

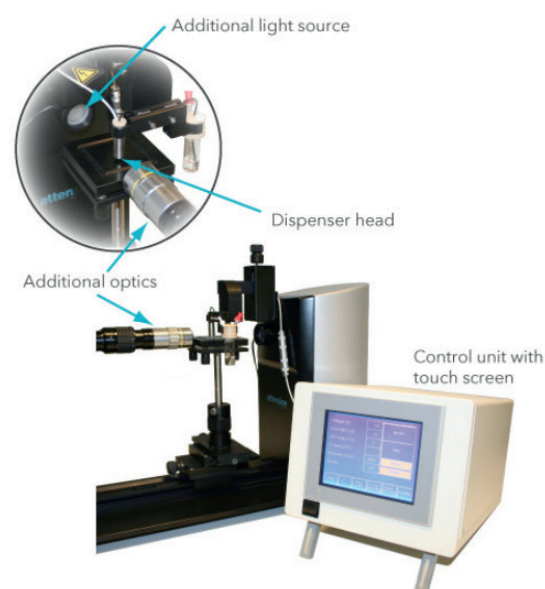
Influence of droplet volume on contact angle

This technology note describes how droplet volume, varying from microliter to picoliter volumes, influences on contact angle.

Introduction

The typical droplet size used in contact angle measurements is between 1 and 10 microliters. When the droplet volume increases, influence of gravity becomes larger. Therefore, larger than 10 microliter droplets are not commonly utilized. Influence of droplet size in microliter range has been widely studied. Drelich [1] has reviewed these studies and concluded that droplet volume has no significant influence on the contact angle with close-to-ideal surfaces, such as clean quartz plates. The ideal surface is considered to be smooth, rigid, chemically homogeneous, insoluble, and non-reactive [2]. However, the larger a contact angle hysteresis is the greater impact droplet volume has on contact angle. Substrate's disparity from ideal surface, such as chemical heterogeneity and surface roughness, causes the contact angle hysteresis. The contact angle hysteresis can be quantified by dynamic contact angle measurement, in which advancing (the largest) and receding (the smallest) angles are defined. It has been demonstrated that the advancing contact angle is less dependent on the droplet volume than the receding angle [2].

In recent years, the interest towards to the picoliter droplets has increased due to emerging inkjet technology and need to analyze small micropatterned and single fiber surfaces. Base diameter of microliter droplets is typically larger than 1 mm, whereas with picoliter droplets the base diameter is in micrometer scale. Therefore, discussion about the effects of droplet size on contact angle has broadened to compare microliter droplets to picoliter droplets. Influence of gravity on the droplet and the rate of the drop size reduction due to evaporation are the two major differences between pico- and microliter droplets [3]. Understanding the fast evaporation phenomena of picoliter droplets is also important to be able to control the drying process in inkjet printing applications. Berson et al. [4] showed that contact angle value has significant effect on this evaporation behavior of picoliter size water droplets. Droplet mass was shown to decrease linearly when initial contact angle is small, whereas decrease was not linear with larger contact angles. Some studies have already showed comparison between pico- and microliter droplets: Taylor et al. [3] demonstrated that picoliter volume water droplets were comparable with those obtained from microliter volume water droplets on a group of commonly used smooth polymer surfaces. They studied the contact angle behavior as



a function of time using high-speed camera. With microliter droplets the contact angles were stable with time, whereas with picoliter droplets contact angle decreased with time occurred in two stages; fast evaporation and spreading during the first 0.5 s, and then slower stage until it reached the receding value. Thus, contact angle versus time curve indicates also hysteresis of the substrate with picoliter droplets. The initial contact angle value of picoliter droplets correlated well with the microliter droplet contact angle values and was also close to literature value. Taylor et al. [3] demonstrated also that with larger droplets and greater influence of gravity, droplet profile fitting model needs to be chosen with care. With picoliter droplets, both Young-Laplace and circular fitting can be used as the free energy of the system at equilibrium is minimized for a spherical shape [3]. With larger droplets (>1 μ l) the circular fitting became inaccurate and Young-Laplace model was shown to give constant value as a function of droplet volume. Yang et al. [5] compared pico- and microliter droplet water contact angles on grooved polymethyl methacrylate (PMMA) surfaces coated with plasma polymers as a first study to investigate anisotropic wetting behavior with picoliter droplets. They found significant differences in water contact angles when

varying the droplet volume from microliters to picoliters, and therefore highlighted the importance of showing drop size alongside contact angle results.

