Evaluation of absorption of micro-droplets on paper for creation of paper-based microstructures*

Toshiharu Enomae, Kazutomo Dougome, and Akira Isogai

Graduate School of Agricultural and Life Sciences, The University of Tokyo, Bunkyo-ku, Tokyo 113-8657, JAPAN

Tel.: +81-3-5841-8199, Fax: +81-3-5841-5271, E-mail: t@enomae.com, http://www.enomae.com/

Abstract

This work clarifies the absorption behavior of micro-droplets of water on treated paper in order to support the design of functional microstructures, such as electronics and micro-fluid channels, on paper. The period of time between when a micro-droplet of water ejected from an ink-jet head lands on the paper's surface and its complete disappearance by absorption was defined as the micro-sizing degree (MSD), and an MSD measurement method was established. The MSD was evaluated using microscopic high-speed video images of the side view recorded every millisecond. Several grades of commercially available ink-jet paper media and laboratory sheets having different levels of water repellency prepared from a pulp and a sizing agent were examined. The MSD of commercial ink-jet papers, which are known to absorb water very quickly, was 3–6 ms. Weakly sized laboratory sheets exhibited a lower MSD of 2–3 ms. The absorption behavior was analyzed in terms of the capillary pressure with and without the Laplace pressure; the theoretical and experimental results agreed moderately well. The results indicated that the Laplace pressure cannot be neglected in the analysis. The MSD of a wet surface where a preceding micro-droplet had already landed was higher than that on a dry or partially wet surface, presumably because water remains inside pores for an unexpectedly long time.

Keywords

Alkyl ketene dimer, ink-jet printing, micro-sizing degree, paper

Introduction

Ink-jet printing systems are currently applied not only for personal use but also for advanced commercial printing capable of outputting variable information from sheet to sheet. Commercial high-grade ink-jet papers with silica or alumina coatings provide the highest image quality. In addition, package printing on curved surfaces by use of a non-contact system and textile printing on nonwoven fabrics were recently reported [1]. Ink-jet technologies such as liquid division into micro-droplets and precise positioning have been applied widely in industries other than conventional printing, for example, production of color filters for liquid crystal TVs and nano-patterning of semiconductors.

^{*} Part of this research was presented at NIP22, Denver, CO, Imaging Science and Technology (2006) and the TAPPI Advanced Coating Fundamentals Symposium, Munich, Germany, TAPPI (2010).

Ink-jet paper that reproduces photo-like quality has been developed and is widely used. Crucial problems with the print quality of plain paper, such as feathering and bleeding, have been alleviated using microscopic ink droplets and non-feathering types of ink. Printing paper compatible with both offset and ink-jet printing is being developed for efficient variable-data printing. In short, ink-jet technology is oriented toward generic printing compatible with all types of paper as well as particularly high image quality when specialized paper is used.

In addition, microelectromechanical systems (MEMS) and other micro-scale electronics can now be fabricated using printing technologies [2]. Fabrication of such functional microstructures on paper would provide portability, eco-friendly disposability, and recyclability at low cost. To achieve this, the lateral spreading, penetration, and solidification of liquid materials must be controlled for conformity with the desired design. As an initial step to realizing this technology, the fundamental interactions between liquid and paper are being investigated at the micrometer level.

Liquid penetration into paper is generally closely related to the paper's water affinity or water repellency, the level of which is described by the sizing degree. This property has been measured by several methods. One of the simplest is the Stöckigt method [3]. A squared paper sheet is given a boat-like shape by folding up the four sides and then floated on a surface of aqueous ammonium thiocyanate. An aqueous ferric chloride solution is dropped onto the boat from above, and the time until three red spots are visually detected is measured. The Stöckigt sizing degree does not represent the surface layer properties involved in ink-jet penetration, and visual judgment can be applied only for moderately to strongly sized paper. The Cobb sizing degree (Cobb value) [4] is defined as the mass of water absorbed in a specific time, which is called the water absorptiveness. For accurate values, long periods of time must be specified. Thus, it is difficult to apply to rapid ink absorption.

