The Improvement of Recycled Newsprint Properties by *In-situ* $CaCO_3$ Loading

Yung Bum Seo,* Young Ho Lee, and Jae Kwon Chung

In-situ $CaCO_3$ loading of old newspaper (ONP) fiber furnish was studied as a method to improve the properties of recycled newsprint paper. The effects of *in-situ* loading on the morphological and physical properties of ONP furnish were examined comparatively with conventional loading methods (addition of ground or precipitated $CaCO_3$, without and with pre-flocculation treatment). The effective residual ink content (ERIC) and macro sticky content began to decrease as soon as the *in-situ* $CaCO_3$ formation started by the injection of carbon dioxide to the reaction tank, where the ONP furnish and calcium oxide mixture was agitated in high shear. When the reaction finished at pH 7, there were no more decreases of ERIC value and sticky content. Improvement of first pass retention and brightness was significant for the *in-situ* $CaCO_3$ loading method. The decrease in breaking length with the addition of $CaCO_3$ in the *in-situ* formation method was equivalent to or slightly lower than that of the $CaCO_3$ pre-flocculation method, which is a method well known to give higher strength properties. Optical images from the FlowCAM® dynamic imaging particle analyzer showed strongly attached organic (fines) and inorganic ($CaCO_3$) materials in the *in-situ* $CaCO_3$ loading method.

Key words: In-situ $CaCO_3$ loading; Recycled fibers; ERIC value; Brightness; Sticky materials; Breaking length; ONP

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INTRODUCTION

More than 90% of fiber furnish for newspaper is from old newspaper (ONP) in the Republic of Korea. In manufacturing duplex paperboard from recycled fibers, old corrugated container (OCC), old magazine (OMG), ONP, and bleached chemical pulp are used, with the bleached chemical pulp on the surface of the board. Among the recycled fibers, OMG is the most expensive, with ONP next and OCC the least expensive. A quality upgrade from low-price furnish to a higher one attracts the attention of papermakers if the process cost is less than the price advantage. In duplex paperboard, upgrading the optical properties of ONP to the OMG level will induce a large cost advantage in Korea.

Kim *et al.* (2012; 2013) showed a large brightness increase in white ledger using the *in-situ* $CaCO_3$ formation method. They used more white ledger furnish for the printing grade paper without losing optical and strength properties by the application of the *in-situ* $CaCO_3$ formation method and by controlling the refining process. Park *et al*. (2012) and Lee *et al*. (2013) also showed that the increase in the optical properties with a bleaching process was inferior to that of the *in-situ* $CaCO_3$ formation method for ONP

furnish. Actually, bleaching ONP caused a significant yield loss in the furnish. Park *et al*. (2012) and Lee *et al*. (2013) separated fibers from fines by fractionation of ONP furnish and examined their morphological changes by scanning electron microscopy (SEM) and optical microscopy using a FlowCAM® dynamic imaging particle analyzer, a new type of colloidal size analyzer capable of showing optical images of colloidal materials. From the optical images, the formation of $CaCO_3$ on the ONP was apparent.

In-situ $CaCO_3$ loading is not a new method for papermakers (Petri 2003; Chauhan *et al*. 2007; Subramanian *et al*. 2007; Kumar *et al*. 2009; Ciobanu *et al*. 2010; Kumar *et al*. 2011), but its application to recycled fibers is relatively new and rare (Ryu *et al*. 2008; Lee *et al*. 2010). Petri (2003) developed 'Superfill', which was made by *in-situ* $CaCO_3$ loading on fractionated fines. Ryu *et al*. (2008) applied the *in-situ* $CaCO_3$ loading method to recycled fibers, resulting in whiteness and opacity improvement. It was also found that recombining the fractionated fines processed by the *in-situ* $CaCO_3$ loading method with previously fractionated long fibers improved the strength properties of the resultant sheets (Lee *et al.* 2013).

