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Methods of contact angle measurement as a tool for characterization of wettability of polymers

Summary — Many problems related to the quality of protective coatings for more sophisticated applications can be solved on the basis of the wettability of their surfaces measurements. The equilibrium (static) or dynamic contact angle (CA) of solids can be measured and the sessile drop method or Wilhelmy method are usually applied. In the sessile drop method CA is measured optically. The measured values of static CA are influenced by evaporation of the liquid, absorption of the liquid by porous substrate (*e.g.* paper, building material) and other chemical or physical interactions occurring on the solid surface.

The Wilhelmy method is based on the measurements of the force which is needed to overcome the resistance of the liquid as the solid plate with known wetted length is immersed in or withdrawn from the liquid of known surface tension. The precision of the contact angle measurements by Wilhelmy method is higher as compared with the sessile drop method. Very important factor highly influencing the quality of CA measurements is the proper selection of applied liquids which should be selected according to the applied measuring method. The careful selection of the method of CA measurements is a crucial factor influencing the possibility of practical application of the results of wettability measurements.

Key words: contact angle, methods of measurement, surface free energy, roughness, hydrophobic properties of polysiloxane/polytetrafluoroethylene system.

Wettability is a very important property characterizing surfaces of polymers, especially of polymeric coating materials. Many problems related to the quality

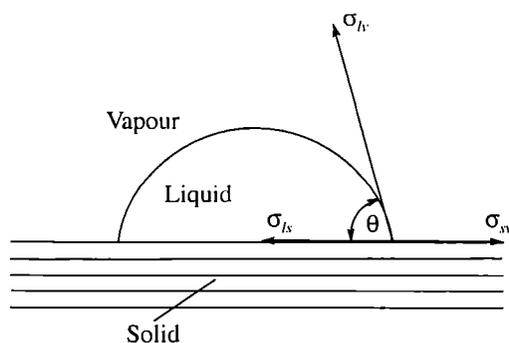


Fig. 1. Wetting of solid surface by a liquid: θ — contact angle, σ_{lv} — surface tension (ST) of a liquid, mN/m ; σ_{ls} — liquid-solid interfacial tension (IT), mN/m ; σ_{sv} — surface free energy (SFE) of solid, mN/m

of protective coatings for more sophisticated application can be solved on the basis of the wettability of their surfaces measurements. The measure of wettability is the contact angle (CA) defined as angle between the tangential line to the liquid drop placed on the solid surface and the solid surface [1] (Fig. 1).

The wetting behavior of a liquid on a solid surface depends on the liquid surface tension (ST) σ_{lv} , liquid-solid interfacial tension (IT) σ_{ls} , surface free energy of the solid (SFE) σ_s (sometimes incorrectly called surface tension of the solid) and contact angle (CA) θ . The relationship of the forces respectively surface/interfacial tensions at the three phase point can be described by Young—Dupré equation:

$$\sigma_{ls} - \sigma_{sv} + \sigma_{lv} \cos \theta = 0 \quad (1)$$

The solid surface is perfectly wetted for $\theta = 0^\circ$ and it is hydrophilic for $\theta < 90^\circ$ while it is hydrophobic for $\theta \geq 90^\circ$.

METHODS OF CONTACT ANGLE MEASUREMENTS

The equilibrium (static) or dynamic CA of solids can be measured and the following methods are usually applied:

- sessile drop method,
- Wilhelmy method.

Sessile drop method

Equilibrium (static) contact angle (CA) measurement

A drop of liquid of known surface tension is placed onto the solid surface using a syringe, and CA is measured optically. The values of static CA measured for the same drop can significantly differ dependently on the time interval between placing the drop on the solid surface and the time of measurement [2] (Fig. 2). The measured values of static CA are influenced by evaporation

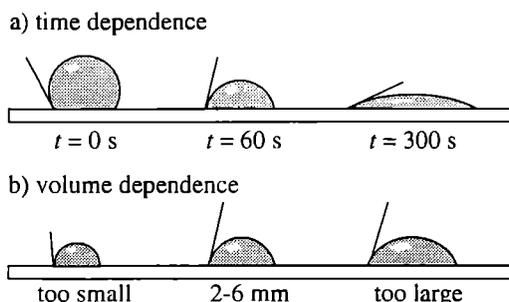


Fig. 2. Effect of time dependence (a) and volume dependence (b) on the measured values of static CA (explanation — see text)

of the liquid, absorption of the liquid by porous substrate (e.g. paper, building material) and other chemical or physical interactions occurring on the solid surface. Without considering all these effects the reproducibility of static CA measurements significantly decreases. The time dependence of static CA can be applied to evaluate time-dependent changes occurring on the solid surface, e.g. drying of paint or coating material, absorption of liquid by the substrate *etc.*

The other factor influencing the accuracy of static CA measurements is the volume of the drop which should give the drop base diameter in the range of 2–6 mm to ensure that CA is independent on the drop volume. In the case of very small droplets, CA is significantly influenced by the surface tension of the liquid, more spherical drops are formed, and thus CA values are overestimated. In the case of too large drops, gravity becomes the dominating factor and CA values are underestimated [3] (Fig. 2).

