

# THOUGHTS ON CONTACT ANGLES AND WETTABILITY

*Mark Strobel and Christopher S. Lyons*  
*3M Company Corporate Process Research Laboratory*  
*3M Center, St. Paul, MN 55144 USA*  
[mastrobell@mmm.com](mailto:mastrobell@mmm.com)

## Introduction

The wetting properties of surface-modified polymers are important for a variety of reasons. Wettability measurements directly define useful polymer properties such as ease of coating. Wettability is also often strongly correlated to the adhesion properties of a surface. Finally, wettability measurements represent a fundamental scientific characterization of any polymer surface. Wetting measurements are probably the most commonly performed and simplest surface analysis technique. The most useful methods for characterizing wettability on solid polymer surfaces are undoubtedly contact angle measurements.

We recently reviewed of some of the practical and theoretical aspects of contact angle measurements [1]. We presented evidence that it is imperative to measure both the advancing and receding contact angles of any liquid of interest. In practical terms, the advancing angle is the angle measured through the liquid at the three-phase contact line when the probe liquid is advanced over a previously un-wetted surface while the receding angle is the angle measured at the contact line when the probe liquid is retracted over a previously wetted surface [2]. Any difference between the advancing and receding angles is referred to as the contact angle hysteresis. It is important to distinguish kinetic effects, which are time dependent, from so-called “thermodynamic hysteresis,” which is an invariant property of the surface [3]. With kinetic effects, changes occur to the liquid-solid system on a time scale that is comparable to the time of measurement so that the observed contact angles appear to change with time. Penetration, swelling, or the rapid reorientation of surface functionalities are possible causes of kinetic effects in contact angle measurements. In thermodynamic hysteresis, there are no changes in the observed contact angles during the course of the measurement.

Reasonably accurate advancing and receding contact angle measurements can be obtained using a number of techniques; however, proper advancing and receding measurements cannot be obtained by simply placing liquid on the surface and then measuring the contact angle of that drop. This method of “plopping the drop” leads to an observed contact angle that is usually closer to the advancing angle than to the receding angle, but is actually neither of the two useful angles. The common use of this so-called “static” sessile-drop technique is a major source of problems with contact angle measurements in industry and in the scientific literature. To obtain valid advancing and receding contact angle measurements, the contact line of the liquid of interest must clearly advance or retract across the surface. The Wilhelmy plate technique for measuring

contact angles on polymer films is generally preferred for a number of sound reasons [1].

On an ideal surface, the advancing and receding angles will be identical. In practice, few, if any, surfaces are ideal. On chemically heterogeneous surfaces, such as surface-modified polymers, the advancing angle is more sensitive to the low-energy components of the surface (along the contact line), while the receding angle is more sensitive to the high-energy components of the surface (again, along the contact line). On surface-modified polymers, the receding angle is the measurement most characteristic of the higher-energy, modified components of the surface and is therefore often the more important of the two meaningful contact angles. In general, adhesion and ease of coating better correlate to the receding angle than to the advancing angle. For example, in the slot-fed die coating of polymer films, the liquid to be coated is physically forced to wet the film surface. The quality of the resulting coating depends upon the liquid film remaining intact prior to drying or curing; that is, not receding from the coated surface or the edges of the film. A low receding angle of the coating liquid on the film prevents “de-wetting” and other coating defects.

An ideal probe liquid for contact angle measurements does not interact with the solid surface. A common error found in the literature is the failure to test if there is any interaction between the probe liquid and the substrate being analyzed. For example, it is important to assess whether any components of a solid surface are soluble in the probe liquid and, if they are, whether any of these dissolved materials alter the surface tension of the liquid. In the case of corona-treated surfaces that have water-soluble low-molecular-weight oxidized materials (LMWOM) [4], the LMWOM will dissolve during contact angle measurements that use water as the probe liquid; therefore, solubility effects are often important on surface-oxidized polymers.

In this work, we utilize a convenient new technique for measuring the receding contact angle of water to investigate kinetic effects and the interactions of a probe liquid (water) with soluble, LMWOM-containing surfaces.

## Experimental

The substrates used for these contact angle investigations were corona-treated biaxially oriented 0.05-mm thick isotactic 3M polypropylene (PP) films. The PP films were treated at corona energies from 0.05 – 17.0 J/cm<sup>2</sup>.