The *in-situ* $CaCO_3$ loading method on ONP improved the brightness, the effective residual ink concentration (ERIC) value, and ash retention greatly (Park *et al*. 2012; Lee *et al*. 2013). In this study, we investigated the mechanism responsible for the ERIC value improvement, macro sticky area changes, retention behaviors, as well as mechanical and morphological changes caused by the *in-situ* $CaCO_3$ loading method. There have been no studies similar to this approach in the published literature.

EXPERIMENTAL

Materials

Deinked ONP obtained from locally collected ONP was donated by Hansol Paper Co. in Korea. Its initial ash content was 23.8% by weight. This furnish was mixed with calcium oxide in a reaction tank with proper agitation in order to obtain ONP furnish with 40% and 60% ash. Pure carbon dioxide was injected at 0.5 L/min to form $CaCO_3$ on the fiber surfaces. Two liters of ONP furnish with 0.75% consistency was charged in the reaction tank (4 L total volume) for each experiment, and pure carbon dioxide was injected at 0.5 L/min to form $CaCO_3$ on the fiber surfaces. The starting reaction temperature was set at 30 °C and increased to the range 33 to 35 °C at the end of reaction. The pH changes were recorded, and the reaction was terminated when pH 7 was reached. For comparison, the ground calcium carbonate (GCC; 2 to 3μm; Omya Korea Co.) and precipitated calcium carbonate (PCC; about 3μm; Hansol Paper Co.) were added to the ONP furnish to meet the same ash levels as the *in-situ* $CaCO_3$ loading case. The filler pre-flocculation method has been shown to provide a higher strength of paper than the other retention methods at the same ash level (Lee *et al*. 2006). Therefore, pre-flocculated GCC and PCC were prepared according to the method described by Lee *et al*. (2006) and added to the ONP furnish to determine the morphological differences in filler distribution.

Methods

Handsheets of 60g/m^2 were prepared from each ONP furnish with and without the retention aid (cationic PAM 0.1% addition, +5 meq/g, CIBA Specialty Chemicals Korea).

A small portion of each ONP furnish was fractionated on a 200-mesh screen, and the morphological changes of each fraction were examined.

The macro-sticky area, ERIC value, and brightness of the handsheet samples were measured to assess the behavior of colored impurities in the ONP furnish during the *in-situ* $CaCO_3$ formation reaction. The macro sticky area was measured with a MasterScreen screening device (Pulmac Systems, USA) using the standard method TAPPI T-277 pm-99 (1999). The brightness (ISO 2470) and ERIC (ISO 22754) values were measured using a Color Touch instrument (Technidyne, USA) according to standard methods.

Scanning electron microscopy was carried out using a S-4800 model (Hitachi, Japan) operating at an accelerating voltage of 5 kV. The samples were mounted on an aluminum stub and sputter coated with a gold alloy. The FlowCAM® dynamic imaging particle analyzer (Benchtop B3 Series, Fluid Imaging Technologies, USA) measured the volume moment mean (D[4,3]) (Xu 2001) and provided optical images of the ONP furnishes.

The first pass ash retention was obtained using the method described by Horn and Linhart (1996), where paper ash was divided by furnish or head box ash, and ash content was analyzed according to TAPPI 211 om-93. The tensile strength was measured using a Micro 350 tensile tester (Testometric 107 Co. Ltd., England) according to ISO 1924.

RESULTS AND DISCUSSION

First-pass retention of ash was measured for ONP furnishes with and without a retention aid, and the results are shown in Fig. 1 for GCC and Fig. 2 for PCC. In Fig. 1, the results of the *in-situ* $CaCO_3$ method without a retention aid did not differ greatly from that with the retention aid. However, GCC retention, both without treatment and with the pre-flocculation method, yielded large differences between furnishes with and without PAM in first-pass retention.

