

## Determination of contact angle hysteresis of water microdroplets evaporating on hydrolyzed PET foils

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*Moderately hydrophobic surfaces of PET foils were gradually hydrophilized by their immersion in NaOH solutions of increasing concentration. Then, the contact angle and geometric factors of microliter water drops, deposited on these polymer surfaces, were automatically monitored as a function of evaporation time. Three stages have been identified from the evaporation course of water droplets, allowing us to determine the advancing and receding contact angle and thus their difference (hysteresis).*

**Key words:** contact angle, contact angle hysteresis, drop dimension, evaporation, wetting

### Introduction

Modification of solid surfaces is a very active field of research. On changing the surface composition, we obtain materials with new surface properties (Semal et al., 1999). One of the basic experiments for gathering information about surface properties of a material is a measurement of the angle between the tangent of liquid drops, raised in the three-phase (triple) line (see the next paragraph), and the solid surface on which the drop is rested. This so-called contact angle of water drops allows a simple and yet effective evaluation of the hydrophobicity especially of a low-energy surface of polymers and is an important parameter in wet processing of solid substrates (Chau et al., 2009; Extrand and Kumagai, 1997; Shanahan and Bourges, 1994).

In principle, a pure liquid on an ideal (flat, homogenous, isotropic, smooth and rigid) solid in the presence of a given environment should give a unique value of equilibrium contact angle  $\theta_e$ , as determined by Young's equation:

$$\gamma_{SV} = \gamma_{SL} + \gamma_{LV} \cos \theta_e \quad (1)$$

where  $\gamma$  represents (constant) tensions with suffixes defining the interface between the pertinent solid (S), liquid (L) and gaseous or vapor phase (V). However in practice, it is rare for such a unique value of  $\theta_e$  to be observed (Shanahan and Bourges, 1994). The problem is that most real surfaces of solids are non-ideal in many respects (roughness, heterogeneity, dissolution, etc.) and drops evaporate. Moreover, many different techniques are adopted, providing different angles even for the same system of phases.

In general, the contact angle values, measured traditionally by a mechanical changing of the drop volume until its three line starts to move, fall into a more or less wide interval between the so-called advancing  $\theta_a$  and the receding  $\theta_r$  contact angle. The difference between them is called the contact angle hysteresis (CAH) (Chau et al., 2009; Erbil et al., 1999).

$$\Delta\theta = \theta_a - \theta_r \quad (2)$$

The interest in CAH is stipulated by the fact that it governs the wetting properties of the solid surface to a large extent (Bormashenko et al., 2008). Indeed, several sources of wetting hysteresis are recognized, of which the major ones are considered to be either chemical (chemical attack, inhomogeneity of chemical compositions of the solid surface, swelling, dissolution, to name a few of them) or physical (surface roughness, local adsorption, molecular orientation, solid strain near the triple line, etc.)

As already mentioned, there also is the mass transfer due to evaporation of the liquid. A contact angle initially imposed in the advancing mode will diminish and tend towards a receding value when the liquid constituting the meniscus starts to evaporate. Unless the atmosphere in the immediate vicinity of the drop is saturated in the vapour of the liquid, this transfer is inevitable and experiments conducted in non-equilibrium conditions may give erroneous values for  $\theta_a$ . Although fairly obvious, this complication in contact angle measurement would seem to have been largely neglected (Shanahan and Bourges, 1994; Monnier and Shanahan, 1995).

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On the other hand, the evaporation phenomenon may serve as an alternative method of determining the contact angle hysteresis since both the advancing and receding contact angles can be identified when the drop is deposited and the contact line starts to shift on the surface, respectively. Thus, in order to find as precise as possible values of contact angles both the experimental techniques (mechanical and evaporational) should be compared. Moreover, a specific role of at least some of these factors can be identified by comparing results of the two techniques. The purpose of this contribution is therefore to measure the time development of contact angle and related dimensions (contact diameter and height) of water droplets evaporating on the PET surfaces, preliminarily hydrophilized by their treatment in increasingly concentrated NaOH solution for 30 minutes at 20 °C. The corresponding changes in the morphology and surface roughness of these foils determined by atomic force microscopy AFM and SEM are presented elsewhere (Škvarla et al., 2010).