For methods more oriented to printability, the Hercules sizing degree [5] is used. An aqueous dye solution is allowed to penetrate a paper sample. The change in light reflectance is monitored from the other side of the paper, and the time required for the reflectance to decrease to a specified value is defined as the sizing degree. More recently, original and modified Bristow-type testers have become popular as a tool for direct measurement of the liquid absorption volume as a function of the duration of liquid–paper contact [6]. Liquid is absorbed into the paper from a slit at the bottom of a liquid supply head. The absorption volume per unit area is determined and plotted against the contact time, which is calculated from the velocity at which the paper crosses the slit width. The shortest available contact time is about 10 ms.

The contact angle is not a direct measure of the absorption volume but is often used to indicate the wettability of media surfaces as well as its change with time. Absorption tests measure the time required for a drop on a paperboard surface to be absorbed, which is determined by a sudden decrease in the gloss [7]. Assuming that the three-dimensional shape of a liquid drop on a paper surface is isotropic, the side view projection, which can be recorded simultaneously with contact angle measurements, yields the volume of the drop. The contact angle is measured using a droplet having a volume ranging from 1 to 30 μ L, which is about 10⁶ times larger than common ink-jet droplets. A 1 μ L sphere has a diameter of about 1.24 mm, which is more than 10 times thicker than common copy paper. Considering the water drop's dimensions, a large volume of water remains on the surface even after the leading edge of the water reaches the opposite side by penetration. Thus, a droplet this large cannot be used to simulate the absorption of a droplet ejected by ink jet.

Questions have arisen about sizing effects. For example, are the sizing degrees or water absorption rates measured using bulk water or macroscopic water drops by conventional methods applicable to the microscopic water droplets used in ink-jet printing? Sizing agents distributed via small particles are reportedly scattered discretely [8]. Although two particles may be deposited at locations several or several tens of micrometers apart, the sizing agent produces an adequate sizing effect owing to the surface tension of the water bridging the two particles. Are water droplets with a diameter smaller than the distance between two size particles absorbed quickly? The drop absorption time has been measured [9], but it was on the order of several decades of milliseconds. Water micro-droplets of about 10 to 30 pL (about 20 to 40 µm in diameter, which is equivalent to the width of a pulp fiber) were ejected from a test ink-jet head and used to determine these properties, which are expected to be on the order of milliseconds, using a high-speed video camera system [10].

In response to these questions, the authors previously reported the absorption rate of water micro-droplets on ink-jet papers having a homogeneous ink-receptive layer [11]. The current report presents the absorption time or micro-sizing degree (MSD), of plain paper with pulp fibers exposed on the surface and compares it to that of commercially available silica-coated ink-jet papers. The water absorption rate is generally measured by Bristow's apparatus and interpreted on the basis of the Lucas–Washburn equation. In this case, the supplied liquid is assumed to be sufficiently abundant, and the reduction in surface area of the bulk liquid during absorption is neglected. This paper also analyzes the absorption mechanism in terms of the driving forces. The intermolecular attraction and surface tension have a much greater effect in a micro-liquid droplet than in a bulk liquid. The surface tension of a micro-droplet's spherical cap on a paper surface is considered to produce high pressure comparable to the capillary pressure. Thus, the absorption mechanisms of liquid micro-droplets could differ from those of a bulk liquid. Because the surface tension and capillary pressure of liquids are both involved in stable patterning of microstructures, it will be useful to understand liquid absorption into a substrate with a micro-porous structure.

Experimental

Samples

The following commercially available ink-jet papers were used. Sample PM is a photo-grade gloss-type PM paper from Epson. Sample QP is Konica-Minolta's gloss-type Photo-like QP paper. Sample HG is a Hi-Grade paper from Mitsubishi Chemical. The liquid ejected as a micro-droplet was de-ionized water unless otherwise noted. Laboratory sheets of different sizing (water repellency) degrees were prepared by adding different amounts of a sizing agent consisting mainly of alkyl ketene dimer (AKD). Two types of AKD (Harima Chemicals, Inc., AK-720H) with different sizing performances were applied. Size L, which exhibits lower performance, was added to dry pulp mass at 0.05, 0.10, and 0.20%, whereas the higher-performance size H was added at 0.10, 0.15, and 0.20%. Polyamide amine epichlorohydrin (PAE) (Seiko PMC Corp., WS-4002) was added as a retention aid at half the amount of AKD. PAE was added first, and the mixture was stirred for 5 min; AKD was then added. Laboratory sheets with no AKD and no PAE were prepared as blank samples. The preparation processes followed ISO 5269-1:2005 except that a pressure of 310 kPa was applied for 5 min with no repetition in the wetpress process.