According to the previous studies it has been demonstrated that droplet volume varying from microliter to picoliter scale has significant influence on wetting and drying behavior of water droplet on non-porous substrates. Chemical and topographical heterogeneity highlights the importance of the droplet volume on the contact angle results. In following case study pico- and microliter droplets contact angle values were compared on non-porous and porous substrates by using wide range of different surface tension liquids to broaden the understanding of the effect of drop volume on the contact angle.

Case study: Experimental comparison of wettability by using pico- and microliter droplets with range of liquid surface tensions on porous and non-porous substrates

Experimental

Contact angles were measured by using Theta optical tensiometer (Attension, Biolin Scientific) equipped with high-speed camera (420 fps), disposable tip pipette (volume 200 μ l) for microliter droplets and picoliter dispenser module with piezoelectric driver for picoliter droplets. The surface free energy of the inkjet paper (HP, Everyday photopaper, 170 g/m²) and low density polyethylene (LDPE) extrusion-coated paper was determined by contact angle measurement by using both microliter and picoliter sized droplets. Measurement liquids were water, diiodomethane (DIM) and ethyleneglycol (EG). The drop size was 5 μ l (2 μ l for DIM) for microliter droplets and 200 pl for picoliter droplets. The Young-Laplace model was used for droplet profile fitting. The recording was started immediately after the drop was out to detect the adsorption of the liquids into solid surface. In case of LDPE coated paper, the contact angle value at 2 s after liquid contact with the surface was used for SFE calculation. For picoliter sized droplets, the first frame was selected as a contact angle value with both LDPE and inkjet paper, due to fast evaporation of the droplet. The surface free energies were calculated by the OneAttension software using the extended Fowkes and the harmonic mean equation (Wu).

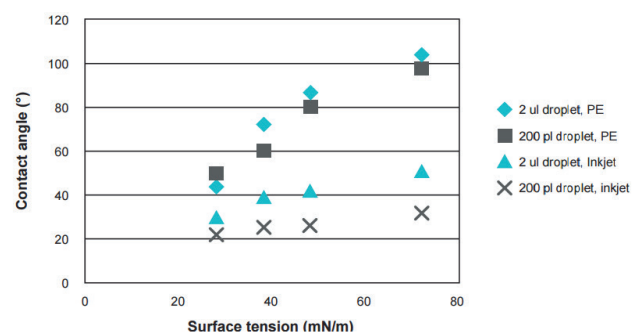
To compare the effect of surface tension on contact angle measured with both micro and picoliter sized droplets, commercially available dyne test inks (Plasmacreat GmbH) were used as measuring liquids. Inks with surface tension values of 28 mN/m, 38 mN/m and 48 mN/m as well as water (72 mN/m) were tested. The droplet size was 2 μ l for microliter size and 200 pl for picoliter size droplets. The measurements were done with the same imaging parameters as for the surface free energy measurements.

Results and Discussion

Results showed that initial contact angles of picoliter droplets correlated well with contact angles of microliter droplet on smooth, non-porous polyethylene surface (Figure 1). The surface tension of the liquid had no significant influence on the correlation. The standard deviation of the measurements was between one and four degrees.

On porous and highly absorptive inkjet paper, droplet volume had a greater influence on contact angles, and picoliter droplets provided lower contact angles compared to microliter droplets as shown in Figure 1. For surface free energy results (Tables 1 and 2) defined from apparent contact angles, influence of droplet volume was less important. The surface free energy value for polyethylene was close to literature values. With inkjet paper the surface free energy was clearly higher compared to polyethylene. This was an expected result as the substrate surface energy should be higher than that of the ink to enhance wetting.

These results accompanied with previous studies [3,4] indicate that picoliter droplets can routinely be used for contact angle measurements and surface free energy determination with smooth, homogeneous and non-porous polymer surfaces. As wetting hysteresis increases with non-ideal surfaces, the influence of droplet volume becomes more important. Surface roughness occurs in many different length scales, which all influence on wettability. The difference between the micro- and picoliter droplets may partly originate from the impact of different roughness scales on the contact angle: As base diameter of picoliter droplet is in microliter scale, macroroughness (0.1-1mm) has no or minor impact on the wetting of picoliter droplet. With porous substrates, also pores occur in different size scales causing the difference between micro- and picoliter droplet contact angles.



[Figure 1]: Contact angle of micro- and picoliter droplets as a function of liquid surface tension on non-porous and porous substrates.

