

## Changes in Crystallinity and Re-swelling Capability of Pulp Fibers by Recycling Treatment

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An integrated technique was purposed for clarifying changes in amounts of amorphous and crystalline regions of fibers as well as for estimating possibility of their irreversible conversion due to recycling treatment. The crystallinity of fibers in handsheets was moderately changed by the recycling treatment as observed by X-ray diffractometry. Because most of the fibers consisting of the stable crystalline region which was hardly affected by the recycling treatment, the change in crystallinity was possibly stemmed from a slight increase in crystallinity of amorphous region of fibers during recycling. The decrease in the amount of the amorphous region by the recycling treatment, which affected the water adsorbability of fibers, was indirectly detected by differential scanning calorimetry. Because of the lack of re-opening of recycled fiber lumens in a wet state, the amount of bound water adsorbed to fiber wall substantially influenced the re-swelling capability of recycled fibers. The loss in re-swelling capability of wet recycled fibers was consistent with sub-morphological changes of fiber wall possibly due to the decrease in the amount of the amorphous region. FT-Raman spectroscopy was found not suitable for determining the effect of recycling treatment on changes in amounts of amorphous and crystalline regions of fibers.

**Keywords:** Amorphous region, Crystallinity, Recycling treatment, Re-swelling capability

### 1. Introduction

Microfibrils in bleached chemical pulp fibers consist of two regions of cellulose: crystalline and amorphous.<sup>1-3)</sup> The crystalline region is normally very stable with highly ordered cellulose molecules hardly accessed by water molecules. On the other hand, water molecules could access and adsorb to the amorphous region consisting of less-ordered cellulose molecules. Because a trace amount of adsorbed water on the surface of crystalline region is almost negligible, the amount of adsorbed water in fibers, which is also called "bound water", almost totally relies on accessible sorption sites of amorphous region.<sup>1)</sup> Therefore, determination of the amount of amorphous region of fibers can be conducted by differential scanning calorimetry (DSC) that is commonly used for determining the amount of bound water in fibers.<sup>1,4)</sup> For a study focusing on the crystalline region of fibers, one of the methods typically used is X-ray diffractometry.<sup>3,5,6)</sup> This method can be used for determining ratios of crystalline region as a crystallinity index that is basically proportional to the peak intensity ratio of reflected X-ray, which is derived from the 200 plane, for the crystalline region to that for the total regions.

As the advantages of these methods are specifically characterized by measurement of either the amount of amorphous or crystalline region, it seems doubtfully to use them separately for determining

changes in amounts of both the regions and discussing their irreversible conversion due to recycling treatment. Though some researchers<sup>7)</sup> stated the possibility of FT-Raman spectroscopy to detect and distinguish the proportional changes in amounts of amorphous and crystalline regions in cellulosic materials conditioned by some chemical and biochemical treatments, it has rarely been applied to study a stepwise effect of recycling treatment on changes in amounts of both the regions of fibers as in a case of DSC.

Therefore, it is the purpose of the present paper to provide an integrated technique of DSC, FT-Raman spectroscopy, and X-Ray diffractometry, which are possibly useful to clarify changes in amounts of amorphous and crystalline regions of fibers including their irreversible conversion due to the recycling treatment. Furthermore, because the re-swelling capability of dried fibers seems to be caused by two phenomena, i.e. the displacement of morphological features in fibers and sub-morphological swelling caused by bound water,<sup>8)</sup> the effect of recycling treatment on re-swelling capability of fibers which is probably related to the amount of bound water in fibers is also demonstrated.

## 2. Materials and methods

Handsheets R0 were made from a virgin hardwood bleached kraft pulp beaten to a freeness of 480 ml CSF (Canadian Standard Freeness), according to TAPPI test methods. As a model of paper recycling process,<sup>9)</sup> some of them were treated in a well-ventilated electric oven at 105 °C for 24 hours and then soaked in de-ionized water for 24 hours before disintegration for making handsheets R1 (recycled once). This procedure is called "recycling treatment" hereafter. The recycling treatment was repeated for one, two and three more cycles to produce handsheets R2, R3 and R4 from some of handsheets R1, respectively. Every handsheet was conditioned at 23 °C with 50 % relative humidity for two months, according to Japanese Industrial Standards (JIS). The amount of bound water and crystallinity were determined by using a differential scanning calorimeter (Pyris 1, Perkin Elmer Instrument Inc., USA) and an X-ray diffractometer with Cu K radiation (RINT 2000, Rigaku, Japan), respectively, with six replications for sheets chosen randomly from conditioned handsheets R0-R4. Small pieces of the rest of handsheets R0-R4 were soaked in de-ionized water for 24 hours and then disintegrated to fiber slurries for determining the aspect ratio of wet single fibers by using a confocal laser-scanning microscope (LSM 510, Carl Zeiss Jena GmbH, Germany). Seventy single fibers were observed for each fiber slurry.<sup>10)</sup> FT-Raman spectroscopy (Magna-IR 860 equipped with Raman accessory, Nicolet Instrument Co., USA) was also attempted for determining changes in amounts of amorphous and crystalline regions of fibers in the handsheets.

