Experimental Comparison of Wettability by Using Pico- and Microliter Droplets with Range of Liquid Surface Tensions on Porous and Non-porous Substrates

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Abstract

Contact angle measurement is a common method to define wettability and liquid-substrate interactions. Since inkjet printing is based on ejection of separate ink droplets on substrate, contact angle measurement is commonly utilized to characterize ink-substrate interactions in inkjet printing. However, the droplet size in contact angle measurements is typically in microliter scale, whereas picoliter droplets are used in inkjet printing. In this work an experimental comparison between micro- and picoliter droplets to evaluate the influence of droplet volume on contact angle has been made. Wide range of liquid surface tensions on porous inkjet paper and non-porous polymer substrates were tested.

Introduction

Major advantage of inkjet technology is its versatility: almost any kind of substrates can be used, such as porous, non-porous, irregular and fragile substrates [1]. A sufficient ink-substrate adhesion is crucial to ensure good print quality. Surface tension of the ink and surface free energy of the substrate are in key roles to ensure good adhesion. Both of these can be modified to promote better adhesion, if it is not in sufficient level with preferred ink-substrate combination.

The ink-substrate adhesion can be assessed with contact angle measurements. Low contact angle shows good wettability and indicates sufficient adhesion. Contact angle is also one of the most sensitive of all surface analytical techniques since only the top nanometer of the surface influence on the initial wetting behavior [3]. As inkjet printing is based on separate ink droplets, contact angle measurement represents well real life ink-substrate wettability. However, typically microliter droplets are utilized in the sessile drop method, whereas the picoliter droplets are used in inkjet printing. In microliter scale it has been known already many years that the effect of droplet size on contact angle depends on substrate homogeneity [2]: The effect of droplet size becomes more relevant when surface heterogeneity and roughness increases, as it is well-known that contact angle value is depended both on surface chemistry and roughness. It has been also showed that an advancing contact angle is less depended on the droplet size compared to a receding angle [2].

In recent years, the interest towards to the picoliter droplets has increased due to emerging inkjet technology. Base diameter of microliter droplets is typically larger than 1 mm, whereas with picoliter droplets the base diameter is in micrometer scale. Thus, small picoliter droplets enable also surface characterization of novel micropatterned surfaces and single fibers. 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]. When the droplet volume increases, the larger the influence of gravity becomes. 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, excluding the mobile hydrogel polymer surface with which water chemically reacted. With picoliter droplets contact angle decrease 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 (>1ul) 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 contact angle 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 water droplet on non-porous substrates. Chemical and topographical heterogeneity highlights the importance of the droplet volume on the contact angle results. In this 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 droplet volume's effect on contact angle.

Experimental

Contact angles were measured by using Theta optical tensiometer (Attension, Biolin Scientific) equipped with high-speed camera (420 fps/1550 fps), disposable tip pipette (volume 200 µl) 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/m^2) 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 µl (2 µl for DIM) for microliter droplets and 200 pl for picoliter droplets. The Young-Laplace model was used for droplet profile fitting. In the case of picoliter droplets, the recording was started immediately after the drop was out to detect the adsorption of the liquids into solid surface. This was especially important with the porous inkjet paper, where the first contact angle value measured was used for surface free energy (SFE) calculation. 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 (Plasmatreat 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 µl 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.

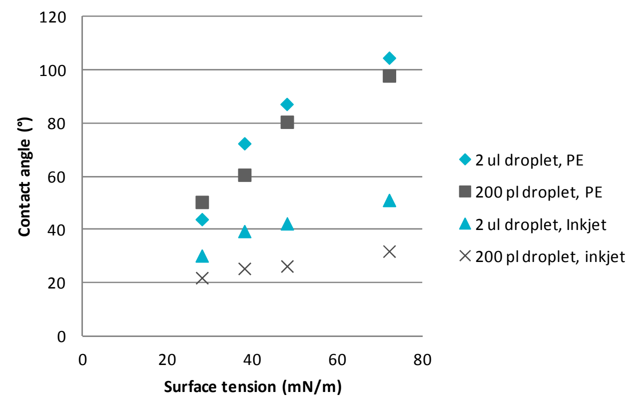

Figure 1. Contact angle of micro- and picoliter droplets as a function of liquid surface tension on non-porous and porous substrates.

Table 1. Surface free energy of LDPE measured with micro- and picoliter droplets.

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

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

		Inkjet paper (micro droplet)	Inkjet paper (pico droplet)
Surface energy	$\square^{tot}$	52,6	53,6
(Extended Fowkes)	$\square^{d}$	38,5	36,5
	$\square^{p}$	14,1	17,1
Surface energy	$\square^{tot}$	57,0	57,2
(Wu)	$\square^{d}$	37,7	33,8
	$\square^{p}$	19,3	23,3

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 (1550 fps).

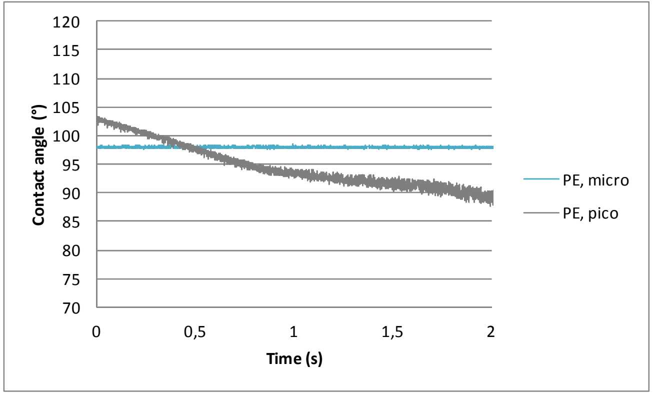

Figure 2. Water contact angle with time (1550 fps) on polyethylene substrate by using micro- and picoliter droplets. The contact angle was stable with time when measured with microliter droplets, whereas with picoliter droplets the decrease in contact angles occurred in two stages.

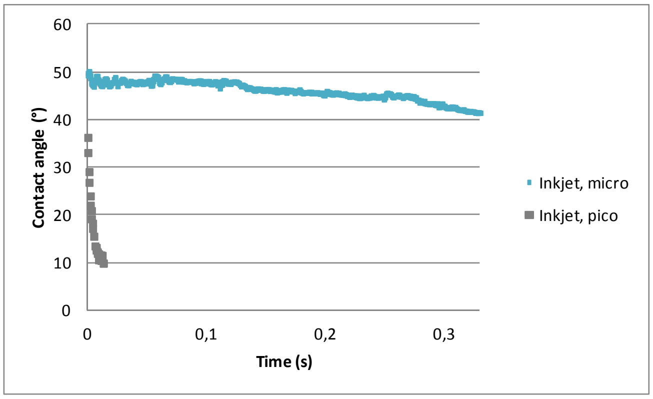

Figure 3. Water contact angle with time (1550 fps) on inkjet paper by using micro- and picoliter droplets. Contact angles decreased with time by using both micro- and picoliter droplets.

Conclusion

As a conclusion, 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.

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Author Biography

Maiju Pykönen received her M.Sc. (Technology) degree in Paper Converting and Materials Chemistry at Department of Materials Science in January 2006 from Tampere University of Technology, after which she worked as a research scientist at Åbo Akademi University, Laboratory of Paper Coating and Converting. During this time her research focused on the effects of plasma surface treatment on fiber-based subtracted and its influence on printability. She received her D.Sc. (Technology) in June 2010. Since November 2010, she has worked as a product manager for Attension tensiometers at Biolin Scientific, Finland.