リサイクルにおける繊維の角質化が繊維交点の潜在結合力に及ぼす影響：共焦点型レーザー走査顕微鏡を用いて

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広葉樹クラフトパルプから調製した手すき紙に、リサイクル処理をモデル化した熱処理を施し、リサイクルを行った。4回のリサイクルによって密度は0.67から0.51 g/cm³に、比引張り強さは46.3から12.9 Nm/gにそれぞれ低下した。リサイクル手すき紙の全体的な結合強度の低下と関係のある微細繊維量の減少と繊維の角質化は、密度と引張強さの低下に影響を及ぼす要素になっていると考えられるため、それらの挙動を調べた。共焦点型レーザー走査顕微鏡（CLSM）を用いた観察によって、微細繊維が繊維表面を覆ったり、繊維間結合部の周囲を埋めたりすることによって紙力を向上させる役割を果たしている可能性が示された。広葉樹クラフトパルプ繊維の断面のCLSM写真は、角質化が起これば湿潤状態での繊維の再膨潤が妨げられることを明らかに示していた。その結果、手すき紙のリサイクルのどの段階においても角質化は紙層形成過程の繊維の柔軟性低下に大きな影響を及ぼしていた。リサイクル繊維は膨潤性と柔軟性に劣るため、リサイクル手すき紙では十分な繊維間の接触がないということもCLSM写真ははっきりと示していた。手すき紙のリサイクルでは、十分な微細繊維量の減少は検出されなかったことから、非結合面積の増加は、再湿潤リサイクル繊維の再膨潤能力又は柔軟性の低下に因ることが示唆された。CLSM観察でも、リサイクル手すき紙の強度低下は明らかに繊維交点の非結合面積の増加に起因するものであることがわかった。

Effect of fiber hornification in recycling on bonding potential at interfiber crossings: Confocal laser-scanning microscopy

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Abstract

Hardwood bleached kraft pulp (HBKP) handsheets were recycled with heat treatment as a model of paper recycling. The apparent density and the tensile index decreased from 0.67 to 0.51 g/cm^3 and 46.3 to 12.9 Nm/g, respectively, after they were recycled for four times. Decrease in fines content and hornification of fibers with recycling, which were related to the reduction in total bonding strength of recycled handsheets, were investigated as possibly influential factors on this behavior. A possibility of strengthening role of fines by covering fiber surfaces including filling peripheral regions of interfiber crossings was presented by confocal laser-scanning microscopy (CLSM). The CLSM micrographs of cross-sections of HBKP fibers evidently showed hornification effect on re-swelling in the wet state, which strongly affected their conformability during wet web forming, in each cycle of handsheets recycling. Recycled fibers showed inferior re-swelling ability and conformability, i.e. they could not provide sufficient interfiber contacts in recycled handsheets, as in CLSM micrographs clearly demonstrated. Because no decrease in fines content was noticeable by handsheets recycling, the increase in un-bonded areas of recycled handsheets is suggested to rely on the reduction in re-swelling ability or conformability of rewetted recycled fibers. The decrease in strength of recycled handsheets was also certainly attributed to the increase in un-bonded areas of interfiber crossings by CLSM.

Keywords: *Confocal laser-scanning microscopy, Hardwood bleached kraft pulp, Hornification, Recycling*

1. Introduction

Recycled paper has been increasingly produced in various grades in paper industry. However, there are still technical problems including reduction in mechanical strength for recycled paper. Especially, chemical pulp-origin paper, that is, fine paper requires a certain level of strength. Howard and Bichard[1] reported that beaten bleached kraft pulp produced handsheets which were bulky and weak in tensile and burst strengths, except in tear strength that was increased, by handsheet recycling. This behavior could be explained by the reduction in re-swelling ability or the reduction in flexibility of rewetted pulp fibers due to fiber hornification and, possibly, by fines loss during recycling processes, which decrease both total bonding area and the strength of paper[1-4]. For thermomechanical pulp (TMP), the reduction in flexibility of wet fibers due to recycling treatment had a strong relation to the reduction in conformability of the wet fibers during paper forming, i.e. paper strength was also reduced due to reduction in interfiber bonding areas, as evidently substantiated by Cao *et al*[5]. Furthermore, they also demonstrated that the specific strength of interfiber bonding was not affected by the recycling treatment. Jang *et al*[6] studied the transverse dimensions of chemical and mechanical softwood pulp fibers in the dry state, which was subjected to the recycling treatment, with a confocal laser-scanning microscope (CLSM). They reported that the decrease in lumen area as well as the significant decrease in fiber wall thickness of the TMP fibers occurred due to the recycling treatment; however, this behavior did not clearly occur in chemical pulp fibers. The credibility of CLSM application for determining the collapse behavior and fibril angle of various fibers has also been demonstrated in many publications of Jang and his colleagues[6-9]. Weise and Paulapuro[10] found a greater reduction in the magnitude of re-swelling of softwood bleached kraft pulp fibers in the wet state using CLSM images of fiber cross-sections. They considered it was a result of repeated wet-and-dry cycles. This result could possibly imply that re-swelling ability of recycled softwood chemical fibers decreased due to the repeated wet-and-dry cycles of the recycling treatment. Furthermore, they also confirmed that the dry state cross-sections of fibers did not significantly change with the wet-and-dry cycles, which was similar to the result of Jang *et al*[6]. Moss and Retulainen[11] applied CLSM technique to clarify the effect of chemical pulp fines on the interfiber bonding in TMP handsheets as a strengthening material. They demonstrated that the chemical pulp fines could possibly strengthen the TMP handsheets predominantly by covering fibers surfaces and filling peripheral regions of interfiber crossings. Though in all these researches the CLSM technique was applied to study the morphological aspects of various types of fibers as well as in the related research fields, they were seemingly quite limited to softwood fibers. Changes in morphological aspects of hardwood bleached kraft pulp (HBKP) fibers directly induced by recycling treatment have not been understood well even by means of the CLSM technique. Understanding of them would lead to important fundamentals of strength recovery of HBKP recycled paper that is sourced partially from HBKP contained in waste office paper and requires strength to be improved. Therefore, the application of CLSM to study the effects of fines and hornification of HBKP fibers, due to the recycling treatment, on the bonding potential at interfiber crossings affecting mechanical properties of the recycled paper is a main objective in this research.

