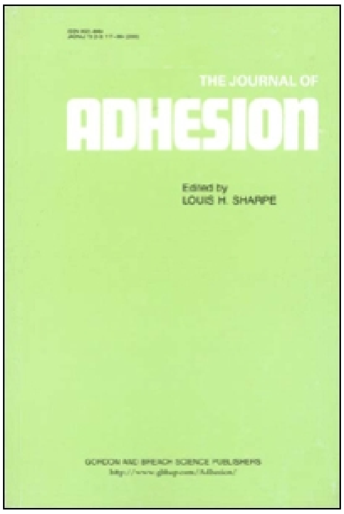

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# Contact Angles and Coating Film Thickness

H. Tavana[a]; N. Petong[b]; A. Hennig[b]; K. Grundke[b]; A. W. Neumann[c]
[a] Department of Mechanical and Industrial Engineering, University of Toronto, Toronto, Ontario, Canada [b] Institute for Polymer Research, Dresden, Germany [c] Department of Mechanical and Industrial Engineering, University of Toronto, Ontario, Canada

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# Contact Angles and Coating Film Thickness

**H. Tavana**
Department of Mechanical and Industrial Engineering,
University of Toronto, Toronto, Ontario, Canada

**N. Petong**
**A. Hennig**
**and K. Grundke**
Institute for Polymer Research, Dresden, Germany

**A. W. Neumann**
Department of Mechanical and Industrial Engineering,
University of Toronto, Ontario, Canada

*The effect of film thickness and surface preparation techniques on contact angles of water, 1-bromonaphtalene, and n-hexadecane on Teflon® AF 1600 polymeric surfaces is studied. It was found that contact angles of water on different thicknesses of spin-coated films ranging from 27 nm to 420 nm are essentially constant. This is due to the homogeneity and smoothness of the coating layers as shown by the scanning force microscopy of the samples. Furthermore, the contact angle measurements with these three liquids on both dip-coated and spin-coated films suggested that the film preparation technique does not affect contact angles dramatically. Interestingly, slightly higher contact angles on dip-coated surfaces were measured. It is also argued that the anomaly of the water contact angle—in the sense that the measured contact angle is much higher than the expected ideal value—is due to specific interactions between water and Teflon®.*

**Keywords:** Film thickness; Dip coating; Spin coating; Teflon AF 1600; Contact angle; Surface tension

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Address correspondence to A. W. Neumann, Department of Mechanical and Industrial Engineering, University of Toronto, 5 King's College Road, Toronto, Ontario, Canada M5S 3G8. E-mail: neumann@mie.utoronto.ca

## INTRODUCTION

Contact angles have been the focal point of many studies in surface science. Because of the difficulty in direct measurement of solid surface energies, contact angle measurements have been widely used as an indirect approach for determination of surface tension of polymeric surfaces [1–8]. To that end, considerable efforts have been made to find criteria for contact angles to be meaningful in the context of Young's equation. It has been shown that systems showing slip-stick of the three-phase line or dissolution of the solid surface by the testing liquid and time-dependent contact angles are not compatible with the Young equation and should be excluded from interpretation in terms of surface energetics. For the purpose of determination of solid surface tensions from contact angles, the solid should be rigid, smooth, and homogeneous [9]. In case of polymeric materials, the easiest way to work toward that goal is by producing thin films using different coating techniques such as spin coating [10–13], dip coating [14], or thermal evaporation [15].

It was shown that contact angles of a group of 10 liquids with bulky molecules on Teflon® AF 1600 polymeric films fall quite perfectly on a smooth curve when plotted as a function of liquid surface tension. This curve corresponds to $\gamma_{\mathrm{sv}} = 13.61 \pm 0.07\,(\mathrm{mJ/m^2})$ and represents the surface tension of this Teflon [16]. Knowing this value, the following equation can be used to obtain the contact angle of water under ideal conditions, that is, in the absence of any specific interaction between water and the Teflon molecules (see [5] for the details of derivation):

