Printability of Ink-jet Printing on Surface-treated Nonwoven Fabrics

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Abstract

The micro scale distribution of ink-jet inks on surface-treated nonwoven synthetic fiber sheets was evaluated with a confocal laser scanning microscope (CLSM) in order to characterize the ink-setting on the surface of the media.

Nonwoven synthetic fiber sheets made from hydrophilic or hydrophobic fibers were prepared. Surface characteristics of the nonwoven sheets varied with corona treatment. The corona-treated application on nonwoven sheets was investigated in order to improve the wettability of the surface of the nonwoven sheets. The corona-treated nonwoven sheets were printed using dye type and pigment type ink-jet printers and the distribution of the magenta inks on the sheets were observed using CLSM.

The micro scale distribution of the inks on the surface-treated nonwoven sheets could be estimated by CLSM nondestructively. Nearly all of the dye type inks did not fix on the hydrophobic nonwoven sheets. After applying corona treatment, the sheet surfaces became more hydrophilic, resulting in an increase of hydrophilic functional groups with the fiber surfaces and the ink set on the sheets. However, the process of ink-setting on the hydrophobic sheets differed with the type of hydrophobic fibers. It was observed that the microstructure of one kind of hydrophobic fiber changed under the corona treatment and more ink fixed on the surface of the fibers. This suggests that not only chemical but also micro structural changes of the sheet surfaces greatly affect the ink-setting on the sheets. In the case of the pigment type ink, more ink was able to set on the hydrophobic sheets compared to the dye type ink.

It was concluded that the wettability and the surface topography of the media had a great effect on the setting of the ink-jet inks and the printing quality. Higher quality ink-jet printing on nonwoven sheets is possible through suitable surface-treatment of the sheet. The CLSM method could be used to evaluate the printability of the media such as nonwoven synthetic fiber sheets.

Introduction

It is very important to understand the mechanisms of ink penetration and setting for all kinds of printing methods. Recently, it has become desirable to develop higher quality printing not only on coated and uncoated papers but also on synthetic fiber paper, nonwoven fabrics and film. In particular, ink jet printing (IJP), flexographic printing and screen printing processes have already been used for various materials. However, fundamental research on the distribution of water-based and oil-based inks on non-cellulose fibers has yet to be studied. Although macro scale printability can be evaluated by visual impressions, it is not sufficient to evaluate micro scale printability using a common optical microscope due to the large degree of surface roughness.

In this report, the micro scale distribution of ink-jet inks on surface-treated nonwoven sheets was studied by confocal laser scanning microscope (CLSM). The main purpose of previous research involving applications of CLSM to prints was to characterize surface roughness [1]. Beland et al. [2] measured surface profiles of matte-coated paper three-dimensionally using CLSM and related perception of gloss to the surface topography. Dickson [3] reported that it was possible to characterize ink pigment position within the surface of printed newsprint sheets by the image analysis techniques of CLSM. Enomae et al. [4] has studied the penetration of dye-based inks for ink-jet by CLSM. We have studied ink penetration into coated and uncoated papers by reconstructed images of CLSM utilizing the fluorescence stain technique to observe the ink vehicle [5, 6]. In this study, the ink penetration and setting within paper coatings or cellulose fibers was investigated by observing fluorescence using the visible laser of CLSM. We also investigated the process of ink-jet ink setting on non-cellulose fibers using CLSM. It was confirmed that the ink-setting behavior of the pigment type ink-jet ink differed by the particle size of the pigment. Furthermore, the fluorescence of the cyan ink on the non-cellulose fibers was detected by CLSM with a UV laser for the first time [7]. It is expected that this method will be applicable to polychrome printing.

Corona treatment is commonly used in the plastics industry to improve the bondability and wettability of polyolefin films and large objects. It is well recognized that corona treatment produces surface oxidation of polymers. The decomposition of hyperoxide groups produces C-OH, C=O and O=C-OH groups on the corona-treated polymer surface [8, 9]. However, the phenomenon of improved ink adhesion on a corona-treated surface is still not fully understood.

