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Upgrading waste paper by *in-situ* calcium carbonate formation

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ABSTRACT

Utilization of the quality-upgraded waste paper in the manufacture of paper and board will reduce the wood consumption and pulping energy. While the optical property of the fibers from recycled old newspaper is very poor, *in-situ* calcium carbonate formation on those fibers by injecting carbon dioxide to the mixed slurry of those pulp and calcium oxide improved their brightness. Upgrading recycled old newspaper to substitute more expensive wood furnish, such as recycled old magazine, was successfully demonstrated in the present study. This study showed that the *in-situ* calcium carbonate formation process improved the optical quality of the recycled old newspaper by covering colored impurities with newly formed calcium carbonate, and improved calcium carbonate retention in papermaking process by attaching them to fibers. The strength reduction by the presence of newly formed calcium carbonate in the paper was recovered by adding strength agent. High ash retention at high ash content under the strong turbulence in the modern paper mill was achieved by the application of the *in-situ* calcium carbonate formation method. The quality-upgrade of recycled fibers and cost saving in the manufacture of duplex paperboard were demonstrated in the mill trial.

1. Introduction

Recycling rate of waste paper in the Republic of Korea was 92.1% in 2013, which was the highest rate in the world (Korea Paper Association). Wood cutting and energy consumption for preparing virgin pulp were decreased by the extensive use of recycled fibers; however, the paper industry that uses these recycled fibers suffers from the ever-worsening quality of raw materials. In manufacturing duplex paperboard from recycled fibers, OCC (old corrugated container), OMG (old magazine), ONP (old newspaper), and bleached chemical pulp are used with the bleached chemical pulp on top in multiply. Among those recycled fibers, OMG is the highest in price in Korea, followed by ONP next and, in the last place, OCC. Quality upgrade from low price furnish to the higher one always attracts the papermaker's attention, if the process cost is less than the price advantage. In duplex paperboard, upgrading optical properties of ONP to the OMG level will be the case for the papermakers in Korea.

Kim et al. (2012, 2013) demonstrated a large brightness increase in the white ledger, which was defined as the recycled fibers from printing paper by using the *in-situ* calcium carbonate ($CaCO_3$) formation method on the white ledger. By the application of the *in-situ* $CaCO_3$ formation method and by controlling the refining process, the researchers could replace more bleached chemical pulp in the writing paper without losing optical and strength properties.

The optical property increase by the bleaching process of ONP was found to be inferior to the *in-situ* $CaCO_3$ formation method (Lee et al., 2013; Park et al., 2012). In reality, bleaching ONP decreased yield significantly as well. Seo et al. (2014) tried to fractionate the *in-situ* $CaCO_3$ formed ONP into long fibers and fines and examined their morphological changes with the SEM micrographs and optical images from FlowCam™ dynamic imaging particle analyzer. FlowCam™ is a new type colloidal size analyzer that is capable of showing all the images of the colloidal materials used for the statistical analysis. From the optical images, it was found that $CaCO_3$ formation was mostly on to the ONP fines. The *in-situ* $CaCO_3$ formation method on ONP significantly improved the brightness, the ERIC (effective residual ink concentration, ISO 22754) value, and ash retention (Lee et al., 2013; Park et al., 2012).

In-situ $CaCO_3$ formation is not a new method to the papermakers (Chauhan et al., 2007; Ciobanu et al., 2010; Dowling et al., 2015); however, its application to recycled fibers was fairly new

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and rare (Lee et al., 2010; Ryu et al., 2008). Ryu et al. (2008) applied the *in-situ* $CaCO_3$ formation method to recycled fibers to result in whiteness and opacity improvement. It was also found that recombining the fractionated fines processed by the *in-situ* $CaCO_3$ formation method with the fractionated long fibers improved the strength properties of the resultant sheet (Kim et al., 2013). Furthermore, Seo et al. (2014) suggested a theory about covering colored materials preferentially by the newly formed $CaCO_3$ in the ONP furnish when the *in-situ* $CaCO_3$ formation method was applied. If it is the case, the *in-situ* $CaCO_3$ formation method may allow a higher brightness and a low ERIC value to the recycled fibers. Petri (2003) developed a new type of filler, 'Superfill', which was made by *in-situ* $CaCO_3$ formation on the fractionated fines and washing out the unattached calcium carbonate after the process.

In the present study, we tried to apply the *in-situ* $CaCO_3$ formation method on the ONP to replace the OMG furnish without lowering essential physical properties such as brightness and ERIC value. The mechanisms of decreasing colored materials and increasing furnish retention in the papermaking process by the *in-situ* $CaCO_3$ formation method were also investigated.

2. Experimental

This section presents the process details and the conditions of how the ONP covered with $CaCO_3$ by *in-situ* formation process was prepared in Section 2.1. Handsheets were made for property comparison and their physical testing methods were listed in Section 2.2.

