ_2^{rec}, The pressed drop method	θ_3^{rec}, The evaporation method	$\Delta\theta_2$ Hysteresis The pressed drop method
PE	103.5±1	70.5±2	105±2	54±3	78±1	51
PP	102.5±1.5	74±3	94±2	79±2	91±1	15
PET	84±2	40.5±2.5	83.5±2	53.5±2.5	56±1	30
PVDF Non-poled	86.5±1.5	48±4	92±2.5	52±2	74±1	40
PVDF poled	87±2	38±3	83.5±3	51±2.5	48±1	32.5
PSU	90.5±2	37.5±2	86.5±3	45±2	47±1	41.5

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 - 8º

Results of CAH Measurements

Receding angle

High discrepancy for all polymer substrates

as high as 24º for PE substrates

Neumann and Chibowski:

Receding contact angles on a dry surface are experimentally conceptually inaccessible

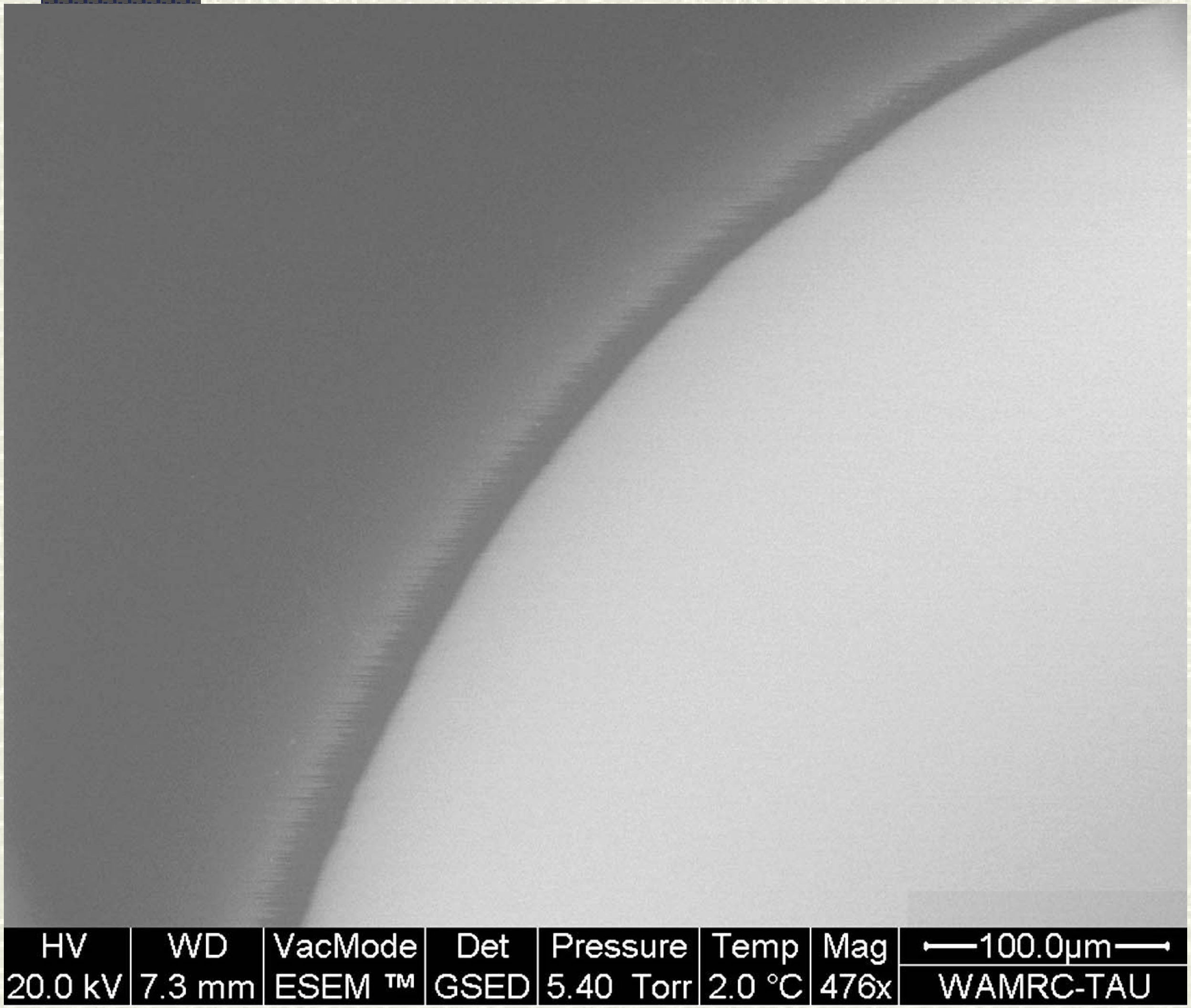
Factors exerting an influence on the contact angle hysteresis

