



INFLUENCE OF EVAPORATION ON CONTACT ANGLES ON HYDROLYZED PET FOILS

ABSTRACT:

This contribution presents results from measuring contact angles on moderately hydrolyzed PET foils immersed in sodium hydroxide solutions of concentration 0% (distilled water), 2%, 4% and 6% at temperatures 20°C and 40°C. Contact angles and geometric parameters on these substrates were monitored as a function of evaporation time. After the evaporation course, four elementary stages have been evaluated, that allow determining advancing and receding contact angles and wetting behavior of these substrates.

KEYWORDS:

contact angle, contact angle hysteresis, drop dimension, evaporation, wetting

INTRODUCTION

Modification of solid surfaces is a very active field of research. By changing the surface composition we obtain a material with new surface properties [Semal et al., 1999].

One of the basic experiments for gathering information about surface properties of PET is the measurement of contact angles of water drops on it. The contact angles allow a simple and yet effective evaluation of the hydrophobicity of a low-energy surface such as polymers and are an important parameter in wet processing of solid substrates [Chau et al., 2009; Extrand and Kumagai, 1997]. Therefore the evaluation of contact angles θ of water on solid surfaces plays an important role in surface characterization [Shanahan and Bourgés, 1994].

In principle, a given 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 θ_e as determined by Young's equation (Eq. 1):

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

where γ represents the interfacial (or surface) tension and the suffixes define the interface. However in practice, it is rare for such a unique value of θ_e to be observed [Shanahan and Bourgés, 1994]. A surface which meets all the requirements of the Young's equation is referred to as an ideal surface. However, most practical surfaces are non-ideal and the measurable contact angle values on such surfaces are referred to as the apparent contact angle θ_{ap} . As a consequence this value is not unique but falls into a

more or less wide interval between the advancing θ_a and the receding θ_r contact angle. The difference between them is called contact angle hysteresis (CAH) (Eq. 2) [Chau et al., 2009].

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

Hysteresis of contact angle is due to deviations of surface from ideal conditions [Erbil et al., 1999]. Interest in CAH is stipulated by the fact that CAH 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, etc.) or physical (surface roughness, local adsorption, molecular orientation, solid strain near the triple line, etc.)

Analogous effects may also be observed when there is 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 forming the meniscus starts to evaporate. Unless the atmosphere in the immediate vicinity of the drop is saturated in the vapor of the liquid, this transfer is inevitable and experiments conducted in non-equilibrium conditions may give erroneous values for θ_a . Although this complication is fairly obvious this complication in contact angle measurement, it seems to have been largely neglected [Shanahan and Bourgés, 1994; Monnier and Shanahan, 1995].

It is therefore important to evaluate relationship between contact angles (advancing and receding) and its variations during evaporation. Whole evaporation

simulates the conditions of advancing contact angle formation in initial phase and then slowly leads to formation of the receding contact angle when contact line is ruptured. The purpose of this contribution is therefore to examine behavior of sessile drop of water on hydrolyzed PET foils in mildest condition during the evaporation. It involves observation values of the contact angle and related changes of drop dimensions: contact diameter d and drop height h as a function of time t . Water drops were placed on different pretreated PET foils that simulate in this case surface roughness.

The morphology and surface roughness of these foils were evaluated by atomic force microscopy (AFM and SEM). Subsequently relationship between surface wettability (contact angles) and related changes of surface tension were evaluated. Results of surface roughness, wettability and changes in surface tension of these pretreated surfaces are presented elsewhere [Škarla 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 temperatures 20 and 40 °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. The PET samples will be in the next text referred to as for example PET4/20 or PET2/40, meaning the PET surface pre-treated in 4 % NaOH at 20 °C or in 2 % NaOH at 40 °C, respectively.

Contact angle goniometry. A sessile drop technique was used to measure the static contact angles of small water drops on the pretreated PET foil samples in air at ambient temperature. All of the measurements were carried out by the Krüss EasyDrop Contact Angle Measuring System, allowing the determination of shape and size of measured drops from their images. The evaluation of digitized video images and the calculation of contact angles were made with the Drop Shape Analysis (DSA1) software. The resulting contact angle values were obtained as averages of both left and right side contact angle of liquid drop every 10 second as well as drop dimensions. Evaporating time varying (from 420 s to 900 s) depending on volume of water drops (from ~4 μl to ~10 μl) and PET sample pretreatment. Drops were deposited on the substrate using microsyringe. During the experiment changes of sizes of contact angles θ and drop dimensions were monitored: contact diameter d and drop height h as a function of time t .

