https://doi.org/10.2352/ISSN.2169-4451.2019.35.69

Quantification of Evaporation, Penetration and Viscosity Increasing Behaviors of Ink Droplets after Landing on Media

Yoshihiro HARADA, Ricoh Company, Ltd., 2-7-1 Izumi, 2430460, Ebina Kanagawa, Japan.

Abstract

In inkjet imaging, in order to obtain high image quality, it is desirable to quickly solidify ink droplets on the media. In order to understand the speed at which the ink droplets solidify, the process was quantified by measurement based on the dynamic light scattering method. In addition, the phenomenon of ink penetration into media, which is one of the factors of solidification, was visualized by the method of optical coherence tomography, and the interface movement speed was quantified. These make it possible to determine whether the ink droplet behaves properly for image quality.

Motivation

In developing an inkjet imaging process, it is important to control the state of the ink during the printing process to achieve both high image quality and high productivity. With an aqueous pigment ink, ink dots are formed by quickly wetting and spreading after landing on the media, and then quick solidification and fixing are performed. This behavior is repeated simultaneously or continuously to form an image by arranging ink dots of target size in order at the target position. If the ink dots do not reach the desired size, the image cannot reproduce a desired color. Also, if the ink dots do not solidify quickly, they coalesce and become unevenly distributed, making it difficult to place the ink dots of the target size at the target position. Therefore, it is necessary to wet and spread ink droplets in accordance with the target image quality and productivity.

The ink dots in inkjet imaging process can basically be formed by the following processes.

(1) Ink droplets collide with the medium.
(2) Ink droplets wet the surface of the medium and spread on it.
(3) The solvent of the ink droplets evaporates.
(4) The solvent of the ink droplets penetrates the medium.
(5) The ink droplets are gradually concentrated and solidified.

Depending on the properties of the ink and media, behaviors of process (2) and later can occur simultaneously. In other words, the viscosity of the ink droplet increases due to the evaporation and penetration of the ink solvent, and the wetting and spreading speeds decrease, thereby interact each other. In order to form ink dots of the target size at the target position, it is required to control these behaviors appropriately.

In particular, as one of the additional methods for rapidly solidifying ink dots, the pre-treatment liquid is applied to the media to assist the viscosity increasing behavior of the ink droplets in advance. The treatment liquid contains flocculants for aggregating dispersed particles such as pigment particles contained in the ink. Flocculants act in the ink droplets landed on the medium to cause the dispersed particles to aggregate. And the viscosity of the ink droplets increases. That is, flocculants have the effect of raising viscosity. If the combination of the ink and the media provides a condition that is easy to penetrate sufficiently, the penetration of the solvent is considered to accelerate the increasing viscosity of the ink droplet, so the pre-treatment step is not necessarily required. However, in such a case, the ink droplets are solidified quickly so that the ink droplets cannot be widely spread, and an extra amount of ink may be required to obtain the target dot diameter. In addition, due to the use of a large amount of ink, for example, when the ink solvent reaches the base layer of offset-coated paper, the paper fibers expand and contract, causing problems such as waving of the printed surface (it is called cockling).

Problem

In this way, it is important to efficiently design an inkjet system for various applications to confirm the behavior and state change of ink droplets landed on the media. However, it is not easy to understand the phenomena that occur in the ink droplet during the imaging process because of its small size and quick behavior.

For example, in order to measure the penetration of ink into media, the penetration speed of ink into paper has been measured with the use of the Bristow method. In this method, it is continued to supply ink to the media being transported. And penetrable rate is estimated from the supply rate. But it is difficult to measure to which depth of the media the ink droplets penetrate.

In order to measure the drying state of the ink, the fluidity of ink has been measured. In this method, it is estimated to evaluate the Brownian motion based on the dynamic light scattering method. However, there are few examples in which the state change of the ink droplet is evaluated for the influence of the media having different penetrability and the pre-treatment of media, or the example associated with the behavior at the time of ink dot formation.

Approach

The purpose of this research is to visualize behaviors and state change during inkjet imaging process, especially the process of ink droplet penetration into media and the process of viscosity increasing, and to make it possible to grasp these phenomena quantitatively. Several observation techniques have been developed for these purposes. The technology to monitor velocity of evaporation, velocity of penetration and velocity of viscosity increasing of ink droplets is described below.