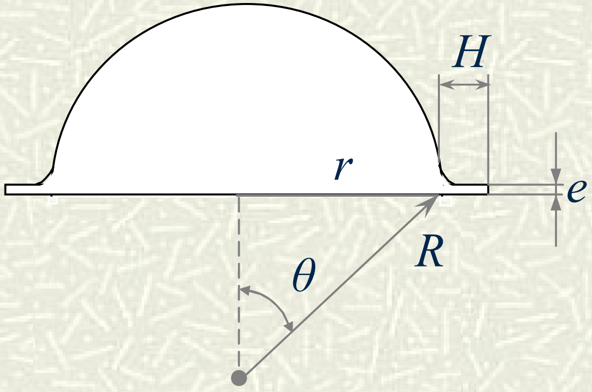
Chemical and physical heterogeneities of the surface

Roughness

Precursor film surrounding the drop

Fine structure of the triple line and the receding contact angle





Taking into account the precursor film

$$E = E_{\text{drop}} + E_{\text{precursor}}$$

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

$$\Delta E_{\text{precursor}} = (\gamma + \gamma_{\text{SL}} + P(e)) 2\pi r H$$

$$\Pi(h) = -\frac{\mathrm{d}P}{\mathrm{d}e}$$

$$R = 2H \frac{\gamma + \gamma_{\text{SL}} + P(e)}{\gamma f(\theta) + \gamma_{\text{SL}} \sin^2 \theta} \sin\theta$$

Quantitative characterization of hysteresis: calculation of CAH energy:

Approach developed by Extrand:

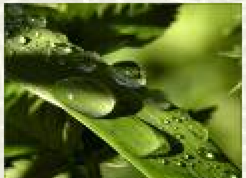
$$d\,g = -\frac{1}{A}\,d\,\mu_s \qquad d\,g = -\frac{R_g T}{A}\,d\ln p$$

g is the surface free energy of the solid and μ_s is its chemical potential

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

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

A - the molar surface area



ρ- the density, M_0 - the monomer weight, *Na* - 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:

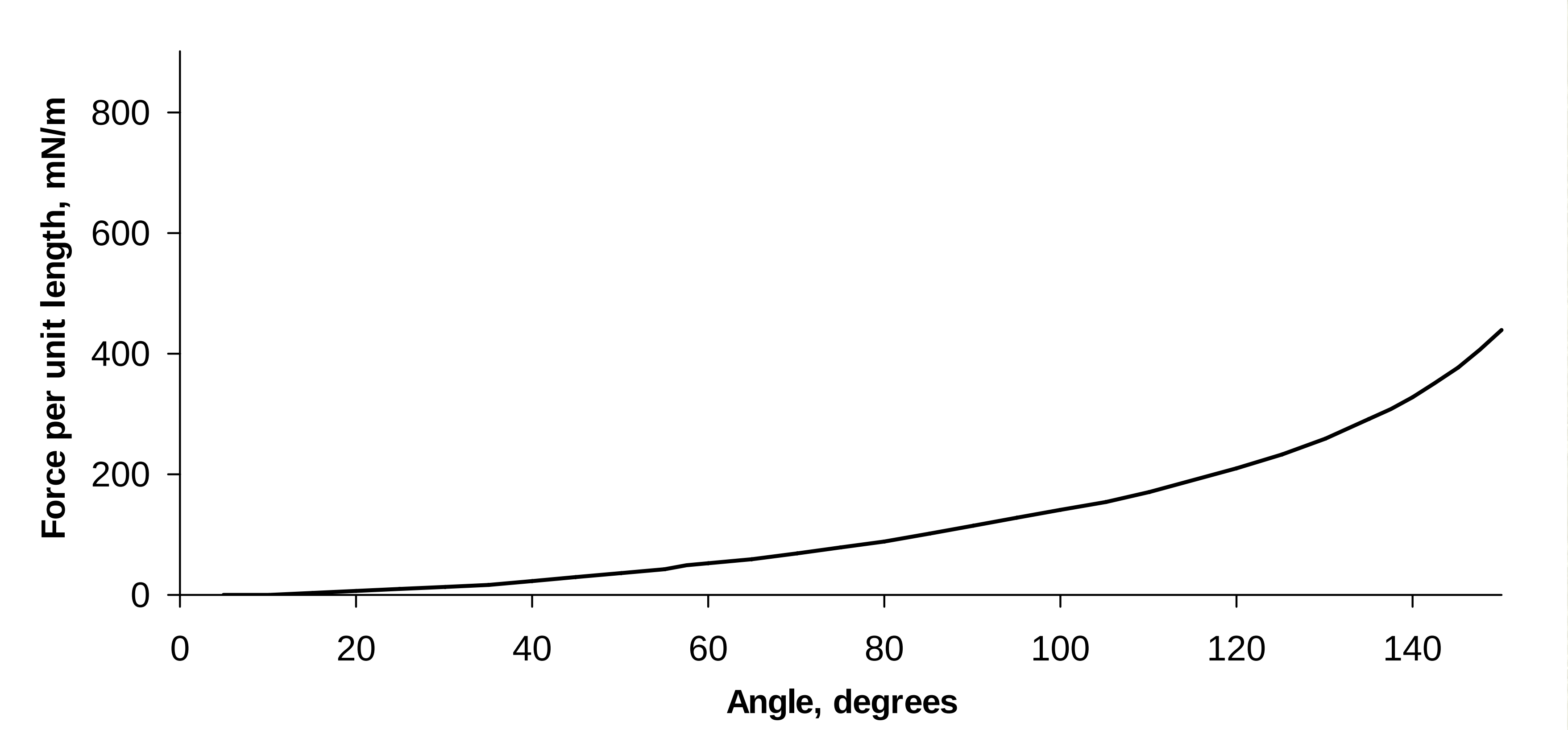
$$\theta = \theta^{adv}$$

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

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

Bormashenko, E.; Pogreb, R.; Whyman, G.; Bormashenko, Ye.; Erlich, M. *Langmuir,* **2007**, *23*, 6501-6503.

The Force per Unit Length of the Triple Line vs. Contact Angle



Quantitative characterization of hysteresis:

Polymer	ε	Δg, mJ/m^2	$\frac{dF}{dl}(\theta^{adv})$, mJ/m^2
PE	2.3	17.7	150
PP	2.2	3.3	150
PET	2.9-3.2	5.1	100
PVDF Non-poled		15.1	110
PVDF poled		13.6	110
PSU	3.14	4.1	110