$$\cos\theta = -1 + 2\sqrt{\frac{\gamma_{\mathrm{sv}}}{\gamma_{\mathrm{lv}}}}e^{-\beta(\gamma_{\mathrm{lv}}-\gamma_{\mathrm{sv}})^2} \tag{1}$$

where $\beta = 0.0001247\,(\mathrm{mJ/m^2})^{-2}$ is a constant obtained empirically from contact angles of many liquids on different polymers [17] and $\gamma_{\mathrm{lv}} = 72.29\,(\mathrm{mJ/m^2})$ is the surface tension of water at 24°C [18]. This yields $\theta = 114.7\,\mathrm{deg}$ as the ideal water contact angle on Teflon AF 1600. However, our preliminary measurements show that the contact angle of water is about 127 deg, which is significantly higher than the ideal value. In the previous study [16], we showed that contact angles of a group of six liquids with bulky molecules that contain electronegative atoms of oxygen and/or nitrogen deviate up to $\sim 3$ deg from the $\gamma_{\mathrm{sv}} = 13.61 \pm 0.07\,(\mathrm{mJ/m^2})$ curve. The deviation in contact angle of water from this curve is obviously much higher. The reason might be because water is a very complicated liquid with anomalous properties. For instance, although it has a very low molecular weight, the boiling point of water is unexpectedly high, implying stronger intermolecular interactions than that expected for ordinary, or even highly polar, liquids [19]. Therefore, it is important to find out whether or not such a discrepancy is an artifact of some kind, such as a consequence of film production techniques or the thickness of the polymeric films.

Little information is available in the literature about the influence of either the thickness of polymeric coatings or the procedure of film production on contact angles. First Langmuir [20] and then Bigelo *et al.* [21] stated that a single monolayer should be sufficient for determination of wetting properties of a solid film. However, this might not be easily achieved in practice. Cho *et al.* have reported contact angles of a water droplet on different thicknesses of Teflon® films produced by spin-coating and thermal evaporation techniques [15]. On spin-coated films of ~5 nm (produced by a 0.01% concentration of the solution), the contact angle of water was 105 deg. Similar values were measured on thermally evaporated films thicker than 3 nm. However, the contact angle decreased to 51 deg when the thickness of a thermally evaporated film was reduced to 1.5 nm. Extrand has investigated the thickness dependence of contact angles for water and ethylene glycol on three different polymeric surfaces: natural rubber (NR), polystyrene (PS), and poly (methyl methacrylate) (PMMA) [22]. The films were produced by a spin-casting technique on both heated silicon wafers and ozone-treated wafers. In the case of NR films, the "critical thickness," that is, thickness above which contact angles do not depend on the film thickness, was found to be 9 nm for heated wafers and 30 nm for ozone-treated wafers. For both PS and PMMA films spin-casted on heated wafers, the critical thickness was as low as 2 nm. In general, inhomogeneity of thin films below a critical thickness was claimed as the cause for variation of contact angle values with thickness.

It is the purpose of this note to elucidate further whether contact angles are merely a property of the coating material or further depend on other parameters such as film thickness and surface preparation techniques. In order to characterize the coating material, advancing contact angle measurements were performed on films of different thickness, produced by different coating conditions and techniques. The polymeric surfaces in this study were prepared by two different methods: spin coating and dip coating, with the main focus on the former technique to produce different film thicknesses as described below.

## EXPERIMENTAL

Silicon Wafers ⟨100⟩ (Silicon Sense, Naschua, NH, USA; thickness: $525 \pm 50\,\mu\text{m}$) were selected as the substrate because of their smoothness, rigidity, and high surface tension. The latter property causes the polymeric coating solution to spread on the surfaces uniformly during the coating process [23]. The substrates were cut into appropriate shapes from the original disks and a hole of approximately 1 mm in diameter was drilled in the center of each surface. To clean the surfaces, they were left in chromic acid. Then hydrogen peroxide (30% pure) was used to remove chromic acid by the resultant chemical reaction. Finally, the surfaces were rinsed with distilled water, ethanol, and isopropanol and were blown dry by nitrogen after each rinsing step. To enhance adhesion of the coating layer to the substrates and its stability, the cleaned surfaces were exposed to the vapor of an adhesion promoter material, 1,1,1,3,3,3-Hexamethyldisilazane (HMDS) (Aldrich, Munich, Germany, 99.9%), for two hours at room temperature.