## 3. Results and discussion

The pattern of X-ray diffraction of a handsheet, as shown in **Fig. 1**, was used for calculating a crystallinity index following the empirical method of Segal et al.<sup>6)</sup> As can be seen in **Fig. 2** the crystallinity indices of handsheets appear to be moderately changed by the recycling treatment. This result

indicates that the crystalline region of cellulose, which is major part of bleached kraft pulp fibers,<sup>1,11)</sup> in the handsheets was quite stable and hardly affected by the recycling treatment whereby the amount of lingo-hemicellulose of the fibers is considerably negligible.<sup>12)</sup> The change in crystallinity index of fibers in the handsheets was possibly reflected by some changes of amorphous region of fibers as the remarkable change in structure of amorphous region of natural cellulose untreated with any chemicals is probably influenced easily by the recycling treatment. As demonstrated in the research of Isogai et al.,<sup>3)</sup> the regenerated amorphous cellulose, which is stable under aqueous conditions as the amorphous region in cellulosic materials, can be changed in its structure to be higher crystallinity and possessed lower water accessibility by irreversible hydrogen bonds formation induced through hydrothermal and dry thermal treatments, respectively. Matsuda et al.<sup>13)</sup> also confirmed that heat treatment promoted hardwood bleached kraft pulp fibers lower water accessibility with the increased irreversible hydrogen bonds in some part of amorphous region in the fibers. Therefore, part of amorphous region of fibers in the present study could possibly be also distorted to lose in their water adsorbability, i.e. due to irreversible hydrogen bonds formation, by the thermal condition in the recycling treatment. This part of the amorphous region lost in water adsorbability is named as "distorted amorphous region" hereafter.

**Fig. 3** demonstrates the noticeable changes in broad endothermic peak areas of handsheets, which were measured by using DSC, due to the recycling treatment. The endothermic peak area attributed to the heat of dehydration of bound water ( $H$ ) of handsheets was calculated based on dried weight of samples following the procedure suggested by Bertran and Dale.<sup>1)</sup> According to our previous research,<sup>9)</sup> the same recycling treatment performed in this study gave handsheets with constant and fairly small amounts of fines content. The negligible loss in carbohydrates and lignin of kraft pulp fibers during recycling is also credible.<sup>14)</sup> Therefore, the change in  $H$  values considerably relied on the change in the amount of bound water adsorbed to fibers in the handsheets. **Fig. 4** shows the decrease in  $H$  values of fibers in the handsheets was affected by the recycling treatment. As can be seen, even though the  $H$  value of R0-fibers was not statistically different from that of recycled fibers, the  $H$  value of the recycled fibers was significantly decreased when they were recycled for three times. This result possibly demonstrates that the inferior adsorbability of water of recycled fibers was influenced by irreversible hydrogen bonds of distorted amorphous region in the fibers which were increasingly formed remarkably through the heating stage of the recycling treatment.<sup>3,13)</sup>

Even though the decrease in  $H$  values represented mostly the increase in the amount of distorted amorphous region of fibers that was induced by the heating stage of the recycling treatment, the good relationship between the crystallinity index and the  $H$  value was still in an agreement as demonstrated in **Fig. 5**. As can be seen, the fibers with high values of crystallinity index have low values of  $H$ , i.e. they have low water adsorbability possibly by increasing in crystallinity of the amorphous region. The increase in crystallinity of amorphous region in the fibers was possible during recycling because the hydrothermal condition was possibly induced, during the initial stage of heating in the recycling treatment, with the moisture content of fibers mostly consisted of bound water adsorbed to the amorphous region.<sup>3)</sup> However, this phenomenon was likely to cause the crystallinity index of fibers in the handsheets to change very slightly by the recycling treatment, which was hardly determined by

conventional X-ray diffractometry, as shown in **Figs. 1** and **2**.

**Figs. 6, 7** and **8** represent the measurement method, the mean values, and the frequency distribution of the aspect ratio of wet single fibers, respectively. Because fully swollen wet fibers with almost completely round cross-sections gave the values of aspect ratio close to 1.00, most of the wet R0-fibers were more swollen than those of the wet recycled ones. Moreover, most of the wet recycled fibers were also irreversibly collapsed after the first recycling time. This phenomenon was similar to the result in our previous research<sup>9)</sup> in which the same kind of chemical pulp fibers and recycling treatment were conducted. Therefore, the re-swelling capability of wet recycled fibers considerably depended on their cell wall swelling because of the lack of re-opening ability of their lumens.

**Fig. 9** demonstrates the relationship between the  $H$  value and the value of the aspect ratio. As can be seen, at low  $H$  values, i.e. small amounts of bound water was adsorbed to fibers, the fibers had a less swelling capability. Because wet fibers could be swelling when the internal strain relaxation of cellulose microfibrils in fiber wall is caused by introducing water molecules to the amorphous region,<sup>10)</sup> this result confirms that the re-swelling capability of recycled fibers collapsed even in the wet state relied strongly on the amount of bound water adsorbed to their cell wall. In other words, the loss in re-swelling capability of recycled fibers was consistent with the loss in the amount of bound water adsorbed to their cell wall, which was possibly caused by the increase in crystallinity and distorted part of amorphous region, as is known as sub-morphological changes of fiber wall.<sup>8)</sup> As a result, both the  $H$  value and the value of aspect ratio could reflect highly sensitively the changes in physical features of fibers affected by the recycling treatment. This finding is proved by the fact that there were certain differences demonstrated significantly among the recycled fibers with both the parameters as shown in **Figs. 4** and **7**. Especially for the DSC, it could probably show that the recycling treatment gave the fibers more uniformity as statistical confidence levels of the  $H$  values were gradually narrowed with recycling times, as also demonstrated in **Fig. 4**. The evaluation method of X-ray diffractometry seems to be lacking in sensitivity of this phenomenon as previously mentioned above and shown in **Figs. 1** and **2**.

