Effect of Surface Roughness on Contact Angle Measurements Obtained with the Surface Analyst™

November 2016

513.469.1800 5129 Kieley Place Cincinnati OH 45217
BTGLABS.COM

Introduction

A frequent question from people who use contact angle measurements to characterize surfaces and control manufacturing processes is, "What effect does surface roughness have on these measurements?" This is a valid question, especially when dealing with surfaces that have a range of textures and roughness levels resulting from variability in molding, casting, machining, and abrasion processes. Without sounding too glib, the answer is "it depends." It depends on the magnitude of the roughness, and it depends on the way in which the liquid drop is deposited on the surface, and it can depend on the contact angle range being measured. However, in most situations where one is using contact angle measurements to control surface cleaning and treatment processes, roughness effects can be ignored. In this white paper we explain and then demonstrate why this is so.

Roughness is not an easily defined surface characteristic. There are many kinds of roughness and many parameters used to quantify roughness. There are also a great number of papers in the literature addressing the effect of roughness on contact angles. However, recent work in this area [1] shows that the best parameter for gauging the influence of roughness on contact angles may be the rise angle, or abruptness of the surface features. This paper goes on to show that the kind of extremely abrupt features that affect contact angle measurements are not typically encountered in surfaces that are prepared for bonding, and concludes that in most cases, roughness was not expected to have a significant influence on contact angles. For example, it's been shown experimentally that polyamide [1] and polyethylene [2] surfaces of consistent surface chemical composition demonstrate contact angles independent of surface roughness.

However, there can be an effect if the scale of roughness is very great. If a surface is extremely rough on a microscopic scale, then the actual surface area under the liquid is greater than the projected area. Thus, because of the greater surface area, the surface energy per unit projected area is higher because there are literally more functional groups per unit area. In this case, if the contact angle of a chemically identical smooth surface is <90°, the measured contact angle can be lower than it would be on a smooth surface. If the contact angle of the smooth surface is >90°, air can be trapped in the asperities below the liquid drop, and in these cases, only a portion of the drop perimeter is in contact with the solid while the rest is in contact with air. This causes the contact angle to increase. This is one approach for creating superhydrophobic surfaces. These extreme cases are not usually encountered in manufacturing situations, however. In general, if two surfaces are of similar roughness profiles, and if the roughness profiles are not extremely sharp, the surface chemical differences will affect the contact angle much more than differences in roughness.

There is another source of roughness effects on contact angle measurements which depends on the way in which the liquid drop is deposited, and arises from pinning of the drop perimeter during drop deposition. This pinning prevents the drop from spreading completely, distorts the drop outline, and results in a non-equilibrium contact angle. This is especially a problem with traditional contact angle measuring instruments that utilize a syringe, a pump, or a 'liquid needle' to deposit the liquid. A significant advantage of the Surface Analyst is the way it creates the drop on the surface from a pulsed stream of nanodroplets. In this technique, called Ballistic Drop Deposition™, the impact of the nanodroplets impart large amounts of kinetic energy into the liquid drop during the deposition process. These impacts advance the drop perimeter over any surface asperities. The drop then recedes slightly in the inter-impact period due to liquid surface tension. This repeated advancing and receding of the drop perimeter during growth greatly reduces the tendency for the drop perimeter to be pinned by surface roughness or small spots of chemical heterogeneity. This creates particularly round drops of uniform, equilibrium contact angles that are reflective of the surface composition, not surface roughness or texture. Because of this, instruments that utilize traditional methods for placing a liquid drop on the surface are much more sensitive to differences in surface roughness than the Surface Analyst.

These principles were demonstrated by comparing contact angles measured using the Surface Analyst with those measured using a benchtop goniometer on a series of surfaces having identical chemical composition but varying roughness. A convenient surface for this purpose was a surface finish comparator (Figure 1). This surface has 21 panels of widely varying roughness and texture; it represents the range of surfaces that are typically encountered in manufacturing processes, with R_a values ranging from 2 to 500 µin. The patterns also vary, from unidirectional to multidirectional to random.

Experimental

The surface finish comparator was first thoroughly cleaned using a multistep process to ensure consistent chemical composition across the entire surface. This consisted of a detergent wash followed with ultrasonic cleaning to remove soils that may have been trapped in the surface profile, and finally a solvent cleaning using Dysol DS-108. We have found that this multicomponent solvent is capable of repeatedly outperforming other solvents in producing a molecularly clean surface with consistent surface energy across large areas. Contact angles of Ballistically deposited drops were measured on each panel using a SA3001 Surface Analyst. Contact angles of syringe deposited drops were also measured using a benchtop goniometer.

Results and Discussion

The contact angles as a function of surface roughness are shown in Figure 2. The Surface Analyst returned an average contact angle for all measurements of 20° with a standard deviation of 1.8°. There was no visible correlation of contact angle with R_a.

The measurements obtained using syringe-deposited drops and measured with a benchtop goniometer averaged 47° with a standard deviation of 3.6°. These measurements also showed no systematic correlation with R_a values. However, the syringe deposited drops showed twice as much scatter about the average as the Ballistically deposited drops.

The Surface Analyst returns a lower average contact angle than the syringe deposited drops because the Ballistic Deposition process establishes a contact angle close to the receding contact angle which is recognized as in general being more sensitive to surface characteristics responsible for adhesion [3]. The much broader distribution of contact angle values obtained using the benchtop goniometer is probably due to the tendency of these drops to be pinned during deposition, preventing achievement of an equilibrium drop shape.