Methods

The landing action and the absorption into paper of water micro-droplets ejected from an ink-jet head were recorded by the microscopic high-speed video recording system shown in Fig. 1. The system consists of a high-speed video camera (For-A, Japan, VFC-1000, black-and-white model) and an optical microscope (Olympus, CX41) with a 10× objective lens. Two ink-jet heads were used: a multi-nozzle type (KIE-2, Konica Minolta, Japan; Fig. 1, top) and a single-nozzle type (PIJ-25NSET, Cluster Technology, Japan; Fig. 1, middle) driven by a controller (WaveBuilder PIJD-1) adjusted to Wave B mode at a discharge voltage of 7.00 kV to stabilize the droplet volume to about 15 pL. The multi-nozzle and single-nozzle heads were used for sizes L and H, respectively.

The sample stage has a smooth vertical surface to which a paper specimen is attached with double-sided tape (Fig. 1, bottom). Backlighting is supplied by diffuse illumination produced by covering the opening for a cold light source with a translucent film. The landing and absorption of micro-droplets ejected from the ink-jet heads were recorded at a speed of 1000 frames/s and a shutter speed of 1/2000 or 1/5000 s. The projected hemisphere of each micro-droplet was recorded as a dark object. The recording period was 4 s per ejection, and the resolution of the recorded images was 256×212 pixels. The distance between the ink-jet head and the paper surface was set to 2 to 3 mm so that the landing velocity would be low enough to ensure capture of the moment of landing. The first stage of micro-droplet deformation immediately after landing, which depends on the surface energies of both the ink and the substrate [12], was deliberately avoided.

To evaluate the absorption rate of a micro-droplet of water, the volume of the hemisphere was calculated from the shape of the projected hemisphere. A prepared slide with an embedded scale was recorded, and the hemisphere volume was calibrated to true values on the basis of a scale of 0.746 μ m per pixel. To measure the shape parameters of the projected hemisphere of a water droplet in video images, the coordinates of two ends of the chord and the zenith were determined visually. The volume, height, and radius of the circular area and the contact angle were then calculated from them, assuming that the hemisphere is part of a circle and that the micro-droplet is isotropic in three dimensions.

Results and discussion

Size of water micro-droplets

The volumes of the water micro-droplets ejected from the ink-jet head varied widely. They can be grouped roughly into tiny, intermediate, and large droplets. The diameters and estimated volumes of each type ejected from the single-nozzle head were 8.0, 20.5, and 36.9 µm and 0.3, 4.5, and 26.4 pL, respectively. It appears that, on ejection, some micro-droplets merged with others, increasing their volume. Thus, the volume of the recorded micro-droplets ranged between 0.3 and 29.2 pL. The volumes were distributed more broadly for the multi-nozzle head because not every micro-droplet was ejected from the same nozzle.

Landing of water micro-droplets

Fig. 2 shows the changes in the shape of the micro-droplets over time after landing on the laboratory sheet prepared with 0.05% and 0.20% added AKD. The horizontal white line that appears in the frames before landing is the top surface of a fiber at the paper's surface. The landing locations were selected prior to ejection so that the fiber axis was as horizontal as possible. Out-of-focus micro-droplets sometimes appeared to pass the front or back of the fiber and fall into the adjacent pore. Therefore, they never spread over the fiber's surface. In some cases, a micro-droplet hung on the tip of a fiber's fibril for several ms and then suddenly disappeared by absorption. This phenomenon is explained in terms of the lotus effect, in which a water droplet rolls off a hydrophobic surface having a porous microstructure containing trapped air. The prepared laboratory sheets, even those with no AKD, pulled in micro-droplets less easily than commercial silica-coated ink-jet papers, and many micro-droplets were seen to float away above the paper surfaces. Repulsive electrostatic forces might have developed between the surfaces of the micro-droplets and the fibers.

