Evaluation of Penetration of Acrylate into Printing Blankets by Confocal Laser Scanning Microscopy

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Abstract

The penetration of an acrylate monomer into blankets was investigated using confocal laser scanning microscopy (CLSM). In order to detect the penetration with CLSM, an oil-soluble dye (Macrolex Yellow 6G) was added to the acrylate monomer. The cleaning solvent for the blanket was stained with Acridine Yellow.

The penetration of the acrylate monomer into blankets could be rapidly and minutely estimated with CLSM stain technique. In addition, the distribution of the acrylate monomer in the blanket after blanket cleaning could also be observed in detail. The acrylate monomer could not be removed from within the blanket after blanket cleaning.

Introduction

In recent years, UV curing inks have become popular in offset printing due to their solvent free nature (Stowe, 2004). Acrylate is used as the vehicle of UV curing inks. The interaction of printing press blankets with acrylate can influence printing results and the integrity of the blanket.

We studied the evaluation by IR imaging of acrylate penetration into printing blankets (Ozaki, 2008). We also reported that we had succeeded, for the first time, in evaluating the penetration rate of each component in a UV curable ink vehicle into the printing blanket using PCA (Principal Component Analysis) data from IR imaging on cross sections of the blanket. The acrylate monomer was shown to penetrate fastest, followed by acrylate oligomer, and pre-polymer, which penetrated very slowly. In addition, we found that the photo initiator transferred together with the acrylate monomer in the blanket.

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In order to evaluate the penetration of the acrylate into the blanket, ultimately it was important to observe the distribution of the acrylate monomer. However, the IR imaging measurement was very slow, and the IR images obtained were rough. We had studied the penetration of solvents into blankets by confocal laser scanning microscope (CLSM) (Ozaki, 2007). Solvents added into blankets with a fluorescent dye could be observed with CLSM. We predicted that this technique could also be used to observe an acrylate monomer.

In this study, the penetration of an acrylate monomer into blankets was investigated using CLSM. The objective of the study was to more rapidly and minutely estimate the penetration of an acrylate monomer into blankets. In addition, we were able to demonstrate how the cleaning solvent can remove acrylate from the blanket.

Experiment

UV curable ink type blanket (blanket-1) and both UV curable ink and oxidation curable ink type blanket (blanket-2) produced by Sumitomo Rubber Co. were used. Rubber had been attached to the reinforcement cloth. The rubber of blanket-1 was isoprene rubber, and that of blanket-2 was acryl-rubber. Fillers had been added in both blankets. The thickness of blanket-1 was about 350μm, and that of blanket-2 was about 550μm.

Di-penta-erythritol hexa-acrylate was used for the acrylate monomer. First, because an acrylate monomer has no fluorescence, a fluorescent dye had to be added to the monomer in order to detect it with CLSM. In the end, we selected an oil-soluble dye (Macrolex Yellow 6G) as the fluorescing agent to dissolve in acrylate monomer. A 0.1 wt% of Macrolex Yellow 6G was completely dissolved in the acrylate monomer. The solvent for cleaning the blankets was 3-metxyle-3-methyl-1-butanol. This solvent was stained with a 0.02wt% of Acridine Yellow.

To prepare samples for IR imaging and CLSM observation, the following procedure was performed. (1) The acrylate monomer with the fluorescent dye was applied at a constant volume (40μl) on the blanket (area :1cm^2). (2) Excess acrylate was wiped off after several hours. (3) The blanket was cut from the rear by a delicate cutter (JUSCO Co.) in order to prevent the acrylate from running with the cutting edge. (4) Finally, the cross sections of the blanket were prepared as samples for IR imaging and CLSM observation.

As another preparation, the following procedure was also performed. (1) The acrylate monomer with the fluorescence dye was applied at a constant volume (40μl) on the blanket (area :1cm^2). (2) The acrylate monomer penetrated into the blanket for 72 hours. (3) The surface of the blanket was cleaned with solvent. (4) The blanket was cut from the rear by a delicate cutter (JUSCO Co.) in such a way as to prevent the acrylate from running

with the cutting edge. (5) Finally, the cross sections of the blanket were prepared as samples for IR imaging and CLSM observation.