The next step was to coat the surfaces. A 6% solution of Teflon® AF 1600 in Fluorinert® FC-75 purchased from Dupont Co. (Mississauga, ON, Canada) was selected as the coating material. Teflon AF 1600 is an amorphous copolymer of tetrafluoroethylene 35% and PDD (2, 2-bistrifluoromethyl-4, 5-difluoro-1, 3-dioxole) 65%, with low surface energy and outstanding characteristics [24, 25]. To produce lower concentrations of the solution and thinner coated films, Teflon AF 1600 was diluted in the solvent FC-75, as discussed later.

Spin coating was selected as the main coating technique because it facilitates production of different thicknesses of the coating material on the substrates. In this technique, film thickness is primarily influenced by spinning speed and concentration of polymeric solution. While increasing the spinning rate tends to decrease the film thickness, a higher concentration of the coating solution would increase it. Different combinations of these two parameters were chosen to produce films of different thickness. Teflon® AF 1600 was dissolved in FC-75 at volumetric ratios of 1:1, 1:4, and 1:8 to produce different concentrations of the solution, and spinning rates of 1000 rpm, 4000 rpm, and 8000 rpm were selected for the coating process.

According to the supplier, freshly coated surfaces must be heated above the glass transition temperature of Teflon® AF 1600, $T_g$ (160°C), to remove the solvent completely. This produces a smooth coating surface and improves adhesion of the polymer to the substrate [24]. Therefore, after the surfaces were coated with Teflon AF 1600, they were kept inside a vacuum oven at 165°C for 24 h. Then the oven was turned off and the surfaces were cooled down gradually to ambient temperature.

To establish whether or not surface preparation techniques influence contact angles, some other surfaces were prepared by a dip-coating method using the most concentrated solution (1:1). Details of preparation of solid surfaces and the coating procedure can be found elsewhere [14].

Ellipsometry measurements were performed both after applying the adhesion promoter layer (HMDS) and Teflon films using a variable angle multiwavelength ellipsometer M-44 (J.A. Woolam Co., Inc., Lincoln, NE, USA). The ellipsometric angles Psi and Delta were measured in a spectral range from 428 nm to 763 nm at three angles of incidence (65 deg, 70 deg, and 75 deg). The thickness and the optical constants were simultaneously determined by curve fitting of the spectra using a Cauchy model. Details can be found elsewhere [26]. The measurements after applying HMDS showed existence of an oxide layer ($SiO_2$) of about 53 nm on the silicon wafer substrates just under the coating layer. The results from ellipsometry measurements of spin-coated and dip-coated Teflon layers will be discussed later.

Prior to performing contact angle experiments, the morphology of the polymer surfaces produced by spin-coating and dip-coating techniques was characterized by scanning force microscopy (SFM; NanoScope III, Digital Instruments, Santa Barbara, CA, USA) in the tapping mode. The AFM results confirmed existence of a smooth and homogeneous layer of Teflon® with RMS mean roughness of 0.3 nm to 0.4 nm (scan size: $20 \times 20\,\mu m^2$) and maximum peak-to-valley distances of about 2 nm and showed no additional structure. Roughness on this scale is not expected to have any influence on contact angles.

The methodology used is a drop shape method known as ADSA-P (axisymmetric drop shape analysis-profile). In this technique, the experimental drop profile is assumed to be axisymmetric and Laplacian. ADSA-P finds the theoretical drop profile that best matches the profile extracted from the image of a real drop. From the best match, ADSA-P not only determines contact angles, but also volume and surface area of the drop, the three-phase contact radius, and the liquid–vapor interfacial tension. The contact angles reported in this paper were determined by sessile drop experiments and were analyzed by ADSA-P. During each experiment, the ambient temperature and relative humidity were $23 \pm 0.5°C$ and approximately 50%, respectively. Details can be found elsewhere [27].

