

HYSTERETIC BEHAVIOUR OF STATIC AND DYNAMIC CONTACT ANGLES ON VARIOUS POLYMER SURFACES: A COMPARATIVE STUDY

Ramon Pericet-Camara*, Carmen L. Moraila-Martínez, Miguel A. Rodríguez-Valverde, Miguel Cabrerizo-Vilchez

Biocolloid and Fluid Physics Group, University of Granada

Facultad de Ciencias – Campus Fuentenueva, Av. Severo Ochoa s/n, 18071 Granada, Spain

rpericet@ugr.es

INTRODUCTION

The understanding of wetting phenomena is a crucial subject in surface science nowadays. Much effort is made not only to comprehend still unclear fundamental aspects, but also in its numerous industrial applications such as irrigation, paints, ink spreading, coatings or oil extraction¹. The wettability of a surface is best described by its macroscopic contact angle θ , which is the angle between the baseline of a sessile droplet of a defined liquid sitting on the solid and the tangent to the liquid-solid interface at the three-phase contact line (TPCL). This angle is the result of the counterbalance at the TPCL of the interfacial energies at solid-liquid γ_{SL} , liquid-vapor γ_{LV} , and solid-vapor γ_{SV} boundaries expressed in the Young's equation for an ideal surface:

$$\cos \theta = \frac{\gamma_{SV} - \gamma_{SL}}{\gamma_{LV}} \quad (1)$$

where θ_Y is called the Young's angle. However, real surfaces present features that are not taken into account in this expression, and impede the access to the Young's angle by experimental means². Facets of real surfaces such as chemical heterogeneity, roughness or softness can provoke the arise of contact angle hysteresis between an advancing or a receding wetting front. Thus, other experimental parameters such as the equilibrium contact angle θ_e , or the advancing θ_A and receding θ_R contact angles, are used in order to characterize the wettability of

real surfaces². θ_A and θ_R represent the contact angles of an imminently moving wetting or dewetting front respectively, and are considered to be the maximum and minimum experimental contact angles of real surfaces. Measured contact angles lie in this range as a result of a series of possible metastates of the system².

In this framework, a group of experimental methods can be found in literature to gauge the above-mentioned wetting parameters such as the Wilhelmy plate method, the sessile drop technique, the captive bubble technique, the capillary rise method or the tilting plate method³. However, the suitability of such methods with respect to each other is a continuous source of discussion, and there are some works realized to compare their performance⁴⁻⁷. To our knowledge, only in one case the tilting plate method was compared to another technique⁶ to discuss its viability.

Herein, we measure the contact angle of various polymer surfaces with the tilting plate technique at incipient contact line movement. The results are discussed and compared with low-rate dynamic contact angles measured with the sessile drop technique on the same polymer surfaces.

MATERIALS AND METHODS

Materials. Polymer sheets (Goodfellow), namely unplasticized polyvinyl chloride (UPVC), polycarbonate (PC), polyethylene terephthalate (PET), polystyrene (PS), poly(methyl methacrylate)

(PMMA) and polytetrafluoroethylene (PTFE), of 2 mm thickness were used as solid surfaces. For contact angle experiments, square sections of about 30 mm side were utilized.

Deionized Milli-Q® water (Millipore, USA) is used along the whole work as liquid medium.

Methods. *Tilting drop technique.* Water drops were deposited on a tilting platform by means of a volume-adjustable micropipette and imaged by a lateral camera (see **FIGURE 1**). Volumes of the drop were 20, 50, 100 and 200 μl . The equipment was a custom built hardware with a fixed CCD camera (A312f, Basler AG) and a halogen light source along with a diffuser for back lighting⁸. The sessile drop platform was inclined in steps of 0.5° tilting angle with respect to the horizontal. The inclination of the stage was measured using a two-axis inclinometer. Image capture and platform tilting were motorized and synchronized through computer control. Tilting steps and image capture were 5 s delayed in order to ensure stabilization of the system.