RESULTS AND DISCUSSION

Typically, the evolution of a sessile drop deposited on a polymer surface demonstrated four distinct stages. In stage I, contact diameter d remained almost

constant in Fig. 1a, b and 2a, b and contact diameter d diminished and variable more rapidly at higher grade pretreatment (Fig. 1c, d and 2c, d). Drop height h diminished slightly and contact angle θ diminished quite markedly at all pretreatments. Initial contact angle θ_0 decreased simultaneously with pretreatment (from ~ 84° to ~ 53°) at 20 °C and (from ~ 82° to ~ 45°) at 40 °C.

In stage II contact diameter d , drop height h and contact angle θ decreased more rapidly than in stage I. In stage III was observed that both drop height h and contact diameter d diminished roughly in proportion, so that the contact angle stayed approximately constant (small plateau in Fig. 1a, b, c, d and 2 a). It is of interest to note that stage III was found to be totally absent at higher pretreatment at 40 °C (Fig. 2b, c, d). Values of contact angle at aforementioned small plateaus in Fig. 1a, b, c, d and 2a may be taken effectively as a receding contact angle θ_r .

Stage IV corresponds to the final disappearance of the sessile drop. It was found to be exceedingly difficult to follow this stage, both the actual size of the sessile drops and the values of its contact angles being very small. Towards the end, θ tends to zero and, as a consequence its value is well below that corresponding to a classic receding contact angle θ_r . Stage IV is poorly understood and is probably influenced by anchoring effect of the triple line on surface heterogeneities. Differences of drop dimensions and contact angles on all of the examined samples in stage IV are caused by surface roughness induced by NaOH pretreatment, imbibitions of water into the pores and crevices of the surface or interactions between water and polar molecules.

For better visualization Fig.3 show dependences of the normalized contact angle θ^* on the normalized time t^* grouped together for triplets of water droplets evaporating on the PET surface pretreated in distilled water (a), 2% (b), 4% (c) a 6 % NaOH (d) at temperature of 20 °C. Analogous dependences for PET surfaces pretreated at 40 °C are presented in Fig.4. We can see immediately that the character of both dependences is changing when the polarity or hydrophilicity of the surfaces rendered by the hydrolysis increase (in the order a to d), irrespective of the size of drops. Normalized values of contact angles and time were calculated according to relationships (Eq.3):

$$\theta^* = \frac{\theta_t}{\theta_i}, \quad t^* = \frac{t}{t_f} \quad (3)$$

The normalized contact angle is defined as the ratio between the contact angle at time t θ_t and the contact angle at initial time θ_i . The normalized time is defined by the ratio between the time of each measurement t and the final time, when the drop has completely disappeared t_f [Cioulachtjian et al., 2010].

Analogous dependences of drops volume V on time t during evaporation on the PET surface pretreated in distilled water, 2 %, 4 % and 6 % NaOH at 20 °C (a) and at 40 °C (b) are presented in Fig.5, irrespective of the size of drops. Volumes of drops were calculated from Eq.4:

$$V = \frac{\pi R^3}{3} \left(\frac{2 - 3 \cos \theta + \cos^3 \theta}{\sin^3 \theta} \right) \approx \frac{\pi h}{6} (h^2 + 3R^2) \quad (4)$$

where R is contact radius, θ is contact angle and h is height of drop.