Quantification of Evaporation

Figure 1 shows a schematic diagram of the experimental setup for quantifying the evaporation rate of ink droplets. A high-speed camera and illumination light are used to record the process in which the ink droplets ejected from the inkjet head land on a non-penetrable medium, evaporate while wetting and spreading, and reduce the volume. The shape change can be grasped by observation of the ink droplet on the media from the horizontal direction of the media surface. Examples of the droplet shape and its time change are shown in Figure 2. If the ink drop is small enough to ignore the effect of gravity, the ink drop shape can be regarded as the part of a sphere. Therefore, if the width and the height of the ink droplet are obtained with the use of image processing, the volume can be estimated by equation (1).

$$V = \pi h(3a^2 + h^2)/6, \qquad (1)$$

where V is the ink drop volume, h is the ink drop height, and a is the ink dot radius. The volume change is calculated by performing this process in the images recorded in time series.

In this report, the volume change of ink droplet obtained by using non-penetrable media is treated as the one caused by evaporation, and the rate of evaporation with penetrable medium is assumed to be the same. However, strictly speaking, it is important to note that the evaporation rate differs depending on ink droplet state which is changed by the behavior such as penetration or aggregation caused by adhesion to different types of media.

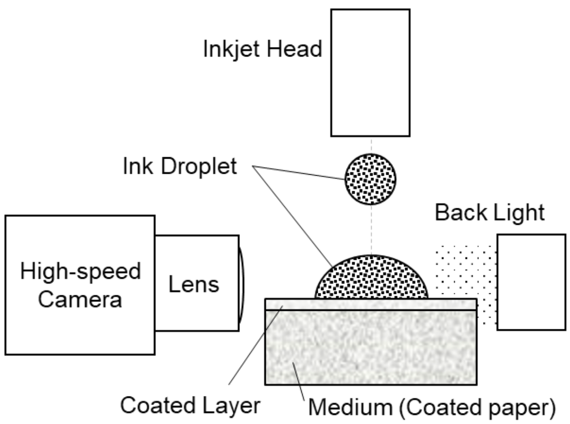

Figure 1. A schematic view of an experimental setup for observation of the shape change of ink droplets landing on media

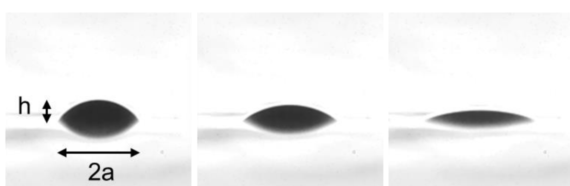

Figure 2. Time sequence (from left to right) of the droplet shape

Quantification of Penetration

Measuring droplet volume decreasing

In order to grasp the penetration velocity of the ink droplet, the volume change of the ink droplet on the penetrable media is measured with the experimental setup shown in Figure 1. The volume change of this case is mainly caused by evaporation and permeation of the solvent. Assuming that the evaporation of the solvent occurs at the same rate as that with the non-penetrable media, the amount of penetration can be estimated by subtracting the amount of evaporation at each time from the measured volume change. This makes it possible to quantitatively determine whether the decreasing of ink droplet volume on the permeable media is due to evaporation or penetration.

Measuring penetration depth

Penetration depth and its change over time were measured with the use of spectral domain optical coherence tomography (OCT). The schematic configuration is shown in Figure 3. This device consists of a Michelson interferometer using a broadband light source and optical fibers. The light output from the light source is split in two directions; one for the measurement sample and the other for the mirror through each lens. The light reflected or scattered by the object and the light reflected by the mirror are again propagated through the same optical fiber as the outgoing path and are guided to the spectrometer. The spectrometer detects the intensity of coupled light from the two directions for each wavelength (or each frequency). The coupled light interferes in the frequency domain if the optical path length of the split light propagating to the object and to the mirror are approximately equal. Intervals of interference fringe observed in the spectrum change depending on the optical path length difference. If the difference of optical path length is small, sparse interference fringes are obtained, and if the optical path length difference is large, dense interference fringes are obtained. If scattered light is generated at each position in the irradiation optical axis direction of the sample, each scattered light is added together and returns to interferometer, and a spectrum which contains several interference fringes is observed. The inverse Fourier transform of the interfered spectrum in the frequency domain estimates the light intensity for each fringe spacing. That is, since the scattered light intensity distribution on the irradiation optical axis can be grasped, the structural information of the sample can be acquired without destruction of the sample.