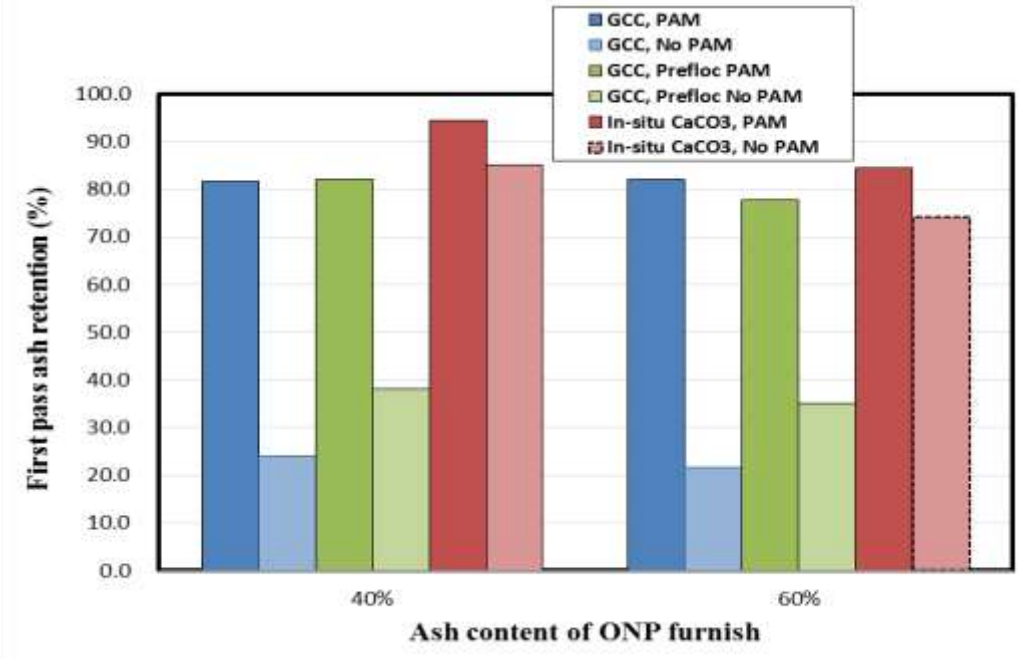

Fig. 1. First-pass retention of GCC and *in-situ* $CaCO_3$ in ONP

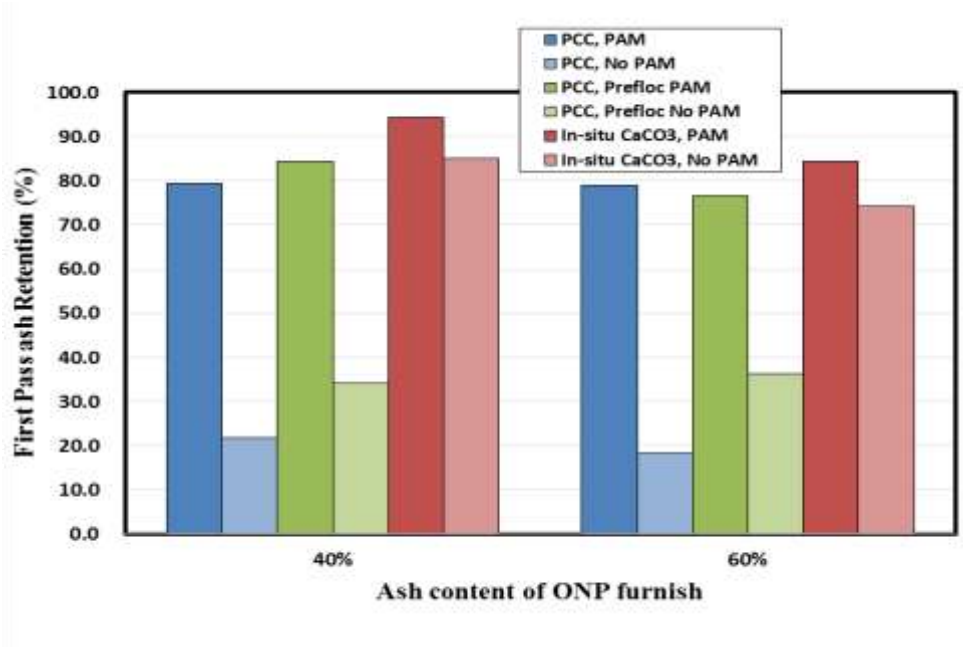

Fig. 2. First-pass retention of PCC and *in-situ* $CaCO_3$ in ONP

GCC pre-flocculation led to better retention than untreated GCC. The results suggest that the *in-situ* $CaCO_3$ method does not require a retention aid for ash retention, while the other methods do. For the ONP furnish only case, the first pass retention of ash was 83.5% with furnish ash of 23.8%. The PCC in Fig. 2 exhibited the same trend as the GCC in Fig. 1.