2.1. In-situ $CaCO_3$ formation on ONP

The ONP and OMG fiber furnish were donated by Hansol Paper Co. in Korea, which were collected locally in the country and were already treated by deinking process in the mill. Their initial ash contents were measured as 18.4% and 17.8% by weight as received for ONP and OMG, respectively. In the *in-situ* $CaCO_3$ formation process, this ONP was mixed with calcium oxide (CaO. Korea Showa Chemicals Co., Korea) in the reaction tank to load 43% of new calcium carbonate in ONP with the provision of proper agitation. Pure carbon dioxide was injected in 0.5 l/min. to form $CaCO_3$ on fiber surfaces. Although the size of the tank was 4 L, 2 L ONP furnish with 1.5% consistency was used. The starting reaction temperature was 30–60 °C, but, at the end of the reaction, temperature was increased by 3~5 °C due to the exothermic reaction. The change of pH was recorded and the reaction was terminated when pH 7 was reached. For comparison, GCC (ground calcium carbonate (2.3 μm in average diameter, Korea Omya Co., Korea) was added in different amounts to the ONP furnish (20–60% by dry weight of the ONP furnish) to make handsheets.

2.2. Preparation of handsheets and physical property measurement

Handsheets were prepared from each ONP furnish with and without retention aid, cationic PAM (Polyacrylamid, 0.1% addition, +5 meq/g, CIBA Specialty Chemicals Korea, Korea) according to the standard method (TAPPI Test Methods T205, 1995).

The ash content (TAPPI Test Method T 413 om-93, 1993), tensile strength (ISO, 1924-1, 1992), and first pass retention (Horn and Linhart, 1996) of the handsheets were measured according to the methods. The tensile strength was measured using a Micro 350 tensile tester (Testometric Co. Ltd., England). The brightness (ISO 2470, 1977) and ERIC value (ISO 22754, 2008) were measured using a Color Touch (Technidyne, USA). For the virgin chemical pulp with 30% GCC case, its ERIC value of the handsheet was measured as 15.4. The lower the ERIC value, the less the dark colored materials in the paper.

3. Results and discussion

This section shows the superiority of *in-situ* $CaCO_3$ formation process on ONP over simple GCC addition process in respect of ash retention and ERIC value (Section 3.2). Their brightness and tensile strength were also compared in Section 3.3. The more expensive OMG was replaced with the less expensive, $CaCO_3$ covered ONP, but no property degradation was noticed when starch was used together (Section 3.4). Paper mill trial results were summarized briefly in Section 3.5, and we presented a model concerning the effect of *in-situ* $CaCO_3$ formation on ONP in Section 3.6.

3.1. Comparison of ONP and OMP furnish handsheet properties

The handsheet properties of the ONP and the OMG obtained from the mill were shown in Table 1. The brightness and ERIC values of two furnishes were quite different, while breaking length, folding endurance, and ash content were similar. Therefore, it is clear that improvement in the brightness and ERIC value of the ONP furnish should be the main goal of the present study. Retention aid, PAM addition increased density and ash, but lowered breaking length and brightness. This means that the PAM addition caused more retention of colored, high-density inorganic materials that hampered wood fiber bonding and lowered brightness. The colored inorganic materials also increased the ERIC values greatly.

3.2. Comparison GCC addition to in-situ $CaCO_3$ formation process

When GCC, which is ground calcium carbonate used as filler in conventional papermaking, was added to the ONP furnish without retention aid, PAM in this case, there was a considerably low first pass ash retention in handsheets (see Fig. 1). The effect of retention aid was greatly pronounced in the GCC addition case (Fig. 1). The amount of ash in the handsheet in the PAM addition case was higher than the added amount of GCC. This is because of the ash already present in the ONP furnish (18.4%) before adding GCC. The role of retention aid is to make GCC and colored small inorganic materials in the ONP furnish attached to the fibers to increases the retention rate. In paper mill, actual first pass ash retention rate is between two extremes; with and without PAM case. The first ash pass retention rate of the mill for 60 g/m^2 basis weight paper with

Table 1
Physical properties of the ONP and the OMG with and without retention aid, PAM.

Item	Basic weight (g/m^2)	Density (g/cm^3)	Bulk (cm^3/g)	Breaking length (km)	Stretch (mm)	Folding endurance (count)	Ash (%)	ISO brightness (%)	ERIC value (ppm)
ONP	61.8	0.46	2.15	4.04	2.89	28.7	7.47	56.0	265.9
ONP,PAM	63.3	0.51	1.67	2.36	2.79	12.8	17.94	49.7	668.7
OMG	61.0	0.49	2.05	4.15	2.92	35.7	7.31	73.6	106.6
OMG,PAM	61.5	0.53	1.89	3.01	1.76	17.3	16.25	69.5	165.2