Figure 4 shows a schematic view of the experimental setup for measurement of penetration depth using OCT. Penetrable media usually have a porous structure. When measuring light is irradiated to the surface, part of the irradiated light is scattered, and the rest part is transmitted. The transmitted light is again scattered and transmitted at a slightly deeper portion in the porous layer. Repeating this, the measurement light propagates while decaying in the media, and generates scattered light at each position. The light backscattered on the measurement optical axis is weakly returned to the OCT system. In OCT, because the scattered light intensity and the generated position are specified, the structure in the thickness direction of the media can be observed.

Ink droplets are deposited using an inkjet head. The measurement light is irradiated to the ink and the media, and the structure in the thickness direction of the ink and the media is observed. As shown in Figure 5, when the ink solvent penetrates into the porous layer of the media, the pores of the porous layer will be filled with solvent. So, the ratio of light scattering and transmission changes. That is, in the region where the solvent penetrates, the transmission of measurement light increases, and the scattered light decrease. The distribution of scattered light intensity after the penetration includes a region with low intensity, which the distribution before penetration does not include. The region is equivalent to the portion where the solvent penetrated. By conducting such analysis over time, it is possible to capture how the penetration area expands.

The OCT uses a low coherence interferometer, and the position where the scattered light is generated is specified based on the optical path length where the measurement light propagates. Therefore, when the measurement light passes through a medium such as ink, the optical path length is extended by the refractive index, which causes a difference in specifying the position. That is, the area where the ink penetrates is observed as a value larger than the actual value. In this method, the penetration depth is corrected by estimating the refractive index of the medium in which the ink solvent is filled in the porous structure and the refractive index was assumed to be about 1.5.

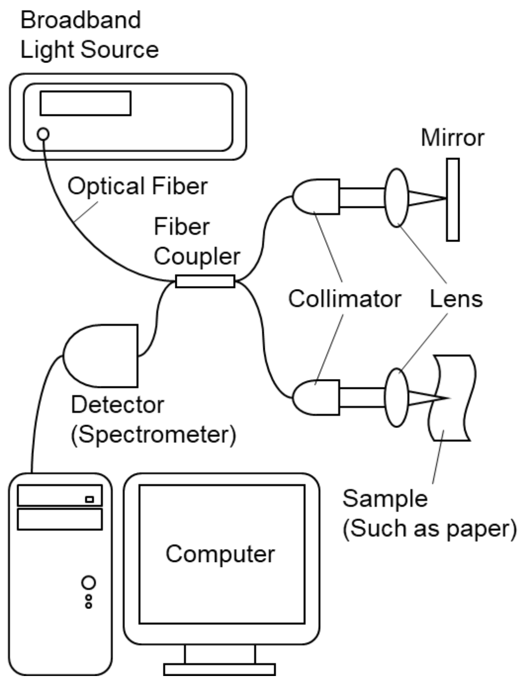

Figure 3. A schematic configuration of spectral domain optical coherence tomography

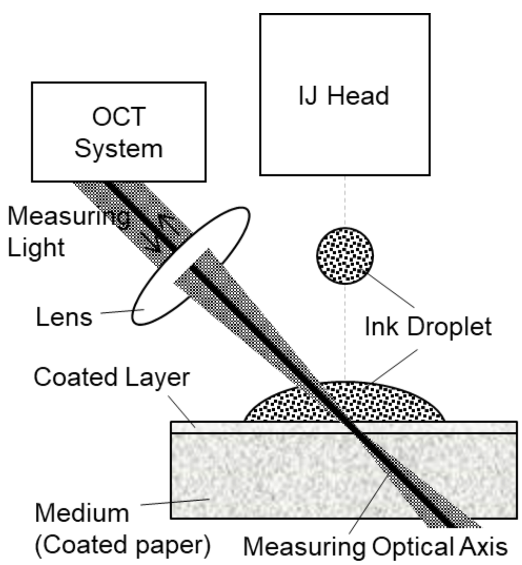

Figure 4. A schematic view of experimental setup for measurement of ink penetration depth into penetrable media based on optical coherence tomography