In this study, the distribution of dye type and pigment type ink-jet inks on corona treated nonwoven sheets was investigated by CLSM in order to characterize the ink-jet ink setting on a variety of materials.

Material and Methods

Samples

A hydrophilic nonwoven sheet (12 g/m^2) made from polyvinyl alcohol (PVA) fibers by a wet process and two kinds of hydrophobic sheets (30 g/m^2) made from core-shell structural fibers were prepared. One kind of core-shell structural fiber named P-Ea (Daiwabo polytech, Japan) is composed of polypropylene (PP) as the core and ethylene acrylic acid (EAA) as the shell, the other fiber named P-Ev (Daiwabo polytech, Japan) is composed of polypropylene (PP) as the core and ethylenevinyl alcohol (EVA) as the shell.

The surface characteristics of these nonwoven sheets were varied with corona treatment. The corona treatment was carried out under the discharge energy of 6.3 x 10^6 J/m^2 for all nonwoven sheets in order to improve the wettability of the sheet surfaces.

The samples were printed using ink-jet printers. The ink-jet printers we used were dye type (Designjet70, Hewlett-Packard, USA) and pigment type (PX-6000, EPSON, Japan) printers. Printing was performed by a normal mode with high print quality. The inks used as water-based ink were the dye type magenta ink (Hewlett-Packard, USA) and the pigment type magenta ink (PX-ink, EPSON, Japan).

Measurement of contact angle

The contact angle of water drop on the surface-treated nonwoven sheets was measured using the contact angle measurement tester. Furthermore, the contact angle of micro ink drop was estimated on the sheets using a microscopic video camera.

Surface observation and analysis

The nonwoven sheet surfaces were observed by scanning electron microscope (SEM; S-3000N, Hitachi, Japan) under the condition of 10 kV accelerating voltage.

The chemical bonding state on the surface of nonwoven sheets were investigated using X-ray photoelectron spectrometer (XPS; PHI-5600ci, PerkinElmer, USA). The measuring conditions were as follows; MgKα (1253.6 eV) X-ray source: 15 kV-200W, vacuum in chamber: 10^{-6} Pa, analysis area: 800 μmφ, take-off angle of the photo electron: 45 degree. The high resolution spectra of C1s were obtained as the narrow scan mode (pass energy: 5.87 eV, step width: 0.5 eV).

Observation by CLSM

A confocal laser scanning microscope (CLSM; TCS-SP5 AOBS, Leica, Japan) was used in this experiment. The laser beam was first irradiated and scanned on a sample, and then the fluorescence emitted from the sample was detected as a fluorescence image. A 3D image was reconstructed from a series of single confocal images accumulated digitally.

The objective lens we selected was an x 63 oil-immersion lens (HC PL APO, NA 1.40) with immersion oil (Refractive Index: 1.518) supplied by Leica. The Z-resolution of the oil-immersion lens is three times better than that of a dry lens with air between the sample and the objective lens. Therefore, it is possible to reduce the optical resolution for a depth up to less than 0.6 μm using an oil-immersion lens [10]. Oil-immersion lenses have been previously used to observe pulp fibers [11, 12]. An excitation wavelength of 488 nm from an Ar laser (50 mW) was used for the observation by CLSM. Confocal images were obtained using XYZ scan modes. A sequence of XY frames (238 x 238 μm^2) was obtained at 0.6 μm intervals in the z (thickness) direction and was stacked as a maximum intensity projection (Z-stack image). The pixel count of each frame was 512 x 512 pixels. The fluorescence emission spectra were obtained using the wavelength scan operation mode of the Leica CLSM.

Results and Discussion

Wettability of nonwoven sheets

The change of the water contact angle on each nonwoven sheet between before and after corona treatment is shown in Fig. 1. The contact angle decreased after corona treatment for all samples. This result shows that the surfaces of all samples became more hydrophilic due to the corona treatment. The reduction rate of the contact angle values by the corona treatment was the greatest for the hydrophobic P-Ea sheet.