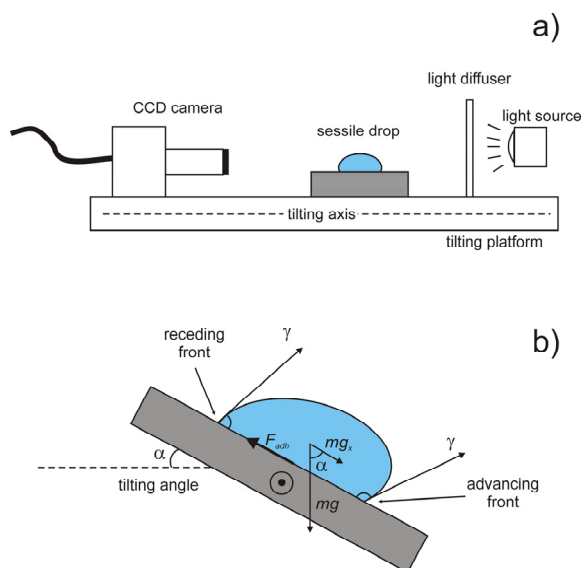


Figure 1. a) Scheme of the tilting device setup. b) Scheme of a tilted drop, the forces acting on it, and its experimental parameters

Profiles of the sessile drops were extracted with homemade software (Contacto[®], J. A. Holgado and

C. Perez, University of Granada, Spain). Horizontal drop profiles were analyzed with Axisymmetric Drop Shape Analysis-Profile (ADSA-P) technique⁹, from which all the sessile drop parameters such as contact angle, contact radius and volume were extracted. Tilted drop profiles were fitted to elliptical arcs by means of Mathematica[®] (Wolfram Research, IL, USA) and the angles of the best-fit curve at the intersection with the drop horizontal were considered as the drop contact angles. For the case of PTFE, two different ellipsoids were fitted to the advancing and the receding half profiles of the sessile drops.

Goniometer sessile drop method. Low-rate dynamic contact angles were measured by imaging the profiles of growing and retracting sessile drops with a CCD camera. Water is injected using a microinjector (Hamilton ML500) (see **FIGURE 2**). Drops of initial volume of 10-20 μl are injected previous to the experiment. Contact line speed is kept constant by applying discontinuous variation of drop volume in time at increasing/decreasing speed of the stepper motor of the syringe pumps¹⁰. Capillary number of the contact line was small enough ($\approx 10^{-6}$) and time between steps of addition/removal of liquid was made greater than the interfacial relaxing time of the drop. Thus, the drop was not altered by hydrodynamic forces¹⁰. Profiles of the growing/shrinking drops were extracted and analysed with ADSA-P technique⁹.

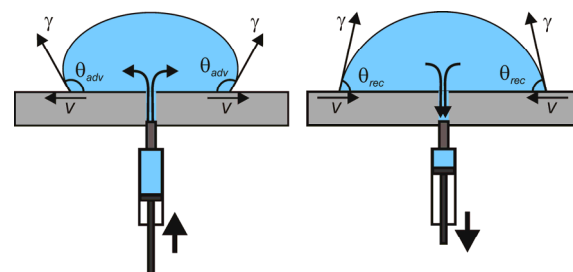


Figure 2. Scheme of the sessile drop technique used to measure low-rate dynamic contact angles.

RESULTS

Tilting drop contact angles. In this section, we measure the evolution of the contact angle of a water drop on the tested polymer surfaces at the lowest and the highest part of the drop, which correspond to the advancing and receding fronts (see **FIGURE 1b**), when the surface is tilted from the horizontal. Simultaneously, the position of the contact line at the lowest and highest points is registered. An example of such measurements for PMMA and PTFE is displayed in **FIGURE 3**. In this, both contact angle and the shift of the contact line from the rest position are represented as a function of the tilting angle.