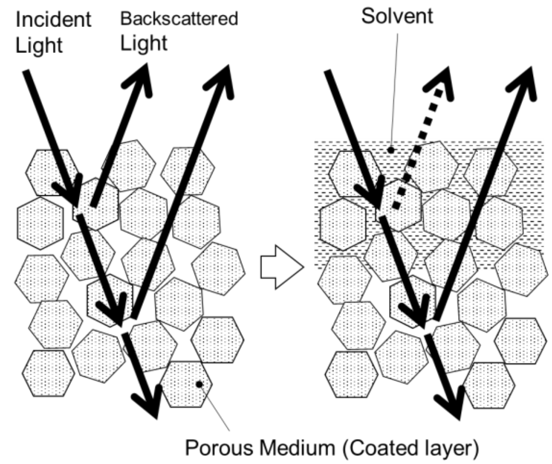

Figure 5. Schematic drawings showing penetration of liquid into porous layer and change of scattered light intensity distribution

Quantification of Viscosity Increasing

The viscosity increasing behavior of the ink droplets landing on the media is measured by a method based on dynamic light scattering. In the aqueous pigment ink targeted in this research, pigment particles and resin particles having particle sizes of less than micrometer are generally dispersed in a solvent. When light is irradiated to the particles of this scale, phenomena such as reflection, diffraction, and scattering are observed depending on the particle diameter and the wavelength of the irradiated light. These phenomena occur for each particle. In the suspension such as pigment ink, the light generated by each particle is combined and observed. When laser is used as the irradiation light which has coherency, the combined light interferes with each other. And the light and shade depending on the place and time is observed in the combine light. This light and shade that occurs on the observation object is called a speckle pattern. Figure 6 shows a photomicrograph of speckle pattern generated on the ink droplet.

On the other hand, the particles dispersed in the ink are in Brownian motion, and the degree of motion is expressed as the diffusion coefficient D by the Stokes-Einstein equation (2).

$$D = \kappa_B T / 3\pi\eta d, \tag{2}$$

where κ_B is Boltzmann's constant, T is temperature, η is viscosity of solvent, and d is particle diameter. The lower the viscosity of the solvent is or the smaller the diameter of the particles is, the greater the Brownian motion becomes. If the viscosity of the solvent increases with evaporation, the dispersed particles aggregate to form coarse particles and to gel. In this process, the degree of Brownian motion becomes low.

When the ink droplet is observed as the sample, the speckle pattern changes with time. Since this change is caused by the degree of Brownian motion of the particles in the ink, the rate of change of the pattern is high if the Brownian motion is quick and low if it is slow. Therefore, if the rate of change of speckle patterns with time changes over time, it is possible to grasp the change over time of the degree of Brownian motion by calculating with moving average processing. That is, it is possible to estimate the change of the diffusion coefficient of the ink. However, this method is not easy to determine whether the cause of the decrease in Brownian motion is the increase in particle size or the increase in solvent viscosity using this method alone. Because both factors contribute to the decrease in ink fluidity, both are treated as a viscosity increasing phenomenon in the same way in this report.

Figure 7 shows a schematic diagram of the experimental setup that performed this measurement. The medium is irradiated with laser light as measurement light in a plane, and an actuator is used to scan the inkjet head discharging droplets continuously (moving in the depth direction in Figure 7). A row of independent ink dots is formed by scanning at a high-speed relative to the jetting frequency. Speckle patterns are generated on the surface of each ink droplet, and the results are observed through a microscope. Time sequence of the speckle patterns are recorded with a high-speed camera.

Regions corresponding to ink dots are extracted from the captured moving image in an image processing manner, and they are arranged in time sequence to calculate the rate of change in the speckle pattern. The correlation coefficient between each image was determined. The viscosity of ink droplet was estimated based on the relationship between the amount of decrease in the correlation coefficient with respect to time change and the calibration curve about the amount of decrease in the correlation coefficient which was prepared using suspensions with different diffusion coefficient beforehand. By performing such an operation on moving averages for speckle pattern images that change with time, the change with time of viscosity is calculated.