For laboratory sheets sized with 0.05% AKD L, as shown in Fig. 2a, wetting and absorption occurred very quickly. This implies that the absorption rate of a water micro-droplet is higher for unsized or weakly sized paper than for ink-jet paper with an ink-receptive layer. When 0.20% of AKD was added, however, as shown in Fig. 2b, the absorption rate was very low. The radius of the circular contact area also remained constant during the absorption process in this case.

Change in shape of water micro-droplet hemisphere

Fig. 3 shows an example of the projected hemisphere of a water micro-droplet on sample QP. The image in which the water micro-droplet first appeared was designated as time 0. This rule of time setting was applied to every water micro-droplet analysis. At 0 ms, the image faintly indicates the micro-droplet's trajectory, suggesting that this frame is very close to the true time 0, which is ideal for determining the landing time. The droplet's height and contact angle decreased with time. In contrast, the radius of the circular contact area initially decreased very little but then started to decrease at 6 ms. Fig. 4 plots these changes in the shape parameters numerically along with the decrease in volume of this water micro-droplet. When the droplet height is low, as in the image at 8 ms, the contact angle data are no longer accurate. This difficulty becomes remarkable as the angle approaches 20°. Although the contact angle decreased, the radius of the circular contact area remained almost constant in the earlier stages of absorption. This phenomenon is believed to be explained as follows. When a water micro-droplet collides with a paper surface, it spreads very quickly over the surface owing to its inertia, forming the advancing contact angle. The shape of the circular contact area is maintained even during penetration of the water until the contact angle matches the receding one. The receding contact angle is subsequently maintained as the contact line recedes toward the inside.

Volume change of water micro-droplet

Fig. 5a shows the volume changes of water micro-droplets on sample QP. The volume decreased nonlinearly with the elapsed time. In Fig. 5b, the same data are re-plotted as a function of the square root of the time; a region of linearity appears at the mid-point in the penetration time in several of the curves. This linearity implies penetration based on the Lucas–Washburn equation,

$$l = \sqrt{\frac{R\sigma\cos\theta}{2\eta}t}$$

(1)

where *l* is the penetration depth, *R* is the capillary radius, σ is the surface tension of the liquid, θ is the contact angle, η is the viscosity of the liquid, and *t* is the time. This equation shows that the surface wetting force $\sigma \cos \theta$ of a liquid is the driving force of penetration and applies well to liquid penetration of such micro-porous media. The initial gentle slope is probably explained in terms of the time required to wet the surface. A gentle slope also appears at the other end of the curves. Considering that the radius of the circular contact area decreased while the receding contact angle was maintained, as shown in Fig. 4, the droplet contracts toward the inside while maintaining its shape. Fig. 6 schematically illustrates the mechanism of water droplet penetration.

Fig. 7 shows the changes in the volume of water micro-droplets on sample PM. As with sample QP, the volume decreased linearly as a function of the square root of the time. The water absorption rate should be reflected in the slope of the volume change. The two photo-grade ink-jet papers, QP and PM, did not show a significant difference in water absorption rate.

Fig. 8 shows video frames of the water micro-droplets and their changes in volume on sample HG, a general grade of coated ink-jet paper. Scanning electron micrographs revealed aggregated silica particles 5 to 20 µm in diameter, and pulp fibers were visible between the particles (not presented here). Therefore, the surface consisted of large, rough silica

aggregates and pulp fibers. The base paper used for ink-jet coating is typically sized to some extent; thus, the water absorbency is expected to be lower than that of the silica particles. However, the initial contact angle was lower for sample HG, as shown in the image at 0 ms, and the water absorption rate was higher than that of photo-grade samples QP and PM. Bristow's test revealed a higher water absorption rate for QP and PM, presumably because the coat weight of sample HG was much less, and any initial quick absorption that might occur was not detected.

Fig. 9 shows the changes in the volume of individual micro-droplets on the laboratory sheets with the square root of the time. The volume of micro-droplets ejected from the head varied widely. However, large droplets did not always show higher MSD values. As noted above, micro-droplets sometimes hung on the tip of fibrils for several ms before being absorbed on sheets with 0.20% added AKD L. This also occurred, but less frequently, for sheets with 0.05% added AKD.

