Determination of the Receding Contact Angle of Sessile Drops on Polymer Surfaces by Evaporation

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The receding contact angles of water drops on PMMA and PET surfaces were determined by using video microscopy to follow the time-dependent evaporation of sessile drops. Depending on the initial drop size, receding angles of $\theta_r = 54-64°$ for PMMA and $\theta_r = 64-66°$ for PET were found with an average hysteresis of 23.5 ± 1.5 and $19.5 \pm 1.5°$, respectively. Advancing and receding angles, θ_a and θ_r, were also determined by the needle-syringe and the inclined plane methods for comparison. The discrepancies from the mean of the maximum and minimum contact angle results of both the needle-syringe and the inclined plane methods were larger than expected for all the polymer surfaces. A general trend was seen with samples giving a larger hysteresis also producing a larger discrepancy for all the samples. The major cause of this discrepancy is the variation of the rate of liquid introduction and withdrawal with the syringe in the needle-syringe method and the drop size effect in the inclined plane method. In this respect the drop evaporation method allows a rate of liquid withdrawal which minimizes (or standardizes) the linear rate of retreat effect on receding contact angle measurement. The literature values are also given for comparison. A discrepancy of 11−15% from the mean for θ_a and 27−32% for θ_r is reported in the literature for these polymers. This is approximately five times more than the previously claimed 2−3% deviation from the mean for θ_a on the same clean homopolymer samples.

Introduction

Contact angle measurements have been a major experimental approach to many problems concerned with the solid−liquid interface. There are, however three different types of contact angles which can be measured. An advancing contact angle, θ_a, can be observed by advancing the liquid boundary over a dry clean surface, and a receding contact angle, θ_r, can be observed by retreating the liquid boundary over a previously wetted surface. In addition, there is the "equilibrium" contact angle, θ_e, which is the direct consequence of Young's equation. The equilibrium contact angle has a value intermediate between θ_a and θ_r. To apply Young's equation, the solid should be ideal with a surface that is chemically homogeneous, rigid, flat at an atomic scale, and free from chemical interaction by vapor or liquid adsorption. When this ideal polymer surface is present, there should be, in principle, a single and unique equilibrium contact angle.[1,2] The contact angle hysteresis is defined as the difference between the advancing and receding (or retreating) angles:

$$\Delta\theta \equiv \theta_a - \theta_r \tag{1}$$

Hysteresis was known almost 80 years ago.[3] On real surfaces, it is common to find hysteresis in the range of 10° or larger; hysteresis in excess of 50° has been reported.[1,2] Hysteresis of contact angle is due to deviations of a surface from the ideal conditions. The existence of the many thermodynamic metastable states for systems having three-phase (solid/liquid/vapor) boundaries results in hysteresis. A different intrinsic θ is associated with each metastable state. In practice, there appear to be five types of causes for hysteresis: Surface roughness,[1,2,4−11] microscopic chemical heterogeneity of the surface,[1,2,8,12−21] drop size effect,[1,2,22−28] molecular reorientation and de-

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formation at the surface,[1,2,29−34] and the size of the liquid molecules to penetrate into the pores and crevices of the solid surface.[1,35] To assess the hysteresis, one must measure both θ_a and θ_r precisely. Although many methods have been developed for the experimental determination of contact angles,[1,2,36,37] there is still controversy on the reliability and the reproducibility of the measured angles, especially for the receding angle.[1,2,19,36,37]

There are three main techniques for measuring the contact angle on flat plates. These are the sessile drop (or captive bubble in liquid), the Wilhelmy plate, and the inclined plane methods. In the sessile drop method, a liquid drop is placed on a horizontal solid surface so that the edge of the drop and its reflected image are both visible when viewed in cross section using a microscope. This allows the tangent to be determined at the point of contact between the drop and the surface. Several measurements are often made on both sides of the drop and an average taken. It is commonly claimed that the accuracy of this method is ±1° or better, and indeed, this may be true for a given observation. However, measurements reported from independent laboratories using this method for the same solid−liquid system have a discrepancy of around 5°.[36] A second method using a sessile drop is due to the school of Zisman.[1,35] In this approach, the tip of a fine platinum wire is used to bring a droplet to the surface and detach it from the wire. More liquid is added, in successive droplets from the wire, and θ_a is measured after each addition. The receding angle is measured by stepwise removal of small increments of liquid so that the liquid is withdrawn by touching the tip of the fine glass capillary to the drop.[1] In many other laboratories,[1,2,28,36] the liquid drop is introduced by means of a micrometer syringe with a fine needle and is held captive while additional liquid is added to the drop until a steady value of θ_a is obtained and the addition of liquid is stopped. Some liquid is withdrawn from the drop in order to measure θ_r by means of the micrometer syringe. In an alternative technique, still based on sessile drops, Neumann and co-workers[37,39] make a small hole in the flat solid sample and first deposit a small drop on this hole. The size of the drop is then increased by feeding liquid to the drop from below the solid surface by a syringe. This procedure prevents the drop oscillating and the destruction of the axisymmetry. They also developed a method to determine both the contact angle and surface tension of the liquid by applying digital image analysis and a computation method named axisymmetric drop shape analysis (ASDA).[37−40] In this method, an objective function is constructed which expresses the error between the physically observed profile and the theoretical Laplacian curve; the function is then minimized using an iterative procedure.