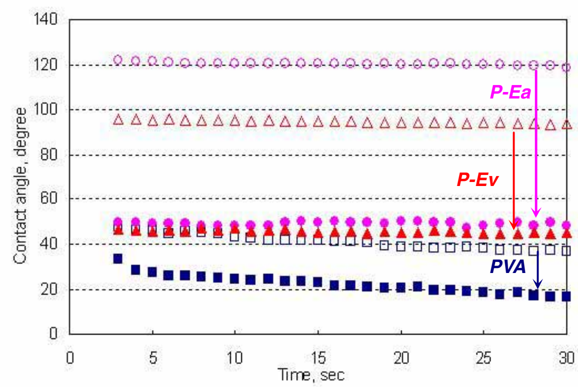


Figure 1. *The Changes of the water contact angle of the nonwoven sheets between before and after corona treatment.*
Before corona treatment; □(PVA), ○(P-Ea), △(P-Ev)
After corona treatment; ■(PVA), ● (P-Ea), ▲(P-Ev)

Surface characteristics of nonwoven sheets

Figures 2-4 are the SEM photographs of the surfaces for the PVA, P-Ea (PP/EAA) and P-Ev (PP/EVA) sheets before (1) and after (2) the corona treatment. In the case of PVA sheet, the binders bonding the PVA fibers have melted greatly after the corona treatment. The surface structure of the P-Ea sheet before the corona treatment was similar to that after the corona treatment. However, the surface structure of the P-Ev sheet changed with the corona treatment. It was observed on the P-Ev sheet that the surface of each fiber would melt and become flat after the corona treatment (Fig. 4(2)). This is attributed to the fact that P-Ev fiber has ethylenevinyl alcohol as the shell of the fiber and the ethylenevinyl alcohol turns into gel when heated up to 120 degree centigrade under moist conditions.

Figure 5 is the C1s high-resolution spectra of PVA (A), P-Ea (B) and P-Ev (C) sheets analyzed by XPS. The intensities at 284.5, 286 and 289 eV are proportional to the contents of C-H, C-O and O-C=O binding state, respectively. After applying corona treatment, the content of the C-H group decreased and that of the C-O and O-C=O groups increased. In this experiment, the contents of the C-O and O-C=O binding states were in proportion to that of hydrophilic C-OH and O=C-OH groups, respectively. This indicates that these sheet surfaces became more hydrophilic due to the corona treatment. This result agreed with that of the contact angle measurement.

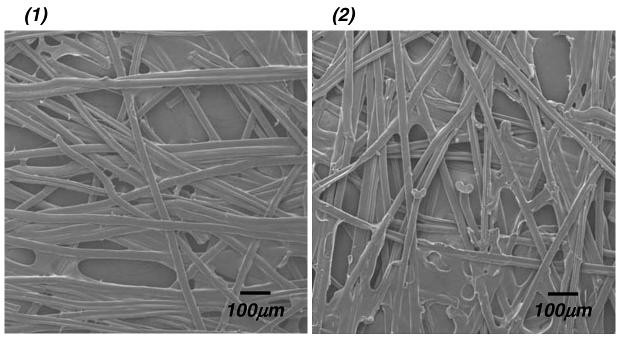


Figure 2. *SEM images of the PVA sheet surfaces before (1) and after (2) corona treatment.*

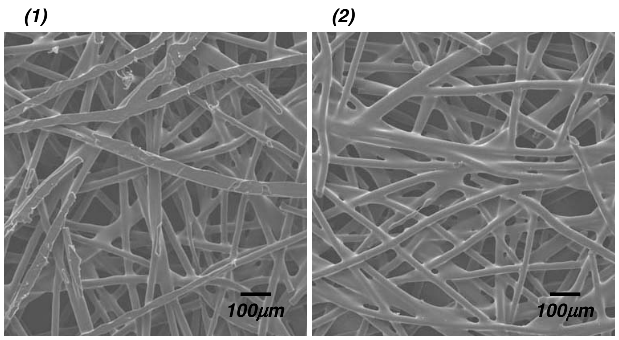


Figure 3. *SEM images of the P-Ea sheet surfaces before (1) and after (2) corona treatment.*