Figure 6.A microphotograph of laser speckle pattern generated on the surface of an ink droplet

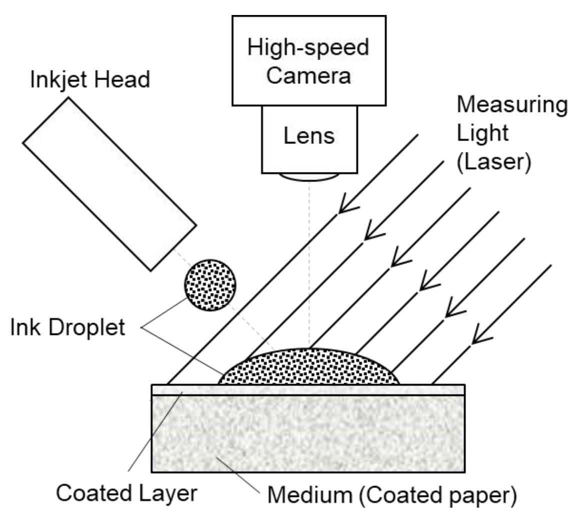

Figure 7.A schematic view of experimental setup for quantification of ink droplet viscosity increasing based on dynamic light scattering method

Result

Several types of media with different penetrability were prepared for one type of aqueous pigment ink. The velocity of penetration and the velocity of viscosity increasing were compared respectively. The media shown in Table 1 were used.

Figure 8 shows the measurement results of the evaporation behavior of aqueous pigment ink droplets on a non-penetrable medium. The observed ink droplet size is about 20pL. According to Figure 8, the ink droplets have been halved in volume by evaporation over about 200 milliseconds. The measurements were performed in laboratory environment, but it can be seen that the volume change due to evaporation cannot be negligible.

Figure 9 shows the change in permeation amount calculated from the volume change of the droplet on each media. The observed ink droplet size is about 20pL.

When sufficient time has passed, it can be seen that more solvent penetrates media #2 and #3 compared to the amount of penetration into media #1.

To investigate the penetration depth, OCT is carried out with various kind of media. Figure 10 shows the observation results of the OCT. Figure 10 (a) shows a schematic view of the OCT image observed during the penetration. The vertical axis represents the position in the thickness direction of the medium, and the origin means the surface of the medium. The horizontal axis represents the time, and the origin means the time when the ink lands on the medium. The time variation of the scattered light intensity distribution is indicated in a greyscale. After the ink lands, the area showing the ink is observed on the OCT image. The medium is displayed in white in a greyscale because the scattered light intensity is large. Penetration ink in the medium suppresses the light scattering. The area where the ink solvent penetrates is displayed in black in the greyscale. The size of the observation is about less than 1nL, which is larger than that of other measurements. Figure 10 (b) and Figure 10 (c) are examples of OCT images showing the penetration phenomena with another media.

For each media, Figure 11 shows the time sequence of the penetration interface position estimated from Figure 10. The plot shows the average behavior based on several measurement results. The vertical axis of the graph represents the position of the penetration interface. The smaller value of the position comes from the deeper penetration. The horizontal axis indicates the time elapsed since the ink adhered to the media. Among the three types of media, Medium #1, #2 and #3, the movement speed of the penetration interface position (shown in Figure 11) also increases as the change in penetration amount (shown in Figure 9) increases. In Medium #2, the penetration velocity decreases in about several hundred milliseconds after ink deposition and does not progress from the penetration depth of about 15 to 20 micrometers. Similarly for Medium #3, the penetration velocity decreases in about several tens of milliseconds and the penetration depth at that time was about 20 micrometers. Since the thickness of the coated layer of the coated paper is approximately 15 to 20 micrometers, whole thickness of coated layer in Medium #2 and #3 is probably penetrated completely. And it is considered that if the ink solvent fills all the voids in the coating layer during penetration, the penetration is suppressed or penetrates at a relatively low speed into the base layer under the coating layer.

Table.1 Media used in the experiment

Abbreviation names	Tested media
Medium #1	Offset coated paper (gloss)
Medium #1A	Offset coated paper (gloss) with pre-treatment
Medium #2	Offset coated paper (matte)
Medium #3	Inkjet coated paper

