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폐지섬유의 세포벽 Micropore속으로 수용성 유기 및 무기화합물의 충전효과(제1보)[*1]

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Impregnation Effects of Water Soluble Organic and Inorganic[*1] Chemicals into Micropore of Cell Wall of Waste Paper Fiber(I)

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요 약

비건조 화학펄프의 세포벽공 속으로 충전제의 충전을 요체로 하는 소위 섬유벽 충전기술은 제지공정의 충전공정을 개선하는데 기여해 왔다. 섬유 세포벽 충전기술이라 함은 펄프섬유의 세포벽공에 두가지 이상의 수용성 염의 이온용액을 1차와 2차로 차례로 흡착시켜 충전제를 침착시키는 기술이다. 즉 이들 두 이온 용액의 세포벽 내에서의 화학반응에 의해 세포벽 세포벽공내에서 물에 부용의 침전을 유발케하는 공정이다.

비록 이 섬유 세포벽 충전기술이 제지공정상 비건조 화학펄프에 적용하도록 고안되었지만, 본 연구에서는 폐지의 재활용을 위해 폐지에 이 충전기술을 시도하였다. 그 결과 무게비율로 폐지섬유의 약 5-6%와 4-5%의 $CaCO_3$와 $SrCO_3$가 각각 충전되었다. 비건조 화학펄프의 그들 값이 17-18%와 16-18%를 나타내는 결과와 비교하여 매우 낮은 값이긴 하지만, 여전히 주목할 만한 결과로 간주되었다. 또한 이 세포벽 충전기술은 실험결과 재래의 충전방식보다 광학적 성질, 물리적 성질 및 강도적 성질이 훨씬 우수함을 보여 주었다.

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ABSTRACT

The fiber wall filling(FWF) technology, which is based on precipitatin of fillers in the micropores of the cell wall structure of never-dried chemical pulp fiber, has been developed to improve filling and loading process in papermaking.

In presenting FWF technique here, micropores of pulp fiber are first impregnated with an ionic solution of water soluble salt and consecutively impregnated with the second salt solution. This procedure generates an insoluble precipitate within the micropores of cell wall by chemical interaction of these two ionic salt solutions.

This is the first attempts to use FWF technology for the quality of waste paper grade which is recycled in papermaking, even though this FWF technology has been impressively improved for never-dried chemical pulp in filling and loading process of papermaking.

The precipitated amount of $CaCO_3$ and $SrCO_3$ reached 5-6% and 4-5% of the waste paper weight respectively, which was measured by ash content of the burned waste paper fiber. On the other way the precipitated amounts of those materials impregnated into never-dried chemical pulp fiber have reached 17-18% and 16-18% respectively.

The micropore loading technique gives optical and physical properties to the handsheets formed with cell-wall-filled fibers which are better than those handsheet properties resulting from conventional loading. The papers made from the cell-wall-filled pulps are stronger than those with the customary location of filler between the fibers.

1. INTRODUCTION

However the inclusion of filler into paper is limited by the mechanical properties of the sheet, it was well-known and ordinary accepted filling process in paper making process. The presence of inert filler particles between pulp fibers gives a critical diminishing effects on paper strength especially at higher filler loading. The higher concentration of filler contents in the paper also creates a number of operating problems such as wire plugging, augmented effluent loading, two-sidedness and dusting etc. in paper making process.

In order to eliminate these detrimental problems in traditional filler loading technology, many new technologies including fiber wall filling(FWF) technique which had been named by Allan (1) have been proposed. The FWF technique is a new technique which makes use of microporosity of never-dried, delignified pulp fiber is well recognized,and the pore size distribution of micropores has been described with and without (2~5) collapse of the pore structure due to drying of pulp fiber.The void volume of micropores before collapse of the structure can amount to about 1.5mL/g of pulp fiber. The collapse of this unique microporous configuration has been used since the 1930s as a means of entrapping materials within cellulose (6). The micropores within the void volume of never-dried, delignified pulp fiber and waste paper fiber are inaccessible to solid filler particles, but can be impregnated by ionic salt solutions. Even though water soluble organic chemicals are directly precipitated into cell wall of pulp and paper fibers, the precipitation of insoluble, inorganic materials into the pulp fiber and waste paper fiber can be achieved by impregnation of one ionic solution of water soluble salt, and consecutively followed by another salt solution through chemical interaction or reaction of this two ionic salt solutions within micropores of them (7-9).