## RESULTS AND DISCUSSION

Distilled water, n-hexadecane, and 1-bromonaphthalene were selected as the testing liquids to perform contact angle measurements on the spin-coated and dip-coated surfaces. The experiments were all performed at low rates of advancing of the drop front between 0.3 and

0.37 mm/min. Figure 1 shows a typical output of ADSA-P for one of the contact angle experiments (corresponding to sample “a” in Table 1). Several traces are shown as a function of time: contact angle, $\theta$; three-phase contact radius, $R$; and drop volume, $V$.

The contact angle measurements were repeated six times, each on a freshly prepared solid surface with a film thickness of 420 nm resulting from the 1:1 (v/v) solution and a spinning rate of 1000 rpm in the spin-coating process. Table 1 summarizes contact angles of water from these measurements. Because the contact angles were constant for all experiments, they were averaged and yielded a mean value of $127.05 \pm 0.08$ degrees.

Similar contact angle measurements were performed with distilled water on Teflon® films of different thicknesses prepared by spin-coating and the results are summarized in Table 2. This table lists the thickness of the coated films as determined by the ellipsometry measurements and the corresponding combinations of the spinning rate and concentration of the polymeric solution. It is seen that by applying different ratios of Teflon® AF 1600 and FC-75 and using a range of spinning rates, coated films with thicknesses ranging from 27 nm to 420 nm have been obtained. It can also be seen that at fairly low concentrations of the coating solution (*i.e.*, 1:4 and 1:8), using different spinning rates but the same concentration of the solution results in the same thicknesses of the Teflon® layer. It is suggested that concentration of the polymeric solution has had the dominant effect in producing the final thickness of the Teflon® layer in the spin-coating technique. The number of contact angle measurements in case of each combination of concentration of the solution and spinning rate is also given.

The key result of Table 2 is that contact angles do not depend on the thickness of the Teflon® AF 1600 films in the range from 27 nm to 420 nm. Within the 95% confidence limits, the contact angles are the same. This is not surprising considering that, except the very first molecular layers, the subsequent layers are not in contact with the substrate and presumably do not interact with it. Therefore, for smooth and homogeneous films the configuration of the polymer molecules is essentially the same at the solid–liquid interface, regardless of the film thickness. It is expected that other polymeric surfaces behave similarly.

To find out whether contact angles are somehow influenced by film preparation techniques, contact angle measurements were performed with water, n-hexadecane, and 1-bromonaphthalene on freshly prepared dip-coated and spin-coated Teflon® AF 1600 surfaces. The thickness of the Teflon® layer on dip-coated surfaces is 470 nm.