The Wilhelmy−capillary rise method eliminates the drop size effects on contact angle measurements. The contact angle determination from the capillary rise at a vertical plate requires knowledge of the density difference between the liquid and the vapor, the liquid surface tension, and the acceleration due to gravity. The contact angle can then be calculated from the measurement of the capillary rise by a cathetometer.[2,36,37,41] The capillary rise method is also suitable for dynamic contact angle measurements, both in advancing and receding mode by following the rise with an electrooptical device.[37] If the capillary pull is measured by an electrobalance instead of capillary rise, this method is called the Wilhelmy−gravitational method.[1,2,36,37] In this dynamic method, a thin plate is mounted vertically above the liquid. The plate is suspended with the bottom edge nearly touching the surface of the liquid to begin the measurement. Later the liquid is raised until it touches the plate. The force on the plate is measured as it is cycled slowly down and up.[2,15,33,36,37,41−45] The advancing angle is the stable angle as the liquid level is raised. The receding angle is the stable angle as the liquid level is lowered from an initially higher point on the plate surface. Although this method is valuable, it has several drawbacks that can restrict the usefulness of the procedure. The perimeter of the plate should be constant, the sample plate must be very smooth and must have the same composition and morphology at all surfaces, and the sample plate must not be swelled by the liquid.

In the inclined plane method, the solid sample is placed on a motor-driven inclined plane. When the plane of the solid surface reaches a critical slope, the drop starts to slide. The measured angle at the downhill edge of the drop approaches θ_a, and the angle at the uphill edge approaches θ_r. The angles should be measured immediately prior to the drop starting to slide.[1,2,21,46−51] However, Good[1] cautioned against this method because it yields values of advancing and receding angles that are strongly dependent on the drop size.

Three main problems exist in association of the measurement of advancing and receding contact angles. The first problem is the variable rates of introducing the drop liquid during determination of θ_a and the variable rates of withdrawal of the liquid during determination of θ_r. The sessile drop method is not particularly well adapted to the quantitative measurement of the dependence of contact angle on the rate of advance or retreat, because a linear rate of change in drop volume does not correspond to a linear rate of motion of the drop front.[36] An appropriate rate is of the order of 0.01−0.10 mm min^{-1} linear advance or retreat by using a motor-driven syringe.[36] Also, it is best to specify the time allowed before measuring the contact angle after the motion stops, e.g. 10−30 s, to obtain more precise data. The second problem is the evaporation

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of the drop liquid. Evaporation may cause the contact angle to decrease and the liquid front to retract so that a receding or mostly an intermediate θ between θ_a and θ_r is observed unintentionally. In practice, a closed chamber can be used to ensure saturation of vapor and so minimize this effect.[1,2,36,37] The third problem is the distortion of the drop surface caused by the needle. If the needle enters the drop at a point very close to the solid, it may obscure the drop profile. If the needle passes through the upper surface of the drop, there will be some capillary rise of the liquid up the needle and distortion of the surface. However, it has been claimed that this capillary rise does not perturb the liquid in the region of the contact line with the solid.[1,36] Removing the needle from the drop does not help, because that makes it impossible to study hysteresis. In summary, the apparent simplicity of the contact angle measurement is quite misleading and the acquisition of thermodynamically significant contact angles and hysteresis values requires painstaking effort.[37]

For sessile drops, liquid evaporation is inevitable unless the atmosphere in the immediate vicinity of the drop is completely saturated with the vapor of the liquid. In contact angle measurement, evaporation has generally been regarded as undesirable. However, in 1962 Mangel and Baer[52] suggested that drop stability on an inclined plane and the mechanism of drop evaporation are both dependent on the same minimum receding angle. The usefulness of their data for drops of water on Teflon is limited because of the very large drops, 19−81 mm^3, used and the relatively infrequent sampling of the contact angle every 8 min. Moreover they did not report the humidity conditions and the drop contact diameter change by time. A later study by Herzberg et al.[53] of droplet evaporation on chloromethylated glass surfaces followed the evaporation of very large drops of 30−60 mm^3 for 80−120 min and reported the change in contact angle for every 5−6 min. They also did not report the ambient relative humidity. Close consideration of the data in both these papers indicates that, late in the evaporation, the contact angle does not decrease linearly but may have peaks in the receding angles. However, any firm conclusions based on the data in these papers is difficult due to the infrequent data collection, relative lack of precision in the angle measurements, and the relatively large drop volume range which exceeds 2−5 mm^3.