2. MATERIALS AND METHOD

2.1 Materials

The never-dried pulp fibers used in this work were bleached commercial red alder, and the waste paper fiber used was mainly news paper.

The water soluble ionic salt solutions used in this work were sodium carbonate, calcium chloride, strontium hydroxide, and the water soluble organic chemical was urea.

2.2 Instruments

Scanning Electron Microscope-Energy Dispersive-X ray Spectrometer(SEM-EDX), Hitachi, Ltd., Japan) was used to investigate the anatomical structures of inorganic chemical impregnation onto micropores of cellulose fibers.

Atomic Absoption Spectrophotometer(AA, Perkin-Elmer, 2380, USA) was used to investigate the effluent concentration of (NH2)2CO from waste paper cellulose fiber impregnated with urea.

2.3 Methods

The never-dried pulp fiber are prepared at different level of moisture content which covers from fiber saturation point of pulp fiber (28~30%) up to 100%. Those never-dried pulp fiber are impregnated with the first water soluble ionic salt solution of sodium carbonate in agitating condition for 30min.

The pulp fiber impregnated with sodium carbonate is filtered with 12cm-diameter Buchner funnel. Those pulp fibers impregnated with sodium carbonate at different consistencies are going to be impregnated with the second water soluble ionic salt solution of calcium chloride at same condition. Dropping calcium chloride solution by spoide on the surface ofthe pulp fiber impregnated with the first solution is employed in this procedure. Thereafter, the insoluble precipitate of calcium carbonate is formed in the cell wall and outer surfaces of the pulp fiber by the chemical reaction of the two salt solutions. The calcium carbonate attached on the outer surfaces of the fiber can be removed through washing of the fiber. Calcium carbonate filled into micropores and precipitated on the surface of pulp fiber can be measured by ash contents of the cellulose fiber precipitated.

To precipitate strontium carbonate into the cellulose fiber, exactly same procedure can be employed as calcium carbonate precipitated. However the second salt solution for strontium carbonate precipitation into cellulose fiber is not necessary because the strontium hydroxide as afirst ionic salt solution within the pulp fiber is converted into strontium carbonate under the atmospheric conditions.

3. RESULTS AND DISCUSSION

The well known chemical reactions of sodium carbonate and calciumchloride are recognized as follows

$$Na_2CO_3 \rightleftarrows 2Na^{+}+CO_3^{--} \text{ -------------- (1)}$$
$$CaCl_2 \rightleftarrows Ca^{++}+2Cl^{-} \text{ ----------------- (2)}$$
$$Na_2CO_3+CaCl_2 \rightleftarrows 2Na^{+}+CO^{--}+Ca^{++}+2Cl^{-}$$
$$\longrightarrow CaCO_3\downarrow + 2NaCl \text{ -------- (3)}$$

The other inorganic chemical which is strontium hydroxide is oxidized asfollows in the air.

$$Sr(OH)_2 \xrightarrow{H_2O} Sr^{++}+3OH^{-} \xrightarrow{\text{공기중의 } CO_2} SrCO_3\downarrow +H_2O$$

The organic chemical used in this work is urea. In the form of urea solution, it is directly absorbed into cellulose fiber.

Figure 1 and 2 are those samples of the SEM picture of cross section of cellulose fiber impregnated with $CaCO_3$ and $SrCO_3$ respectively. Moisture content of cellulose fiber to impregnate filler materials into fiber wall of it shows significant effects on precipitated amount expressed as percent calcium carbonate and strontium carbonate based on oven dry weight of cellulose fiber to be impregnated in this Figure 1.