2. Materials and Methods

Handsheets preparation and measurement of mechanical and physical properties

According to TAPPI test methods, all of handsheets R0 were first made from a virgin HBKP beaten for 5,000 revolutions in a PFI mill to obtain a freeness of 480 ml CSF (Canadian Standard Freeness).

In order to simulate a part of recycling process, the following treatment was conducted as a model treatment in paper recycling. That is, a laboratory-level treatment was applied to some of the handsheets by keeping them in a well-ventilated electric oven at 105 ℃ and then soaked in de-ionized water, both for 24 hours, before disintegration for making handsheets R1 (recycled once). This procedure is named as "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. The handsheets R0-R4 were each randomly determined six replications for subsequent mechanical and physical properties tests, also according to TAPPI test methods.

Fiber and fines analysis

Some sheets of handsheets R0 to R4 were soaked in de-ionized water for 24 hours and then disintegrated to fiber slurries; post-R0 slurry to post-R4 slurry. Parts of them were each subjected to analysis for fines content and mean fiber length with a fiber quality analyzer (FQA, OpTest Equipment Inc., Canada). Other parts of the rest of them were each stained with acridine orange, a fluorescent dye, and filtered with filter paper for retaining fines. A small piece of the wet dyed fibers and fines retained on the filter paper were cut out and placed on a slide glass, and a piece of cover glass was mounted on the top before subjecting to CLSM (LSM 510, Carl Zeiss Jena GmbH, Germany) observation. The micrographs of XY plane and XZ or YZ sectional plane of the dyed fibers and fines, both in the wet and dry states, were taken using a 65x water immersion lens. Micrographs of only XZ or YZ sectional plane of the dyed fibers, which were perpendicular to their fiber axes, were used for the interpretation of changes in the cross-section and phenomena induced by the recycling treatment.

3. Results and Discussion

Fig. 1 shows that apparent density and tensile index of the handsheets decreased from 0.67 for R0 to 0.51 g/cm^3 for R4 and 46.3 for R0 to 12.9 Nm/g for R4, respectively. These results suggest that the decrease in fines content of handsheets and the hornification of recycled fibers reduced the total bonding strength in those recycled handsheets. Fig. 2 shows typical wet HBKP fines in the post-R0 slurry observed by CLSM. These fines could play a role of strengthening material, as suggested by Moss and Retulainen[11)]. As can be seen in Fig. 3, a thin layer of fines covered a surface of a dry fiber from post-R0 slurry and filled the peripheral region of the interfiber crossing potential to make a bond in the dry state, which is similar to the CLSM micrograph demonstrated by Moss and Retulainen[11)]. However, there was not any difference in fines content between any pairs of post-R0 to post-R4 slurries as shown in Fig. 4. Because all the slurries used for the fiber and fines analysis were prepared by the same method, the constant fines content of post-R0 to post-R4 slurry was possibly caused by the similarity in fines retention during handsheet making, i.e. similar amounts of fines were retained in wet webs consisting of fibers of equivalent lengths. The mean fiber length that was also constant with cycles of the recycling treatment as also shown in Fig. 4 which strongly supported this interpretation. Fig. 5 shows the hornification effect on the re-swelling ability of HBKP fibers when soaked in water. It can be noticed that the recycling treatment had great influence on re-swelling of fiber walls of recycled HBKP fibers and the collapse of their lumens. In the dry state, however, the change in transverse dimension of fibers through the recycling treatment was hardly noticeable because the lumens completely collapsed as shown in Fig. 6. This behavior in the wet and dry states was similar to that of the softwood chemical fibers studied by Jang *et al*[6) and Wiese and Paulapuro[10). Less swollen fibers wall and more collapsed lumens of wet recycled fibers tend to loose conformability for promoting good interfiber contact during a handsheet making process because the plasticity of fiber walls directly depends on their swelling ability[12). Fig. 7 gives a representative example to prove this mechanism. It can also be seen that wet-collapsed fibers of post-R4 slurry lost their conformability and produced loose contact at the interfiber crossing in the dry state, whereas wet-swollen ones of post-R0 slurry were fairly collapsed but maintained superior conformability to produce good interfiber contact in the dry state. These results also strongly suggest that rewetted fibers in post-R0 slurry, which were not subjected to the recycling treatment, still had good re-swelling ability and conformability for improving good interfiber contact. Therefore, it undoubtedly implies that virgin fibers had much superior swelling ability and conformability to produce good interfiber contact in the first handsheets (R0). Furthermore, the fiber behavior of post-R4 slurry could possibly be applied for predicting those of the other fibers of the recycled slurries because of the similarity in re-swelling ability and dried cross-sections of them all as can be seen in Figs. 5 and 6. As a result, it is no exaggeration to say that the recycled fibers had the inferior re-swelling ability and conformability, i.e. they could not produce the good interfiber contact in the recycled handsheets. The top micrograph of Fig. 8 shows a gap representing a loosely bonded or un-bonded area, which possibly often occurred in the recycled handsheets, at the interfiber crossing of dried fibers of post-R4 slurry. Because none of the handsheets used in this research was calendered, un-bonded areas including interfiber gaps in the handsheets were measured in terms of light scattering coefficient[13-14). Fig. 9 shows that measured light scattering coefficients of all the recycled handsheets were significantly higher than those of handsheets R0. This finding strongly suggests that there were larger interfiber un-bonded areas in the recycled handsheets than that in handsheets R0. Though there was a possibility that fiber wall breakage created light scattering surfaces, but it was not noticeable in any of the samples observed with the CLSM. Fig. 10 shows the strong relationship between the light scattering coefficient and the tensile index of the handsheets. This relationship could possibly explain that the decrease in strength of the recycled handsheets was mainly related to their increased un-bonded areas if the specific strength of interfiber bondings in the handhseets was not affected by the recycling treatment at all, as clearly recognized by some experts[5). As can be seen, the handsheets with high light scattering coefficients had low strengths. According to all the results mentioned so far, the increase in un-bonded areas of the recycled HBKP handsheets is also suggested to rely on the reduction in re-swelling ability or conformability of rewetted recycled HBKP fibers during the handsheet making process. This hypothesis was proved by the significant increase in light scattering coefficient and decrease in tensile index of the recycled handsheets while there was no significant difference in fines content among post-R0 to R4 slurries.