**Fig. 10** shows the intensity and pattern of FT-Raman spectrum of R0-fibers were similar to those of FT-Raman spectrum of R4-fibers. Because changes in intensity of FT-Raman spectrum at 900 and 1098  $\text{cm}^{-1}$  represent to changes in amounts of amorphous and crystalline regions, respectively,<sup>7)</sup> therefore, the FT-Raman spectroscopy was found not suitable for determining the change in the ratio of amorphous and crystalline regions in the fibers affected by the recycling treatment. This is possibly caused by the fact that the ratio was not statistically different between R0-and R4-fibers, as shown in **Figs. 2** and **4**, and not caused by changes in chemical aspects of fibers due to the recycling treatment. Moreover, a possible cause for the similarity of the two FT-Raman spectra is that the sample preparation and treatments in the present study were different from those in others' research.

#### 4. Conclusion

The crystallinity index of fibers in the handsheets was moderately changed by the recycling treatment. This phenomenon is suggestively caused by some part of amorphous region of fibers in the

handsheets was slightly changed to be higher crystallinity during recycling. Because of the lack of re-opening of recycled fiber lumens in the wet state, the amount of bound water adsorbed to fiber wall substantially influenced the re-swelling capability of recycled fibers. The loss in re-swelling capability of recycled fibers was consistent with the loss in the amount of bound water adsorbed to their cell wall, which was possibly caused by the loss in amorphous region, as is known as sub-morphological changes of fiber wall. Only the DSC and the measurement of the aspect ratio of wet single fibers could sensitively determine the changes in physical features of fibers affected by the recycling treatment. The FT-Raman spectroscopy was found not suitable for determining the effect of recycling treatment on the changes in amounts of amorphous and crystalline regions of fibers.

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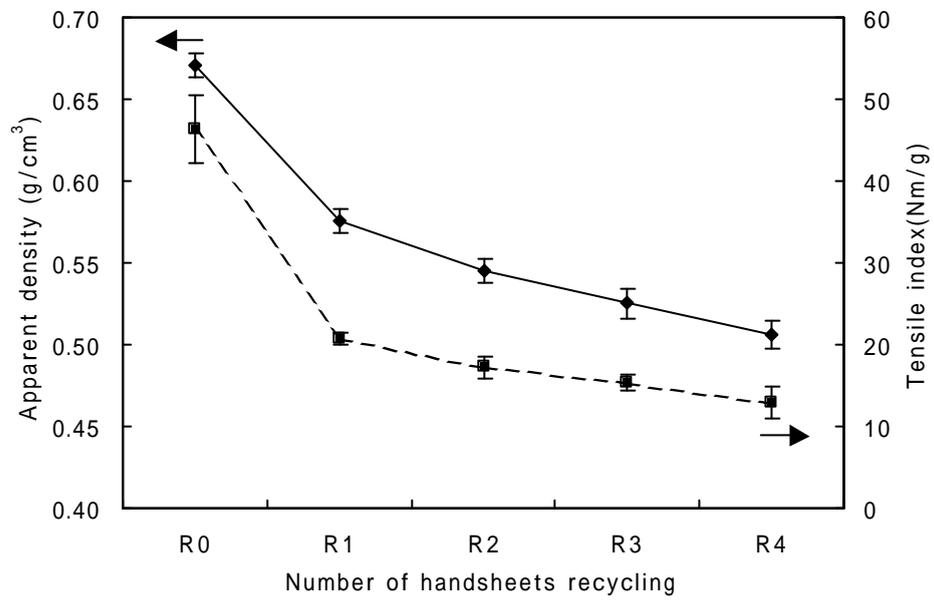


Fig. 1. Decrease in apparent density and tensile index of HBKP handsheets due to the recycling treatment. A pair of bars denotes a range of 95% confidence level.