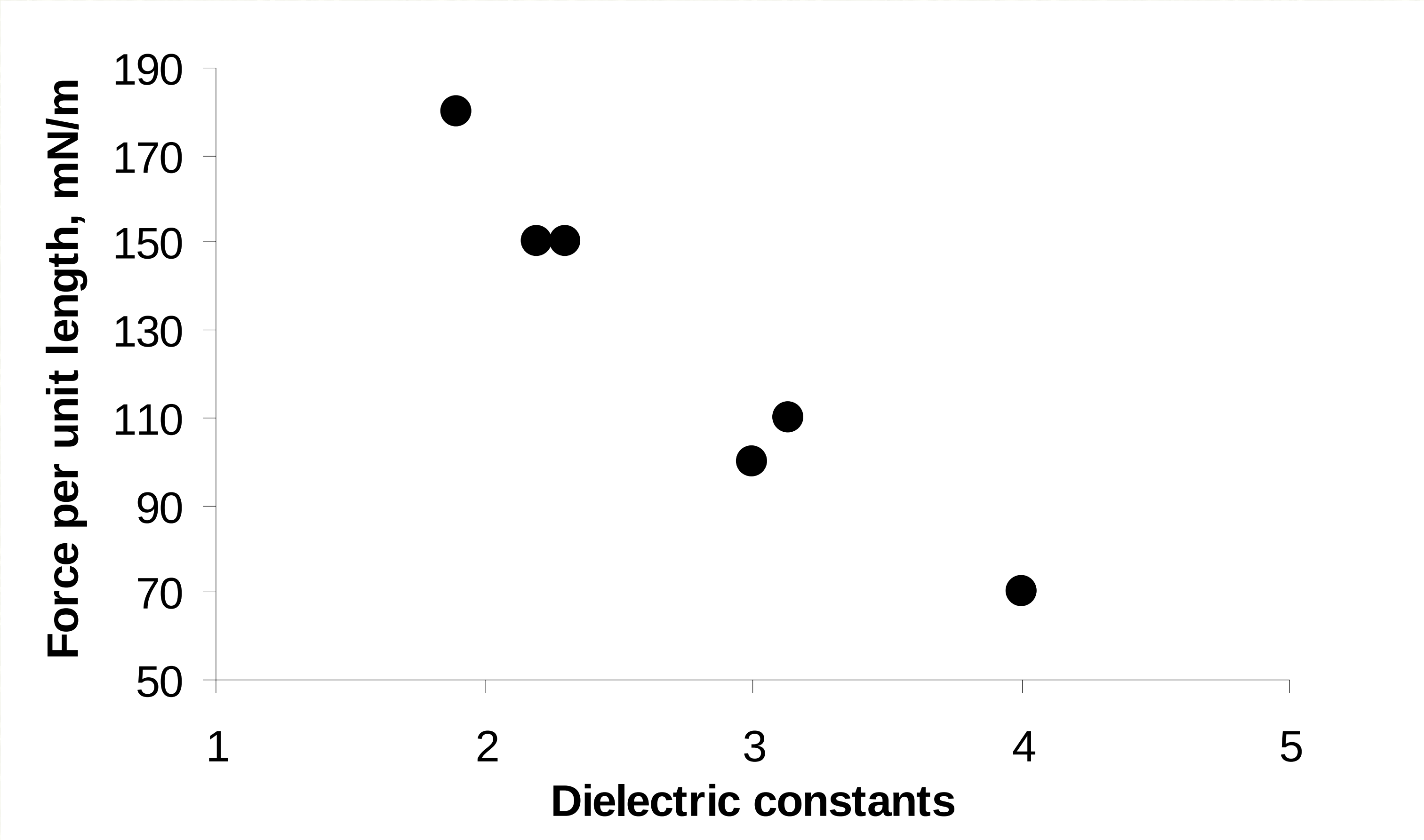
The potential barrier to be surmounted by the triple line to jump:

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

$$\delta U = \frac{\mathrm{d}F}{\mathrm{d}l}(\theta^{adv})\delta r \approx 10^{-10} - 10^{-11}\ \frac{\mathrm{J}}{\mathrm{m}}$$

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:

1. Bormashenko, E.; Bormashenko, Y.; Whyman, G.; Pogreb, R.; Musin, A.; Jager, R.; Barkay, Z. ***Langmuir***; 2008; **24,** 4020-4025

2. E. Bormashenko, R. Pogreb, G. Whyman, Ye. Bormashenko, M. Erlich, ***Langmuir***, 2007, **23**, 6501-6503.

3. Whyman G, Bormashenko E., Stein T., ***Chemical Physics Letters***, **450**, 2008 355–359.

4. E. Bormashenko, Ye. Bormashenko, T. Stein, G. Whyman, R. Pogreb, ***Langmuir***, 2007, **23**, 4378-4382.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