The suggestion that local peaks exist in the receding contact angle as droplets evaporate is consistent with recent reports[54−62] on the evaporation of small droplets resting on plane surfaces. For initial contact angles of less than 90° evaporation proceeds with a decreasing contact angle and a pinned contact radius, and this persists for much of the evaporation time. Toward the end of the evaporation, the contact radius finally begins to recede. The contact angle at this point may therefore represent a natural receding angle.[55] Moreover, it is possible that the contraction of the contact radius does not proceed smoothly but rather undergoes a stick−slip motion so giving rise to local peaks in the receding angle.[56] In the study reported here, an attempt is made to determine the precise receding contact angles of small water drops on poly(methyl methacrylate) (PMMA) and poly(ethylene terephthalate) (PET) surfaces by applying video microscopy. This technique enables a more accurate comparison between contact angles measured from successive images and provides the facility to examine brief rapid changes occurring within a relatively long experiment. Receding angles obtained by withdrawing the liquid by a microliter syringe connected with a fine needle and by applying the inclined plane methods up to the vertical position on the same sample surfaces are also reported for comparison.

Experimental Section

Experiments were performed using ultrapure water, which had been triply distilled, deposited as a sessile drop onto flat and smooth polymer substrates. PMMA and PET (Mylar of DuPont) polymers were used as substrates. All polymer surfaces were cleaned off all the impurities and oily material by washing with ethyl alcohol and then wiping with a piece of paper containing dilute soap solution and later washing with distilled water thoroughly and dried at 50 °C for 4 h under 1−2 mmHg vacuum. Water droplets were deposited from a microliter syringe onto the freshly prepared polymer substrates, and the water drops were allowed to evaporate in still air in the closed weighing chamber of a Mettler AE200 balance. Two water drops, one small and one large size, were formed at different times on different locations of the same sample of polymer surfaces in order to check the drop size effect. The temperature for all experiments was measured by a thermocouple probe located in the chamber and was constant at 22.8 ± 0.2 °C. The relative humidity in the chamber was measured by using a hygrometer (Polymeter, Casela, London Inc.) located inside the chamber. The relative humidity of the room was checked with a wet and dry bulb temperature rotating hygrometer (Brannon Thermometer Ltd., U.K.). The relative humidity in the chamber was constant at (41.8 ± 0.8)% RH. The polymer surfaces were sufficiently reflective to enable an optical profile of a droplet and its reflection to be obtained. The evolution in the profile of the droplet was then recorded onto videotape operating at 25 frames/s by using a video camera equipped with a suitable objective. The images were subsequently transferred onto a personal computer using a Data Translations DT-3152 scientific framegrabber card working at a resolution of 768 × 576 and a one-to-one pixel aspect ratio. Digital image analysis was performed using a simple thresholding routine to obtain the profile. The UTHSCSA ImageTool program was used, together with in-house routines, to perform the image analysis. These routines gave angles similar to those obtained using the simple visual measurement option within the image processing package. Advancing and receding contact angle determinations by the needle-syringe method were also carried out on the same polymer samples by using a stainless steel needle (outer diameter = 0.496 mm) connected with a microliter syringe. The water introduction and withdrawal were done by applying different rates manually by hand, and thus were monitored by video recording the profile during the process. Contact angles were determined by the visual angle measurement option of the image analysis program because of the difficulties introduced by the presence of the needle in the drop. Inclined plane experiments were done by increasing the angle of tilt, ϕ, manually after forming the water drop on the polymer surface. The sample was attached to a triangular glass device by means of double-sided tape. All three angles, θ_a, θ_r, and ϕ, were determined on the images of the profiles by the visual angle measurement option of the image analysis program.

Results

A deposited drop has a contact diameter that is initially pinned, and this remains so for a long period during the evaporation (Figure 1). During this period the contact angle decreases systematically as shown in Figures 2 and

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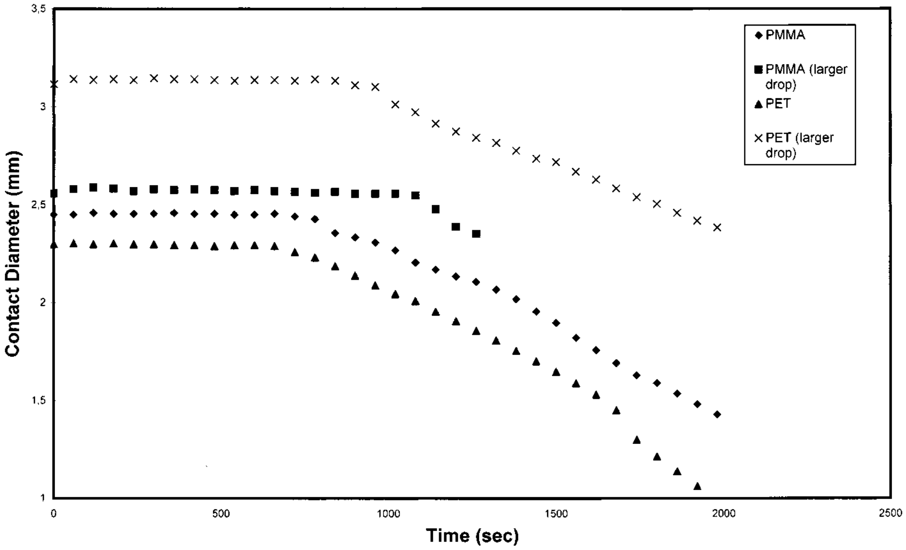

Figure 1. Contact diameter change with time for water drops on PMMA and PET surfaces by video microscopy and image analysis.