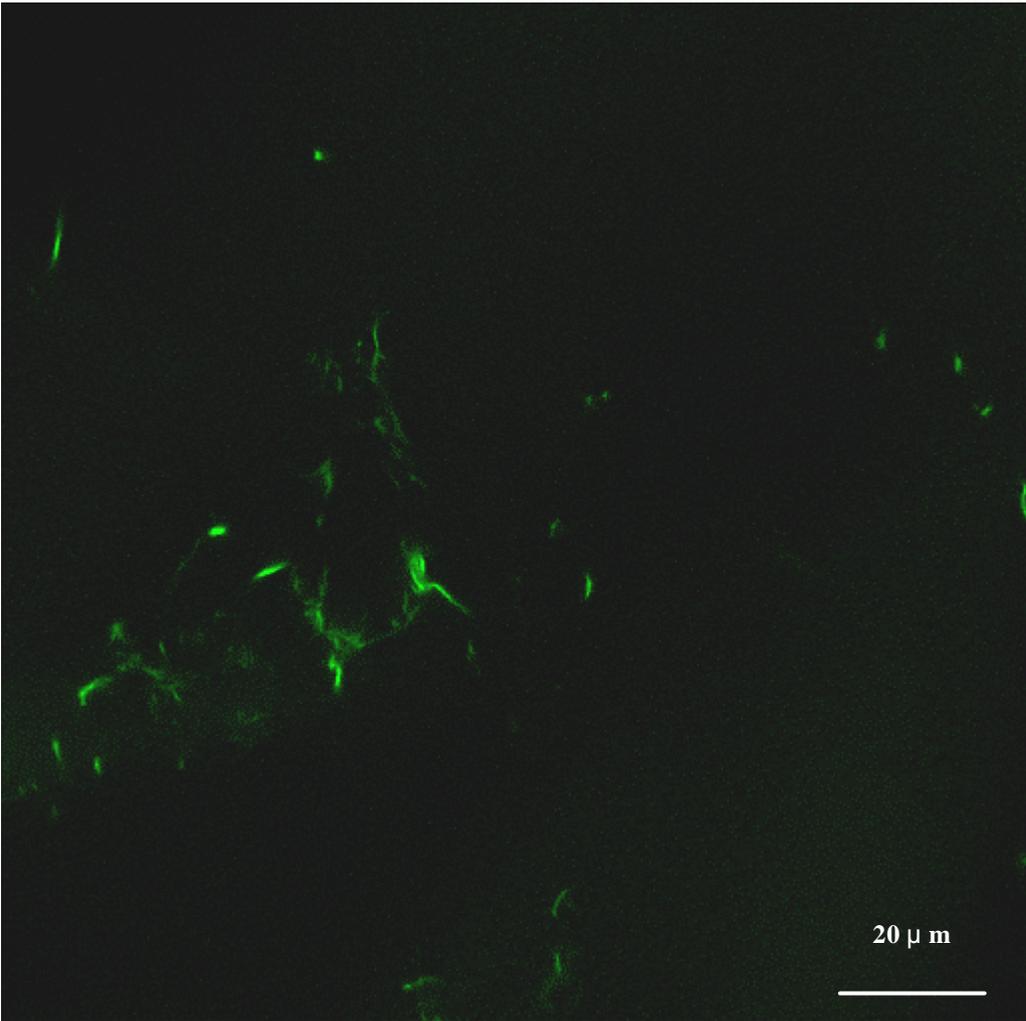


Fig. 2. CLSM micrograph of typical fines in post-R0 slurry.

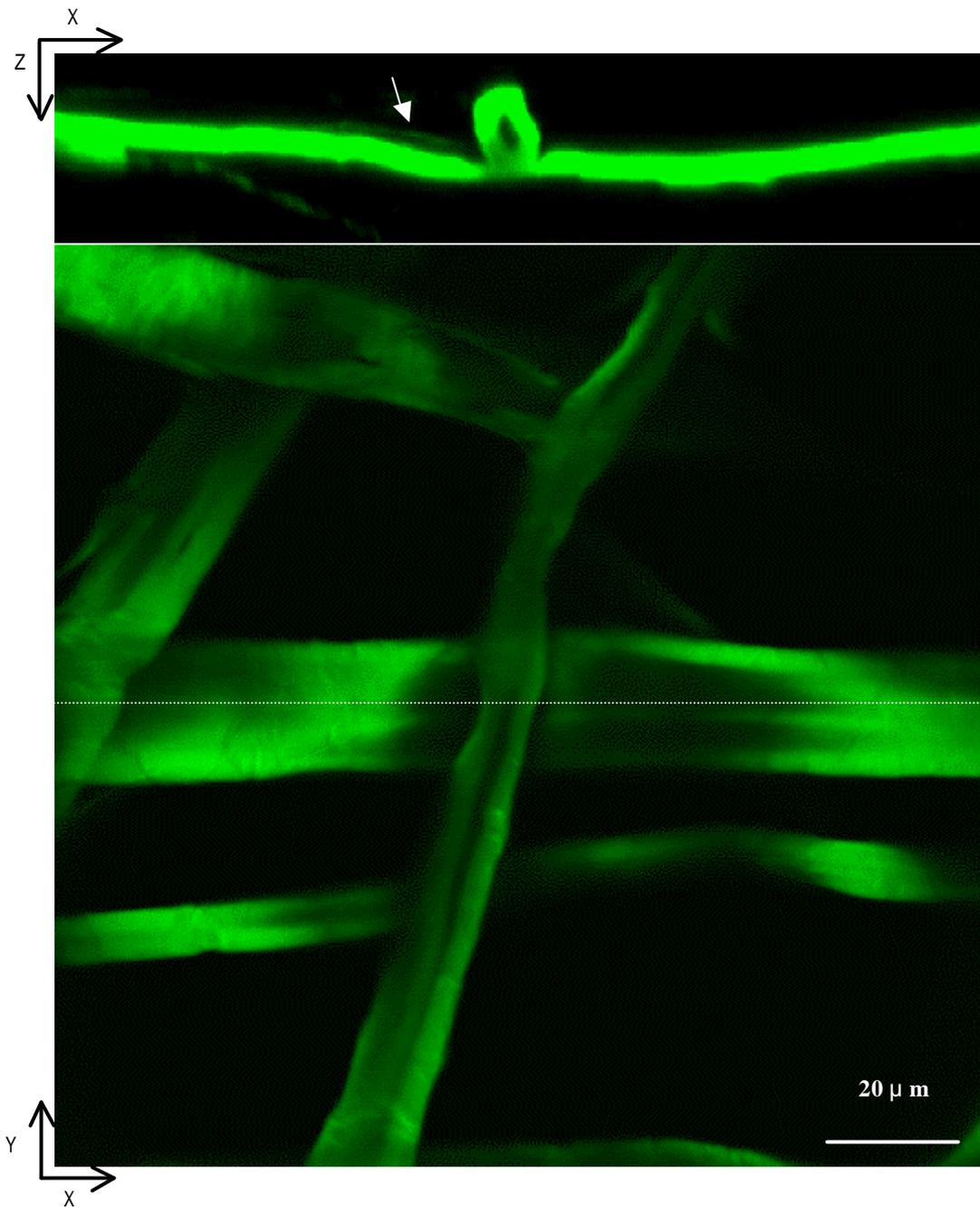


Fig. 3. CLSM XZ-sectioned micrograph (top) along the dotted white line in XY-micrograph (bottom) shows a thin layer of fines (arrowed) covering a fiber surface of post-R0 slurry surface in the dry state at the potentially interfiber crossing as a kind of strengthening material.