Recently, the accuracy of the optical measurements has been increased what gives precision rise as compared with common technique. For example, the drop

image is recorded by CCD-camera and digitalized by a video card, and the determination of CA is performed automatically by using a software for a drop shape analysis. Thus, precise user-independent values of CA can be obtained. However, surface free energy, characterizing the whole surface, cannot be calculated by using this method.

Nevertheless, the automatic measurement of the static CA has been applied as a quality control method for the production of printed circuits because CA at precisely chosen point of the surface can be measured.

Dynamic contact angle (DCA) measurement

The sessile drop method can also be applied for DCA measurements. In this case the needle of the syringe remains in the drop while the volume of the drop is increased at constant flow rate (Fig. 3). The drop advances over the solid surface and continuously wets new area of

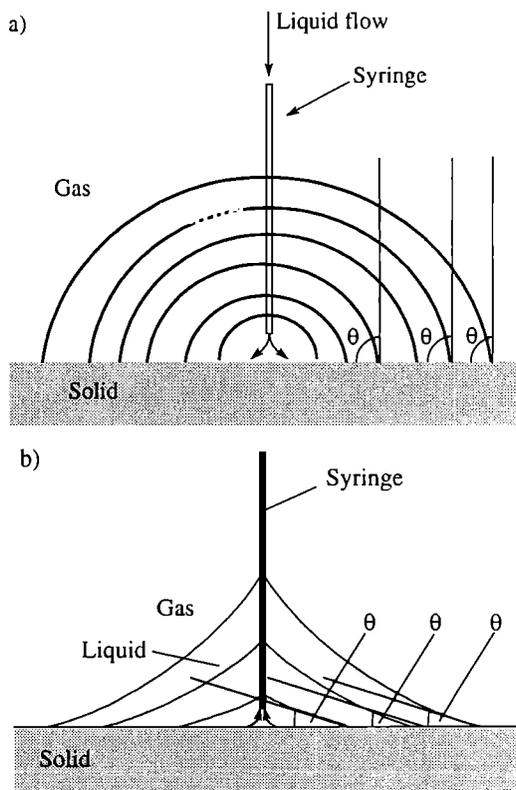


Fig. 3. Sessile drop method — dynamic CA measurement: (a) — advancing contact angle (ACA), (b) — receding contact angle (RCA) (explanation — see text)

the surface. As the drop advances the advancing contact angle (ACA) can be measured manually or automatically (Fig. 3a). To measure receding contact angle (RCA) the needle also remains in the drop and the drop recedes together with decreasing in the volume of the drop (Fig. 3b). RCA value is always lower as compared with ACA value. The difference between ACA and RCA values is

called *DCA* hysteresis and it is mostly resulted from the surface roughness of the solid.

Some disadvantages of this method should be noted that the results of *DCA* measurements, in particular *RCA* ones, obtained by using this method show a significant uncertainty. Moreover, the measured values provide the information on *DCA* in a single point of the surface, thus the whole surface is not characterized and *SFE* values characterizing the whole surface can not be calculated.

Wilhelmy method

Wilhelmy method is based on the measurements of the force which is needed to overcome the resistance of the liquid when the solid plate with known wetted length is immersed in or withdrawn from the liquid of