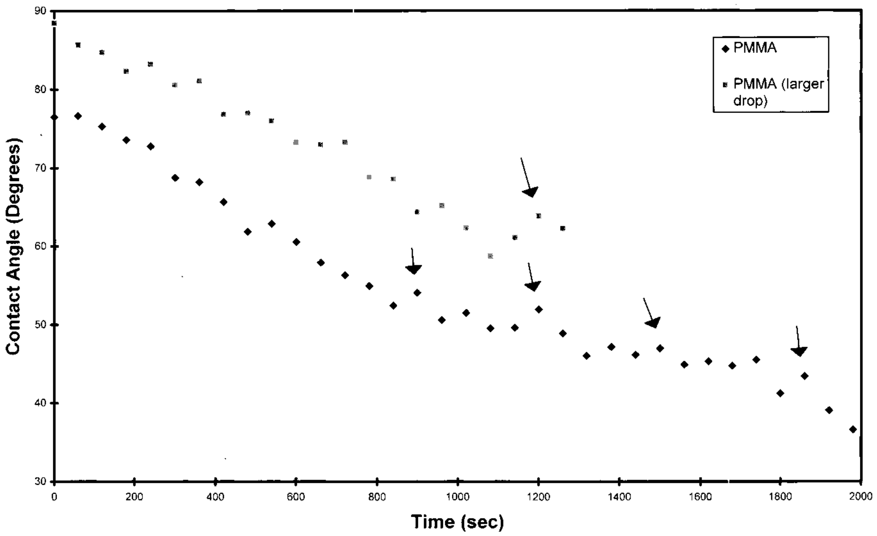

Figure 2. Contact angle change with time for water drops on PMMA surface by video microscopy and image analysis.

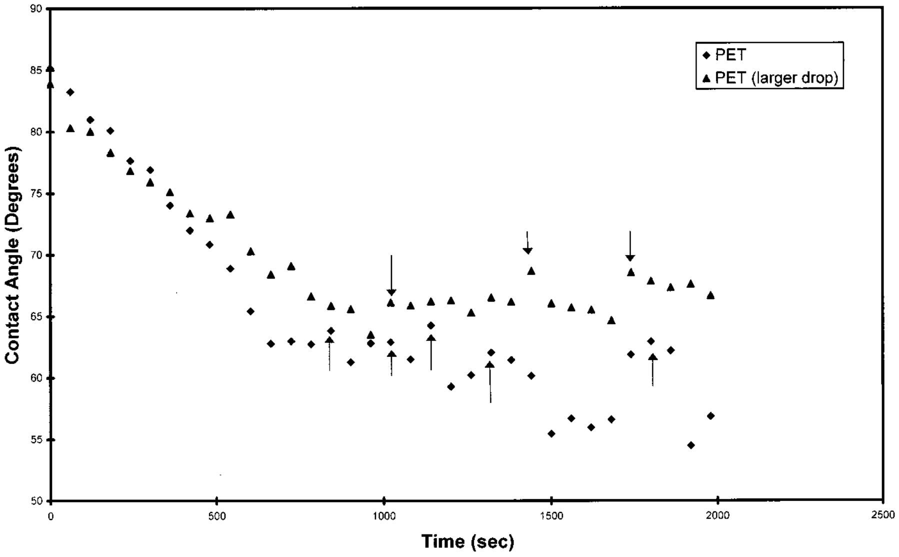

Figure 3. Contact angle change with time for water drops on PET surface by video microscopy and image analysis.

3 for PMMA and PET, respectively. The initial contact angles, θ_i, cannot be regarded as the true advancing angles because there was a time of 5−10 s between the formation of the drop and the withdrawal of the needle. However, all the θ_i values should be close to θ_a since extrapolating the rate of change back to the deposition time implies a

Table 1. Initial Contact Angles, Contact Radii, and Volumes of Water Drops on Polymers with the Times of Drop Contraction and Receding Contact Angle Determination by Evaporation

polymer	θ_i (deg)	initial r_b (mm)	initial V (mm^3)	θ_r (deg)	$\Delta\theta$ (deg)	time of receding θ (s)	time of d decrease (s)
PMMA	77	1.23	2.72	54	22	900	780
PMMA	89	1.28	3.88	64	25	1200	1080
PET	85	1.15	2.67	64	21	840	720
PET	84	1.56	6.27	66	18	1020	900

Table 2. Advancing and Receding Contact Angle Results Obtained by Needle-Syringe and the Inclined Plane Methods[a]

polymer	θ_a (needle syringe)	θ_r (needle syringe)	θ_a (inclined plane)	θ_r (inclined plane)	ϕ (angle of tilt)	θ_a (lit.)	θ_r (lit.)
PMMA	79−92	42−56	66−89	54−78	40−63	64−86	30−58
PET	86−98	52−66	70−93	59−75	41−85	71−88	28−49

[a] Literature values are given for comparison. All the contact angle values are in deg.