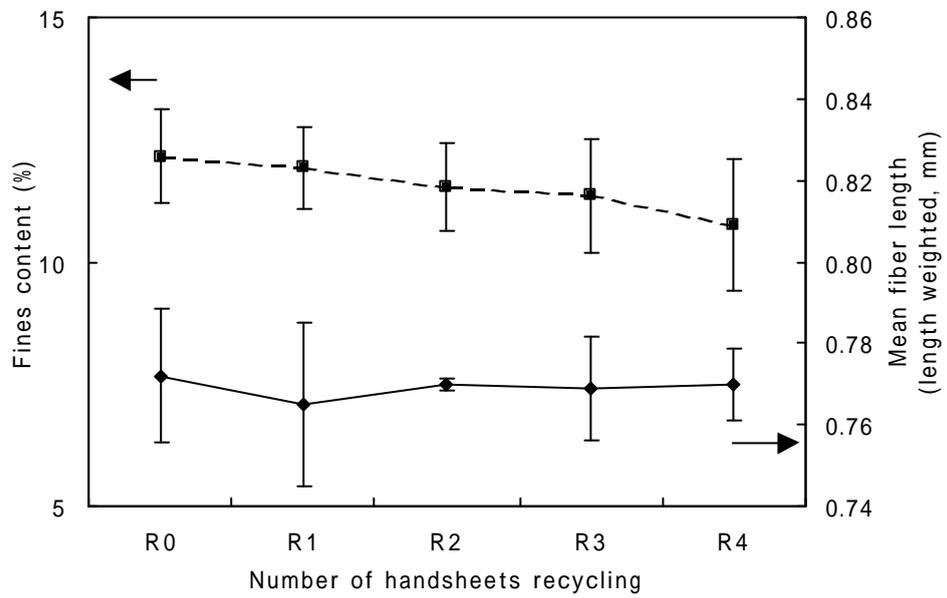


Fig. 4. Fines content and mean fiber length of post-R0 to R4 slurries. A pair of bars denotes a range of 95% confidence level.

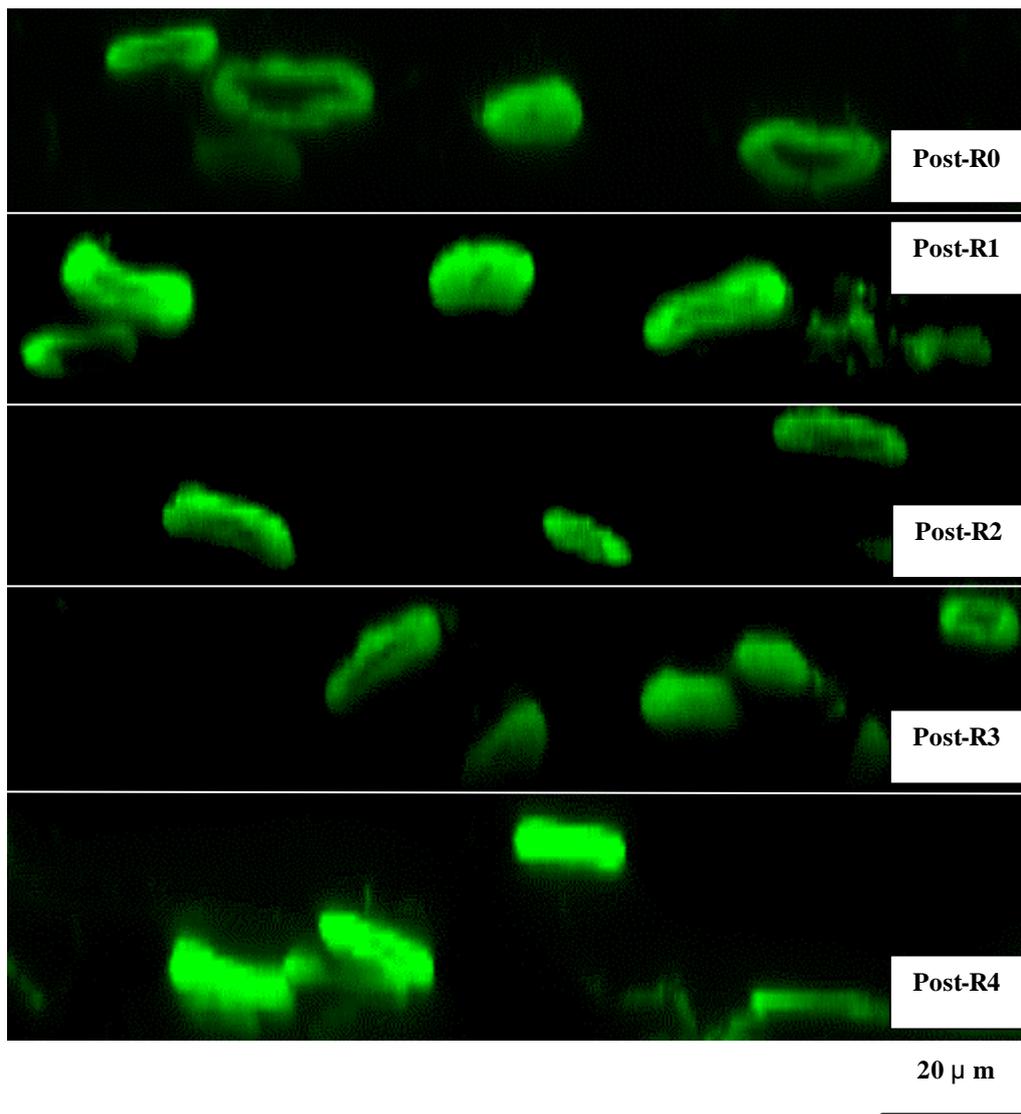


Fig. 5. CLSM micrographs of HBKP fiber (wet) cross-sections show the stepwise effect of recycling treatment on the re-swelling ability.