Fig. 1 and 2 show the Scanning Electron Microscope Energy Dispersive-Xray Spectrometer(SEM) pictures of cross section of oak and red alderfiber cell wall impregnated with $CaCO_3$ and $SrCO_3$ respectively. It is not easy to find out the loading material of $CaCO_3$ and $SrCO_3$ in the cell wall, however the swelling thickened cell wall of them suggested that those cell walls have to be filled with those loading materials.

Fig. 3 shows aging effect of strontium hydroxide reacted into strontium carbonate in the fiber wall impregnated by carbon dioxide in the atmosphere. Aging effect of strontium hydroxide into strontium carbonateis proportionally increased upto 24hrs of aging after impregnation of it into

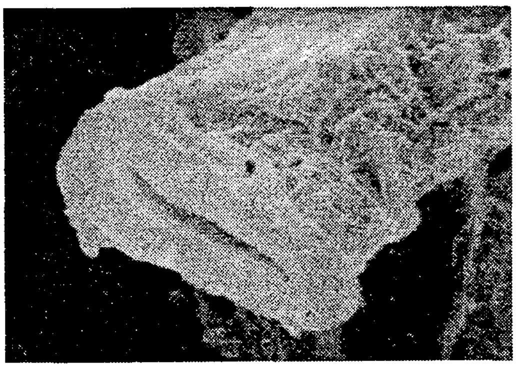

Fig. 1. The SEM picture of cross section of oak fiber cell wallimpregnated with $CaCO_3$ (10)

Fig. 2. The SEM picture of cross section of red alder fiber cell wallimpregnated with $SrCO_3$ (11)

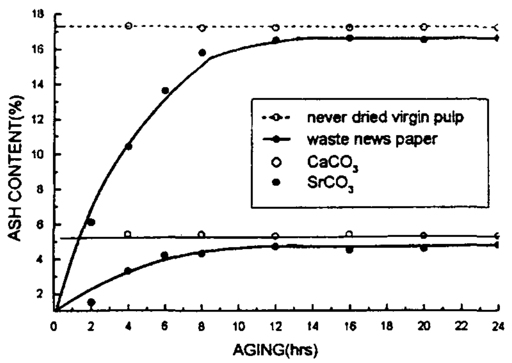

Fig. 3. Aging effects of calcium carbonate and strontium hydroxidereacted into strontium carbonate in the waste news paper filled with.

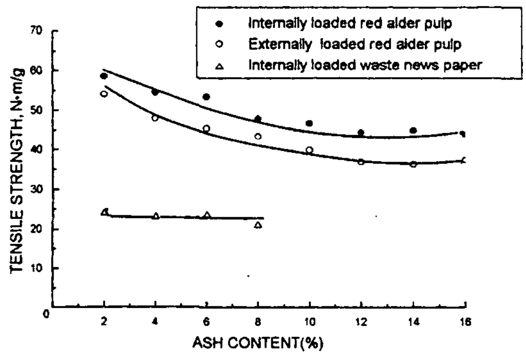

Fig. 4. Ash content effect on tensile strength with different fiber typeand filling materials.

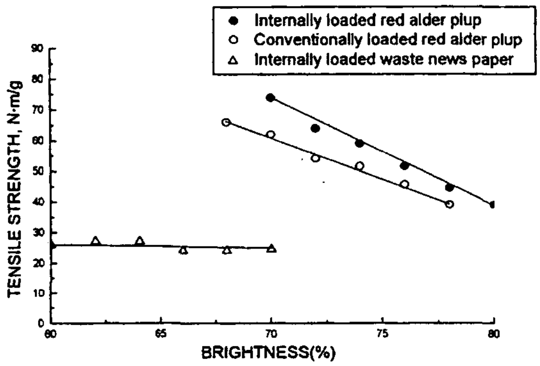

Fig. 5. The variation of tensile strength versus the brightness withdifferent fiber type and filling materials.