4. Conclusions

The strengthening role of fines layer, the adverse effect of hornification of recycled HBKP fibers on the re-swelling ability, and gaps at interfiber crossings of dry recycled fibers were proved to affect strongly the potential of interfiber bondings in the handsheets by the powerful function of CLSM. The increase in un-bonded areas including interfiber gaps in the recycled handsheets is suggested to rely on the reduction in re-swelling ability or conformability of recycled fibers during the handsheet making process. The unique CLSM micrographs in this research also showed that the fibers treated with the recycling treatment had the inferior re-swelling ability and conformability, i.e. they could not produce the good interfiber contact in recycled handsheets. The decrease in strength of recycled HBKP handsheets was confirmed as being due to the increase in un-bonded areas of interfiber crossings.

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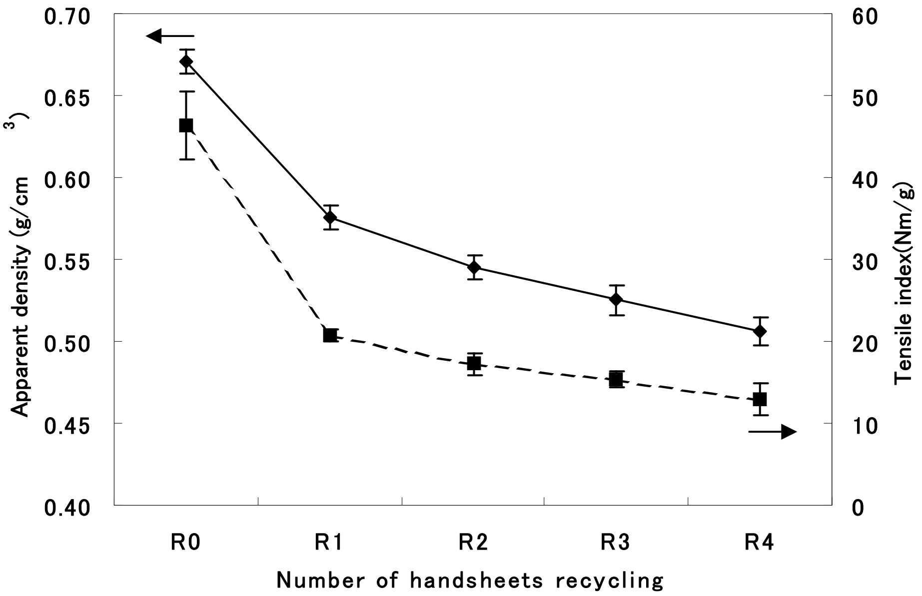

Fig. 1. Decrease in apparent density and tensile index of HBKP handsheets due to the recycling treatment. A pair of bars denotes a range of 95% confidence level.