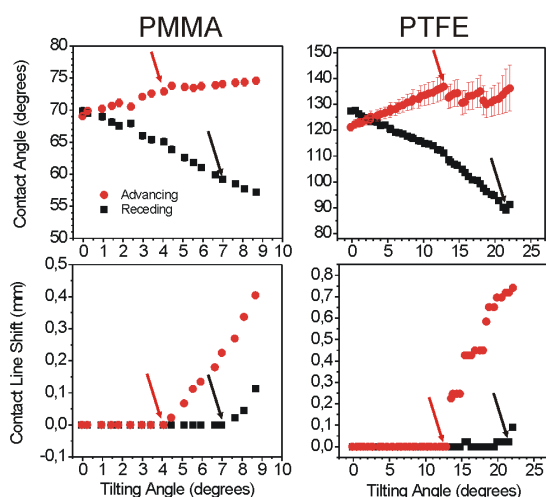


Figure 3. Contact angle and contact line shift from rest of sessile water drop of 100 μ l volume on PMMA and PTFE surfaces at the advancing and receding fronts. The arrows point the positions at which the contact line starts to move.

Parameters of the advancing and the receding front are differentiated. While the advancing front presents an increasing contact angle with increasing tilting angle, the contact angle of the receding one decreases as shown in **FIGURE 3**. This is expected since the drop deforms its shape due to the action of the gravity. As a consequence of the platform tilting, the gravity vector shifts from the normal, and it counteracts the adhesion force of the drop (see **FIGURE 1b**). After certain tilting angle, the gravity

force becomes more important than the adhesion force, and the contact line starts to move. This effect happens at different tilting angles for the advancing and receding fronts. Typically, the advancing front slides beforehand. Indeed, the contact angle after the deposition of the drop is frequently closer to the limiting advancing contact angle of the surface. The instants at which the contact line starts to move, both at the advancing and the receding fronts, are pointed by an arrow in **FIGURE 3**. The angles at which the contact line shifts are named maximum and minimum contact angle for the advancing and receding front respectively. It is still under discussion whether those are equal to the advancing and receding angles of the surface¹¹. Experiments of tilting sessile drops on PMMA and PTFE surfaces are realized varying the drop volume, and the results are summarized in **FIGURE 5**. In there, maximum and minimum contact angles are displayed in bar graphs, and results for every drop volume are compared. The maximum contact angle for PMMA is in the range of 59-73.9° depending on the drop volume. The receding one is 34-57.5°, and the hysteresis is 22-26°. On the other hand, PTFE presents a maximum contact angle of 126-141°, whereas the minimum one is 81-86° and the hysteresis is 40-60°. Clearly, contact angles of PTFE show a more intense hydrophobic nature compare to those of PMMA. Additionally, contact angle hysteresis is higher for PTFE. Its average surface roughness is 2.75 μ m as measured with a confocal profilometer, whereas PMMA presents 88 nm as surface roughness. The higher hysteresis of PTFE may well have its origin in its higher surface roughness.

Low-rate dynamic contact angles. Some results in the measurement of advancing and receding contact angles are shown in **FIGURE 4** for the case of PMMA and PTFE. The upper graphs show the contact radius of the sessile drop measured as a function of injection dimensionless time. The lower

graphs display the dynamic contact angle as a function of the contact radius of the growing drop, for red symbols, or the decreasing drop in black symbols. Both at the advancing and the receding region, a linear relation between contact radius and time indicate a regime of constant speed of the contact line. Thus, the average dynamic contact angles are obtained at that regime. This corresponds to the plateau regions in the contact angle vs. radius graphs. Again, the mean values of advancing and receding contact angles as measured with this technique are represented in **FIGURE 5** and compared to the ones obtained with the tilting plate method. PMMA presents an average advancing contact angle of $77.2 \pm 0.5^\circ$ and the receding one is $49.6 \pm 0.7^\circ$ with a mean hysteresis of 27.6 ± 1.2 . On the other hand, PTFE has an average advancing contact angle of $145 \pm 5^\circ$ and a receding one of $101.1 \pm 2.1^\circ$ with a mean hysteresis of $44 \pm 7^\circ$. The hydrophobic characteristics of PTFE are again confirmed with the higher values of advancing and receding contact angles with respect to those of PMMA, as well as the more hysteretic behaviour probably due to a higher surface roughness. This may as well be an explanation of the more erratic behaviour of the contact line of the drop on PTFE. As can be observed in **FIGURE 4**, error bars are larger and a few pinning events of the contact line may be found in the graphs. PMMA presents more similar behaviour between the advancing and the receding front, and contact angles are more stable along the constant speed regime of the contact line. Experiment results shown are averaged over the results of five different drops. The small size of the error bars of the results in the constant speed regime indicate the high reproducibility of this technique for all the investigated polymers, and specifically for the two here displayed.