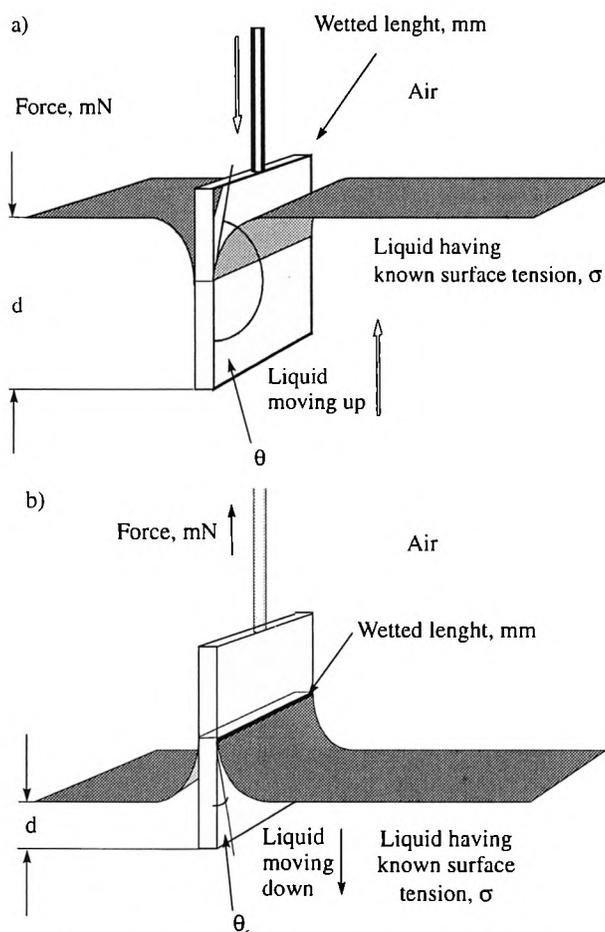


Fig. 4. Wilhelmy method: (a) — ACA; (b) — RCA [2] (explanation — see text)

known surface tension (Fig. 4) [2]. Contact angle (θ) is related to the surface tension of the liquid (σ) by Wilhelmy equation:

$$\sigma = \frac{F_w}{L \cos \theta} \quad (2)$$

where: F_w — Wilhelmy wetting force, L — wetted length.

The transformation of eq. (2) gives:

$$\theta = \arccos \frac{F_w}{\sigma \cdot L} \quad (3)$$

The values of all parameters in eq. (3), i.e. F_w , L and σ , should be measured.

The force (F) acting on the plate during immersion of the plate into the liquid depends on the immersion depth and its two components can be distinguished:

$$F = F_w + F_a \quad (4)$$

where: F_w — constant for given plate-liquid system, F_a — buoyancy force given by equation.

$$F_a = \rho \cdot g \cdot L \cdot d \quad (5)$$

where: ρ — liquid density, g — gravitation constant, d — immersion depth.

The average values of ACA and RCA are determined by extrapolation of the curve $F(d)$ to zero im-

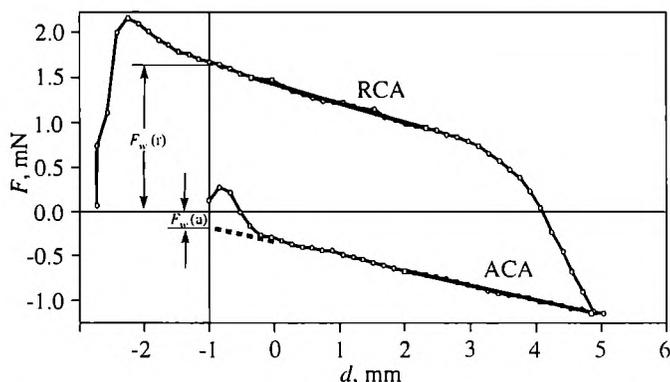


Fig. 5. Plot of the force (F) versus immersion depth (d) when plate is immersed into (ACA) or receded out (RCA) of a liquids; F_w — see eq. 4 (sample: stainless steel, liquid: water) [2]

mersion depth which sets the buoyancy term $F_a = 0$ giving $F = F_w$ (Fig. 5). The calculated values of CA represent an average CA for whole surface area, so the whole tested surface of the plate should be as homogeneous as possible.

A force measurement is often more precise than an optical angle observation, so the precision of the contact angle measurements by Wilhelmy method is higher as compared with the sessile drop method. The reproducibility of force measurements as high as ± 0.1 mN/m is often reported.

SURFACE FREE ENERGY CALCULATION

The values of *SFE* can be calculated based on *DCA* measurements. The selection of *SFE* calculation method is very important due to the existing limitations related to the energy range covered by the method.

The equation of Owens, Wendt, Rabel, Kaeble based on polar and dispersive interactions approach gives the best results for polar systems of low *SFE* [4]. The equation of Wu based on the harmonic mean gives sufficiently accurate results for low energy systems like organic solutions, water soluble polymers and organic pigments.

Surface and interfacial tensions result from an irreversible change of free energy (G_{ls}) on the unit of newly formed interface surface [4] according to the equation:

$$G_{ls} = \sigma_{ls} - \sigma_s - \sigma_{lv} \quad (6)$$

It should be noted that $G_{ls} = -W_A$ (W_A — thermodynamic work of adhesion).