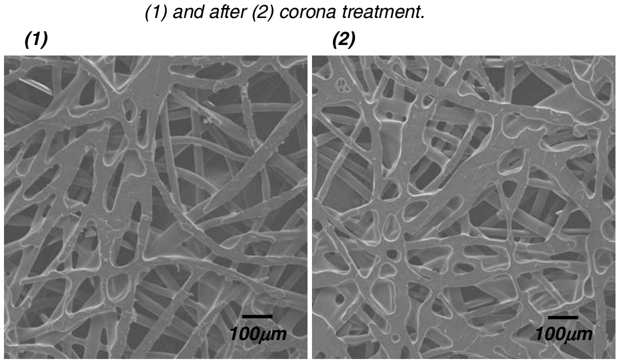
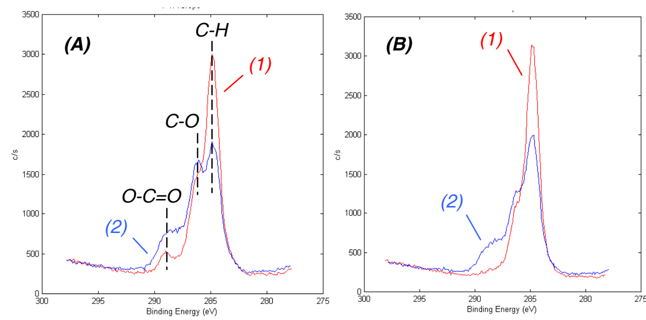


Figure 4. *SEM images of the P-Ev sheet surfaces before (1) and after (2) corona treatment.*



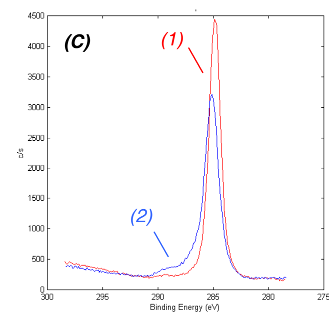


Figure 5.
Cls high resolution spectra on the PVA (A), P-Ea (B) and P-Ev (C) sheets analyzed by XPS.
(1) Before corona treatment
(2) After corona treatment

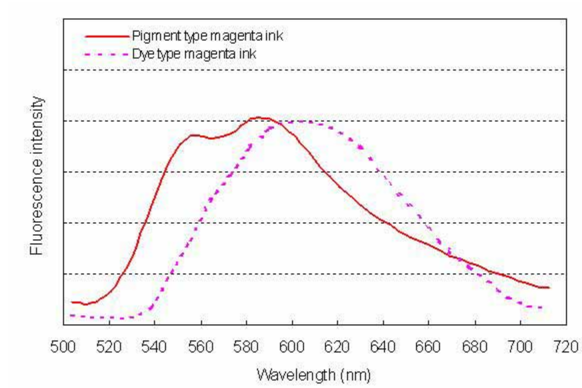


Figure 6. *Fluorescence spectra of the ink-jet magenta inks.*

Fluorescence of magenta inks

Figure 6 shows the fluorescence spectra of dye type and pigment type magenta inks at the excitation wavelength of 488 nm. The dye type magenta ink had one peak while the pigment type magenta ink had two peaks. It is expected that two fluorescent components are included in the pigment type magenta ink. It is thought that the component having fluorescence around 600 nm derives from the magenta pigment included in the ink and that having fluorescence around 540 nm might be serving as the dispersive agents [7].

Distribution of dye type ink on nonwoven sheets

The distribution of magenta ink on PVA, P-Ea and P-Ev fibers could be directly observed by CLSM. The magenta ink emitted strong fluorescence at the excitation wavelength of 488 nm. However, these fibers did not emit any fluorescence at this wavelength.

Figure 7 is the reconstructed images of the orthogonal projections for the PVA sheet printed with the dye type magenta ink before (1) and after (2) the corona treatment. The fluorescence images around 600 nm are expressed as a red color overlapped with the monochromatic transmission image. In each of the reconstructed images, the top left image is a Z-stack image compiled from a series of XY-plane images. The bottom image is an XZ-plane which is sectioned virtually along line 1 (the horizontal line in the XY-plane image). Finally, the top right image is an YZ-plane which is sectioned along line 2 (the vertical line in the XY-plane image).