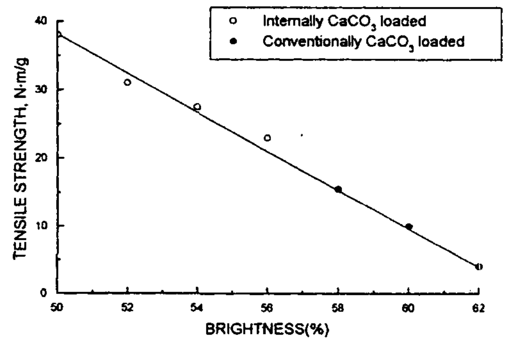

Fig. 6. The variation of the tensile strength versus the brightness forwaste news paper loaded.

the fiber wall of waste news paper. After 24hr, the tendency to be strontium carbonate is stopped, in which the highest turns out to be 4-5 percent based on oven dry weight of waste news paper fibers. On the other aspects, the precipitation of $CaCO_3$ and $SrCO_3$ into never dried chemical pulp fiber have reached 17-18% and 16-17% respectively. Generally the efficiency, of $CaCO_3$ filled into the fiber is a little higher than that of $SrCO_3$

The physical properties of the handsheets made from the various types of loaded never-dried virgin pulp nad waste news paper fiber are summarized in Figures 4, 5 and 6.

In Figure 4, for the red alder pulps, at similar ash contents, the tensile strength of the corresponding papers is greater for the never-dried internally loaded pulp than for the conventional externally loaded pulp or externally loaded news paper. In other words, for as pecified paper strength, the *in situ* precipitation technique allows the placement of more filler in the paper. The news paper filled shows significant lower tensile strength than those of red alder pulp, however there is no significant difference in tensile strength at different ash content range of it.

Another way to analyze these results is to compare the physical properties for different papers having similar optical characteristics in Figure 5. From the results in Figure 5, it can be observed that for brightness of the pulp the never-dried, internally cell wall loaded pulps yield papers with improved tensile strength, since at equal brightness values the papers made from never-dried, cell-wall-loaded pulp exhibit a greater tensile strength than conventionally loaded sheets.

Then data demonstrate the benefits of loading pulp in a never-dried condition. As expected, it was found that under the same conditions air-dried pulp(exterally loaded pulp) could only be loaded to a lesser extent than never-dried pulps.

In Fig. 6 the optical properties were as expected, better for the conventionally filled paper because the filler is outside the fibers,where it can have the maximal visual effect, even though these results show internally $CaCO_3$ loaded pulp exhibit a greater tensile strength than conventionally filled sheets of waste news paper.

Table 1. The variations of the effluent concentrations of $(NH_2)_2CO$ between never-dried red alder pulp cellulose and waste paper cellulose.

sample \ concentration(ppm)	first effluent	second effluent
red alder cellulose	3825	2604
waste paper cellulose	5924	786

Table 1 shows that the effluent concentration of $(NH_2)_2CO$ from never dried pulp fiber cellulose is significantly higher than that from waste paper cellulose. Those results can be clearly explanined by the difference of an atomical structure between these two cellulose fibers.

As mentioned above the never dried pulp fiber cellulose which contains lots of micropores within the void volume due to delignification of pulp fiber has more opportunities to impregnate soluble chemicals than the waste paper cellulose does. The micropores of waste paper cellulose has been collapsed during aging of the paper(12-16), and the microporosity of it is much reduced, even though it still has poly hydroxyl group to absorb and impregnate the water soluble chemicals.

4. CONCLUSION

As a tentative conclusions, the analogous technology of the fiber wall filling technique(FWF) applying for waste news paper shows the possibilities to improve waste paper quality for recycling, when it is re-used for carton box, corrugated liner board or wrapping paper etc. The technique also shows the possibility to use waste paper cellulose as a matrix for slow release of water soluble chemical impregnated into the cellulose.

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