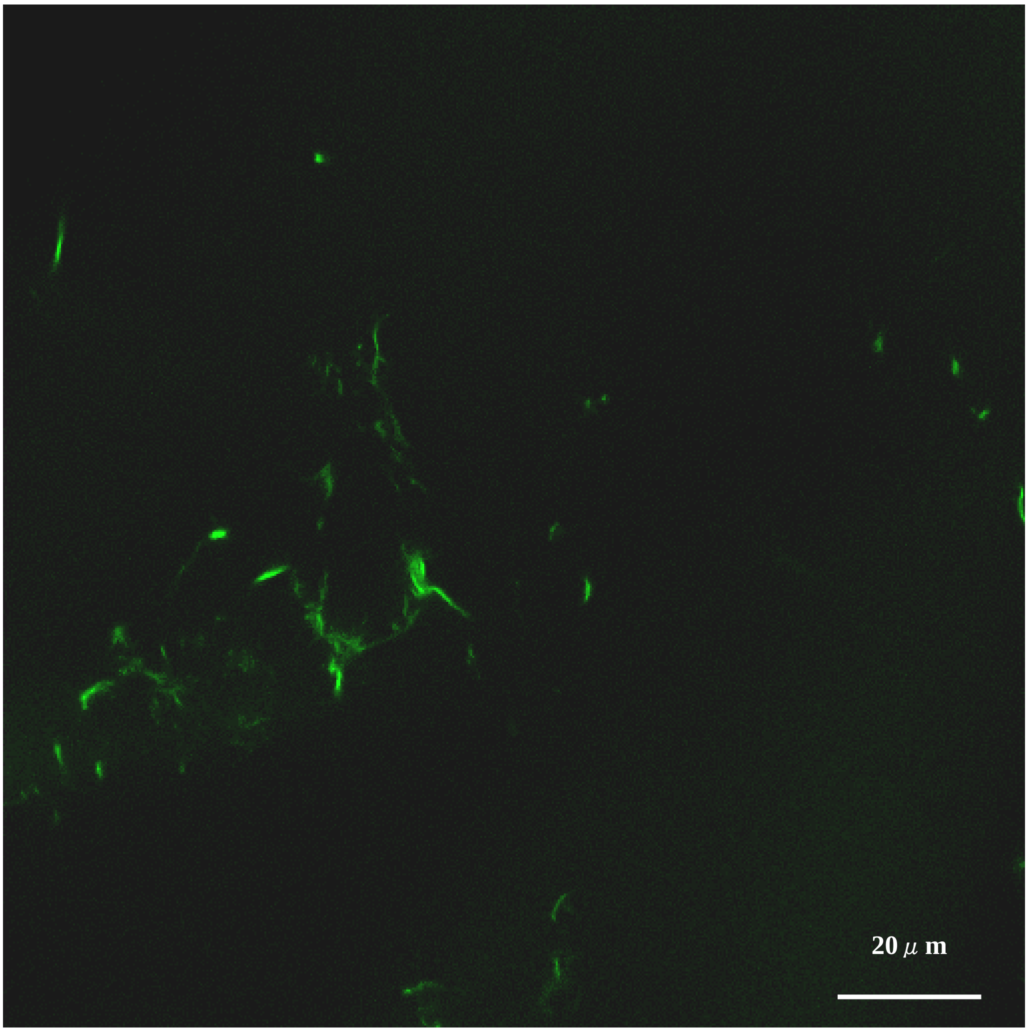

Fig. 2. CLSM micrograph of typical fines in post-R0 slurry.

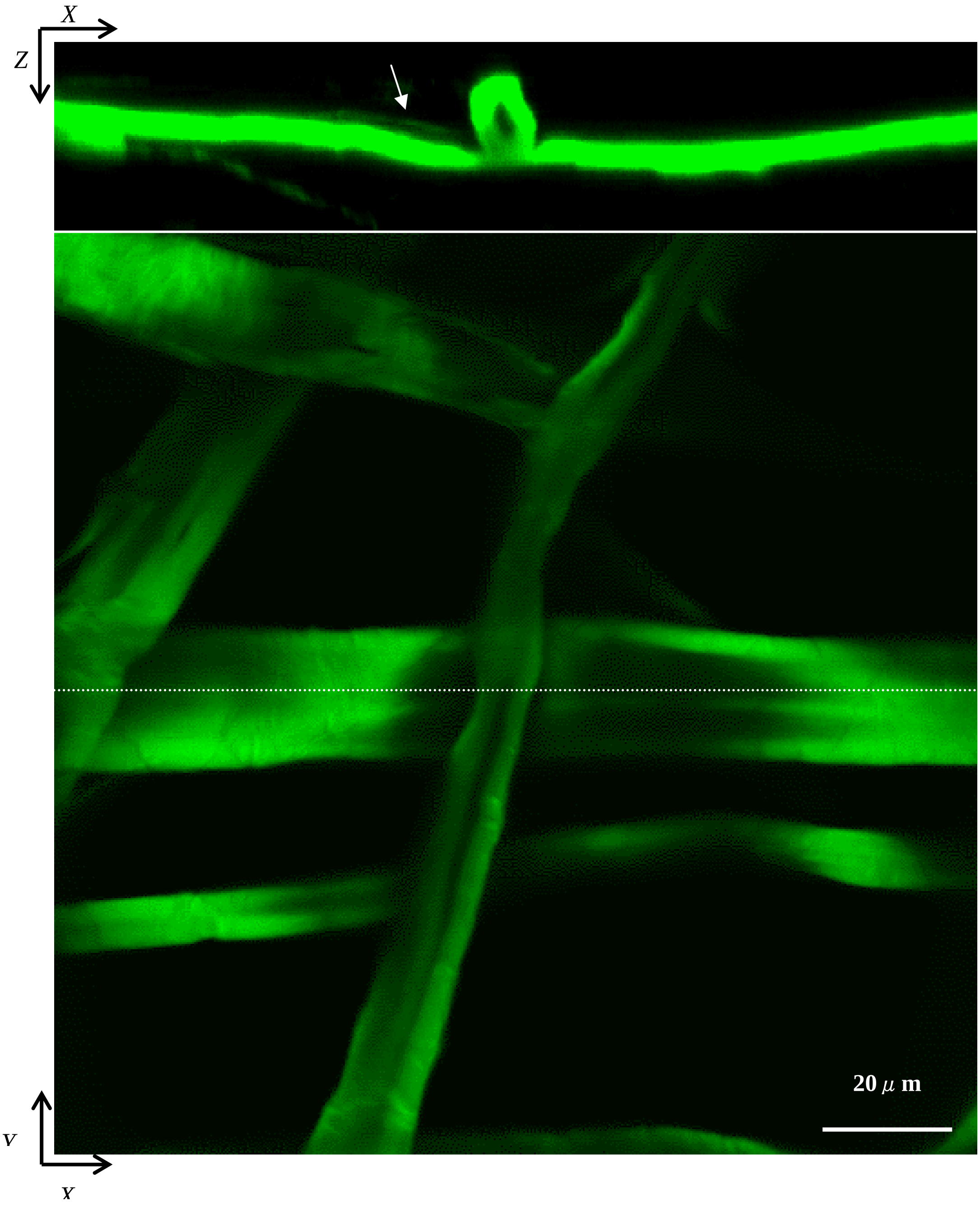

Fig. 3. CLSM XZ-sectioned micrograph (top) along the dotted white line in XY-micrograph (bottom) shows a thin layer of fines (arrowed) covering a fiber surface of post-R0 slurry surface in the dry state at the potentially interfiber crossing as a kind of strengthening material.