For the brightness, Figs. 3 and 4 showed that the *in-situ* $CaCO_3$ method led to much higher brightness than the other methods at 40% and 60% $CaCO_3$ addition. The PCC resulted in higher brightness than with the GCC, but the difference between them was minimal when compared to the enormous increase caused by the *in-situ* $CaCO_3$ method.

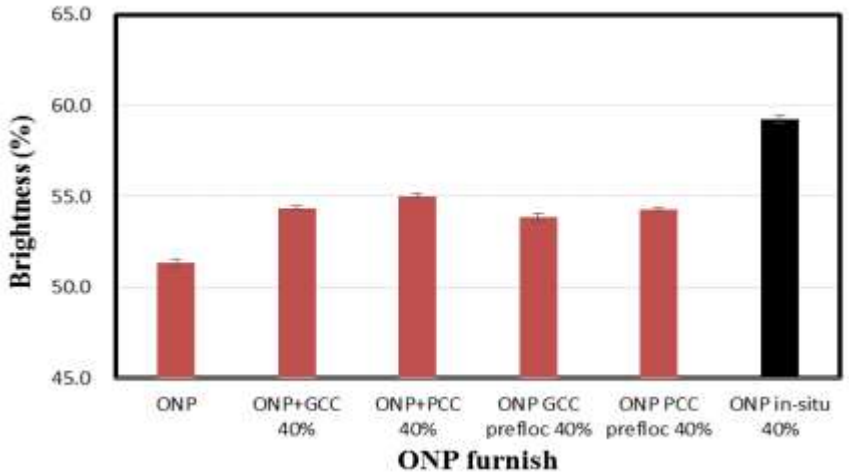

Fig. 3. ISO brightness of handsheets from ONP furnishes with 40% $CaCO_3$ ash content and 0.1% PAM addition

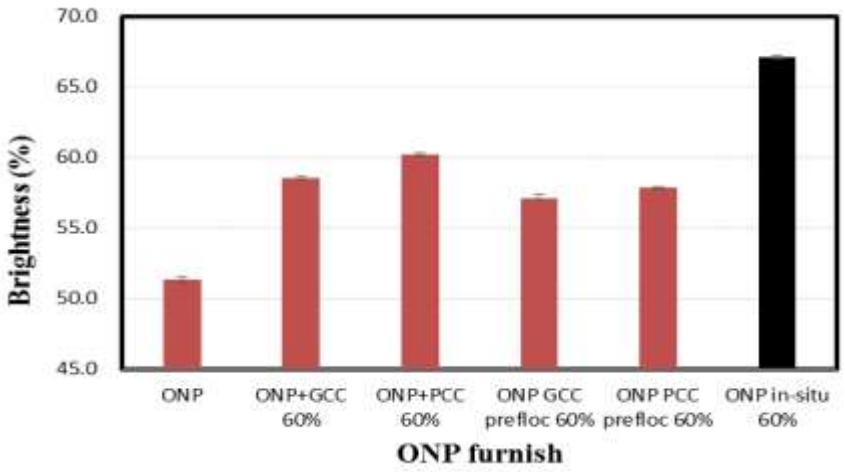

Fig. 4. ISO brightness of handsheets from ONP furnishes with 60% $CaCO_3$ ash content and 0.1% PAM addition