CRITICAL SURFACE TENSION

Fox and Zisman [5] developed the method of determination of critical surface tension (*CST*) of solids based on plotting $\cos \theta$ as a linear function of σ_{lv} for homologous series of liquids of low differences in polarity. *CST* of solid denoted as σ_k , is a value corresponding to σ_{lv} if a solid surface is ideally wetted by a liquid *i.e.* at the contact angle equals to zero. The value of σ_k is determined from the plot of $\cos \theta = f(\sigma_{lv})$ as *CST* value for $\cos \theta = 1$. Although the precision of the method is sufficiently high, the application of this method is limited in the information it provides, because there is no splitting into polar and dispersive parts.

CONTACT ANGLE HYSTERESIS

The difference between the *ACA* and *RCA* values, mentioned before as *DCA* hysteresis, occurs in each measurement [6]. The ideal state, *i.e.* $ACA = RCA$, is possible if the solid surface is ideally smooth, chemically homogenous and the measurement is carried out sufficiently slowly to achieve the equilibrium of all surfaces. The *DCA* hysteresis measurement provides the information on the structure of the surface. Johnson and Dettre [7] studied rough surfaces and they defined the roughness factor (r) as the ratio of the $\cos \theta$ value of real surface and that of ideal one:

$$r = \frac{\cos \theta}{\cos \theta_i} \quad (7)$$

where: θ , θ_i — contact angles of real surface and ideal one, respectively.

The rough surfaces which cannot be totally penetrated by a liquid ($\theta > 90^\circ$) form so called composite surface, in which air is occluded on the surface irregularities leading to the local strains. In such case the dependence between θ_i and θ is different from the ratio described by equation (7) and a more complex equation should be applied [8, 9].

DCA hysteresis can result also from chemical heterogeneity of the surface, even for smooth surfaces. High

DCA hysteresis always occurs for block copolymers containing blocks of distinct differences in *SFE*. Moreover, homopolymers such as PTFE, PVC, PMMA also may have heterogeneous surfaces where the low *SFE* component is the polymer while the residues of catalyst or initiator build in during polymerization can act as high *SFE* components.

The model of heterogeneous surfaces, analogous to the model of rough surfaces was elaborated by authors of [7]. Other morphological and chemical differences in the surface structure due to the orientation of polymers [10, 11], as well as migration of polymer components, especially low molecular ones, to the surface can be estimated by *CA* measurements [12].

SELECTION OF LIQUIDS FOR THE INVESTIGATIONS OF WETTABILITY

Very important factor highly influencing the quality of *CA* measurements is the proper selection of applied liquids which should be selected according to the applied measuring method. The application of mixtures of liquids or liquids containing impurities should be avoided for each method of measurements. The composition of such liquids can be changed due to the differences in the vapour pressure of particular components and then very quick changes of *CA* values can be observed [13, 14]. Moreover, in the case of mixture of liquids, the differences in absorption of the components of the mixture at the interfacial surface influence *CA* values [3].

Of course, the solid surface cannot be dissolved or swollen by the applied liquid because in this case *CA* value can also be changed. If the measured *CA* values are used to calculate *SFE*, the liquid should be selected according to the requirements of the calculation method. For calculation of *SFE* by Owens and co-workers method or Wu method, liquids of known values of disperse and polar parts of the surface tension have to be applied. For *CST* determination the series of liquids of small differences in polarity should be selected. Generally, these liquids should belong to the following groups:

- non-polar liquids, *e.g.* homologous series of *n*-alkanes or di-*n*-alkylesters,
- polar liquids without hydrogen bonds such as halogenated hydrocarbons or esters,
- polar liquids able to form hydrogen bonds, *e.g.* water, glycerine.

The crucial requirement for the selection of liquids is contact angle $\theta \neq 0$. The *n*-alkanes can be applied only for characterization of low *SFE* polymer surfaces, *e.g.* fluoropolymers, while they are unsuitable for characterization of high *SFE* surfaces, such as PVC and PET [15].