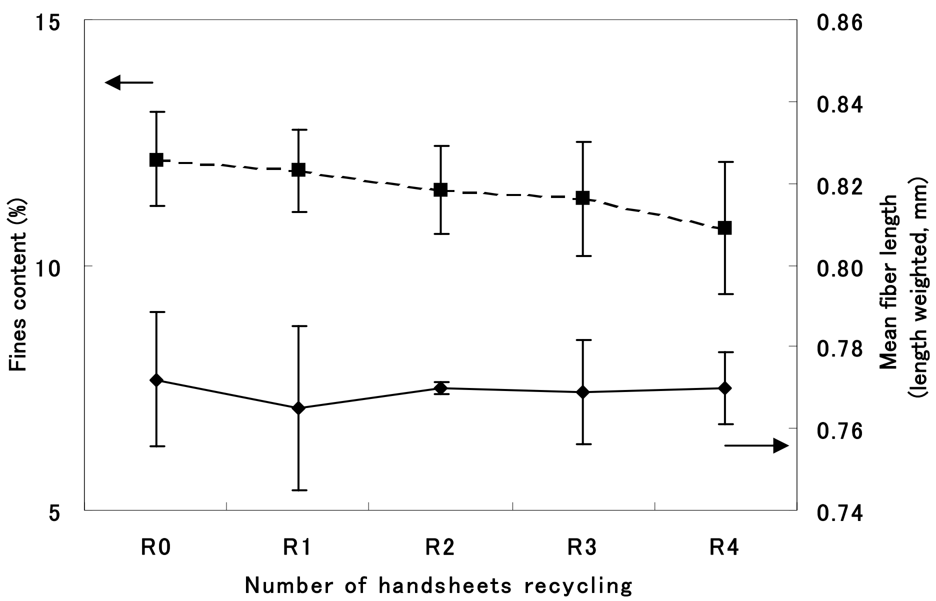

Fig. 4. Fines content and mean fiber length of post-R0 to R4 slurries. A pair of bars denotes a range of 95% confidence level.

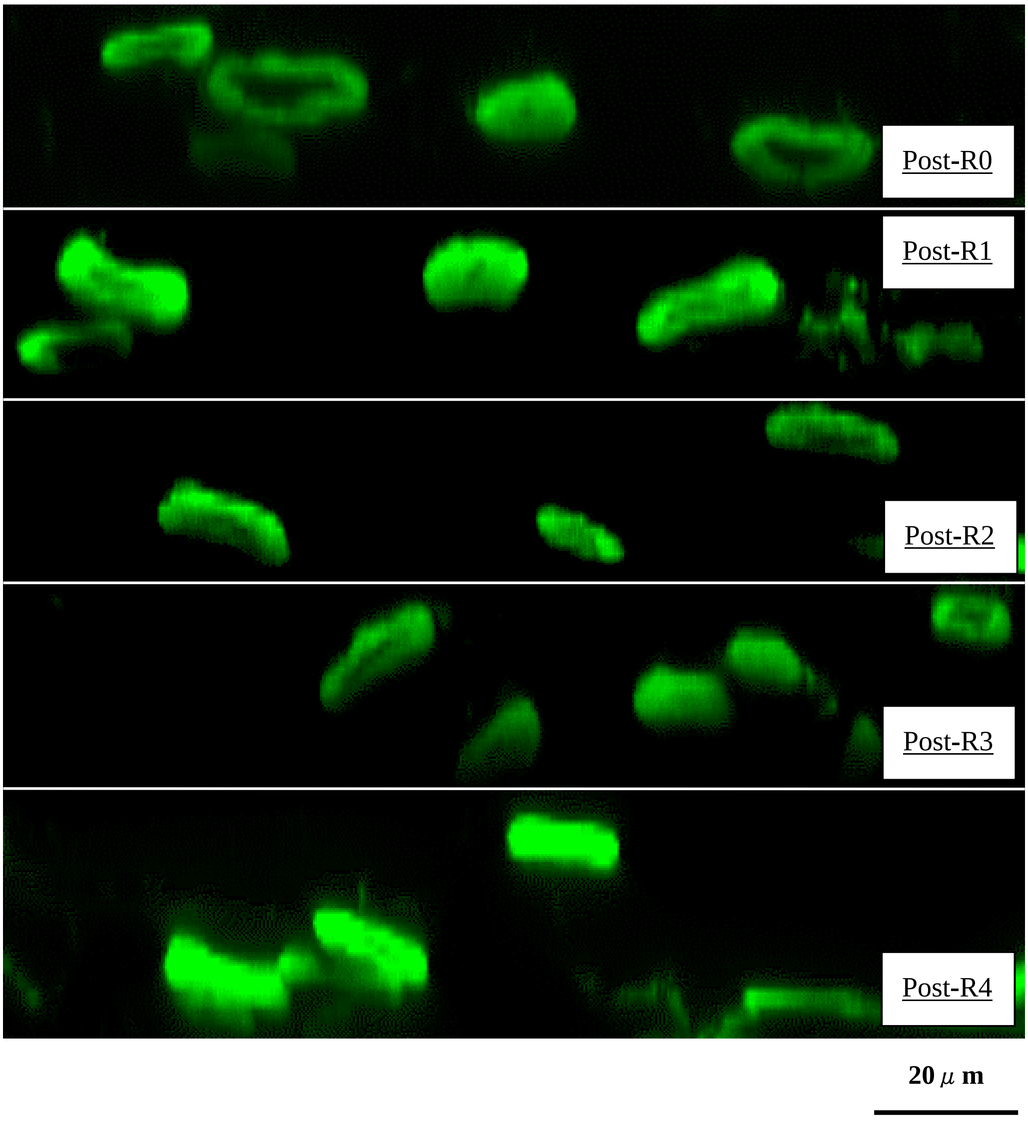

Fig. 5. CLSM micrographs of HBKP fiber (wet) cross-sections show the stepwise effect of recycling treatment on the re-swelling ability.