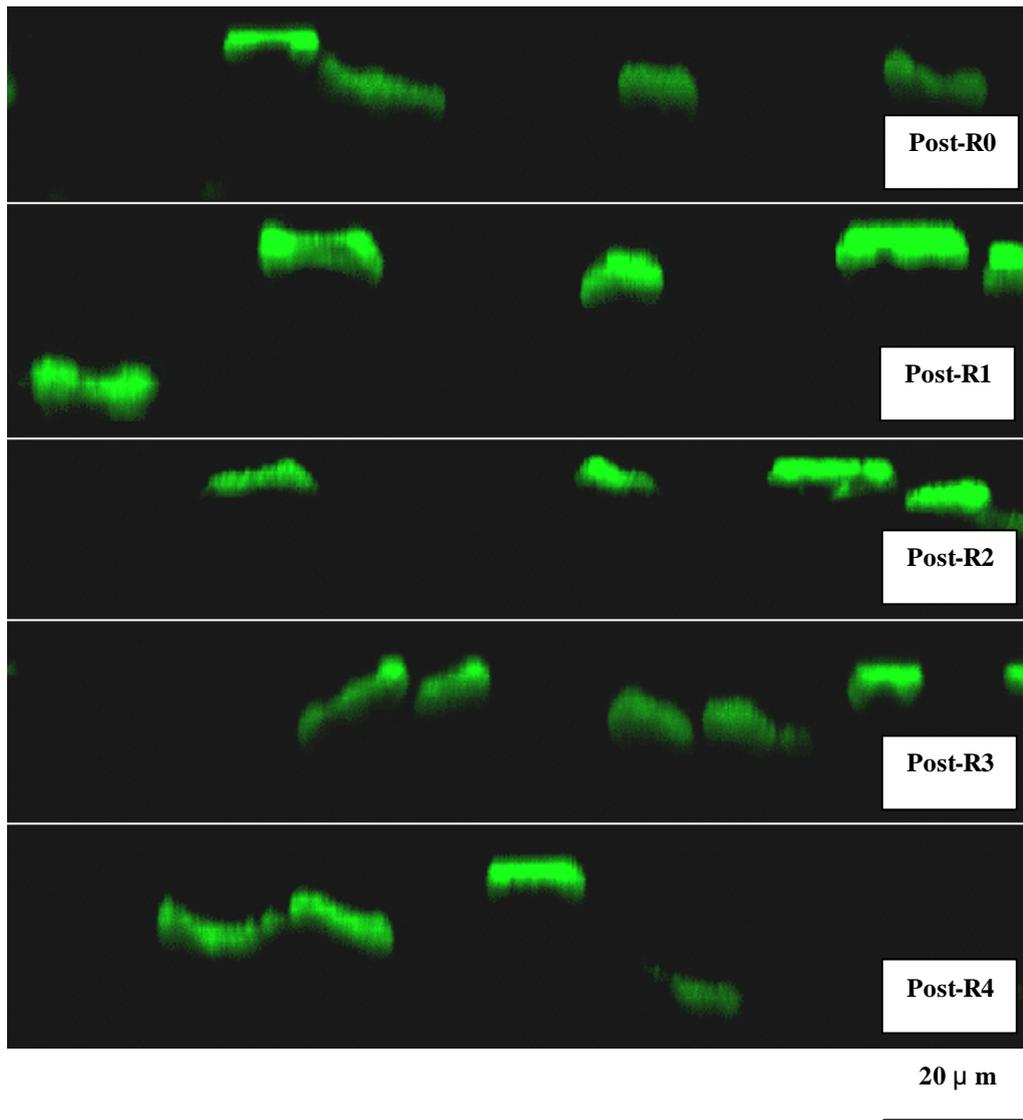


Fig. 6. CLSM micrographs of HBKP fiber (dry) cross-sections at the same location as in Fig. 5.