For the ERIC value, large decreases due to the *in-situ* $CaCO_3$ method are shown in Figs. 5 and 6. There were almost no differences in the ERIC value with and without retention aid for the *in-situ* $CaCO_3$ method. This may mean that there are almost no floating colored impurities, if any, in the ONP furnish after the *in-situ* $CaCO_3$ process. If this is indeed the case, where did they go? The large increase of brightness for *in-situ* loa ding (Fig. 3–4) supports the idea of the disappearance of colored impurities. We suppose that during the *in-situ* $CaCO_3$ loading process, the colored impurities or sticky materials acted as the initial nuclei for $CaCO_3$ formation; these newly-formed, $CaCO_3$ particulates may stick together or aggregate to create micron-size fillers, which also attach to fibrous materials in ONP. Therefore, almost no colored materials were left floating in the liquid phase. Further study is necessary to find the evidence of the newly-formed, $CaCO_3$ particulates that covered colored particulates.

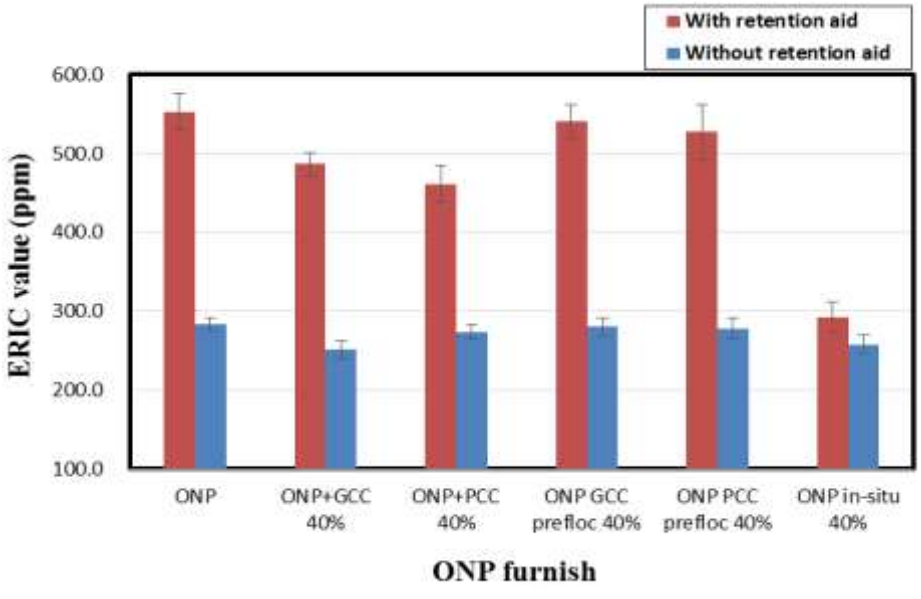

Fig. 5. ERIC values of handsheets from ONP furnishes with 40% $CaCO_3$ ash content and with and without 0.1% PAM addition