The way the magenta ink was unevenly distributed on the PVA fibers before the corona treatment is shown in Fig. 7(1). In contrast, after the corona treatment most of the ink evenly covered the PVA fibers that have a concave shape as shown in Fig. 7(2).

Figure 8 shows the reconstructed images of the P-Ea sheet printed with the dye type magenta ink before (1) and after (2) corona treatment. The fluorescence images showing ink is assigned to red. In the case of the hydrophobic P-Ea sheet, only a minor amount of dye type ink could be observed by CLSM before the corona treatment because most of the ink did not fix on hydrophobic P-Ea sheet but instead passed through the P-Ea sheet. After corona treatment, the ink tended to fix at fiber crossing points. This is because the sheet surfaces became more hydrophilic with the increase of C-OH and O=C-OH groups on the sheet surfaces due to the corona treatment, as shown in the results of the contact angle measurement (Fig. 1) and the surface analysis by XPS (Fig. 5).

It was found that the distribution of the ink on the hydrophobic P-Ev sheet was much different from that of P-Ea sheet after the corona treatment. Figure 9 shows the reconstructed images of the distribution of the magenta ink on P-Ev fibers. Magenta ink is assigned to red. The ink spread over and fixed on the surface of the P-Ev sheet but did not penetrate into the sheet after the corona treatment as shown in Fig. 9(2). It was also observed on the cross section images of CLSM that magenta dye

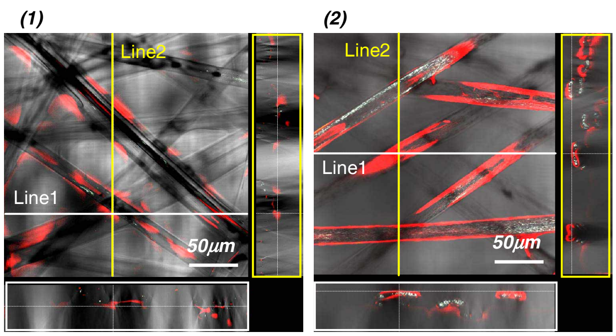


***Figure 7.** Reconstructed images of the orthogonal projections for the PVA sheet, before (1) and after (2) corona treatment, printed with the dye type magenta ink.*

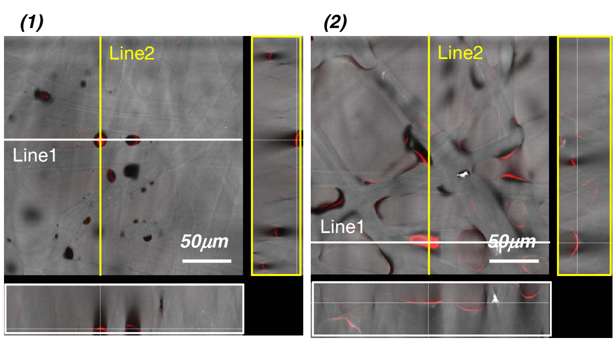


***Figure 8.** Reconstructed images of the orthogonal projections for the P-Ea sheet, before (1) and after (2) corona treatment, printed with the dye type magenta ink.*

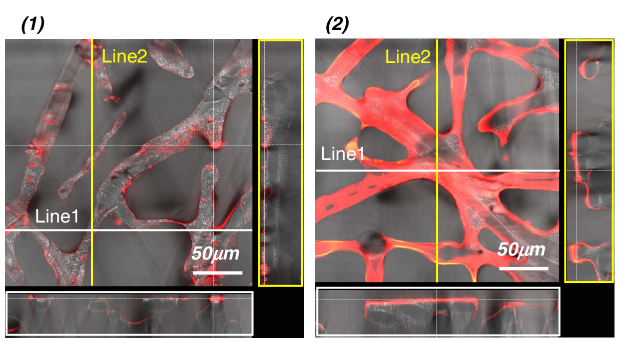


***Figure 9.** Reconstructed images of the orthogonal projections for the P-Ev sheet, before (1) and after (2) corona treatment, printed with the dye type magenta ink.*