## Experimental

### Samples pretreatment

Samples of PET foils cut from post-consumer plastic bottles were used. The foil samples with the size of ca. 50×50 mm and without any preliminary cleaning procedure were immersed in a series of aqueous sodium hydroxide solutions with concentration of 0, 2, 4 and 6 wt % NaOH at the temperatures of 20 °C and stirred continuously for the period of 20 minutes. The NaOH-treated samples were taken out of the bath, rinsed with a large amount of distilled water to remove the remaining NaOH and air dried at 35 °C.

### Contact angle goniometry

Water microdroplets with the volume ~4 µl to ~10 µl were deposited on the pretreated PET foil surfaces by a microsyringe in the moist air surrounding and at the ambient temperature. The shape and geometric parameters (contact angle  $\theta$ , base diameter  $d$  and height  $h$ ) of these drops were automatically determined from their digitized images every 10 seconds from putting the drops down to the surfaces by the Krüss EasyDrop Contact Angle Measuring System with the Drop Shape Analysis (DSA1) software. The total evaporation time varied, depending on the volume of drops and the PET pretreatment, ranged from ca. 300 to 900 seconds.

## Results and discussion

Initially, the contact angle of the water drop on the PET surface pretreated in distilled water was found to continuously decrease from the initial value of 78° with increasing evaporation time while its base diameter stayed constant (Fig. 1a). This is, apparently, the “pinned” stage of evaporation of drops, i.e. the constant contact area mode. Subsequently, the contact angle stops to decrease after the elapse of 300 seconds, just when the base diameter starts to diminish. We ascribe this to the beginning of the constant contact angle mode of drops shrinking toward their centre (“unpinned” stage) and consider the contact angle ( $\approx 54.5^\circ$ ) as the receding one. Interestingly, a few steps can be identified one after the other on the base diameter-vs-time dependence, reflecting repeated contractions of the drop interrupted by short pauses. Consequently, steps of contact angle are observable in parallel with these in the contact diameter, accompanied with an overall decline in the contact angle during the constant contact angle mode lasting between 300 and 850 s. A similar phenomenon has also been noticed by Kim et al. (2007) for water droplets with the initial weight smaller than ca. 5 mg, evaporating on smooth hydrophobic PAMS polymer films (0.3 to 0.4 nm rms roughness). In fact, in their experiment the contact angle was not detected to fall down through out the whole constant angle mode only if a biggest drop was used. It is important to emphasize however that the contact angle values of all the drops diverged, irrespective of their size, from an unique (a “true” receding) value at the beginning of the mode. It should also be mentioned that contractions and the corresponding step by step decrease in the contact angle of n-decane drops on PTFE from the value of ca. only 36° have been attributed to the surface roughness (not specified) of the hydrophobic polymer rather than to the droplet size by Bourges-Monnier and Shanahan (1995). Nevertheless, no such effects were observed in their study when following water drops on polished but still quite rough epoxy surface ( $R_a = 0.1$  mm) during the constant contact angle mode and the latter mode was even absent on a very rough epoxy surface ( $R_a = 1.4$  mm). This fact excludes the role of surface roughness as a possible reason of the step-like character of the constant contact angle mode of the evaporation process of water drops deposited on hydrophobic surfaces. Finally, the drop on the untreated PET surface started to vanish after 850 seconds, as documented by the abrupt decrease in the base diameter of the drop.

On PET previously treated in 2 % NaOH solution, the contact angle varies with time in a similar way as the PET immersed in water only but the receding contact angle at the beginning of the drop shrinkage

( $\approx 46.0^\circ$ ) is lower and proceeds to decline with a lower rate. Also, the drop vanishes earlier, i.e. after 550 seconds. For more hydrophilic PET pretreated in 4 % NaOH, a shrinkage point of the water drop is even less pronounced but it can still be identified at 160 – 180 seconds from which time the receding contact angle seems to diminish slowly. Unfortunately, no pinning is detectable for PET pretreated in 6 % NaOH solution so that the receding contact angle could not be determined.