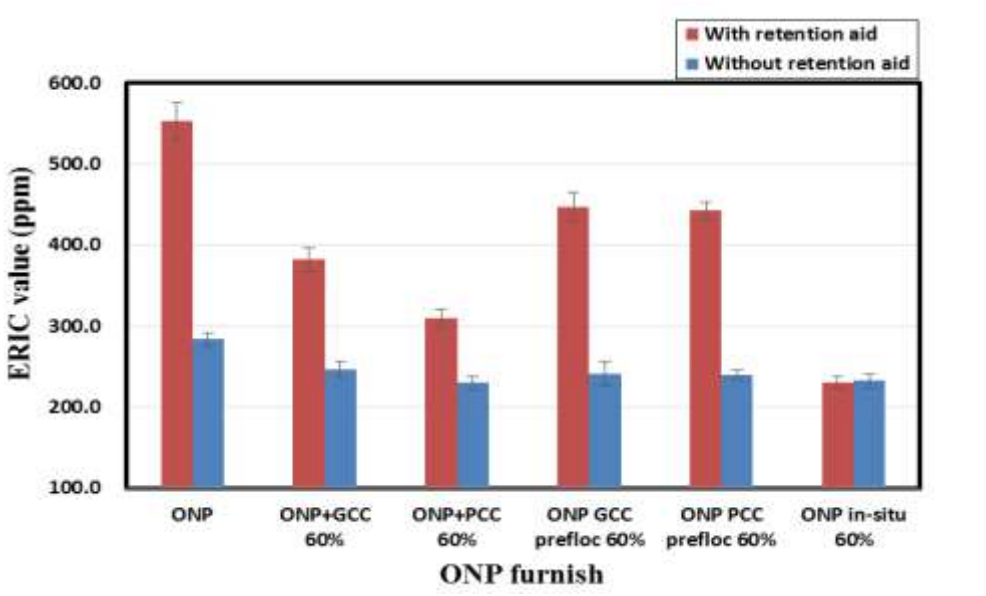

Fig. 6. ERIC values of handsheets from ONP furnishes with 40% $CaCO_3$ ash content and with and without 0.1% PAM addition

Figure 7 shows the change in the macro sticky area during the $CaCO_3$ formation reaction, as measured by the standard method TAPPI T-277 pm-99 (1999). The final ash content of the ONP furnish in this figure was about 60%. As *in-situ* $CaCO_3$ formation proceeded, the sticky area decreased; when the reaction stopped at pH 7.0, there was no more decrease in the sticky area.

The sticky areas for simple addition of GCC and PCC to ONP were 1844 and 1552 mm^2/kg, respectively, at a 60% ash level. The same trend was shown for the ERIC value in Fig. 8.

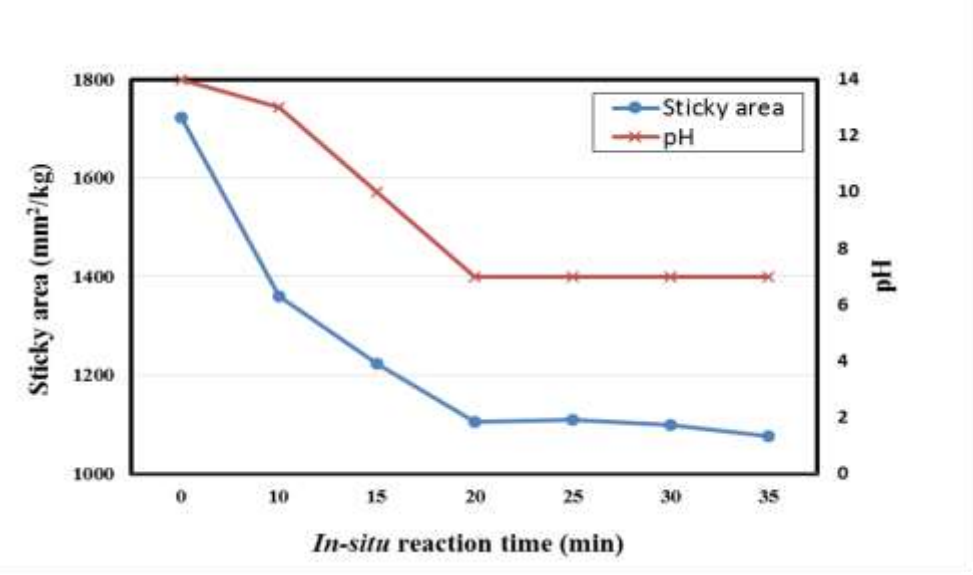

Fig. 7. The macro sticky area and furnish pH as a function of reaction time of *in-situ* $CaCO_3$ formation