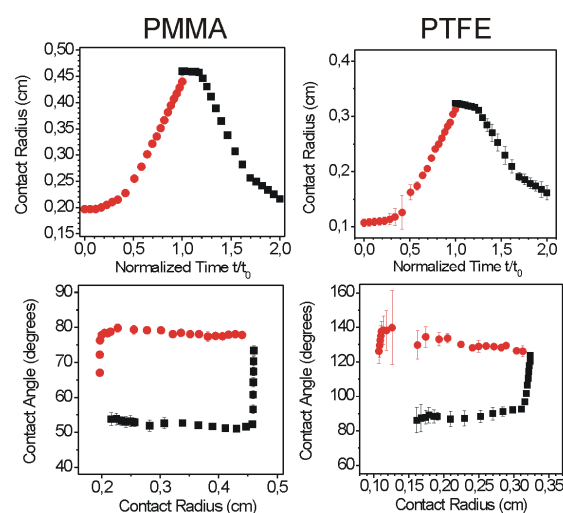


Figure 4. Measurements of low-rate dynamic contact angles of water on PMMA and PTFE. Red circles correspond to advancing front of the sessile drop and black squares are the receding one. Contact angle and contact radius of the dynamic drop are represented, as well as time where liquid is injected (advancing regime) or extracted (receding regime) from the drop.

DISCUSSION

In **FIGURE 5**, results of experimental contact angles from the techniques used herein are displayed and compared. Values of the contact angle at the advancing front are fairly similar for tilting drop and low-rate dynamic contact angles. However, disagreement is more severe when contact angles in the receding front are compared, especially regarding measurements with PMMA. This feature is also found when comparing the performance of the tilting drop technique with the Wilhelmy plate method⁴. Similar trends are found when comparing both methods with the rest of studied polymer surfaces. The reason for these discrepancies can be found in the different characteristics of these techniques. Krasovitski and Marmur¹¹ already pointed out that contact angles at advancing and receding fronts do not have to be the same at tilted drops and at expanding and contracting drops on horizontal surfaces. One has to understand that low-rate dynamic contact angle measurement scans the contact angle along a

certain area of the surface, and an average value is extracted. The measurement is realized with a fixed camera, and only the profile of the drop perpendicular to it is imaged. Still, the contact angle is measured along the diameter of the final drop. Certainly, the result represents better the wettability of the surface. Moreover, dynamic contact angles of uniformly moving TPCL are proved to agree well with static ones⁵. On the other hand, for the tilting drop method, the resulting contact angles are those measured at an immobile contact line. Thus, they are strongly dependent on the position of the drop and its contact line at the surface. Additionally, it has been reported the dependence of the contact line shape of a tilted drop on its adhesion force⁸. As a consequence, it has been determined that in a tilted drop experiment, the maximum and minimum measured contact angles are dependent on the overall contact angle distribution along the contact line. The irregularities of the contact line shape due to the deposition methods can be a source of irreproducibility of the contact angles at advancing and receding fronts. For this, a novel work of Antonini *et al.*¹² proposes a method to overcome this problem. Therein, the contact line shape and its distribution of contact angles along the line are reconstructed through the analysis of a number of profile images of the drop, which are obtained by turning the camera around the drop platform, and the zenithal one. As a result, the adhesion force of the drop is calculated with 1% error. The analysis of our system by using this method may help to improve the accuracy of our measurements.