Fluorescent images were obtained using a confocal laser scanning microscope (Leica TCS-SP5). A x10 dry lens (HC PL APO, NA 0.4) was used to observe the blankets in cross section. The digital zoom was set to double magnification. Excitation wavelengths of 458nm and 514nm from Ar laser (Power: 50mW) were used. Acridine Yellow has strong fluorescence at the excitation wavelength of 458nm, while Macrolex Yellow has strong fluorescence at the excitation wavelength of 514nm. A dichronic beamsplitter, which separates the fluorescent wavelength from the excitation wavelength of an Ar laser, was used (DD458/514). The pinhole size was set at the optimum value for each objective lens (Wilson, 1995). The detected wavelengths ranged from 470nm to 550nm for the excitation wavelength of 458nm and ranged from 535nm to 635nm for the excitation wavelength of 514nm. In addition, reflected images were obtained as light from 505nm to 515nm for the excitation wavelength of 514nm in order to observe the shape of the blankets. Fifteen confocal frames in the z-direction were taken at 3μm steps beginning from a depth of 6μm in order to prevent contamination (Fig. 1), and the CLSM images were shown as a stacked image. The image size of each frame was 1024x1024 pixels. The fluorescence image is expressed as the maximum intensity projection.

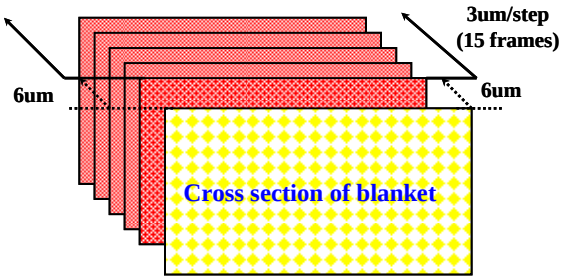

Figure 1. *Schematic diagram of CLSM measurement.*

IR imaging was carried out with an IR imaging system (Spotlight-300: Perkin Elmer Co.). A cross section of each sample was set on the sample stage of the IR microscope. The reflection mode was used to measure samples. The measurement area was adjusted to 1950μm x 530μm. 26458 spectra were obtained in this area because the IR beam size was 6.25μm x 6.25μm. It took about 20 minutes to measure one sample even with this high-speed detection system. The spectral range was from 4000cm^{-1} to 720cm^{-1} at 8cm^{-1} spectral resolution. All reflection spectra for the IR imaging were converted to an absorbance, after a Kramers-Krönig (K-K) transformation was executed. The strain of the reflection spectra can be revised by K-K transformation. We obtained frequency maps based on the absorption peak of the stretching vibration of carbonyl group (C=O) at 1735cm^{-1}.

Results and Discussion

The observation of penetration of acrylate monomer into blanket with CLSM

Figure 2 shows single frequency maps at 1735cm^{-1} (C=O stretching vibration) on the cross section of blanket-1 after several hours. Practically no penetration of the acrylate monomer was observed immediately after dropping it onto the blanket. However, the acrylate monomer had penetrated to the middle of the blanket rubber 6 hours after dropping. And after 24 hours it had become distributed throughout the blanket rubber.

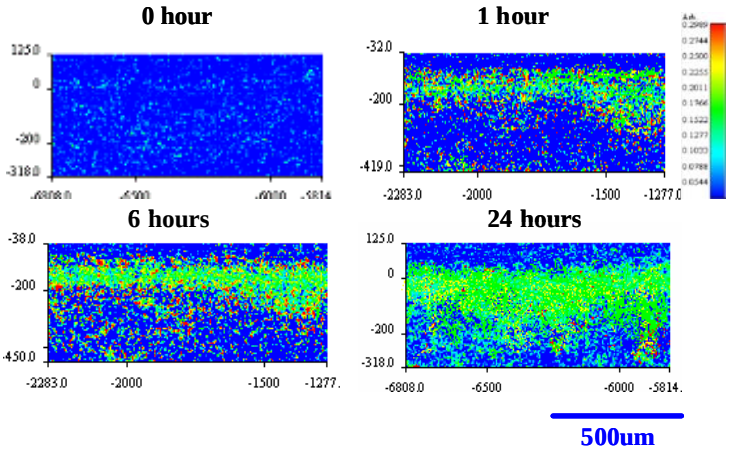

Figure 2. *Single frequency maps at 1735cm^{-1}(C=O stretching vibration) of acrylatemonomer on cross section of blanket after various time periods.*

Figure 3 shows the CLSM stacked image of the cross section of blanket-1 4 hours after dropping the acrylate monomer. The green represents the reflected light as the cross sectional shape of the blanket, and the red represents the fluorescent light as the distribution of the acrylate monomer. The fluorescent light was detected in the entire cross section. In Figure 2, however, the acrylate monomer had penetrated only half the thickness of the blanket rubber 6 hours after dropping. Because fluorescent light was detected throughout the cross section, it would appear that traces of fluorescent dye were deposited to the cross section of the blanket while cutting the blanket. To avoid observing such contamination, CLSM images were taken from positions deeper than 6μm (Fig. 1).

Figure 4 shows the CLSM stacked image after removing the cross section image. The fluorescent light was distributed to the middle of the blanket. The reinforcing cloth (bottom) is shown in red because it has its own fluorescence at the excitation wavelength of 514nm. While it takes 20 minutes to obtain the IR image, it takes only 3 minutes to obtain the CLSM

image.