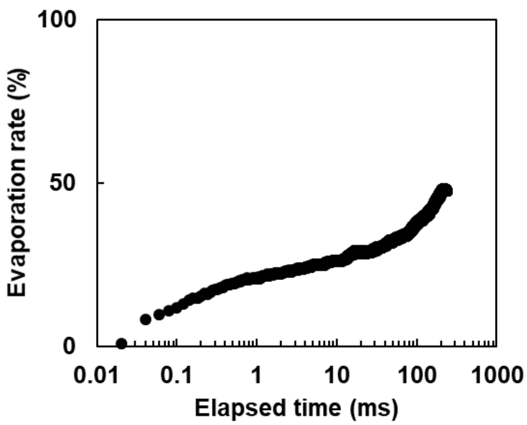

Figure 8. Temporal change of ink volume reduction on non-penetrable media

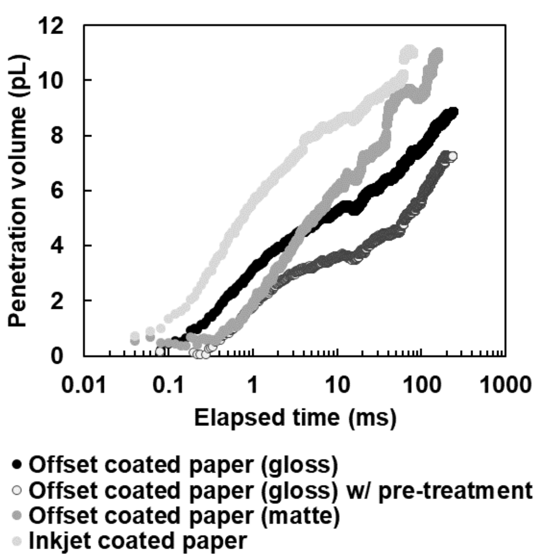

Figure 9. Temporal change of ink penetration amount

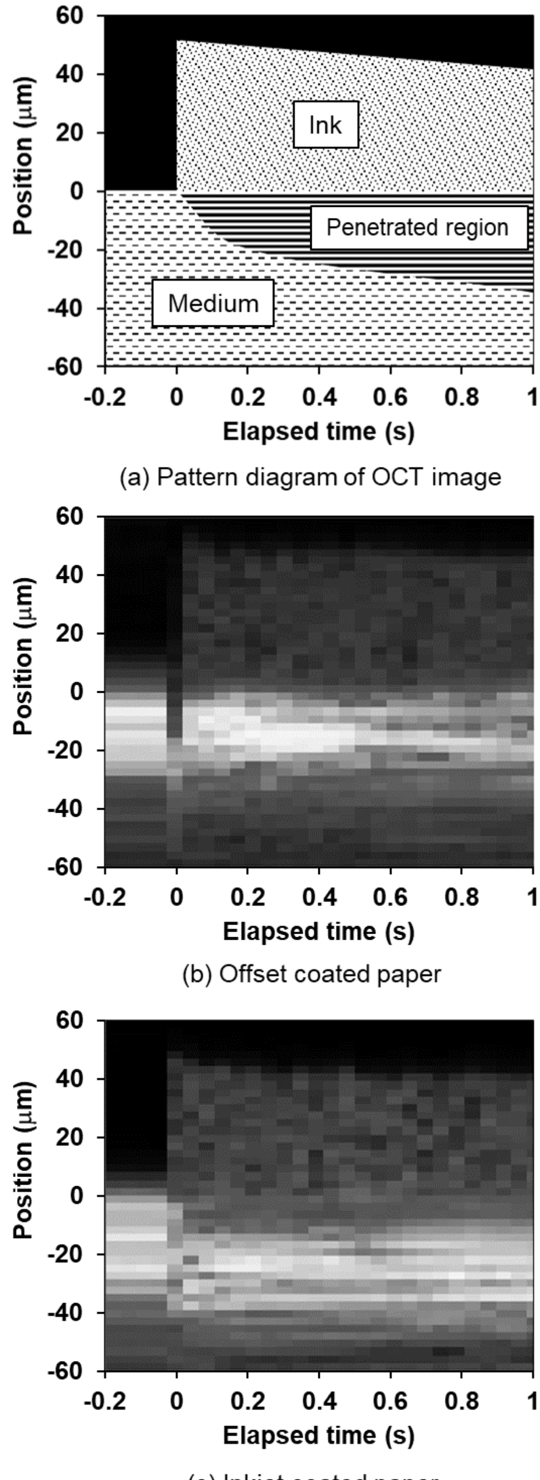

Figure 10. Observation result of penetration behavior by OCT

Focusing on pre-treated Medium #1A and untreated Medium #1, there is a difference of about 20% between the two in Figure 9. Penetration is probably suppressed with Medium #1A. On the other hand, there is no significant difference in penetration depth between the two in Figure 11. With the Medium #1A, the wetting and spreading of the ink droplet is suppressed as compared with the Medium #1. However, for both media the speed of penetration into the coated paper is the same. Therefore, it is considered that the difference in the amount of penetration was caused by the difference in ink dot diameters dominantly.