Table 3. Average Advancing and Receding Contact Angle Results Obtained by Needle-Syringe and the Inclined Plane Methods with Their Percentage Deviation from the Mean[a]

polymer	θ_a (needle syringe)	θ_r (needle syringe)	θ_a (inclined plane)	θ_r (inclined plane)	θ_a (lit.)	θ_r (lit.)
PMMA	85 ± 8%	49 ± 14%	78 ± 15%	66 ± 18%	75 ± 15%	44 ± 32%
PET	92 ± 6%	59 ± 12%	81 ± 14%	67 ± 12%	80 ± 11%	39 ± 27%

[a] Literature values are given for comparison. All the contact angle values are in deg.

change of no more than 2°. Perhaps surprisingly, when the contact radius begins to contract, no immediate change in the trend of the contact angle can be observed. However, after a further time of around 120 s the contact angle increases and reaches a local maximum. These peaks are shown in Figures 2 and 3 by the arrows. This was true for all drops on both surfaces and irrespective of the drop size. Table 1 summarizes the initial contact angles and contact radii, drop volumes, the time required for the first contact angle peak, and the time required for the first decrease of the drop contact diameter, *d*.

Regarding the PMMA surface, the smaller drop of water showed four receding angle peaks, 54, 52, 47, and 43° after 900, 1200, 1500, and 1860 s, respectively as seen in Figure 2. There was an average decrease of 4 ± 1° in the receding angle determined for every contraction step occurring at approximately 300 s intervals. The larger drop showed one peak at 64° after 1200 s. Since this drop was formed to investigate the drop size effect on θ_i and the first θ_r, the consecutive peaks were not recorded. When eq 1 was applied by assuming $\theta_i \approx \theta_a$, an average hysteresis of $\Delta\theta = 23.5 \pm 1.5°$ was found for both drops. The larger the drop size, the higher both of the θ_a and θ_r was seen for PMMA surface. The contact diameters of both drops were constant up to 780 and 1080 s, respectively, and decreased linearly after that period. During the contact diameter decrease stage no other drop contraction was detected by the image profiles as seen in Figure 1. The local peaks in the receding angle peaks as shown in Figure 2 may indicate that the detected diameter decrease is the sum of many rapid microcontractions in the drop profile, which are not easily observed by viewing the profile.

Regarding the PET surface, the smaller drop of water showed five receding angle peaks, 64, 63, 64, 62, and 63° after 840, 1020, 1140, 1320, and 1800 s, respectively, as seen in Figure 3. There was no steady decrease of the receding angle for this polymer surface, and an average θ_r of 63 ± 1° was obtained for all the peaks. The larger drop of water showed three peaks at 66, 69, and 69° after 1020, 1440, and 1740 s, respectively. An average θ_r of 68 ± 1° was obtained for the three peaks. When eq 1 was applied by assuming $\theta_i \approx \theta_a$, an average hysteresis of $\Delta\theta = 19.5 \pm 1.5°$ was found for both drops. The contact diameters of both drops were constant up to 720 and 900 s, respectively, and decreased linearly after that period. The drop size effect on the θ_a and θ_r was found to be minimal for PET surface as indicated by the close lines in Figure 3. Similarly to the PMMA surface, no drop contractions were detected from the image profiles during the contact diameter decrease stage, but again the receding angle peaks may indicate that microcontractions are occurring.

When θ_a and θ_r values were determined by manually advancing and receding the water drop, by means of a needle connected with a microliter syringe, quite varying results were obtained. This appears to be due to variations in the rate of liquid flow and the size of the drops. The maximum and the minimum θ_a and θ_r values obtained by this method are given in Table 2. Similarly when θ_a and θ_r values were determined by the inclined plane experiments, quite scattered results were obtained for varying sized drops; these are given in Table 2 together with the maximum and minimum tilt angle applied. The literature values are also given in this table for comparison. The average θ_a and θ_r values obtained from both methods are given in Table 3 with their percentage deviations from the mean.