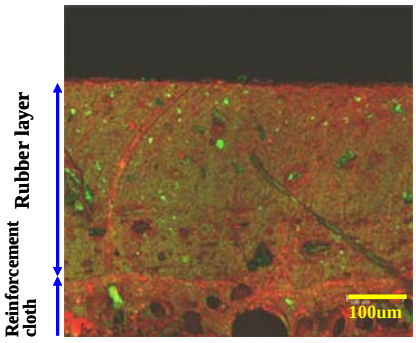

Figure 3. *CLSM stacked image of cross section of blanket-1 4 hours after dropping acrylate monomer.Green represents the reflected light as the cross sectional shape of blanket. Red represents the fluorescent light as the distribution of acrylate monomer.*

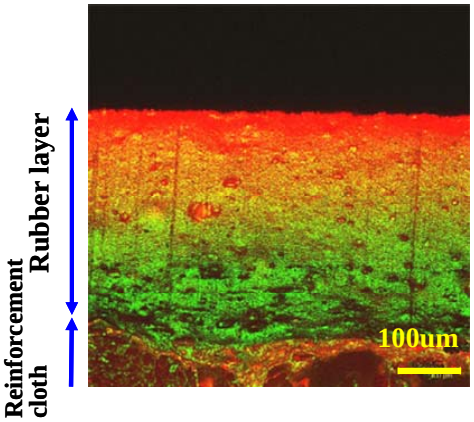

Figure 4. *CLSM stacked image of blanket-1 after removal of cross section image. Green represents the reflected light as the cross sectional shape of blanket. Red represents the fluorescent light as the distribution of acrylate monomer.*

Figure 5 shows the CLSM images of cross sections of blanket-1 at different times after acrylate was dropped on the blanket. The figures show that acrylate gradually penetrates into the blanket. In comparison to the IR images (Fig. 2), the distribution of acrylate into the blanket could be observed in more detail using CLSM.

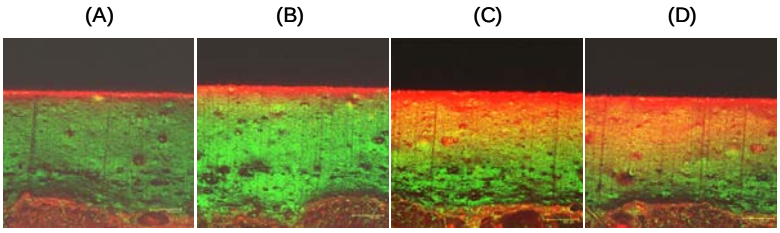

Figure 5. *CLSM images of cross section of blanket-1 at four intervals after acrylate was dropped on blanket. (A), (B), (C) and (D) show section at 0.5, 2, 4, and 12 hours after dropping. Green represents reflected light and red represents fluorescent light.*

Figure 6 shows the relationship between the penetration depth and time after acrylate dropping. The penetration depths obtained from the CLSM images were similar to those from the IR images.

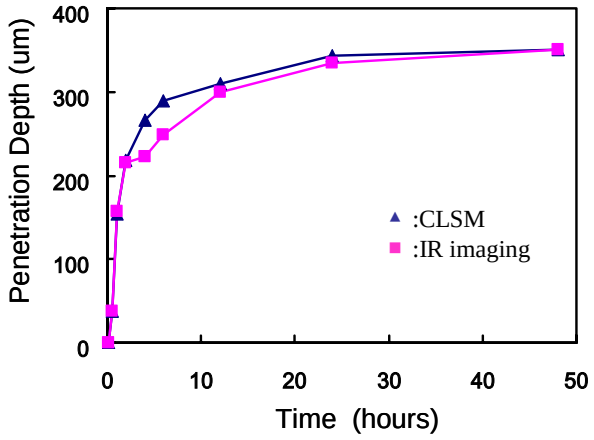

Figure 6. *Relationship between penetration depth and time after acrylate dropping.*

Figure 7 shows the relationship between the penetration rate of two blankets and time after dropping. The thickness of the blanket rubber was set as 100 % of penetration rate, and the penetration rates of acrylate monomer between blanket-1 and blanket-2 were compared. The penetration rates of

the acrylate monomer in blanket-1 were slightly faster than those in blanket-2. It was shown that the penetration of the acrylate monomer could be more easily and rapidly estimated with the CLSM staining technique.