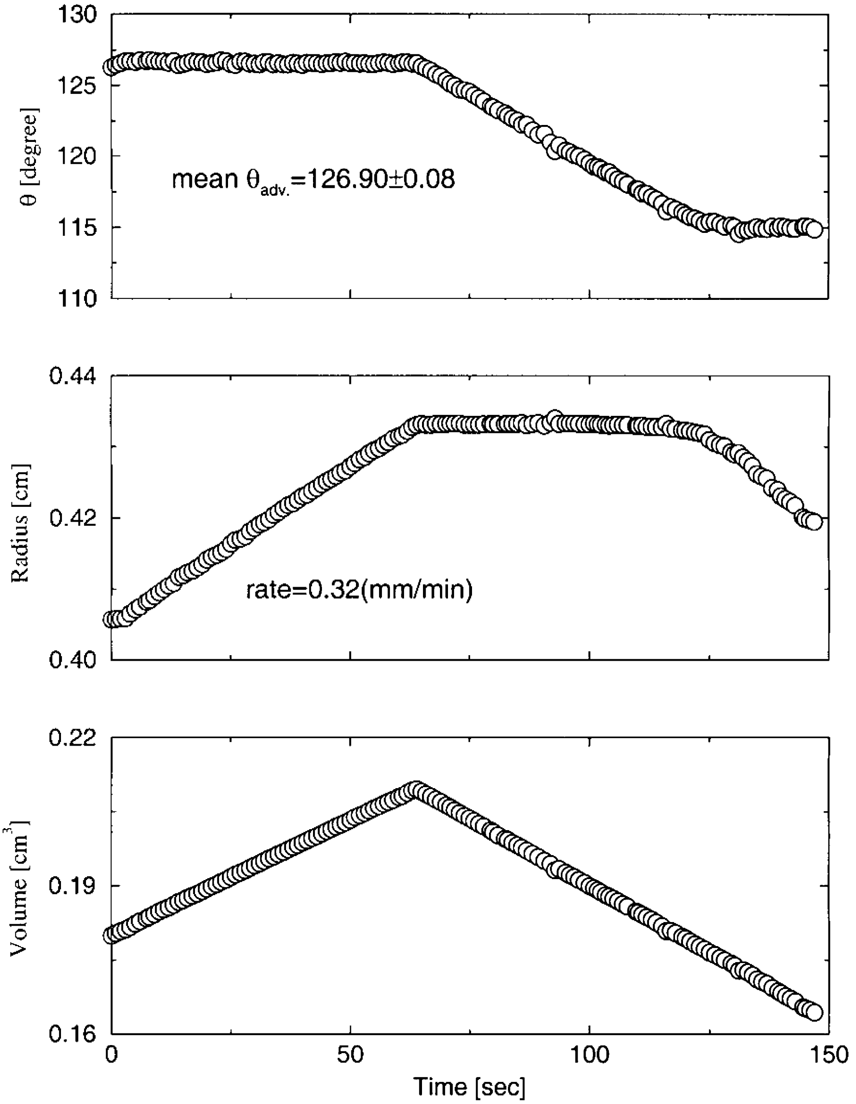

**FIGURE 1** A typical output of ADSA-P for a sessile drop experiment of distilled water on Teflon® (sample "a" in Table 1) prepared by spin coating. Several traces are given as a function of time: contact angle, the three-phase contact radius, and drop volume.

**TABLE 1.** Contact Angles of Water on Teflon®-coated Surfaces from Seven Measurements and the Corresponding Three-Phase Line Velocities

| Sample | Three-phase line velocity (mm/min) | Advancing contact angle (deg) |
|---|---|---|
| a | 0.32 | 126.90 ± 0.08 |
| b | 0.35 | 126.81 ± 0.06 |
| c | 0.31 | 126.87 ± 0.06 |
| d | 0.32 | 127.02 ± 0.08 |
| e | 0.37 | 127.42 ± 0.10 |
| f | 0.35 | 127.00 ± 0.08 |
| g | 0.32 | 127.31 ± 0.11 |
| | | mean: 127.05 ± 0.08 |

The thickness of the Teflon layer is about 420 nm. The samples were prepared with a 1:1 (v/v) solution of Teflon AF 1601 and FC-75 at the spinning rate of 1000 rpm.

The experiments were all performed at low rates of advancing of the three-phase line. The mean value of contact angle from these experiments and the corresponding number of measurements are given in Table 3. The mean contact angle of water on the spin-coated surfaces is the grand average value from Table 2. The contact angles are essentially the same on both types of surfaces for each liquid, indicating that for solid surfaces of high quality, the coating technique does not have a dramatic effect on advancing contact angles. It is interesting, however, that the mean values are consistently slightly higher for the dip-coated surfaces than for spin-coated surfaces. If this effect is real, it might indicate that, since film formation in the dip-coating technique is slower, the polymer molecules might be able to assume a surface configuration of slightly lower surface tension.

**TABLE 2** Contact Angles of Water on Films of Different Thickness

| Teflon® AF 1600 FC-75 (v/v) | Spinning speed (rpm) | Film thickness (nm) | No. of measurements | Mean advancing contact angle (deg) |
|---|---|---|---|---|
| 1:1 | 1000 | 420 | 7 | 127.05 ± 0.08 |
| 1:4 | 1000 | 150 | 5 | 127.11 ± 0.11 |
| 1:4 | 4000 | 72 | 3 | 127.04 ± 0.19 |
| 1:4 | 8000 | 72 | 3 | 126.86 ± 0.13 |
| 1:8 | 4000 | 27 | 4 | 127.10 ± 0.23 |
| 1:8 | 8000 | 27 | 4 | 127.07 ± 0.20 |
| | | | | mean: 127.04 ± 0.19 |

The effect of concentration and spinning speed is also illustrated.