Discussion

Bourges and Shanahan reported the evaporation of water and *n*-decane drops on various substrates and named stage II where the drop height and contact angle decreases while contact radius remains constant and stage III where the height and contact radius decreases while contact angle remains constant and corresponds to a receding angle on smooth surfaces.[55] They also reported the decrease of drop height, contact diameter, and contact angle step by step for *n*-decane drop on the PTFE surface where the decrease of the contact radius is accompanied by a slight increase of drop height and contact angle during a step. As seen in Figures 1−3, these stages were also reproduced in our drop evaporation experiments although we monitored the evaporation in still air having 42% relative humidity whereas Bourges and Shanahan applied nearly dry atmosphere by using a silica gel dish in the evaporation chamber.[55] Later, Shanahan developed a simple theory for "stick−slip" behavior during drop evaporation, in which the wetting front remains static for most of the time but from time to time moves quite abruptly.[56] He argued that the reduction in drop volume by evaporation must lead to a lack of capillary equilibrium during the period of contact line is pinned. The shape of the drop at any instant in time can then be used to estimate the excess free energy. His argument was that triple line motion required this energy to exceed an hysteresis potential barrier due to the solid surface. For an ideal solid surface, the triple line should recede smoothly, and for a system having large hysteresis, jumps should be large and infrequent.[56] This model excluded the effects of gravity, line tension, and pseudo-line tension and, importantly, any dynamic effects from the evaporation process. In particular, internal flow was assumed to be negligible and this assumption, which suggests that the rate of change should not be important, may not be true.[63]

The discrepancies from the mean of the maximum and minimum contact angle results of both the needle-syringe and the inclined plane methods were larger than expected for the polymer surfaces as seen in Table 3. A general trend was seen with the larger the hysteresis, the larger is the discrepancy for all the samples. When advancing contact angles in the needle-syringe method were considered, the discrepancy from the mean was minimum; it was between 7 and 8% but was larger than the expected 2−3%. The receding angles had a discrepancy of nearly the double of the advancing angles for the needle-syringe method for PMMA and PET surfaces. The major cause of this discrepancy was the variation of the rate of liquid introduction and withdrawal with the syringe. Theoretically, the three-phase line should always move steadily and without changes in the contact angle on the ideally smooth solid. However, in the actual experiment, even a very slow supply of liquid to the drop causes no immediate and steady motion of the triple line. At the beginning θ rises continuously to a certain maximum value which should be considered as the true θ_a. Then the three-phase line starts moving in the form of short jump, resulting in a small reduction of the contact angle. So it is rather difficult to obtain the maximum θ_a. The reverse is also true for the receding angle so that a molecular band is left behind during the retreat of the liquid front and the influence of the gradient of surface concentration will be different for retreat than for advance. If the polymer surface restructuring takes place during the retreat, it is rather difficult to obtain the minimum θ_r. Spelt et al.,[38] who pointed out that the maximal receding contact angle will only become evident at very low rates of liquid withdrawal, suggested it is a common mistake to measure this angle too quickly. Doing so provides an exaggerated estimate of the contact angle hysteresis. Li and Neumann[19] applied a model to describe the effect of surface heterogeneity on the contact angle hysteresis and concluded that even a very small amount of surface heterogeneity may cause the receding angle to be less reproducible. In particular, it depends on the contact angle measurement technique and the rate of recession of the three-phase line. In this respect the drop evaporation method allows a minimum rate of liquid withdrawal which minimizes the linear rate of retreat effect on receding contact angle measurement. We calculated a linear retreat rate of 0.02−0.05 mm min^{-1} from Figure 1 after the constant contact diameter period, depending on the rate of drop evaporation. A rate of 0.01−0.10 mm min^{-1} linear advance or retreat by using a motor-driven syringe is recommended in the literature.[36] However, even when such rates for liquid delivery and withdrawal in the needle-syringe method for the contact angle measurements are complied with, it is difficult to compare the results of contact angle measurements on the same polymer types in independent laboratories. The same conclusion can also be drawn from the 11−15% discrepancies from the mean of the literature values of θ_a and 27−32% of θ_r for the polymers as seen in Table 3. Such a large discrepancy may be accepted for the receding angle values of the individual samples due to their different surface properties resulting in different contact angle hysteresis. However the 11−15% discrepancies from the mean of the literature value of θ_a are approximately five times more than the claimed value of 2−3% deviation from the mean for θ_a on the same kinds of polymers.[1,36] This result shows that the discrepancies of θ_a of the same liquid on the same kinds of polymers between independent laboratories have previously been underestimated.

The results of inclined plane methods showed even worse discrepancies from the mean for both advancing and receding angles. The drop size effect on the contact angle seems to be the major cause of this discrepancy, because when small-sized drops were used, the increase in the tilt angle did not result in a regular increase of θ_a and a regular decrease of θ_r. Furmidge[48] reported that both θ_a and θ_r vary with the time of contact between liquid and the solid. Rotenberg et al.[50] stated that, on an inclined surface, a static drop will have a range of contact angles with values varying between $\theta_a \geq \theta_{max}$ and $\theta_{min} \geq \theta_r$. Wolfram and Faust[49] reported that small drops do not slide even for a 90° tilt angle, which was also confirmed by Bikerman.[46] Overall, the inclined plane method did not appear suitable for contact angle determinations in agreement with ref 1.