Fig. 10 shows the changes in the volume of water micro-droplets upon landing on laboratory sheets treated with size H with 95% confidence intervals attached to every data point of a mean value. The data points were plotted down to certain volumes and not to volume zeros because some micro-droplets were completely absorbed early and the reasonable mean volumes could not be calculated only from the remaining micro-droplets, that is, those chosen nonrandomly. The three absorption curves for the AKD-added sheets have fairly wide 95% confidence intervals. This result suggests that the three curves can be regarded as equal in absorption rate and compared with theoretical curves as a whole in the following section. The mean MSD was 380–450 ms for the three types of sheets irrespective of the amount of size H added. Sizing effects tend to saturate at high levels of added sizing; therefore, the 0.1% addition level provided sufficient water repellency. However, the wider 95% confidence intervals suggest that more sites lacked AKD when less sizing agent was added as summarized in Table 1.

Theoretical analysis of absorption

The velocity of liquid absorption into porous media has been investigated theoretically using the Lucas–Washburn equation (1) historically [13] and more recently using the Davis–Hocking model, which describes a porous medium saturated by a liquid [14] and a dry porous medium [15]. For non-porous media with a water-absorbent polymer, the diffusion model was shown to be appropriate, and the case of a porous medium was compared to it [8]. The ink absorption velocity of pigment-based inks has also been determined [16]. The driving forces for liquid sorption into porous media are the capillary pressure, Laplace pressure, and hydrostatic (gravitational) pressure,

$$\Delta P = \frac{2\sigma\cos\theta}{R} + \frac{2\sigma}{r} + \rho gh, \qquad (2)$$

where ΔP is the total absorption pressure, *r* is the radius of the spherical cap of a micro-droplet remaining on the medium's surface, ρ is the density of the liquid, *g* is the gravitational acceleration, and *h* is the height of the spherical cap. The gravitational pressure in the third term is far less than the other two pressures, especially for a micro-droplet. The Laplace pressure is usually neglected for bulk liquids such as film-shaped ink deposits above a medium in conventional printing systems. It is also often neglected for ink-jet printing because the radius of curvature of a micro-droplet is larger than the capillary radius for pigmented microporous layers with small pore sizes [13, 17, 18]. On the fiber-exposed surfaces of uncoated paper such as the laboratory sheets, however, the pore radius is 1 µm or greater at the medium's surface, which is comparable to a micro-droplet's radius of curvature. Therefore, the Laplace pressure cannot always be neglected.

The volume V and radius r of the spherical cap are functions of time t. It was assumed that the radius of the circular contact area has a constant value a and the contact angle at the edge of the spherical cap continues to decrease during absorption, as shown in Fig. 6, although θ , the advancing contact angle in the capillaries, is constant. If the liquid flow in capillaries is assumed to follow Poiseuille's law, and the gravitational pressure is neglected,

)

$$\frac{dl}{dt} = \frac{R^2 \Delta P}{8nl} \,. \tag{3}$$

Equations (2) and (3) give

$$\frac{dl}{dt} = \frac{R^2}{8\eta l} \left(\frac{2\sigma\cos\theta}{R} + \frac{2\sigma}{r} + \rho g h \right).$$
(4)

Substituting $\rho gh = 0$, $V = V_0 - \phi \pi a^2 l$, and $-\frac{dV}{dt} = \phi \pi a^2 \frac{dl}{dt}$ into equation (4) yields

$$-\frac{dV}{dt} = \frac{R^2}{8\eta} \frac{(\phi \pi a^2)^2}{V_0 - V} \left(\frac{2\sigma \cos\theta}{R} + \frac{2\sigma}{r}\right),\tag{5}$$

where ϕ is the porosity of the medium, and V_0 is the initial volume of the spherical cap at t = 0. In equation (5), every value is constant except V and r. Thus, it is difficult to determine V as a function of t. However, if some values are substituted for r, the right-hand side value is determined by using the relationship

$$V = \frac{\pi}{3} \left\{ 2r^3 - \left(2r^2 + a^2\right)\sqrt{r^2 - a^2} \right\}.$$
 (6)

If dv and dt are observed starting at $V = V_0$ and t = 0, respectively, the relationship between V and t can be illustrated graphically.