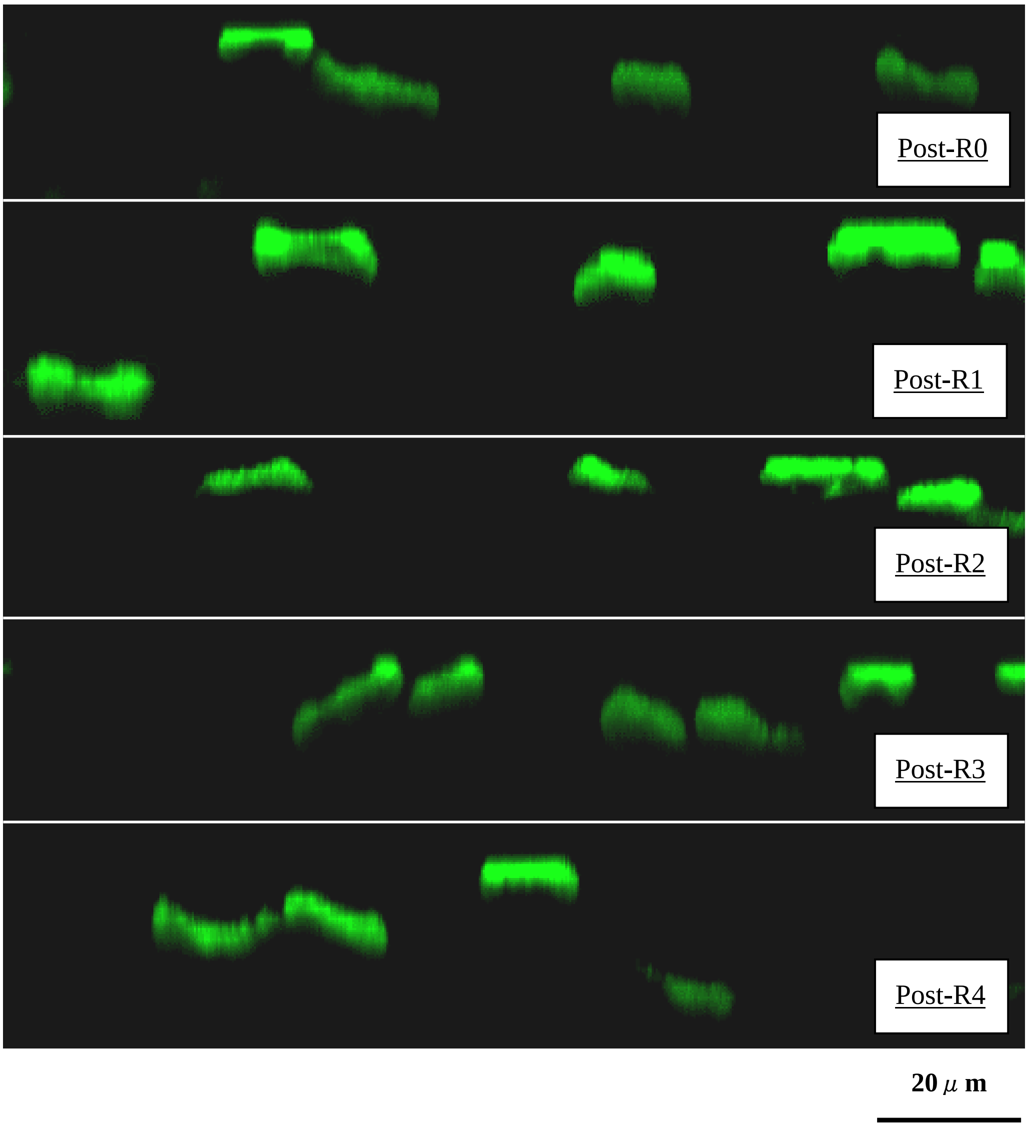

Fig. 6. CLSM micrographs of HBKP fiber (dry) cross-sections at the same location as in Fig. 5.