Figure 12 shows the results of measurement of the viscosity increasing various media obtained from the laser speckle analysis. The vertical axis indicates the viscosity, and horizontal one indicates the elapsed time after the droplet landing. It takes a long time to reach a certain viscosity in the order of Medium #1, #2 and #3. This is consistent with the slow order of penetration velocity, and the viscosity increasing with these media is probably due to the solvent penetration. On the other hand, with the Medium #1A, the viscosity increased faster than that with the Medium #1. The flocculating agent applied as a pre-treatment agent diffuses into the ink droplet, and aggregation and gelation of the particles cause the rapid increase of the viscosity with the pre-treated Medium #1A. The difference in penetration between Medium #1 and #1A is most likely caused by the suppressing penetration due to the viscosity increase. There is a possibility that the difference in penetration between Medium #1 and #1A also originates from the effect of suppressing penetration based on the theory of capillary phenomenon by viscosity increasing of the ink, in addition to the effect due to the difference in ink dot diameters. It should depend on the ability of aggregation or gelation of the pre-treatment.

Conclusions

The ink droplets and media after landing were visualized, by means of shape change observation with a high-speed high-magnification camera, observation by optical coherence tomography, and laser speckle observation based on dynamic light scattering. Using them, the evaporation velocity, penetration velocity (change in penetration amount of droplet and change of penetration depth), and velocity of viscosity increasing were measured quantitatively.

It has become possible to measure the velocity of the state change that occurs in the ink droplet during the imaging process and the behavior that causes the change. As a result, it is possible to directly confirm whether the ink or process is suitable for the medium and whether the ink droplet behaves as intended so that high image quality and high productivity can be realized.

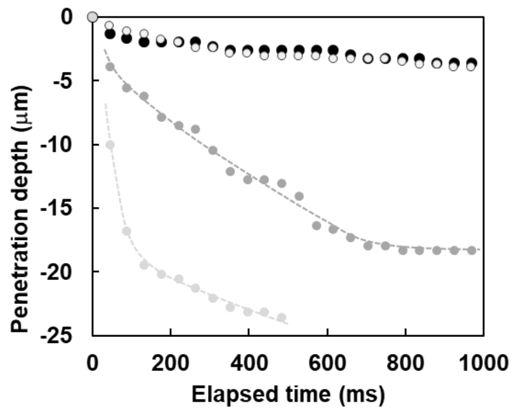

Figure 11. Temporal change of ink penetration interface position measured by observation result of OCT

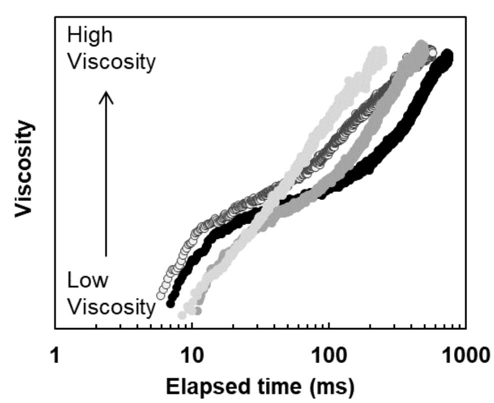

Figure 12. Temporal change of viscosity of ink droplet measured by laser speckle observation

References

[1] T. Enomae, F. Onabe, M. Usuda, Tappi J. 44(7):811–820 (1990)

[2] T. Enomae, F. Onabe, M. Usuda, Tappi J. 45(2):285–291 (1991)

[3] Hanne M. van der Kooij et al., Scientific Reports **6**, 34383 (2016)

[4] Y. Harada, M. Mohri, Proceeding of Printing for Fabrication 2018, Society for Imaging Science and Technology (2018), pp. 135-138.

Author Biography

Yoshihiro Harada obtained his master's degree in quantum engineering at the Nagoya University in Japan in 2009. In the same year, he joined Ricoh Company, Ltd. He has been engaged in the development of optical measurements and evaluation techniques for inkjet imaging process using knowledges he has been learning since he was in the university.