**TABLE 3** Comparison of Contact Angles of Distilled Water, 1-Bromonaphthalene, and n-Hexadecane on Teflon® Films Prepared by Dip-Coating and Spin-Coating Techniques

| Liquid | Dip-coating $\theta$ (degs) | No. of measurements | Spin-coating $\theta$ (degs) | No. of measurements |
|---|---|---|---|---|
| Distilled water | $127.58 \pm 0.19$ | 6 | $127.04 \pm 0.19$ | 26 |
| 1-Bromonaphthalene | $89.90 \pm 0.19$ | 4 | $89.51 \pm 0.17$ | 2 |
| n-Hexadecane | $69.68 \pm 0.11$ | 6 | $69.48 \pm 0.09$ | 2 |

The results suggest that the measured high contact angle for water cannot be caused by film production techniques or coating film thickness and must be due to physical interactions between water and Teflon® AF 1600. A similarly large difference between expected and measured contact angle has been reported by Yang *et al.* [28]. They investigated the effect of surface treatment on the contact angle of water on self-assembled monolayers (SAMs) of octadecanethiol adsorbed on nonannealed and annealed gold. The nonannealed surfaces show a contact angle of 119.1 deg, which is unexpectedly high for a surface that presumably should expose only methyl groups at the surface. However, annealing the evaporated gold surface before formation of the SAM reduces the contact angle to 106.9 deg. This value is very close to the water contact angle of 104.6 deg on n-hexatriacontane [29]. This could be expected because both surfaces consist of $CH_3$ groups. The quality of n-hexatriacontane surfaces was so good that no contact angle hysteresis was observed for water. The results of infrared spectroscopy (IR) and atomic force microscopy (AFM) of the SAMs of octadecanethiol suggest that polycrystallinity and surface defects of nonannealed surfaces result in less-packed monolayers and brings about additional intermolecular interactions between water molecules and the methylene groups. This in turn contributes to an increase in the contact angle value.

However, there must be very different reasons for the discrepancy between the observed and expected ideal contact angle in the present case. It was argued above that intermolecular interactions contribute to contact angle deviations of about 3 deg from the $\gamma_{sv} = 13.61 \pm 0.07\,(\mathrm{mJ/m^2})$ curve for liquids with bulky molecules containing electronegative atoms. Moreover, the contact angle deviations for 1-bromonaphthalene and n-hexadecane from this curve are 0.07 and 2.07 deg, respectively. In the latter case, the contributing factor was the alignment of n-hexadecane molecules at the vicinity of the solid surface. The much larger deviation of $\sim$12 deg for water is presumably a consequence of the fact that it is the most polar liquid with very small molecules that can promote strong intermolecular interactions with the polymer. As a minor point, the contact angles of one and the same liquid on the Teflon® AF 1600 films used in this and previous studies [14, 16] shows that the polymer films are identical. For example, 1-bromonaphthalene contact angle was reported as $69.80 \pm 0.44$ deg [16], which is essentially the same as the value in Table 3.

The contact angle hysteresis for water compared with the other two liquids studied here confirms further the previous discussion: The hysteresis for water is about 12 deg with receding angles dependent on the solid–liquid contact time, while 1-bromonaphthalene and n-hexadecane show a constant 6–7 deg contact angle hysteresis.

## SUMMARY

In summary, it was shown that advancing contact angles of water on the spin-coated Teflon® AF 1600 surfaces do not depend on the film thickness in the range from 27 nm to 420 nm. Furthermore, by performing contact angle measurements with water, n-hexadecane, and 1-bromonaphthalene on both dip-coated and spin-coated Teflon surfaces, it was shown that the coating technique does not influence advancing contact angles dramatically. Interestingly, slightly higher contact angles were measured with these three liquids on dip-coated surfaces than on spin-coated ones. The results indicate that the large contact angle deviation of water from the expected value is not an artifact of experimental procedures but is due to physical interactions between water and the polymer.

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