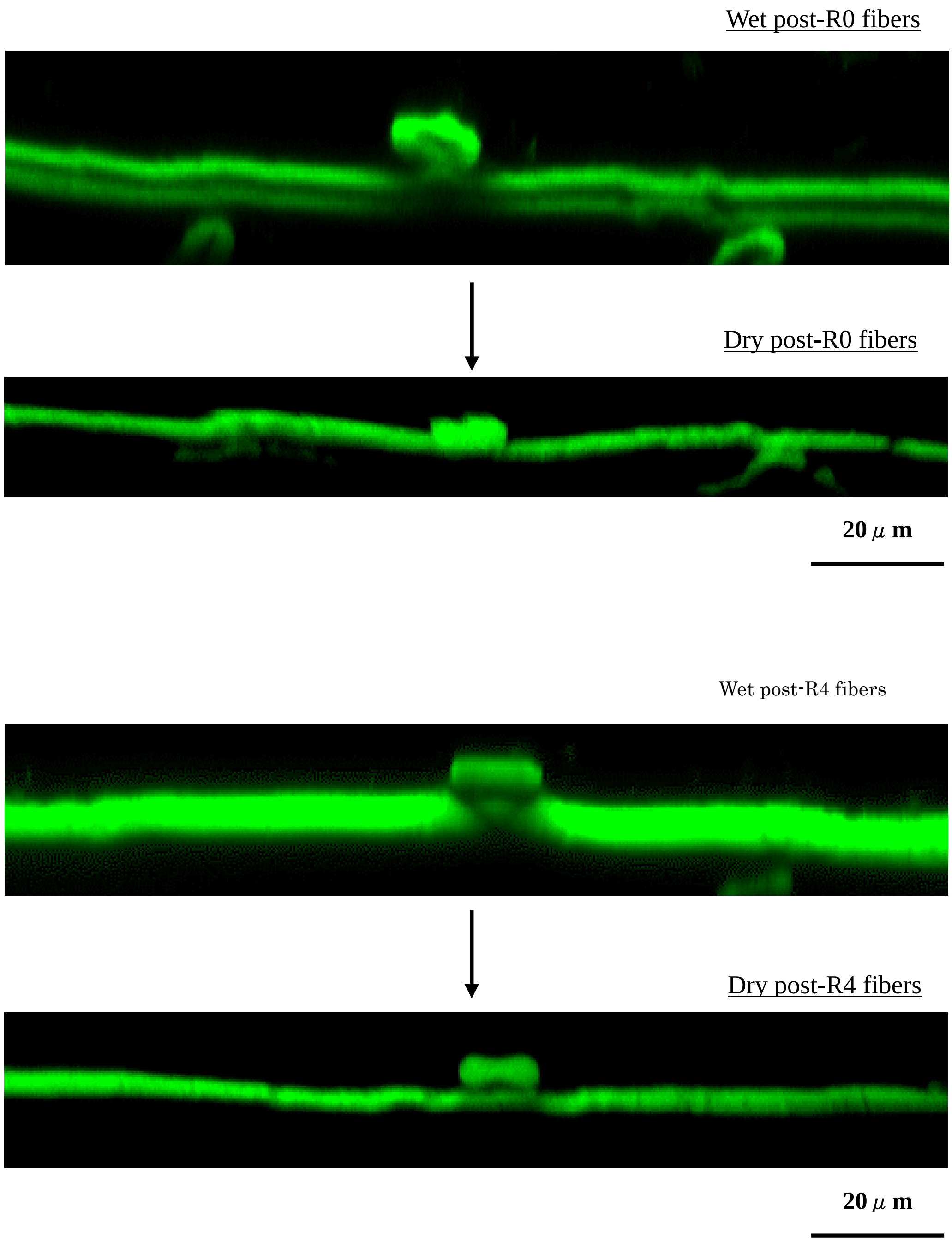

Fig. 7. CLSM micrographs of HBKP fiber cross-sections at the interfiber crossings show the conformability of wet-swollen fibers of post-R0 slurry is superior, for promoting the good interfiber contact in the dry state, to that of wet-collapsed fibers of post-R4 slurry.