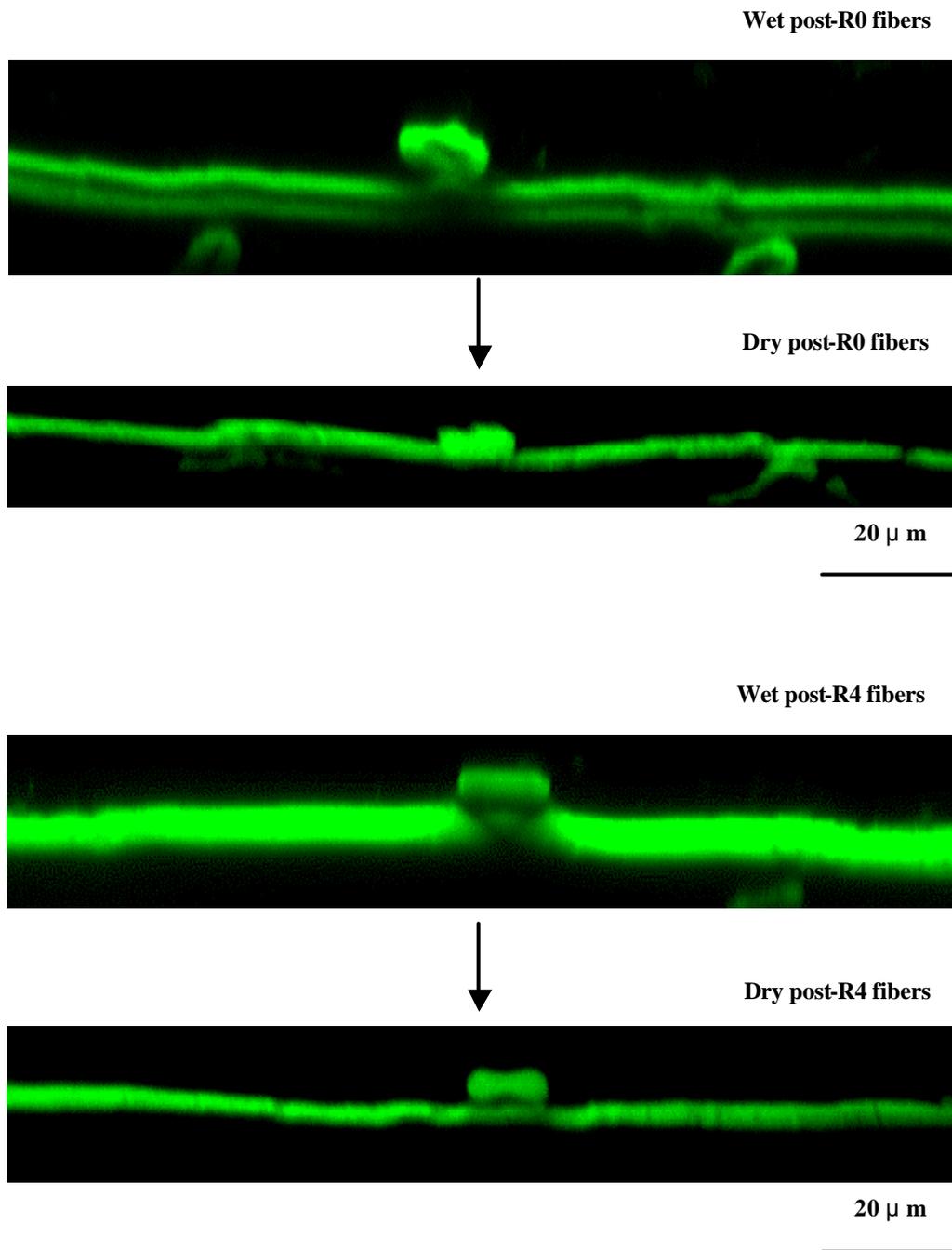


Fig. 7. CLSM micrographs of HBKP fiber cross-sections at the interfiber crossings show the conformability of wet-swollen fibers of post-R0 slurry is superior, for promoting the good interfiber contact in the dry state, to that of wet-collapsed fibers of post-R4 slurry.