Conclusions

- Careful experiments on clean metal surfaces having a range of R_a values from 2 to 500 µin showed no systematic influence of surface roughness on contact angle.

- Ballistically deposited drops deposited using the Surface Analyst returned extremely consistent and repeatable values across the entire range of surfaces, with a standard deviation of <2°.
- Syringe deposited drops showed a higher contact angle with 2x more point-to-point variation.
- For surfaces such as these, surface cleanliness and point-to-point consistency of cleanliness have a much greater effect on contact angles than surface roughness for typical surfaces encountered in manufacturing.

References

1. C. W Extrand, “Contact Angles and Their Hysteresis as a Measure of Liquid-Solid Adhesion”, Langmuir **20** 4017-4021 (2004).
2. S. R. Holmes-Farley, R.H. Reamey, T.J. McCarthy, J. Deutch, G.M. Whitesides, “Acid-Base Behavior of Carboxylic Acid Groups Covalently Attached at the Surface of Polyethylene: The Usefulness of Contact Angle in Following the Ionization of Surface Functionality”, Langmuir **1** 725-740 (1985).
3. M. Strobel, S.M. Kirk, L. Heinzen, E. Mischke, C.S. Lyons, J. Endle, D. Poirier, G. Dillingham, “Contact angle measurements on oxidized polymer surfaces containing water-soluble species”, Journal of Adhesion Science and Technology **29** 14, 1483-1507 (2015).

Figure 1. Surface finish comparator used for gauging effects of surface roughness on contact angle measurements. This device consists of nickel plated steel.

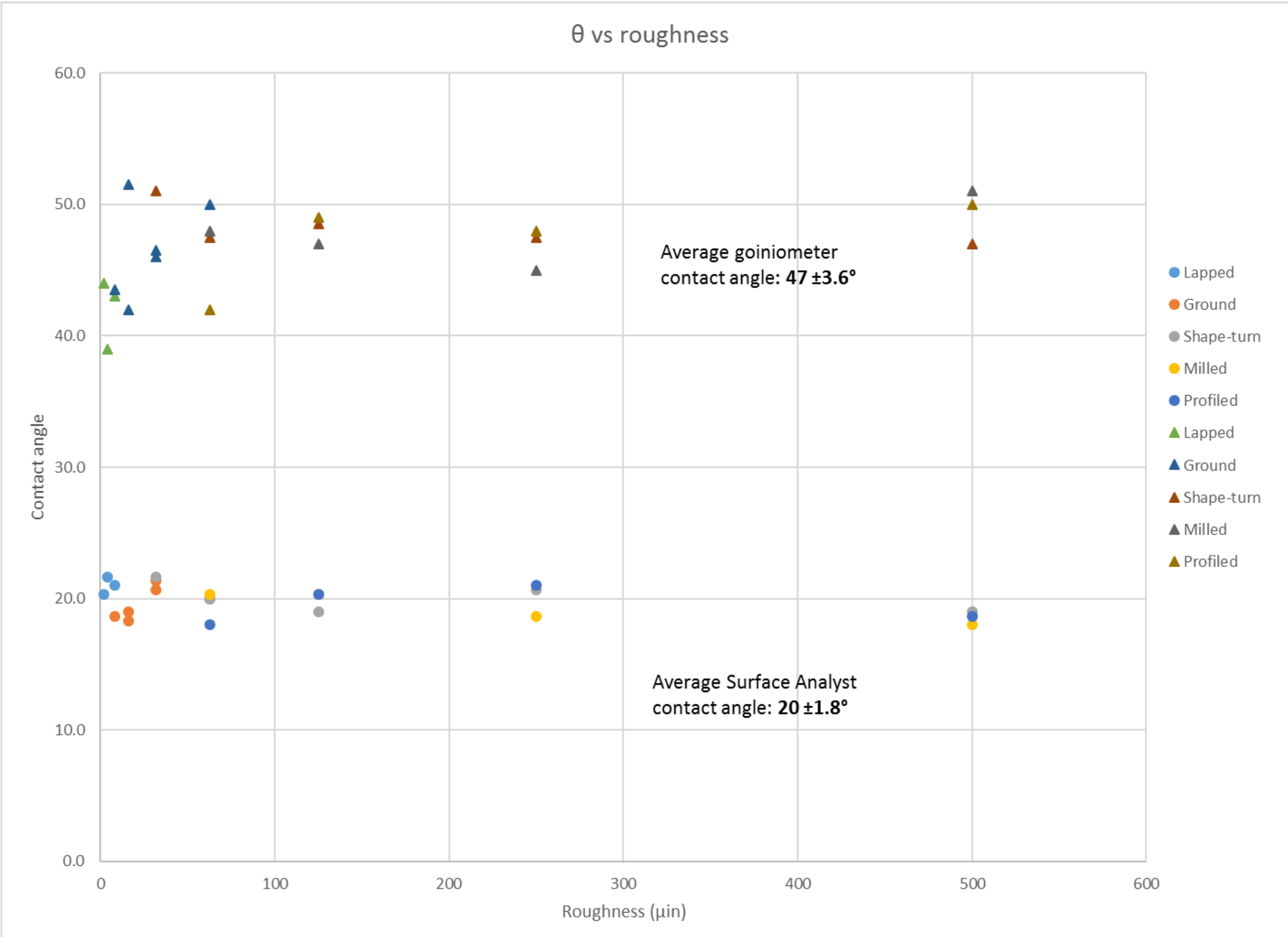

Figure 2. Contact angles obtained from the surface finish comparator in Figure 1 after careful cleaning.