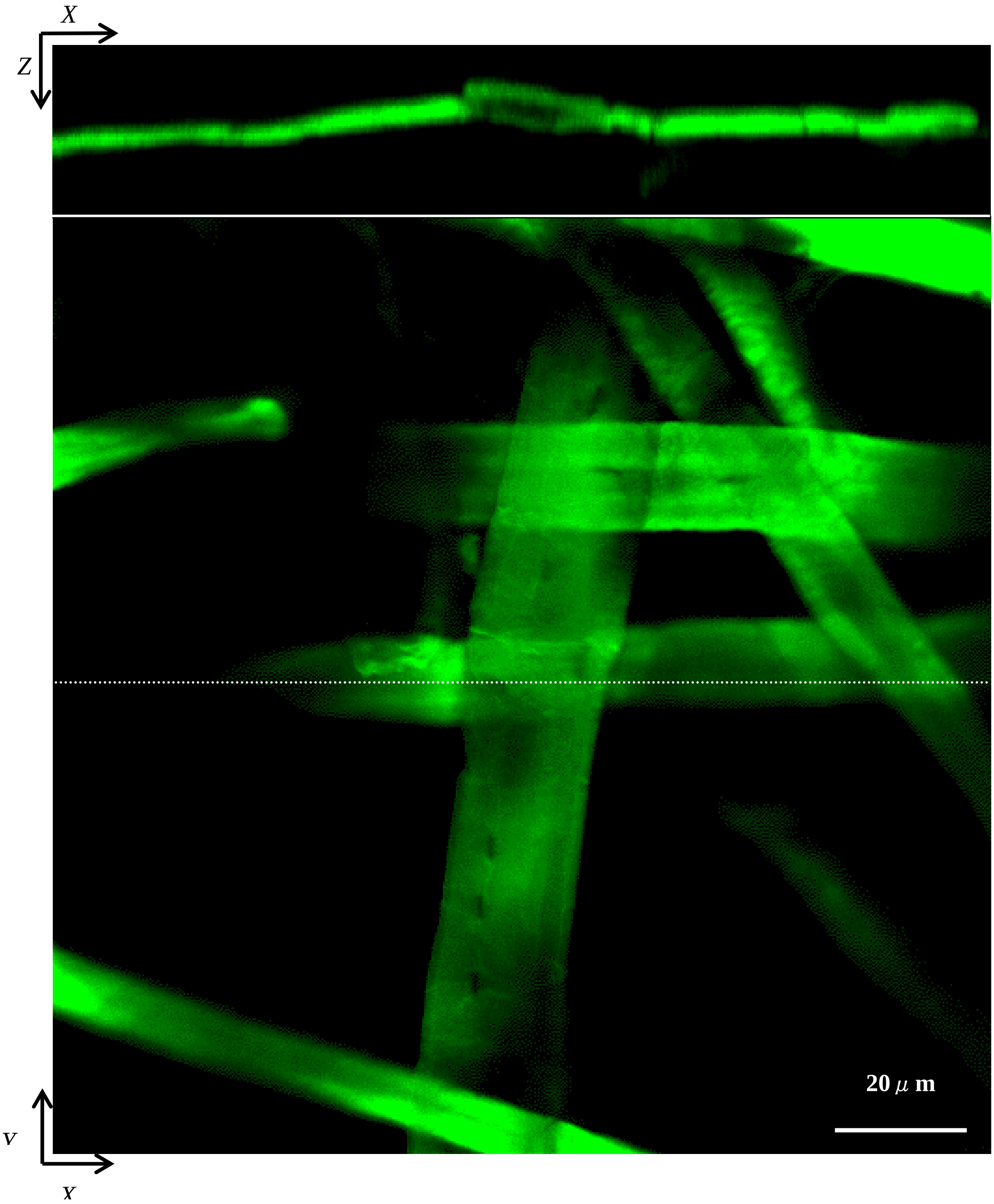

Fig. 8. CLSM XZ-sectioned micrograph (top) along the dotted white line in XY-micrograph (bottom) shows an un-bonded area at the interfiber crossing of dried fiber of post-R4 slurry.

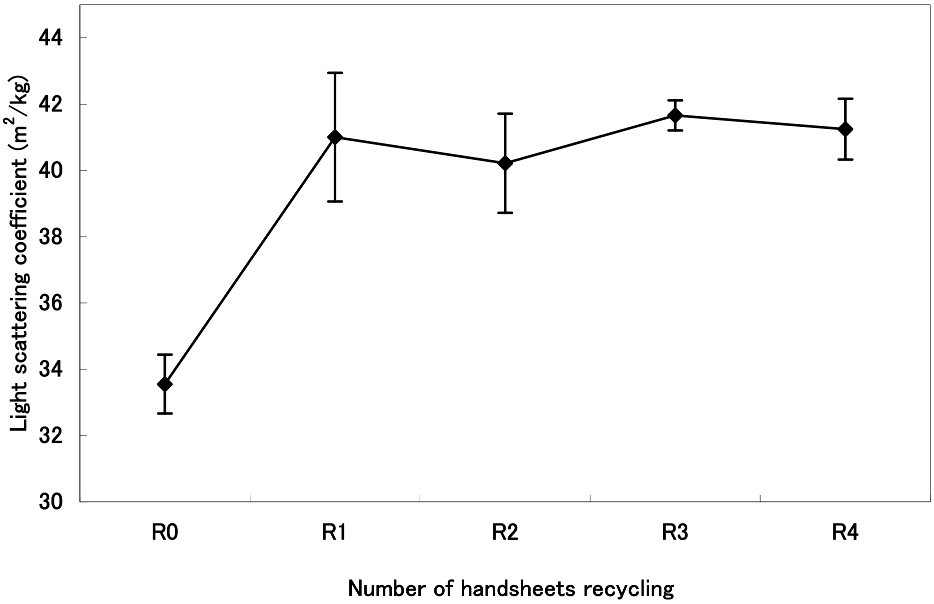

Fig. 9. The increase in light scattering coefficient of recycled HBKP handsheets due to the recycling treatment. A pair of bars denotes a range of 95% confidence level.

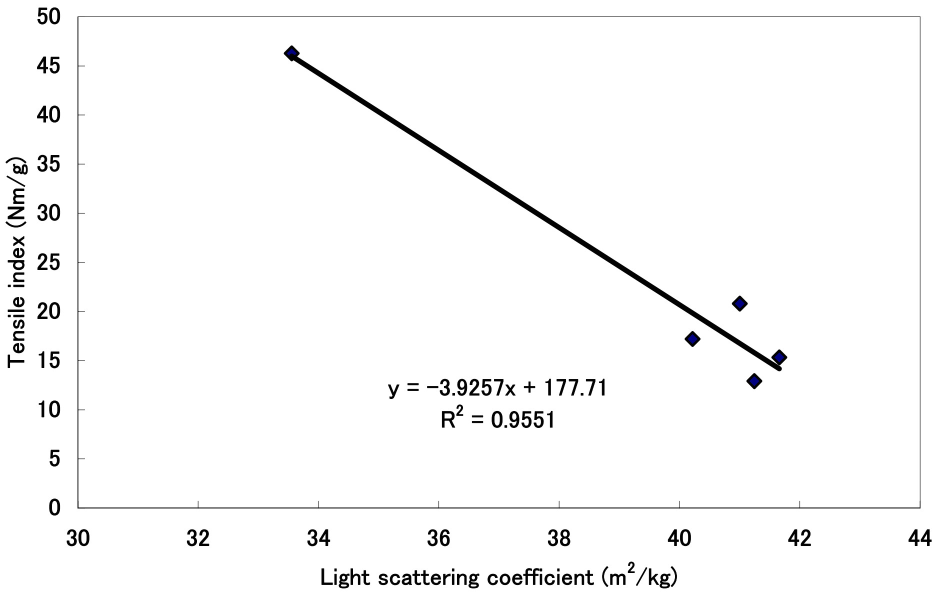

Fig. 10. Relationship between light scattering coefficient and tensile index of HBKP handsheets.