Measurements of the advancing and receding contact angles of water were made using the Wilhelmy plate method on a ThermoCahn Radian DCA 332 dynamic con-

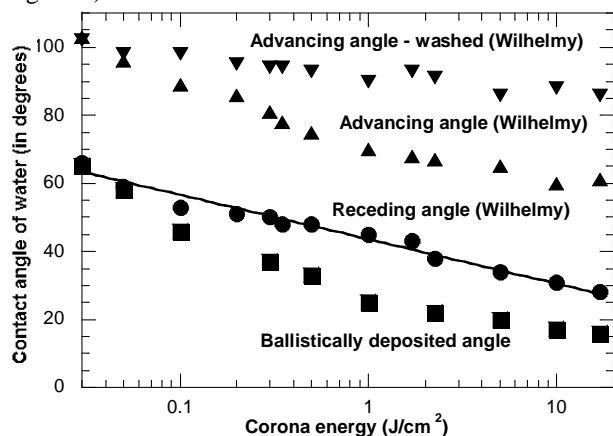
tact angle instrument. The stage speed was 50  $\mu\text{m/s}$  and the submersion distance was 6 mm. The volume of water used for the contact-angle measurements was *ca.* 50  $\text{cm}^3$ . The untreated PP film had advancing and receding water contact angles of 109° and 83°, respectively.

The treated films were washed with water using the ThermoCahn instrument. In the Wilhelmy plate method, washing of the surface is accomplished by the cycle of forcing the PP film into the water bath (advancing angle), holding it for one minute in the water, and then retracting the film (receding angle). Immediately after this washing, a second Wilhelmy measurement cycle generates the contact angles for the water-washed materials. When determined by the Wilhelmy plate method, the receding contact angles are thus always measured on “washed” surfaces because the PP is immersed in water prior to the measurement of the receding angle. Hence, no difference in the receding angle for unwashed and washed samples is detected. By using the ThermoCahn microbalance, we determined that, even after dissolution of the LMWOM, the surface tension of the water did not change after these two cycles of immersion.

Contact angle were also measured by the “ballistic-drop method” using a Brighton Technologies Group Surface Analyst instrument. In this method, about twenty 0.09  $\mu\text{L}$  drops of water are ballistically deposited in *ca.* 1 s to form a drop with a volume of 1.8  $\mu\text{L}$  on the PP surface. An image of the deposited drop is then gathered at a defined time (the “settle time”) after the drop deposition process is complete. From the image, the drop diameter is determined and the contact angle is then calculated. The settle time can be varied from 0.02 – 10 s. The ability to measure a contact angle almost immediately after the liquid contacts the surface enables the study of transient phenomena, such as kinetic effects or dissolution.

## Results and Discussion

When the contact angle of water is determined using the ballistic-drop method, the measured angle is always much closer to the receding angle (as determined by the Wilhelmy plate method) than to the advancing angle (see Figure 1).



**Figure 1.** The contact angles of water as measured by the Wilhelmy and ballistic-drop methods for corona-treated PP as a function of corona energy.

When water is deposited on a surface ballistically, it is not obvious that the water would retract from a previously wetted surface to yield a receding angle. In fact, casual observation of the drop deposition process leads to the expectation that an advancing angle is measured because the water is seemingly deposited onto a previously unwetted surface. However, high-speed imaging of the ballistic-deposition process shows that the droplets impinge on and then move over the surface prior to coalescing into the final drop that is analyzed by the instrument. The process of coalescence typically involves the movement of numerous tiny droplets from previously wetted surfaces into the final drop. In this instance, droplet coalescence is analogous to the retraction of the liquid contact line, which is the definition of a receding contact angle.

For a drop to form a receding angle on a surface, a change in the shape of the drop must occur. The necessary shape change in the drop can be regarded as an activation energy barrier to motion. In the ballistic-drop method, the droplets have kinetic energy that is converted into interfacial energy upon impingement on the surface. The supplied energy enables the liquid to advance beyond the volume and shape that is associated with the receding angle. When the ballistic deposition process stops, surface tension forces cause retraction of the liquid contact line through the minimization of interfacial energy, which, in turn, leads to the measured receding contact angle.

Despite the clear indication in Figure 1 that the angles measured by the ballistic-drop method are much closer to the receding angles than to the advancing angles measured by the Wilhelmy method, there is not agreement between the two measurement methods except for PP treated at low corona energies. This discrepancy in receding angle measurements is a result of kinetic effects, specifically, the dissolution of LMWOM into the water drop on a time scale that is comparable to the settle time. Table 1 shows the contact angles measured on corona-treated PP as a function of settle time.

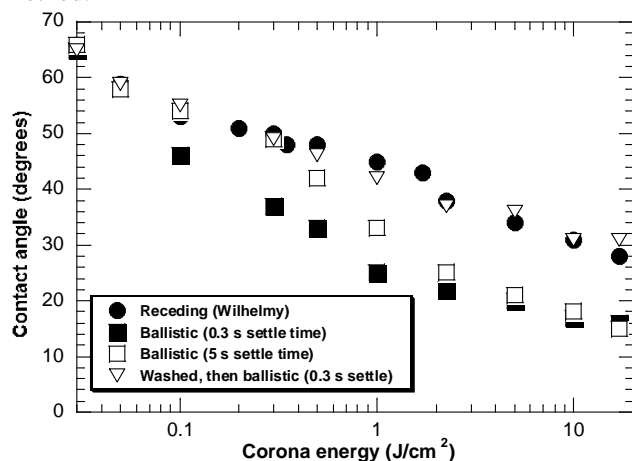
**Table 1.** The contact angle of water as measured by the ballistic-drop method as a function of settle time for PP films corona treated at an energy of 0.5  $\text{J}/\text{cm}^2$ .