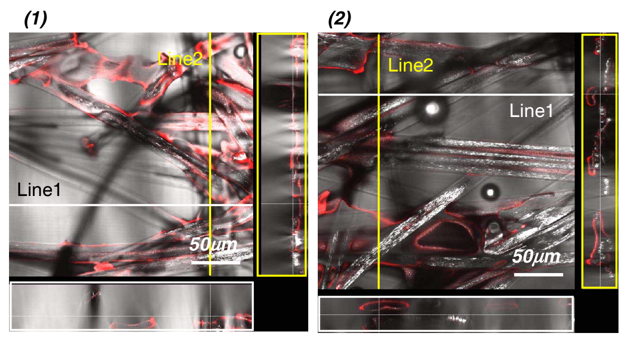


***Figure 10.** Reconstructed images of the orthogonal projections for the PVA sheet, before (1) and after (2) corona treatment, printed with the pigment type magenta ink.*

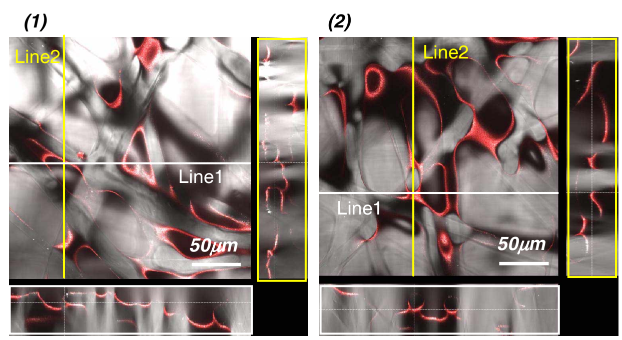


***Figure 11.** Reconstructed images of the orthogonal projections for the P-Ea sheet, before (1) and after (2) corona treatment, printed with the pigment type magenta ink.*

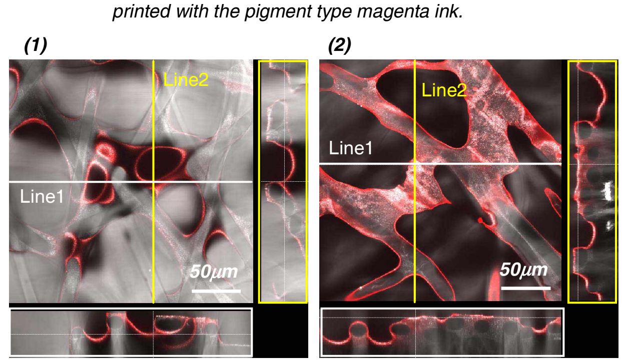


***Figure 12.** Reconstructed images of the orthogonal projections for the P-Ev sheet, before (1) and after (2) corona treatment, printed with the pigment type magenta ink.*

type ink sets on P-Ev fibers, because the shell part of P-Ev fibers melted and flattened after the corona treatment, which agreed with the result of SEM observation. It was concluded that the dye type ink fixed on the flattened surface of the P-Ev fibers as a result of the corona treatment. In contrast, the surface structure of the P-Ea fiber did not change as a result of the corona treatment. Therefore, the ink did not spread over the P-Ea sheet surface and fixed at only fiber crossing points.

From the results of the contact angle measurement and the surface analysis by XPS, the surface of P-Ea sheet became more hydrophilic than that of P-Ev sheet. However, more dye type ink fixed on the P-Ev sheet than on the P-Ea sheet after the corona treatment. These results suggest that the micro structural changes of the fiber surfaces by the corona treatment had greater effect on the ink-setting for the sheets than the resulting chemical changes. It is concluded that not only chemical but also micro structural changes of the sheet surface caused the behavioral changes of the ink-setting.

Distribution of pigment type ink on nonwoven sheets

Figures 10-12 are the reconstructed images of the orthogonal projections for the PVA, P-Ea and P-Ev sheets, before (1) and after (2) the corona treatment, printed with the pigment type magenta ink. These figures express the fluorescence images around 600 nm as a red color. These reconstructed cross section images show that the pigment type ink set on the surface of the sheets with or without the corona treatment. This is because the wettability of the sheets does not greatly affect the process of setting of the pigment type inks on the sheets when compared with the dye type ink.