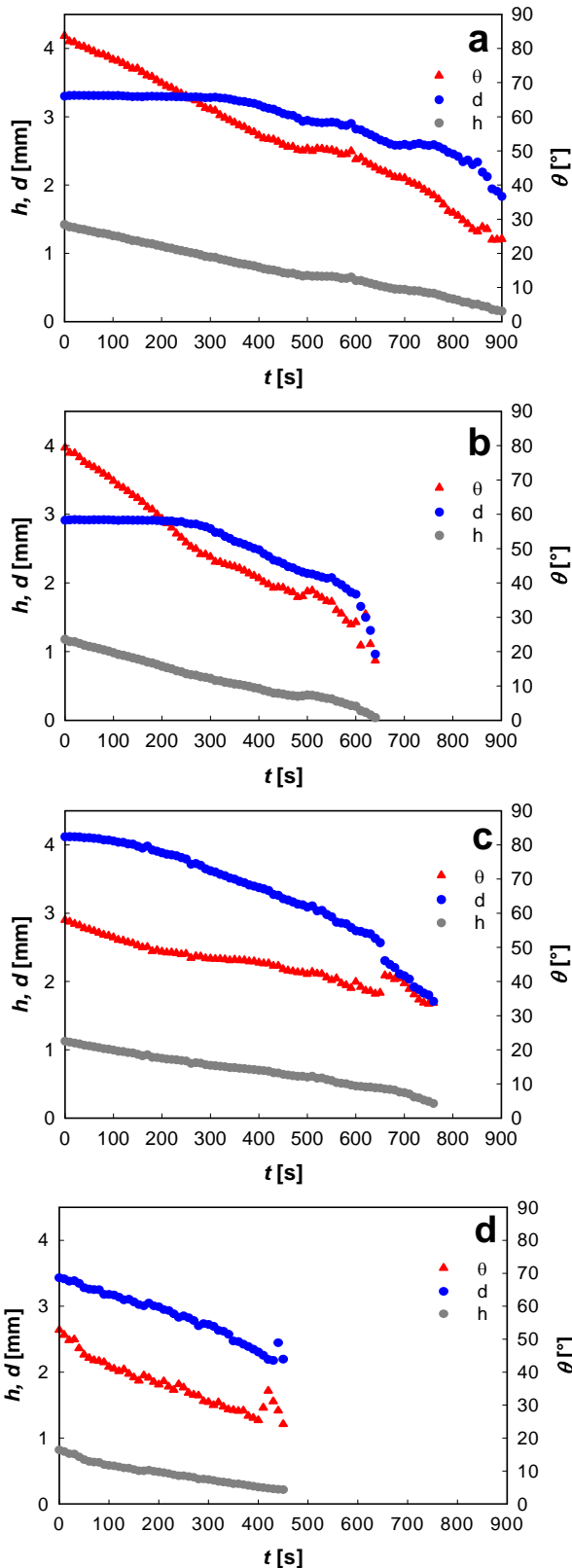


Figure 1. Contact angle (θ), contact diameter (d) and drop height (h) as a function of time (t) at 20 °C. Sample pretreatment: PET0/20 (a), PET2/20 (b), PET4/20 (c) and PET6/20 (d).