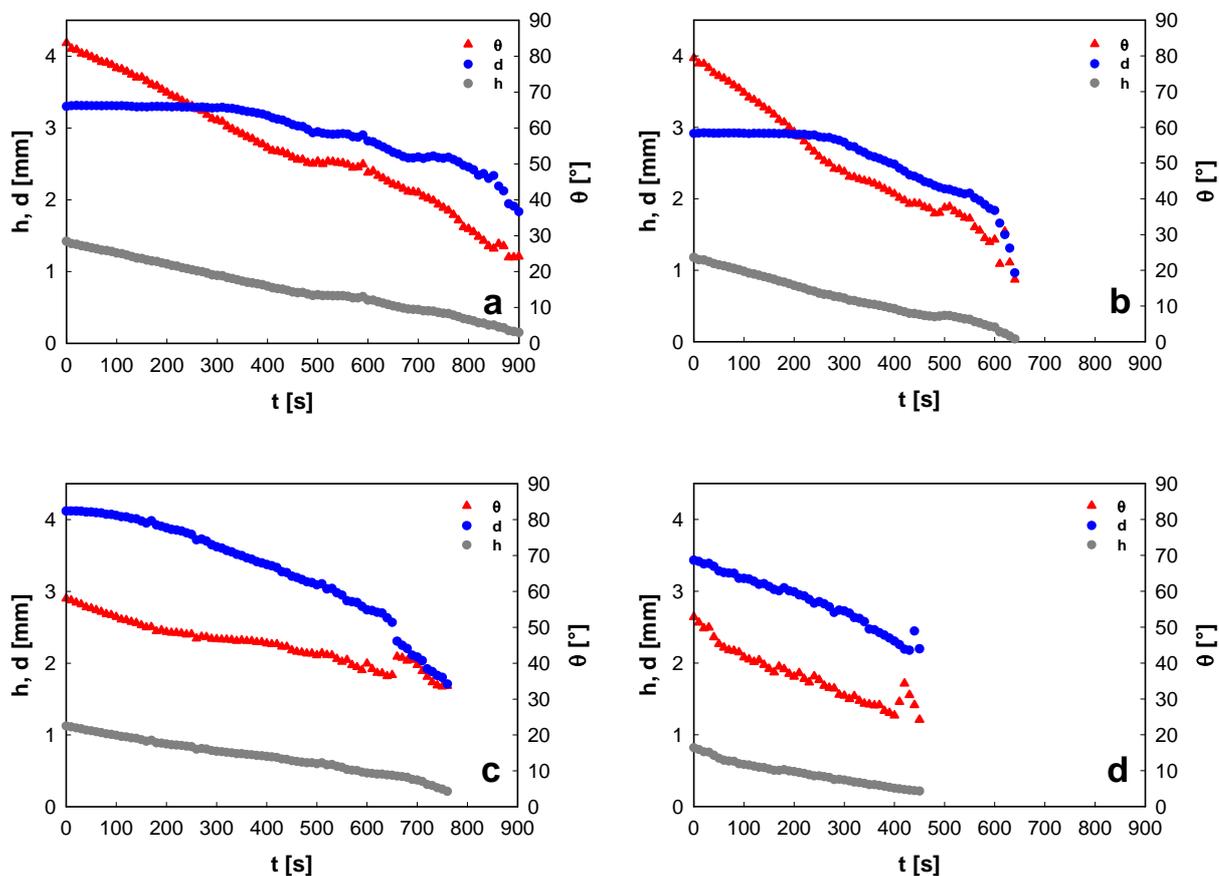


Fig. 1. Time evolution of contact angle ( $\theta$ ), base diameter ( $d$ ) and height ( $h$ ) of selected water droplets on PET foils pretreated in distilled water (a), 2 % (b), 4 % (c) and 6 % (d) NaOH solution at 20 °C (see the legend inserted).

## Conclusions

In general, sessile drops of water deposited on the solid surface of PET foils exhibit an initial contact angle only for a short period of time in open air at ambient temperature. The value of such an advancing contact angle decreases proportionally with concentration of the pretreatment NaOH of partially hydrophobic PET surfaces making them increasingly hydrophilic. During the evaporation of water droplets, three basic stages can be detected. Initially, the contact angle decreases while contact diameter remains almost constant (stage I). In the stage II, the contact diameter diminishes but the contact angle stays approximately constant or decreases mildly, providing a small plateau at which the receding contact angle can be determined. In the stage III the contact diameter as well as the contact angle start to decline and the drop disappears rather abruptly.

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