In the case of the hydrophobic P-Ea sheet, pigment type ink fixed at the fiber crossing points unlike the dye type ink, as shown in Fig. 8 and 11. The results indicate that pigment type ink tends to set evenly on the hydrophobic sheet because it contains solid pigments. The pigment type ink distributed on the surface of the P-Ev sheet and did not penetrate into the P-Ev sheet after the corona treatment. This result corresponds with that of dye type ink on the P-Ev sheet (Fig. 9).

Conclusion

The distribution and the process of setting of the ink-jet inks on the corona-treated nonwoven sheets were investigated by CLSM. It was concluded that the distribution of the inks on the nonwoven sheets can be observed nondestructively and that the micro scale wettability between the inks and the sheet surfaces can be evaluated using CLSM.

It was confirmed that the wettability between the ink-jet inks and the sheet surfaces has a great effect on the process of ink-setting on the sheets. After applying corona treatment, the sheet surfaces became more hydrophilic and more dye type ink fixed on the sheets for all samples. The distribution of the ink on the hydrophobic sheets after the corona treatment differed with the type of hydrophobic fibers. It was concluded that not only chemical but also micro structural changes of the sheet surface had an influence on the behavior of setting and the micro scale distribution of the ink on the sheets. In the case of pigment type ink, the wettability of the sheets did not greatly affect the process of ink-setting when compared with dye type ink. It should be considered that the pigment type ink containing solid pigments was able to set on the hydrophobic sheets.

CLSM technique could be used to evaluate the printability of various materials such as nonwoven synthetic fiber sheet and paper. It is also expected that this technique can be applied to polychrome printing.

References

[1] Beland, M. C. and Mangin, P. J., Three-dimensional evaluation of paper surface using confocal microscopy, Surface analysis of paper, pp.1-40, (1995).

[2] Beland, M. C., Lindberg, S. and Johansson, P.A., Optical measurement and perception of gloss quality of printed matte-coated paper, J. Pulp Paper Sci., 26 (3) pp. 120-123, (2000).

[3] Dickson, A. R., Quantitative assessment of ink pigment position within the surface of a newsprint sheet, Appita J., 58 (4) pp. 272-276, (2005).

[4] Enomae, T., Ivutin, D., and Isogai, A., Three-dimensional distribution of ink-jet inks in paper acquired by confocal laser scanning microscope, 58th APPITA Annual conference & Exhibition Proceedings, pp. 577-588, (2004).

[5] Ozaki, Y., Bousfield, D. W. and Shaler, S. M., Three-dimensional characterization of ink vehicle penetration by confocal scanning laser microscope, J. Pulp Paper Sci., 31 (1) pp. 48-52, (2004).

[6] Ozaki, Y., Bousfield, D. W. and Shaler, S. M., Observation of the ink penetration in the coated paper by confocal scanning laser microscope, TAGA Annual conference Proceedings, pp. 68-69, (2005).

[7] Hamada, H. and Ozaki, Y., Observation of the distribution of ink on non-cellulose fibers by confocal laser scanning microscope, Nordic Pulp Paper Res. J., 21 (5) pp. 59-63, (2006).

[8] Foeldes, E., Kalman, E. and Fekete, E., Appl Polym Sci, 76(10), pp.1529-1541 (2000)

[9] Zenkiewicz, M., J Adhes Sci Technol, 15, (14), pp.1769-1785 (2001)

[10] Sterlzer, E. H. K., The intermediate optical system of laser scanning confocal microscopes, Handbook of Biological Confocal Microscopy, pp. 139-153, (1995).

[11] Jang, H. F., Robertson, A. G. and Seth, R. S., Optical sectioning of pulp fibers using confocal scanning laser microscopy, Tappi J., 74 (10) pp. 217-219, (1991)

[12] Jang, H. F., Robertson, A. G. and Seth, R.S., Transverse dimensions of wood pulp fibers by confocal laser scanning microscopy and image analysis, J. Material Sci., 27, pp. 6391-6400, (1992)

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