When the individual polymer surfaces are considered by using video microscopy, the larger the drop size, the higher both of the θ_a and θ_r values was seen for the PMMA surface. We found $\theta_i = 77-89°$ and $\theta_r = 54-64°$ depending on the drop size. The increase in the receding contact angle is qualitatively in agreement with the "stick−slip" model proposed by Shanahan.[56] The energy per unit length of the contact line depends on the contact radius so that a smaller change in contact angle is required to depin the contact line given the same hysteresis barrier. When eq 1 was applied by assuming $\theta_i \approx \theta_a$, an average hysteresis of $\Delta\theta = 23.5 \pm 1.5°$ was found for both drops. Various advancing and receding contact angles of water drops on PMMA surfaces were reported in the literature depending on the method used. Dann[64] reported $\theta_a = 74°$. Herzberg and Marian[23] examined the effect of drop size on contact angles on the PMMA surface by evaporation. They measured the advancing angles by using the needle-syringe method in a saturated atmosphere chamber, and the needle was left in the drop. They reported that despite precautions taken to maintain these drops in a saturated atmosphere drop size reduced due to evaporation. For drops of initial volume 0.1−0.4 mm^3, the average θ_a was 67°, for 1−4 mm^3, volume θ_a was 71°, and when the drop volume was raised to 20 mm^3 by the addition of 1−2 mm^3 amounts, θ_a was found to be 72°. However, when a large drop of 20−30 mm^3 was formed, θ_a was 86°. Evaporation within their chamber occurred, and θ decreased from 72 to 66° in 17 h by losing the 8% of its volume. They concluded that the observed variation of θ is a manifestation of hysteresis and because of the unavoidable evaporation and the distortion of the captive needle, conditions for maximum θ_a were never realized on a PMMA surface.[23] Good and Koo[22] also examined the effect of drop size on

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contact angles. They employed both the needle-micrometer syringe sessile drop technique and the capillary rise at a vertical plate technique. In both techniques, the angle measurements were made within about 10 s after stopping the liquid addition or the motion of the vertical plate. They reported $\theta_a = 64-74°$ and $\theta_r = 29.5-51.0°$ for the sessile drop method, and both θ_a and θ_r increased with the drop size similar to our observations. They also reported the vertical plate results as $\theta_a = 74.4 \pm 1.2°$ and $\theta_r = 54.3 \pm 1.1°$, which were in good agreement with the limiting θ of the large drops. They attributed the drop size effect to the presence of a negative pseudo-line tension.[22] Busscher et al.[8] examined the effect of surface roughening. They measured θ_a and θ_r after the droplet has been forced to advance over the surface by moving the solid while keeping the microsyringe in the droplet. Thus one edge of the drop exhibits θ_a, while the other edge shows θ_r. They reported $\theta_a = 64-79°$ and $\theta_r = 42-58°$ with varying roughness of PMMA surfaces. They also measured an intermediate angle, which they named as "equilibrium θ" when the drop rests on the solid surface freely. The values of these types of angles were very close to θ_a.[8] Lin et al.[65] applied a video-enhanced sessile drop technique. The parameters of location of apex, radius of curvature at apex, and the capillary constant were calculated from the best fit between the edge coordinates and the theoretical curve obtained from the Laplace equation. By control of the humidity of the air phase surrounding the drop, this technique can measure the advancing and receding contact angles. When 95% RH was applied, they detected a slow increase in the diameter of the drop and attributed it to an advancing angle. They opened the chamber after 60 s and equilibrated the drop surrounding with the 65% RH in about 20 min. The contact angle decreased by evaporation, and they assumed the last contact angle as the receding angle. They reported $\theta_a = 79.9°$ and $\theta_r = 46.0°$ for their PMMA surface and claimed that the technique is capable of giving a contact angle with a 0.2° precision. Their receding angles were somewhat low due to reporting only the angle after drop contraction rather than the angle of the last stage of evaporation. When the inclined plane method was used, Kawasaki[47] reported $\theta_a = 75°$ and $\theta_r = 35°$ for the drop on a PMMA vertical wall having a tilt angle of $\phi = 90°$. Extrand and Kumagai[51] examined the relation between the drop shape and the contact angle on an inclined plane and concluded that roughness did not influence the hysteresis as much as the chemical nature of the surfaces. They reported $\theta_a = 77 \pm 1.1°$ and $\theta_r = 47.7 \pm 1.1°$ for the water drop on a smooth PMMA surface.[51] When all the advancing angles reported in the literature are averaged, $\theta_a = 74 \pm 11°$ was obtained which corresponds to a 15% deviation from the mean. In two of the references,[8,22] the hysteresis was reported as $\Delta\theta = 20-23°$, which is very close to our results in Table 1. The reason for the average decrease of 4 ± 1.5° in receding angles determined for every contraction step may be attributed to the time-dependent surface restructuring of PMMA due to the H-bonding between water and ester groups present at the polymer surface. Interpreting the successive contraction steps within the Shanahan model[56] becomes more difficult because the meaning of the "equilibrium" contact angle for calculating the excess free energy change is less clear.