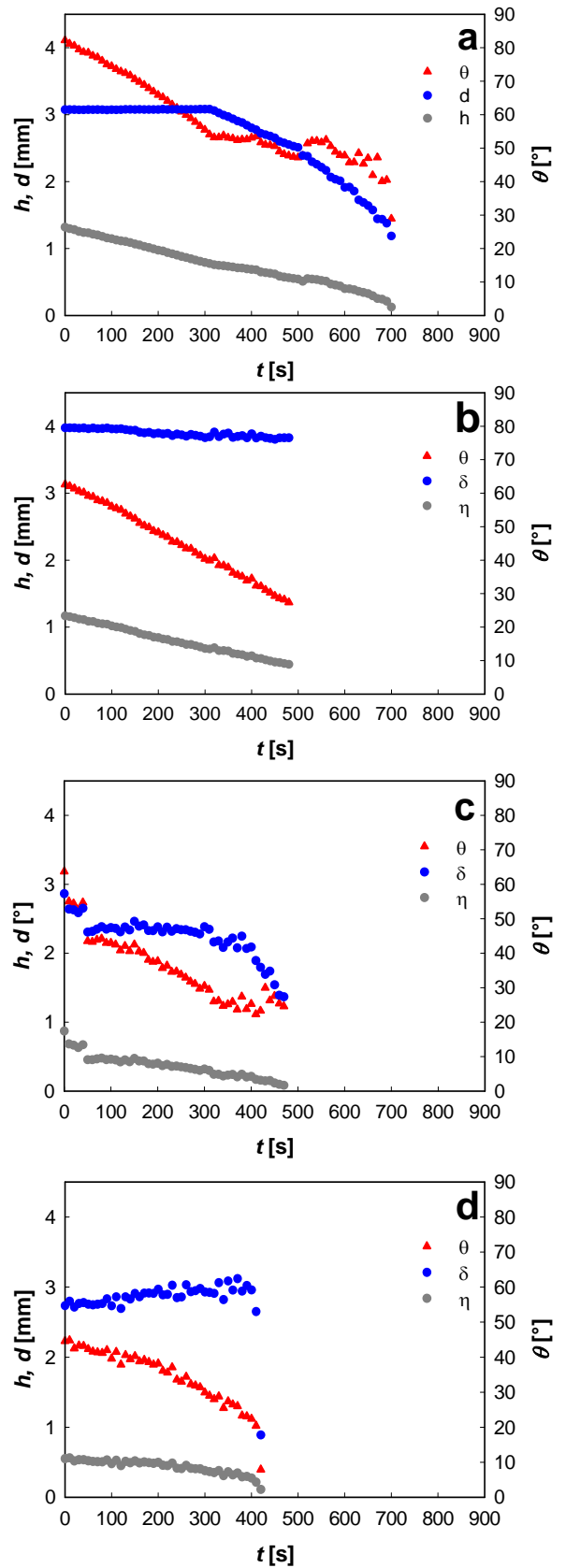


Figure 2. Contact angle (θ), contact diameter (d) and drop height (h) as a function of time (t) at 40 °C. Sample pretreatment: PET0/40 (a), PET2/40 (b), PET4/40 (c) and PET6/40 (d).