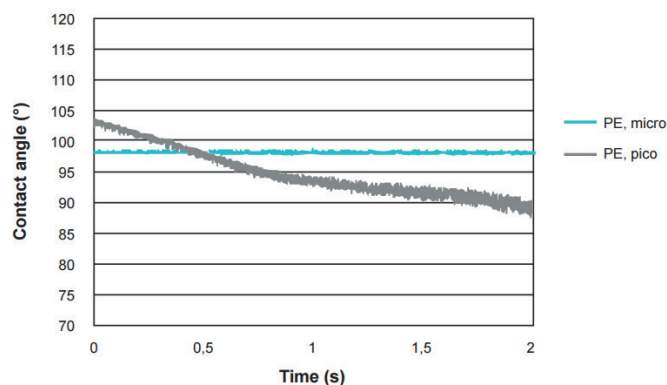
Fast evaporation of the picoliter droplet caused differences in contact angle versus time curves. The results for polyethylene substrate (Figure 2) correlated well with the previous study by Taylor et al. [3]. The contact angle was stable as a function of time when measured with microliter droplets. With picoliter droplets, the decrease in contact angles occurred in two stages: In the first stage, the decrease in contact angles was faster until approximately one second, after which it continued slower. With inkjet paper, the contact angles decreased with time by using both micro- and picoliter droplets. With picoliter droplets, the decrease was extremely fast and decrease occurred with one stage. It was also noted that with picoliter droplets the contact angle value stabilized immediately, whereas with microliter droplets the stabilization took more time (until ~0.1 s) and caused variation in contact angle results. This phenomenon was visible only by using high-speed camera.

		LDPE (micro droplet)	LDPE (pico droplet)
Surface energy	γ^{tot}	52,6	53,6
(Extended Fowkes)	γ^{d}	38,5	36,5
	γ^{p}	14,1	17,1
Surface energy	γ^{tot}	57,0	57,2
(W u)	γ^{d}	37,7	33,8
	γ^{p}	19,3	23,3

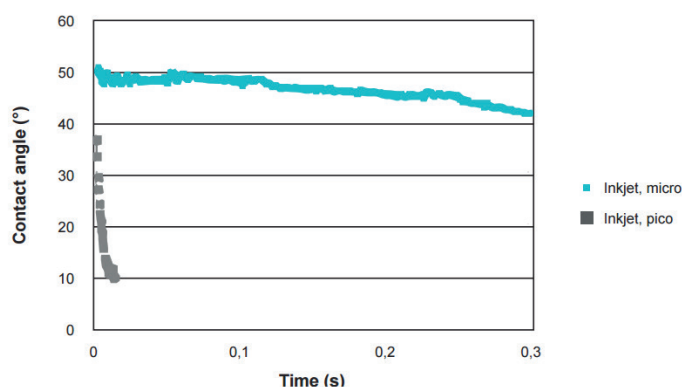
[Table 1]: Surface free energy of LDPE measured with micro- and picoliter droplets

		LDPE (micro droplet)	LDPE (pico droplet)
Surface energy	γ^{tot}	32,3	33,0
(Extended Fowkes)	γ^{d}	32,3	32,8
	γ^{p}	0,0	0,2
Surface energy	γ^{tot}	33,8	35,4
(W u)	γ^{d}	33,5	34,4
	γ^{p}	0,2	1,0

[Table 2]: Surface free energy of inkjet paper measured with micro- and picoliter droplets.



[Figure 2]: Water contact angle with time (420 fps) on polyethylene substrate by using micro- and picoliter droplets. The contact angle was stable with time when measured with microliter droplets, whereas with picoliter droplets the decrease in contact angles occurred in two stages.



[Figure 2]: Water contact angle with time (420 fps) on inkjet paper by using micro- and picoliter droplets. Contact angles decreased with time by using both micro- and picoliter droplets.

As a conclusion for the case study, the results suggest that droplet volume, varying from microliter to picoliter volume, is a critical parameter influencing on contact angle also with porous substrates in addition to chemically or topographically heterogeneous substrates. When absorption and spreading behavior as a function of time is assessed, droplet volume should be considered also with smooth and homogeneous surfaces due to different evaporation behavior.

Conclusion

In this application note it has been showed that droplet volume and contact angle hysteresis has a strong linkage: With closeto-ideal substrates droplet volume has no significant influence on contact angle. However, with substrates having larger contact angle hysteresis (e.g. due to chemical heterogeneity and surface roughness) it is critical to keep droplet volume constant if samples are compared. The advancing contact angle has been shown to be less depended on the droplet volume than the receding angle. Due to fast evaporation of picoliter droplet, the contact angle decrease as a function of time reaching the receding angle. The initial contact angle of picoliter droplet was demonstrated to correlate best with the contact angle of microliter droplet.

References:

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