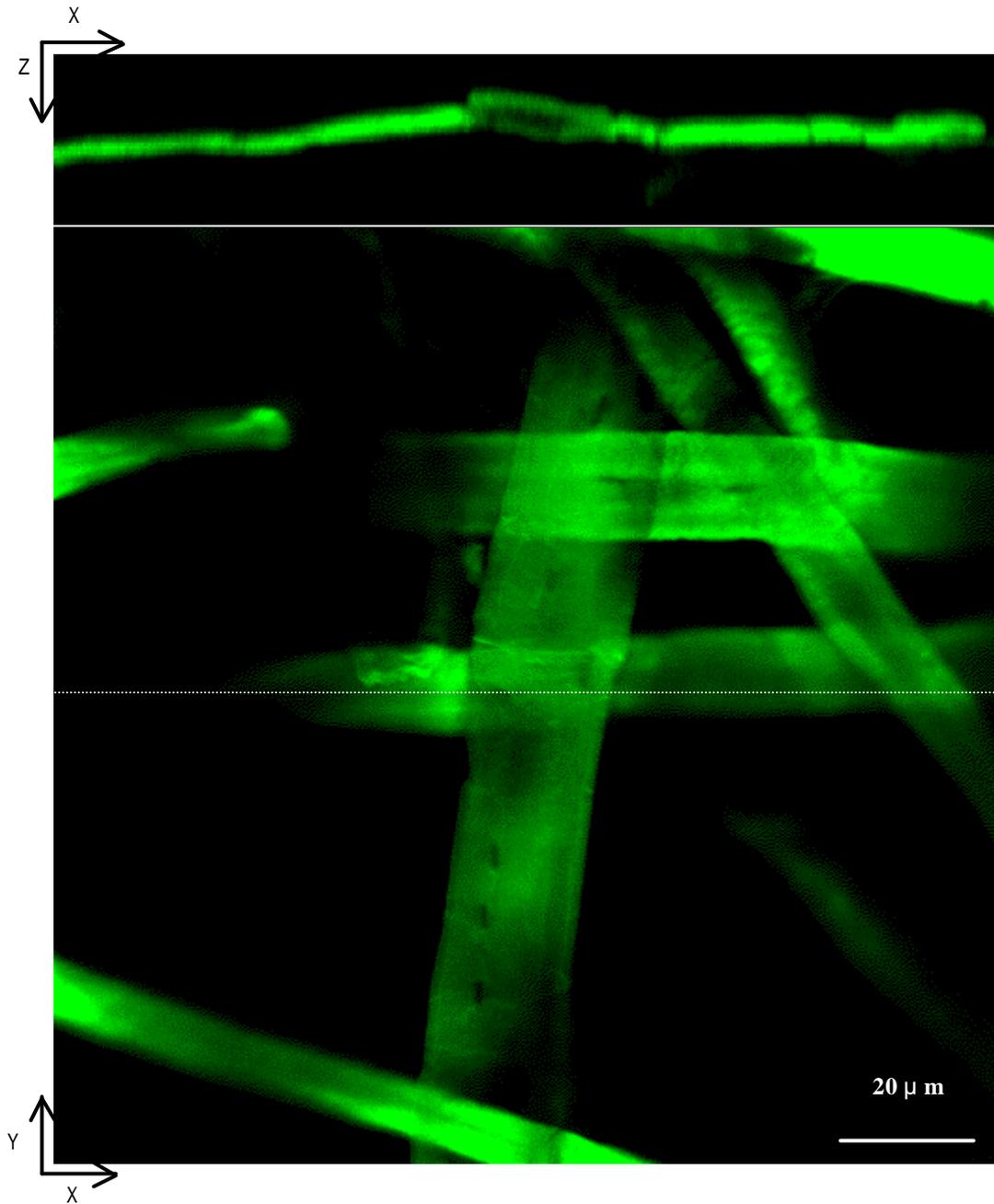


Fig. 8. CLSM XZ-sectioned micrograph (top) along the dotted white line in XY-micrograph (bottom) shows an un-bonded area at the interfiber crossing of dried fiber of post-R4 slurry.

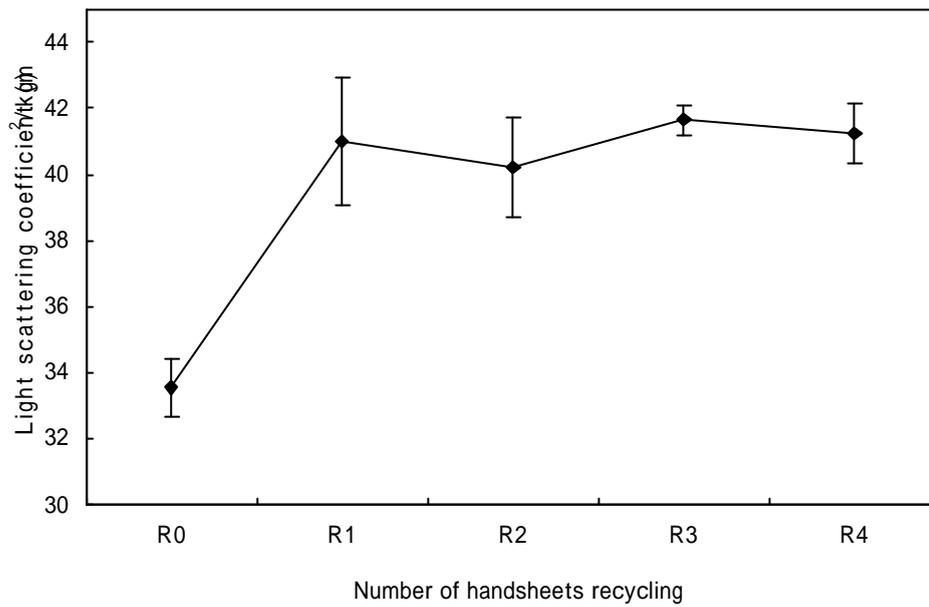


Fig. 9. The increase in light scattering coefficient of recycled HBKP handsheets due to the recycling treatment. A pair of bars denotes a range of 95% confidence level.

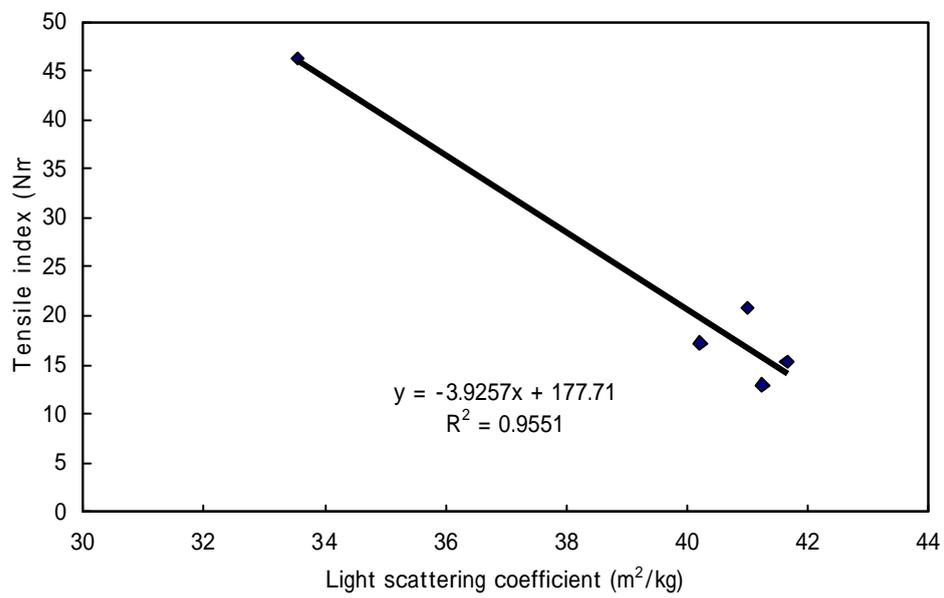


Fig. 10. Relationship between light scattering coefficient and tensile index of HBKP handsheets.