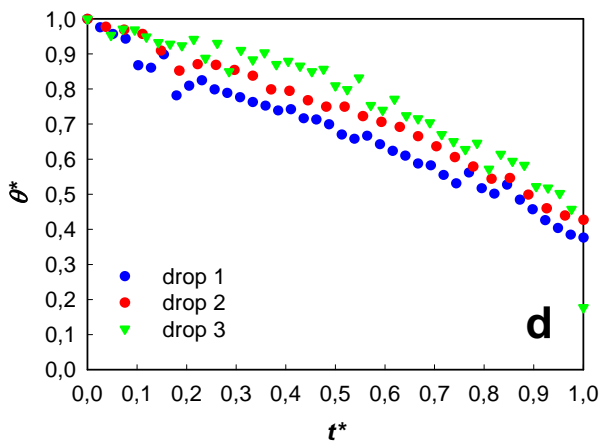
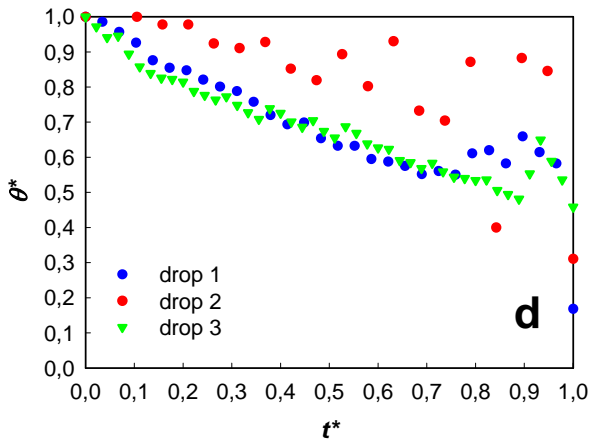
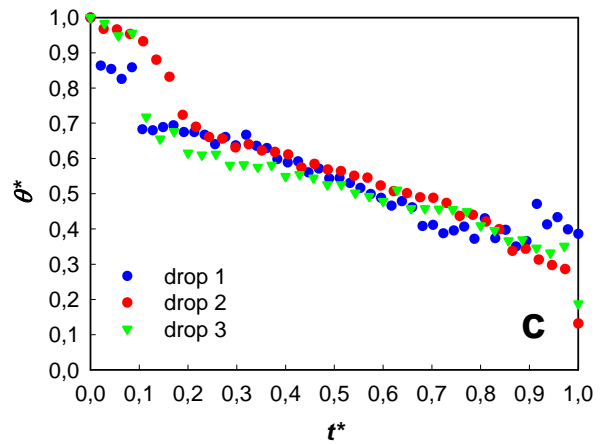
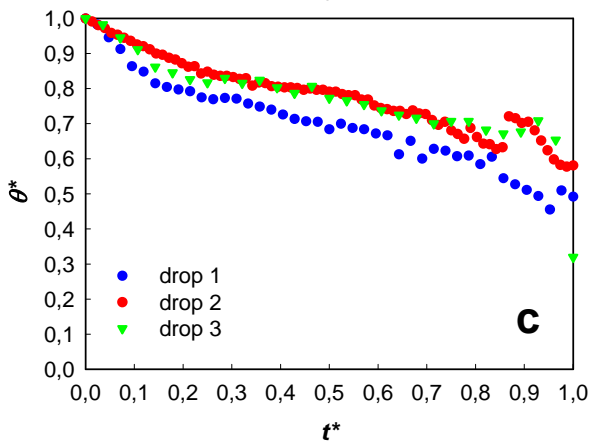
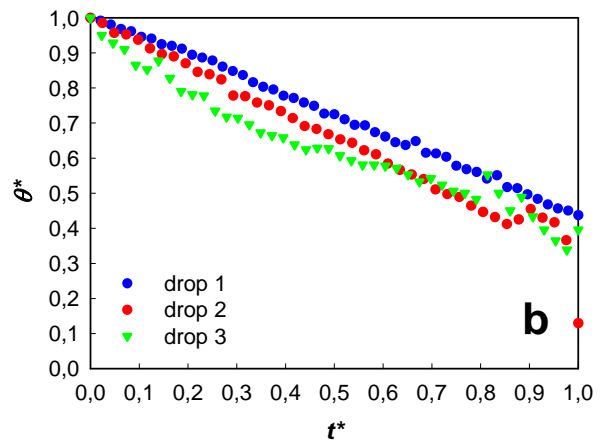
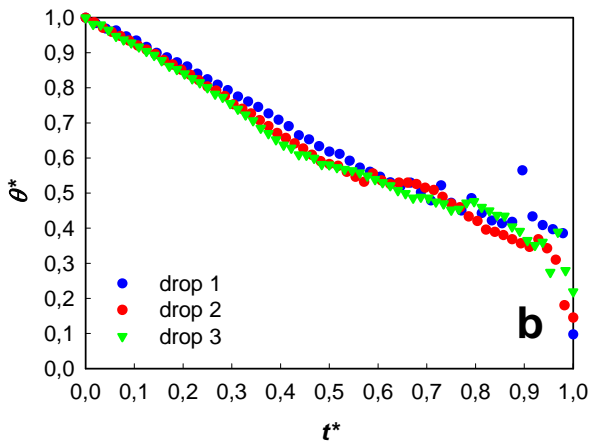
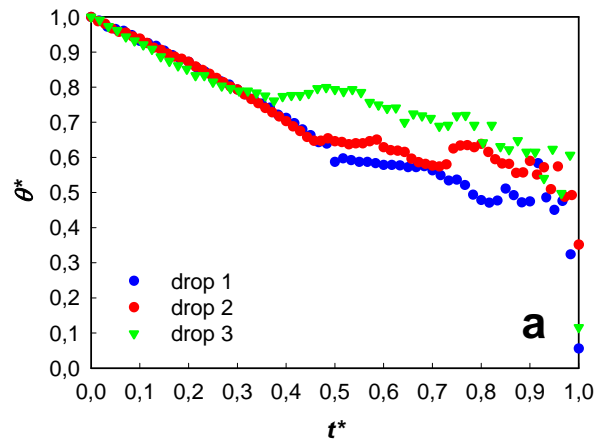
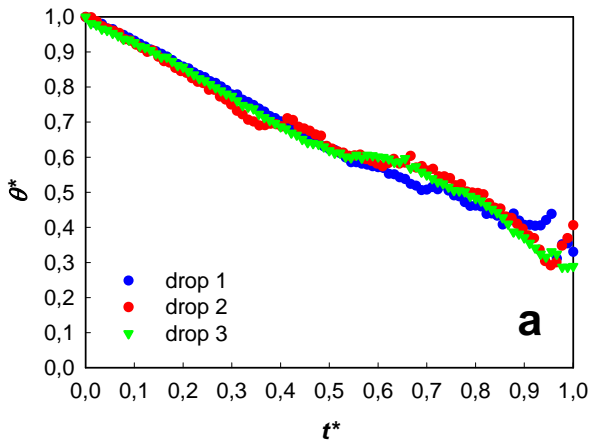