Fig. 11 shows the absorption curves predicted by equation (5); the Laplace pressure $2\sigma/r$ is considered and neglected for both sized and unsized papers. To draw these curves, the known physical constants of $\sigma = 72.8$ mN/m and $\eta = 1.00$ mPa·s were applied, and ϕ was calculated from the paper and cellulose densities. *R* has not been measured, but 2.1 µm, which is the measured value for generic uncoated paper, was used [19]. The values of θ , *a*, and $r_{t=0}$ were those calculated from the initial dimensions of the micro-droplets recorded essentially as specified in the caption of Fig. 11 so that V_0 would agree approximately with the measured values in Fig. 10. The curves predicted with and without the Laplace pressure are reasonably different from each other. The difference becomes remarkable when the capillary pressure is reduced by the presence of larger pore sizes or higher contact angles, that is, for low-density or sized paper, respectively. Both of the predicted curves for the sized laboratory sheets match the experimental ones shown in Fig. 10. It was difficult to judge the importance of considering the Laplace pressure. For unsized laboratory sheets, the predicted curves showed slower absorption than the experimental ones, presumably because of the effect of swelling of cellulosic materials, which resembles that of an absorbent polymer.

The experimental curves shown in Fig. 10 deviated downward to some extent from a linear regression for the sized paper. This deviation is presumably attributed to the evaporation of water from the micro-droplet surfaces. If the evaporation rate is assumed to be roughly proportional to the area of a water/air interface and this area does not change much until near the end of the absorption process, the water micro-droplet volume decreases as a linear function of time by evaporation. If the evaporation effect is put on the absorption curves, the volume reduction curves in Fig. 10 will deviate downward on a scale of a square root of time. The effect of evaporation should be examined precisely because it is closely related to microstructure formation after drying.

Absorption of a water micro-droplet on a wet surface

Coincidentally, several water micro-droplets landed close to each other on sample PM. Fig. 12a shows video frames recording four water micro-droplets that landed continuously on the surface. The first droplet (0 to 6 ms) and the third droplet (200 to 216 ms) appear on the left, the second (124 to 130 ms) appears in the middle, and the fourth (210 to 216 ms) appears on the right. The second and fourth water droplets landed at a distance from the first and second, respectively, of approximately half the radius of the circular contact area. The absorption patterns of the second and fourth water droplets were similar to that of the first droplet, which landed on a dry surface, in terms of the change in the volume of the on-paper spherical cap, the radius of the circular contact area, and the contact angle. When an area of about one-third of that of the circular contact area is already wetted, it does not seem to affect a droplet's absorption behavior. However, for the third droplet, which happened to land on exactly the same location as the first one, the volume decreased more slowly than for the other droplets, and the contact angle was lower at the same time after landing. Wet pore walls are believed to have low contact angles θ and to absorb water more quickly than dry ones. However, absorbed water might remain inside the pores and plug them for longer times than expected for diffusion and evaporation.

Micro-sizing degree

In Fig. 2a, the spherical cap of a micro-droplet was recorded in only two frames. In this case, the MSD was 2 ms. It follows that in order to standardize the sizing degree, we can assume that *n* frames including a micro-droplet in contact with a paper surface indicate that the MSD is *n* ms on average, with maximum errors of ± 1 ms at 1000 frames/s. Therefore, lower MSDs tend to have relatively larger experimental errors. For samples other than the laboratory sheets treated with size H, the multi-nozzle type head was used. From this head, satellite (small) and coalesced (large) droplets were sometimes generated. The MSDs for every clearly recorded micro-droplet were determined irrespective of the droplet size, and the mean values were calculated. Table 1 lists the mean MSDs with 95% confidence intervals for all the samples examined. Therefore, the calculated MSDs have relatively broad distributions. When 0.10% or less of AKD L was added, the MSD did not vary significantly. When 0.20% was added, however, it increased to extremely high values. Ink-jet papers having an ink-receptive layer that contains silica or alumina particles are known to absorb water quickly. However, the hydrophilic fiber surfaces of

an unsized or even weakly sized laboratory sheet absorbed water much more quickly. Sample HG showed the lowest MSD among the silica-coated ink-jet papers used.