Contact Angle Measurement	Receding Angle (°)
Wilhelmy plate:	48
Ballistic-drop:	
0.1 s settle time	34
0.3 s	33
0.5 s	37
1.0 s	40
3.0 s	42
5.0 s	43
10.0 s	44

On these treated films, visual observation of the water drop shows that the drop rapidly, but clearly, shrinks in aerial coverage after ballistic deposition. Our hypothesis is that the water contact angle on many samples of corona-treated PP changes as a function of settle time because the water-soluble LMWOM is dissolving into the water drop on a time scale of a few seconds. For example, at a settle time of only 0.1 s, the liquid front is still resting on the extensive LMWOM that is generated by the corona treatment. As the water remains in contact with the surface, the high-energy LMWOM dissolves into the water, thereby lowering the wettability of the surface and leading to an increase in the observed contact angle as the settle time increases to 3 s and more.

Depending upon the settle time used with the ballistic-drop method, different surfaces are analyzed. When settle times of 0.1 – 0.3 s are used, the measured contact angle appears to reflect the not-yet-dissolved (unwashed) LMWOM. When a settle time of > 5 s is used, the method appears to be analyzing the equivalent of a water-washed surface, subject to the effect of dissolved LMWOM on the measured contact angle.

Figure 2 shows the effect of settle time and washing on the contact angles as measured by the ballistic-drop method.



**Figure 2.** The receding contact angles of water as measured by the Wilhelmy and ballistic-drop methods (as a function of settle time and washing) for corona-treated PP.

When the corona-treated PP is first washed with water and *then* the contact angle is measured by the ballistic-drop method at a 0.3 s settle time (symbol ▽), the measured angle is nearly identical to the receding angle as measured by the Wilhelmy plate technique (symbol ●). When ballistic-drop method is used at the 5 s settle time (symbol □), then the measured contact angle agrees with the Wilhelmy receding angle at low corona energies where the amount of LMWOM is minimal, but deviates towards the 0.3 s settle time values (symbol ■) as the energy of treatment increases and the amount of LMWOM increases.

The correspondence of the Wilhelmy receding angle and ballistic-drop methods on washed samples shows that the ballistic-drop method measures an accurate receding

angle *when there are no kinetic effects present*. When water-soluble LMWOM is found on the unwashed corona-treated surface, the contact angles that are measured by the ballistic-drop method are dependent upon kinetic effects (at the 0.3 s settle time) or upon the interaction between the probe liquid and the soluble surface (at the 5 s settle time). At short settle times, the ballistic drop method actually analyzes the LMWOM surface itself before the LMWOM dissolves into the water drop. Because LMWOM is more oxidized than the underlying insoluble “washed” surface [4], it seems reasonable that the LMWOM has a lower receding contact angle than the washed surface. Thus, the ballistic-drop angle, which is measured on the LMWOM before it dissolves into the water, is lower than the Wilhelmy receding angle, which is always measured on the washed, LMWOM-free surface.

At the longer settle times, the LMWOM dissolves into the water. Because the water volume used in the ballistic-drop method is *much* less than that used in the Wilhelmy plate technique, the dissolved LMWOM can have a detectable effect on the surface tension of the water. This drop in the surface tension of the probe liquid is sufficient to lower the measured contact angle of that modified liquid drop on the corona-treated PP. Thus, as the amount of LMWOM on the surface grows with increasing corona energy, the contact angles measured at the 5 s settle time gradually trend downward.

## Conclusions

Use of a ballistic-drop method for contact angle measurement enables exploration of kinetic wettability effects and the interaction of a probe liquid with a solid surface. The ballistic-drop method enables the measurement of a receding contact angle on water-soluble LMWOM because the measurement can be made before the probe liquid (water) can dissolve the LMWOM. This is an excellent example of a kinetic effect in which the contact angle can change on a time scale that is comparable to the time of the measurement. The ballistic-drop method is the only analytical test known that can actually measure the water wettability of the water-soluble LMWOM that is such an important characteristic of corona-treated surfaces.

Dissolution of LMWOM into the small volume of water used in ballistic-drop method nicely illustrates the issues that can be associated with using a probe liquid that can interact with the solid surface.

## References

1. M. Strobel and C. S. Lyons, *Plasma Process. Polym.*, 2001, **8**, pp 8-13.
2. L. Gao and T. J. McCarthy, *Langmuir*, 2009, **25**, pp 14105-14115.
3. F. Garbassi, M. Morra, and E. Occhiello, *Polymer Surfaces*, 1994, Wiley, Chichester.
4. M. Strobel, M. J. Walzak, J. M. Hill, A. Lin, E. Karbasheski, and C. S. Lyons, *J. Adhesion Sci. Technol.*, 1995, **9**, pp 365-383.