Figure 3. Dependence of the normalized contact angle on the normalized time of water droplets evaporating on the PET surface pretreated in distilled water (a), and 2 % (b), 4 % (c) and 6 % (d) NaOH solutions at 20 °C.

Figure 4. Dependence of the normalized contact angle on the normalized time of water droplets evaporating on the PET surface pretreated in distilled water (a), and 2 % (b), 4 % (c) and 6 % (d) NaOH solutions at 40 °C.

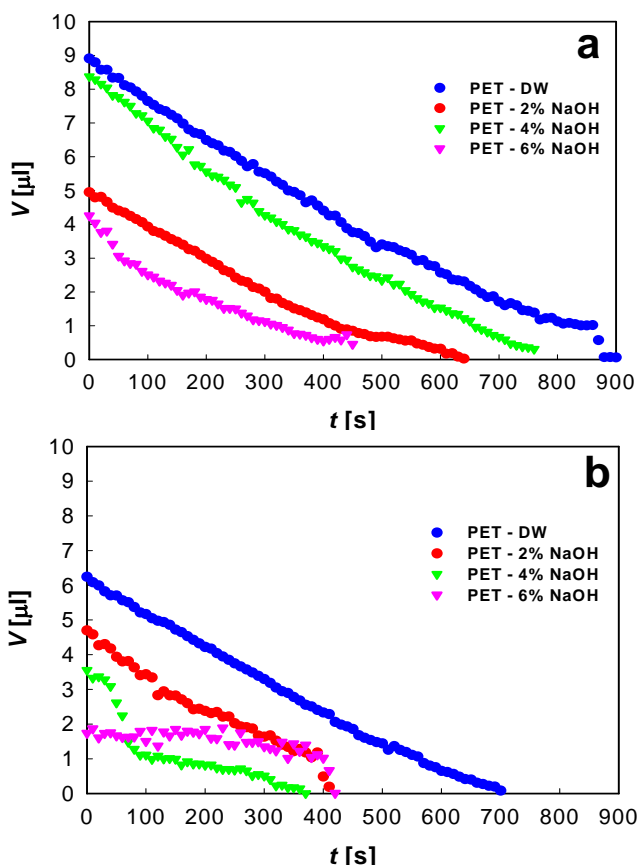


Figure 5. Dependence of the volume of water droplets on the PET surface pretreated in distilled water, 2% NaOH, 4% NaOH and 6% NaOH solutions at 20 °C (a) and at 40 °C (b).

CONCLUSION

Sessile drops of water deposited on a solid surface of PET foils present an advancing contact angle only for a short period in air at ambient temperature. Initial contact angles decrease proportionally with pretreatment of PET samples as well as in course of evaporation when liquid evaporates from drop meniscus. During evaporation four basic stages were observed. Initially, drop height and contact angle decrease while contact diameter remains almost constant. Modest discrepancies of contact diameter we can see at higher grade of pretreatment (PET4/20, PET6/20 and PET4/40, PET 6/40).

Values of contact angles are between the initial advancing values and a receding contact angle; lower than the classic receding angle measured on equally pretreated PET foils (result not shown here) obtained by mechanical retraction of triple line.

The reasons for these lower values of receding contact angle are not absolutely clear, but it may be related to the fact that evaporation alone reduces the contact angle.

In stage III was observed that both drop height and contact diameter diminished roughly in proportion, so that the contact angle stayed approximately constant and produced small plateau (initial values of receding contact angles). Stage III is absolutely absent at higher pretreated PET samples.

Finally, the drop disappears and drop dimensions and contact angles tending to zero. This stage is very difficult clarify experimentally because it is probably caused by surface roughness of PET surface derivable from NaOH pretreatment (incipient alkaline hydrolysis) and other reactions taking place at PET surface (swelling, dissolution etc.).

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