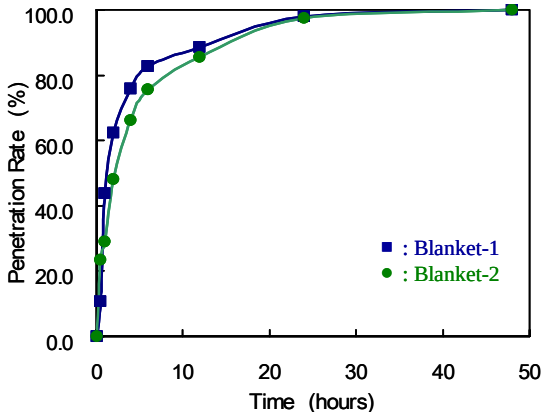

Figure 7. *Relationship between penetration rate of two blankets and time after dropping.*

The observation of acrylate monomer and cleaning solvent in blanket before and after cleaning

Figure 8 shows the CLSM image of the cross section of blanket-1 filled with the acrylate monomer before blanket cleaning. The acrylate monomer was shown to penetrate throughout the blanket rubber, as seen by the pervasiveness of red, which represents the fluorescent light of the monomer.

Figure 9 shows the CLSM images of blanket-1 after blanket cleaning. (A) shows, in red, the fluorescent light as the distribution of the acrylate monomer. (B) shows, in green, the fluorescent light as the distribution of the cleaning solvent. (C) shows an overlay of the distributions in (A) and (B). The acrylate monomer was removed to a depth of about 100μm from the blanket surface. Comparing the fluorescence image in (A) with that in (B), it was confirmed that some of the cleaning solvent overlapped the acrylate monomer in (C). However, the cleaning solvent did not significantly penetrate the blanket, and as a result the acrylate monomer was not removed from the blanket. In the case of the pure blanket, the cleaning solvent quickly penetrated into the blanket rubber. From this we concluded that the acrylate monomer in the blanket rubber could not be removed, because it inhibited the penetration of the cleaning solvent into the blanket.

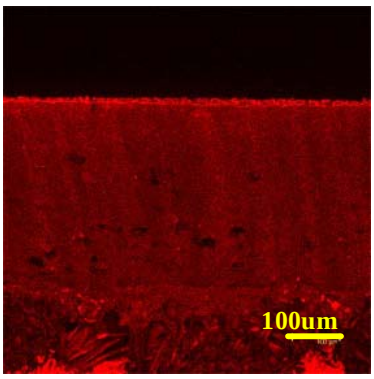

Figure 8. *CLSM image of blanket-1 before cleaning. Red represents the fluorescent light as the distribution of the acrylate monomer.*

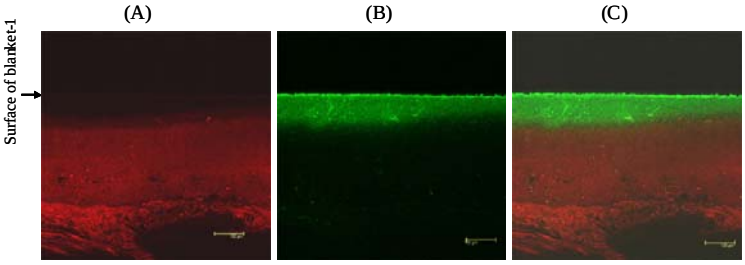

Figure 9. *CLSM images of blanket-1 after cleaning. (A) Red represents the fluorescent light as the distribution of the acrylate monomer. (B) Green represents the fluorescent light as the distribution of the cleaning solvent. (C) Overlay of (A) and (B) showing slight penetration of solvent into monomer.*

Figure 10 shows the CLSM image of blanket-2 after blanket cleaning. This image is an overlay of images showing the fluorescence of the acrylate monomer (red) and the cleaning solvent (green). As in blanket-1, the cleaning solvent only penetrated to the surface of the blanket, and the acrylate monomer was removed to a depth of about 100μm from the blanket surface.

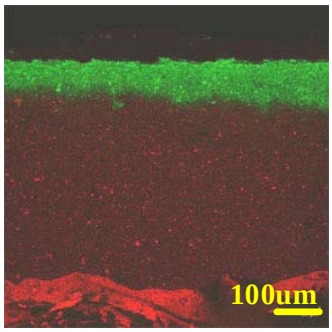

Figure 10. *CLSM image of blanket-2 after solvent cleaning*
Red shows acrylate monomer, green shows cleaning solvent.

Because the acrylate would remain in the blanket rubber even after cleaning, pre-conditioning operations would no longer be necessary in the printing work.

Conclusions

Using the CLSM staining technique, it was possible to observe the penetration of an acrylate monomer into a blanket in great detail. The CLSM technique is also very useful because the measurement times were five times shorter than those of IR imaging.

The distribution of the acrylate monomer and the cleaning solvent in the blanket after blanket cleaning could also be minutely observed using the CLSM double-staining technique. In this case, the acrylate monomer could not be removed from within the blanket after blanket cleaning because the solvent could not penetrate into the blanket.

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