PRACTICAL APPLICATION OF CA MEASUREMENTS

The results of dynamic contact angle measurements were applied to the optimization of the formulations of

coating materials based on polysiloxane/polytetrafluoroethylene (SIL/PTFE) system with excellent hydrophobic and antigraffiti properties [16]. The wettability of SIL/PTFE surface, measured by DCA and SFE , decreases in general, if PTFE content increases. The increase in ACA values from *ca.* 93° for SIL/PTFE system containing less than about 20 wt. % PTFE to *ca.* 115° for the system containing over 35 wt. % of PTFE is accompa-

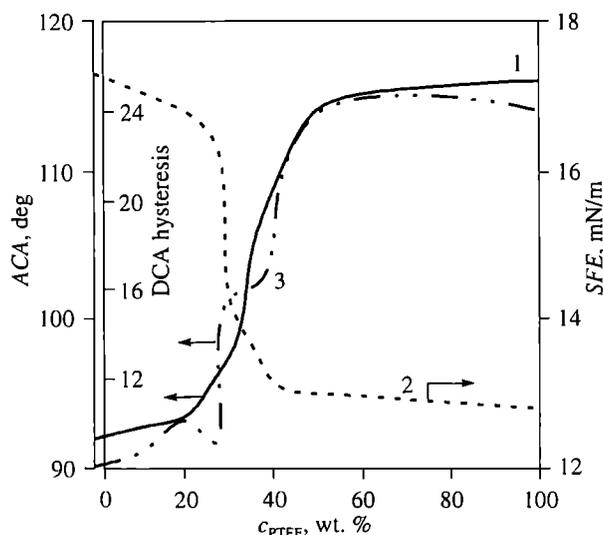


Fig. 6. SIL/PTFE system — the effect of PTFE content (c_{PTFE}) on ACA (1), SFE_{total} (2) and DCA hysteresis (3) values (own results)

nied by the decrease in SFE values from *ca.* 17 mN/m to *ca.* 13 mN/m, respectively (Fig. 6, curves 1 and 2).

Moreover, an increase in DCA hysteresis with increasing PTFE content was also observed in general, and it indicates an increase in surface roughness. However,

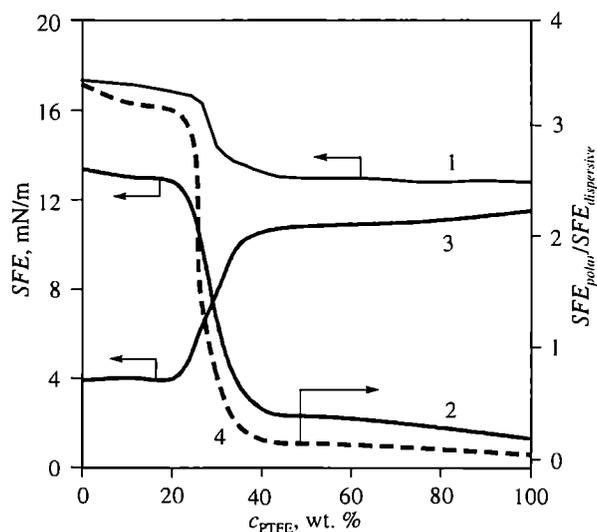


Fig. 7. SIL/PTFE system — the effect of PTFE content (c_{PTFE}) on SFE_{total} (1), SFE_{polar} (2) and $SFE_{dispersive}$ (3) values, and on $SFE_{polar}/SFE_{dispersive}$ ratio (4) (own results)

an inflexion of the hysteresis curve was observed for PTFE content about 20 wt. % and the decrease in hysteresis values in the range of 20–30 wt. % of PTFE. It indicates that the minimum of roughness exists in this range of PTFE content (Fig. 6, curve 3).

The most significant effect is the change in the type of interactions from polar ones (Fig. 7, curve 2) for PTFE content below 20 wt. % to dispersive ones (Fig. 7, curve 3) for PTFE content over 35 wt. %. Thus, the ratio of $SFE_{polar}/SFE_{dispersive}$ decreased rapidly in the region of 25–35 wt. % of PTFE (Fig. 7, curve 4). These results were in good correlation with application tests which indicated very good antigraffiti properties in the region of 20–30 wt. % of PTFE.

FINAL REMARKS

— Methods of CA measurements are useful tools for precise determination of wettability of polymer surfaces. Especially, the precision of the contact angle measurements by Wilhelmy method is higher as compared with the sessile drop method. A force measurement is often more precise than an optical angle observation and the reproducibility of force measurements as high as ± 0.1 mN/m is often reported.

— Higher precision and reproducibility of CA measurements can be reached by using computer-aided apparatus. Recently, the accuracy of the optical measurements has been increased what gives precision rise as compared with common technique. For example, the drop image is recorded by CCD-camera and digitalized by a video card, and the determination of CA is performed automatically by using a software for a drop shape analysis. Thus, precise user-independent values of CA can be obtained.

— The careful selection of the method of CA measurement is a crucial factor influencing the possibility of practical application of the results of wettability measurements for the optimization of polymeric coating materials. Based on these measurements many problems related to the quality of polymeric coatings can be solved and new materials improving quality of life can be developed.

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