AKD particles melt under heat treatment and cover the paper's surface, but only a certain ratio of the entire area [9]. Exposed unsized surfaces might be wetted easily by water micro-droplets and trigger quick absorption even on strongly sized paper. Therefore, it was predicted that for micro-droplets, sizing agents such as AKD might not function properly. Emulsified particles of AKD are adsorbed on the fiber surfaces during dehydration in the papermaking process. However, for the laboratory sheets with 0.20% of added AKD H, it takes several tens of milliseconds for every micro-droplet to be completely absorbed. This is significantly longer than the time required on the laboratory sheets with 0.10% or less of added AKD H. Thus, strongly AKD-sized paper exhibits homogeneous water repellency of micro-droplets with diameters of as small as a few micrometers.

Conclusion

The micro-sizing degree (MSD) is defined as the period of time between when a micro-droplet of water ejected from an ink-jet head lands on a paper surface and its complete disappearance by absorption. MSD values were evaluated using microscopic high-speed video images of a side view for several grades of commercially available ink-jet paper and laboratory sheets having different levels of water repellency. The laboratory sheets were prepared from a kraft pulp with added AKD. The MSD of commercial ink-jet papers, which are known to absorb water very quickly, was approximately 3–6 ms. In contrast, it was approximately 2–3 ms for uncoated laboratory sheets with 0.10% or less of added AKD H. The MSD for laboratory papers with 0.20% of added AKD H was approximately 45 ms. The absorption of water micro-droplets was analyzed considering the capillary pressure with and without the Laplace pressure as driving forces. The difference due to considering or ignoring the Laplace pressure became remarkable when the capillary pressure was reduced by the presence of larger pore sizes or higher contact angles, that is, for common uncoated printing paper. The MSD of a wet surface where a preceding micro-droplet had already landed was higher than that of a dry or partially wet surface. The knowledge obtained in the study will be useful in the design and fabrication of microstructures on commercial paper.

Acknowledgment

The authors express special thanks to Mr. Kazumasa Matsumoto, Konica Minolta, for giving us the opportunity to use the KIE-2 system. They also thank the Japan Society for the Promotion of Science (JSPS) and the Japanese Society of Printing Science and Technology (JSPST) for their financial support: Grant-in-Aid for Scientific Research (B) No. 22380092 (2009) and Research Fund for Printing Technology (2009 and 2011), respectively.

Type of paper	MSD, ms
Commercially available ink-jet paper	
QP	6.3±1.4
PM	4.8±1.0
Landing on dry or partially wet surface	7.3±1.3
Landing on wet surface	18
HG	3.3±0.7
Laboratory sheets	
Unsized	2.1±0.4
Sized by AKD L addition, %	
No AKD addition	2.1±0.4
0.05	3.4±2.5
0.10	2.3±0.7
0.20	44.9±21.2
Sized by AKD H addition, %	
No AKD addition	3.1±1.1
0.10	380±120
0.15	420±70
0.20	450±60

Table 1 MSD values of commercially available ink-jet papers and laboratory sheets sized to different degrees



Fig. 1 Multi-nozzle (top) and single-nozzle (middle) ink-jet heads and microscopic high-speed video camera system (bottom)



Fig. 2 Landing of water micro-droplets on laboratory sheets prepared with (a) 0.05% and (b) 0.20% added AKD



Fig. 3 Changes in projected spherical cap of water micro-droplet on sample QP recorded every 2 ms



Fig. 4 Changes in volume and shape parameters of a single water micro-droplet recorded in video images shown in Fig. 2



Fig. 5 Changes in volume of water micro-droplets on sample QP with (a) time and (b) square root of time



Fig. 6 Schematic of water micro-droplet absorption mechanism



Fig. 7 Changes in volume of water micro-droplets on sample PM with square root of time



Fig. 8 Changes in projected spherical cap of water micro-droplet on sample HG recorded every 2 ms (left) and changes in volume of droplets with square root of time (right)



Fig. 9 Volume changes with square root of time in water micro-droplets above surface plane of laboratory sheets prepared by adding different amounts of AKD sizing to dry pulp mass



Fig. 10 Volume changes with square root of time in water microdroplets after landing on laboratory sheets prepared with AKD size H. Error bars indicate 95% confidence intervals.