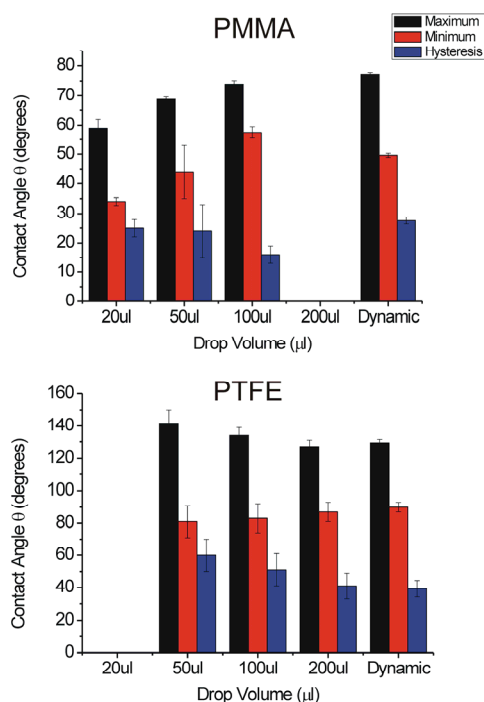


Figure 5. Bar graphs showing experimental contact angles of sessile water drops of the indicated volumes in X axis on PMMA and PTFE surfaces. The different colors indicate the angles at the advancing front (maximum), receding front (minimum), and its difference (hysteresis). Dynamic indicates low-rate dynamic contact angles.

CONCLUSIONS

Contact angle measurements of water drops are realized on various polymer surfaces using the tilting drop method and goniometer sessile drop technique. With the former, contact angles at advancing and receding front at the previous instant for the contact line to start to slide are obtained. Low-rate dynamic contact angles are acquired with the latter technique. Contact angles at advancing front agree fairly well with the two methods, whereas the angles at receding fronts present discrepancies. Considering the high reproducibility of measurements with the sessile drop technique, one can admit that improvements on the tilting drop method have to be accomplished. Future measurements involve reconstruction of the contact line path and their contact angles through a novel

procedure in order to improve the accuracy of the technique.

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REFERENCES

- (1) De Gennes, P. G.; Brochard-Wyart, F.; Quéré, D. *Capillarity and wetting phenomena*; Springer: New York, 2004.
- (2) Chibowski, E. *Advances in Colloid and Interface Science* **2007**, *133*, 51-59.
- (3) Butt, H.-J.; Graf, K.; Kappl, M. *Physics and Chemistry of Interfaces*; 2nd ed.; Wiley-VCH: Weinheim, 2006.
- (4) Krishnan, A.; Liu, Y.-H.; Cha, P.; Woodward, R.; Allara, D.; Vogler, E. A. *Colloids and Surfaces B: Biointerfaces* **2005**, *43*, 95-98.
- (5) Kwok, D. Y.; Gietzelt, T.; Grundke, K.; Jacobasch, H. J.; Neumann, A. W. *Langmuir* **1997**, *13*, 2880-2894.
- (6) Lander, L. M.; Siewierski, L. M.; Brittain, W. J.; Vogler, E. A. *Langmuir* **1993**, *9*, 2237-2239.
- (7) Rodríguez-Valverde, M. A.; Cabrerizo-Vilchez, M. A.; Rosales-Lopez, P.; Paez-Duenas, A.; Hidalgo-Alvarez, R. *Colloids and Surfaces a-Physicochemical and Engineering Aspects* **2002**, *206*, 485-495.
- (8) Pierce, E.; Carmona, F. J.; Amirfazli, A. *Colloids and Surfaces A: Physicochemical and Engineering Aspects* **2008**, *323*, 73-82.
- (9) Wege, H. A.; Holgado-Terriza, J. A.; Rosales-Leal, J. I.; Osorio, R.; Toledano, M.; Cabrerizo-Vilchez, M. K. *Colloids and Surfaces a-Physicochemical and Engineering Aspects* **2002**, *206*, 469-483.
- (10) Tavana, H.; Neumann, A. W. *Colloids and Surfaces A: Physicochemical and Engineering Aspects* **2006**, *282-283*, 256-262.
- (11) Krasovitski, B.; Marmur, A. *Langmuir* **2005**, *21*, 3881-3885.
- (12) Antonini, C.; Carmona, F. J.; Pierce, E.; Marengo, M.; Amirfazli, A. *Langmuir* **2009**, *25*, 6143-6154.