The drop size effect on θ_a and θ_r was found to be minimal for the PET surface. We found $\theta_i = 84-85°$ and $\theta_r = 64-66°$ depending on the drop size. The lack of dependence of the receding contact angle on drop size, despite the evident contact angle hysteresis, is no longer consistent with Shanahan's model.[56] When eq 1 was applied by assuming $\theta_i \approx \theta_a$, an average hysteresis of $\Delta\theta = 19.5 \pm 1.5°$ was found for both drops. Ellison and Zisman[66] measured $\theta_a = 81°$ on the PET surface by adding small increments of water by a fine platinium tip. It was shown that in stretched PET films not only are the polymer chains oriented in the direction of drawing but also the benzene rings all lie in a plane oriented normally to the surface of the film. They proposed that there is very little hydrogen bonding with the water drop because the PET surface has only ether oxygen (−O−) groups at the top and not ester groups, so PET is unable to make an H-bond. Dann[64] reported $\theta_a = 71°$ on the PET surface. Hayes and Ralston[44] measured $\theta_a = 85-88^o$ and $\theta_r = 47-49°$ by applying the dynamic Wilhelmy gravitational plate method on the PET surface. They pointed out that evaporation and liquid vapor pressure has an effect on the relaxation of the three-phase contact line and interferes with the measured force.[44] Tretinnikov and Ikada[33] measured $\theta_a = 82.0-82.6^o$ and $\theta_r = 45.9-50.5°$ with their modified Wilhelmy balance method. They explained this large hysteresis by the time-dependent reorientations of the polymer surface in the water drop. They also pointed out that the speed of the sample immersion (between 1 and 50 mm min^{-1}) has considerable effect on the contact angles of polar polymers such as PET. The advancing angle increases and the receding angle decreases as the immersion speed becomes higher.[33] When the inclined plane method was used Extrand and Kumagai[51] reported $\theta_a = 75.3 \pm 2°$ and $\theta_r = 27.7 \pm 1.5°$ for the water drop on a PET surface. When all the advancing angles reported in the literature are averaged, $\theta_a = 81 \pm 8.5°$ was obtained which corresponds to a 11% deviation from the mean. In two of the references,[33,44] the hysteresis was reported as $\Delta\theta = 32-39°$, which is nearly double our results. Since our average $\theta_i = 85°$ was only 5% larger than the average literature θ_a, the reason for this difference appears to be the low receding angles reported in the literature. This is consistent with our own measurements using the needle-syringe and the inclined plane methods applied on the same PET sample, where we also measured similarly low receding angles of $\theta_r = 52-59°$ when compared with $\theta_r = 64-66°$ by the drop evaporation method.

Conclusions

The receding contact angles of water drops on PMMA and PET surfaces were determined by following the time-dependent drop evaporation with a video-microscopy technique. Increased values of initial and receding angles were seen for increasing drop size on the PMMA surface. We determined $\theta_r = 54-64°$ depending on the drop size with an average hysteresis of $\Delta\theta = 23.5 \pm 1.5°$. On the PET surface, we found $\theta_r = 64-66°$ depending on the drop size, although the drop size effect was found to be minimal for PET surface. An average hysteresis of $\Delta\theta = 19.5 \pm 1.5°$ was found. θ_a and θ_r were also determined by the needle-syringe and the inclined plane methods for comparison. In the needle-syringe method where the syringe was applied manually, scattered results were obtained according to the rate of liquid flow and the size of the drops. Similarly in the inclined plane experiments, quite varying results were obtained due to the drop size effect. The discrepancies from the mean of the maximum and minimum contact angle results of both the needle-syringe and the inclined plane methods were larger than expected

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for the polymer surfaces. A general trend was seen with a larger hysteresis indicating a larger discrepancy for all the samples. The major cause of this discrepancy is the variation of the rate of liquid introduction and withdrawal with the syringe in the needle-syringe method. In this respect the drop evaporation method allows a minimum rate of liquid withdrawal which minimizes (or standardizes) the linear rate of retreat effect on receding contact angle measurement. A standard procedure ordering a constant rate of liquid delivery and withdrawal in the needle-syringe method is required in order to compare the results of the contact angles on the same polymer types in independent laboratories.

The literature values were also given for comparison. It is realized that a discrepancy of 11−15% from the mean of θ_a is present for the same kinds of polymers and this is approximately five times more than the previously claimed 2−3% deviation from the mean for θ_a on the same polymers with the needle-syringe method.[1,36] The literature values and our experimental results of the inclined plane methods showed even worse discrepancies from the mean for both advancing and receding angles. The drop size effect on the contact angle seems the major cause of this discrepancy. Overall, considerable care is needed in interpreting contact angle determinations from the inclined plane method.

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