Fig. 11 Predicted volume changes of water micro-droplets on laboratory sheets. For sized sheets, $a = 21.3 \text{ }\mu\text{m}$, $r = 21.6 \text{ }\mu\text{m}$, $\theta = 80.4^{\circ}$, and $\varphi = 0.547$ are assumed. For unsized sheets, $a = 22 \text{ }\mu\text{m}$, $r = 27.5 \text{ }\mu\text{m}$, $\theta = 53.1^{\circ}$, and $\varphi = 0.557$ are assumed.



Fig. 12 (a) First water droplet in initial frames, second droplet away from the first by half the drop size, third droplet on the same location as the first droplet, and fourth droplet away from the second by half the drop size, with graphs of (b) volume, (c) radius of circular contact area, and (d) contact angle

References

- Hamada H, Bousfield DW, Luu WT (2009) Absorption mechanism of aqueous and solvent inks into synthetic nonwoven fabrics. J Imaging Sci Technol 53:050201-050206
- Sekitani T, Takamiya M, Noguchi Y, Nakano S, Kato Y, Sakurai T, Someya T (2007) A large-area wireless power-transmission sheet using printed organic transistors and plastic MEMS switches. Nat Mater 6:413-417
- Japanese Industrial Standard, JIS P 8122 Paper and board Determination of sizing Stöckigt method
- 4) ISO 535:1991 Paper and board Determination of water absorptiveness Cobb method
- 5) TAPPI TEST METHODS T 530 om-02 Size test for paper by ink resistance (Hercules-type method)
- 6) Kuga S, Kataoka H, Enomae T, Onabe F, Yagi N, Fukami O (1994) Development and application of dynamic scanning absorptometer—Rapid and improved measurement of Bristow's method. Japan TAPPI J 48:730-734 [in Japanese]
- 7) TAPPI TEST METHODS T 835 om-03 Water absorption of corrugating medium: water drop absorption test
- Asakura K, Iwamoto M, Isogai A (2005) Effects of fatty acid components present in AKD wax on emulsion stability and paper sizing performance. J Wood Chem Technol 25(1-2):13-26
- Yip KL, Lubinsky AR, Perchak DR, Ng KC (2002) Measurement and modeling of drop absorption time for various ink-receiver systems. Proc IS&T's NIP18, IS&T, Springfield, pp. 378-382
- Ivutin D, Enomae T, Isogai A (2005) Ink dot formation in coating layer of ink-jet paper with modified calcium carbonate. Proc IS&T's NIP21, Springfield, pp. 448-451
- Enomae T, Mori Y, Isogai A (2006) Micro liquid absorbency of ink-jet media. Proc IS&T's NIP22, IS&T, Springfield, pp. 604-607
- Blayo A, Pineaux B, Gandini A, Medledge F (2000) A study of the dynamic spreading of inks onto various ink-jet substrates. Proc IS&T's NIP16, Springfield, pp. 225-228
- Schoelkopf J, Gane PAC, Ridgway, CJ, Matthews GP (2002) Practical observation of deviation from Lucas–Washburn scaling in porous media. Colloids Surf., A 206:445-454
- Davis SH, Hocking LM (1999) Spreading and imbibition of viscous liquids on a porous base.
 Phys Fluids 11:48-57
- Davis SH, Hocking LM (2000) Spreading and imbibition of viscous liquids on a porous base II. Phys Fluids 12:1646-1655
- Desie G, Deroover G, Voeght F De, Soucemarianadin A (2004) Printing of dye and pigmentbased aqueous inks onto porous substrates. J Imaging Sci Technol 48(5):389-397
- 17) Desie G, Van Roost C (2006) Validation of ink media interaction mechanisms for dye and pigment-based aqueous and solvent inks. J Imaging Sci Technol 50(3): 294-303
- Lundberg A, Ortegren J, Alfthan E, Strom G (2011) Microscale droplet absorption into paper for inkjet printing. NORD PULP PAP RES J 26(1):142-150

19) Enomae T, Onabe F, Usuda M (1990) Surface properties and pore structure of coated paper as measured by liquid penetration methods. Japan TAPPI J 44(3):391-398