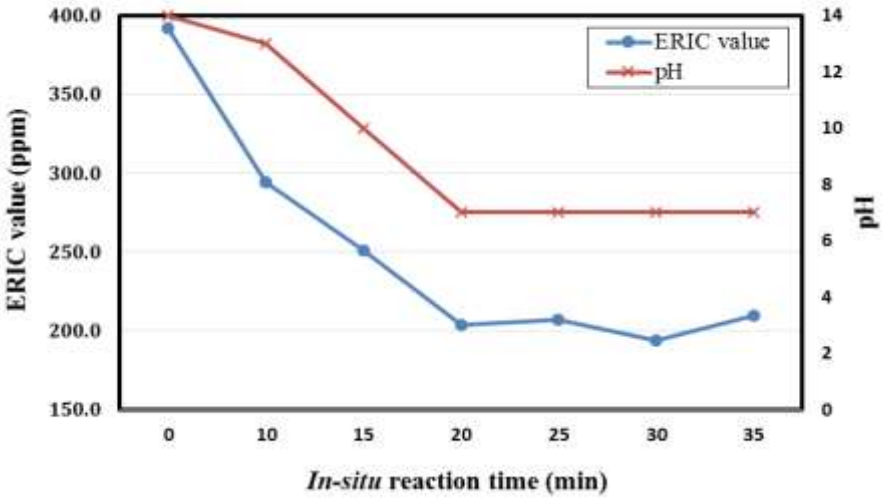

Fig. 8. ERIC value and furnish pH as a function of reaction time of *in-situ* $CaCO_3$ formation

The ERIC values for simple addition of GCC and PCC were 367 and 314 ppm, respectively, at a 60% ash level. At pH 7, the ERIC value decreased to 200 ppm with the *in-situ* $CaCO_3$ formation method. It is believed that the retention aid in papermaking, cationic PAM in this case, captures the anionic materials, which may have dark color. When those colored materials are retained on the paper sheet, the ERIC value increases. This means that no such colored anionic materials were left in the liquid phase of the ONP furnish after the *in-situ* $CaCO_3$ formation. Therefore, the ERIC value of 200 ppm might come from the solid phase of the ONP furnish. The brightness increase due to the *in-situ* $CaCO_3$ method in Figs. 3 and 4 may have been caused by a reduction of the colored materials in liquid phase, which, otherwise, attached to the paper sheet by retention aid, PAM.

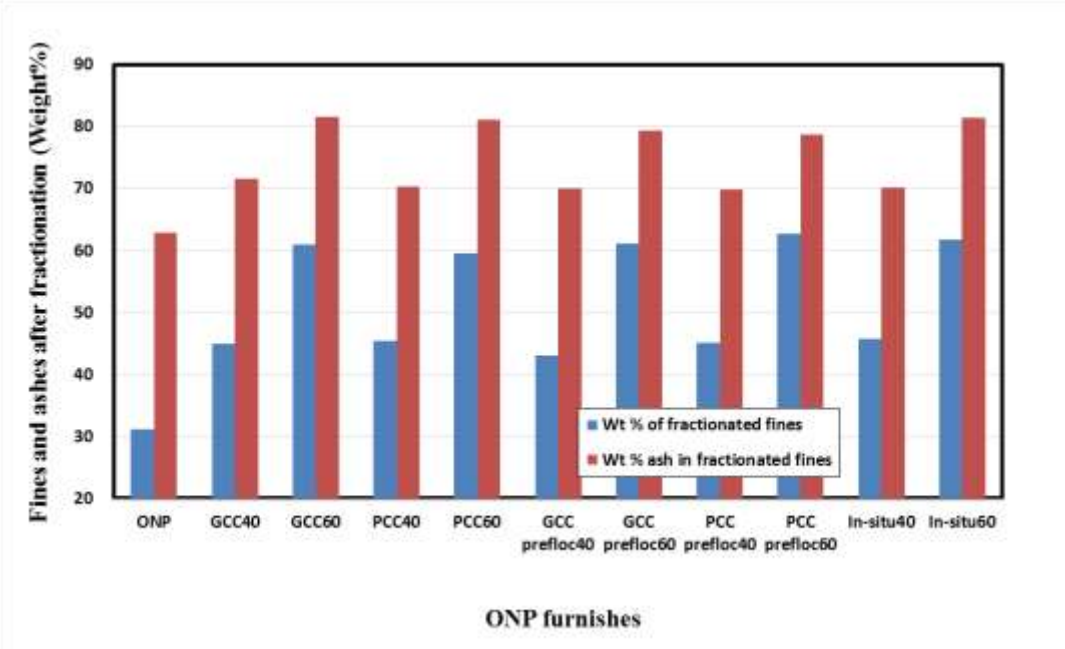

Fig. 9. The weight% and ash contents of fractionated fines in ONP

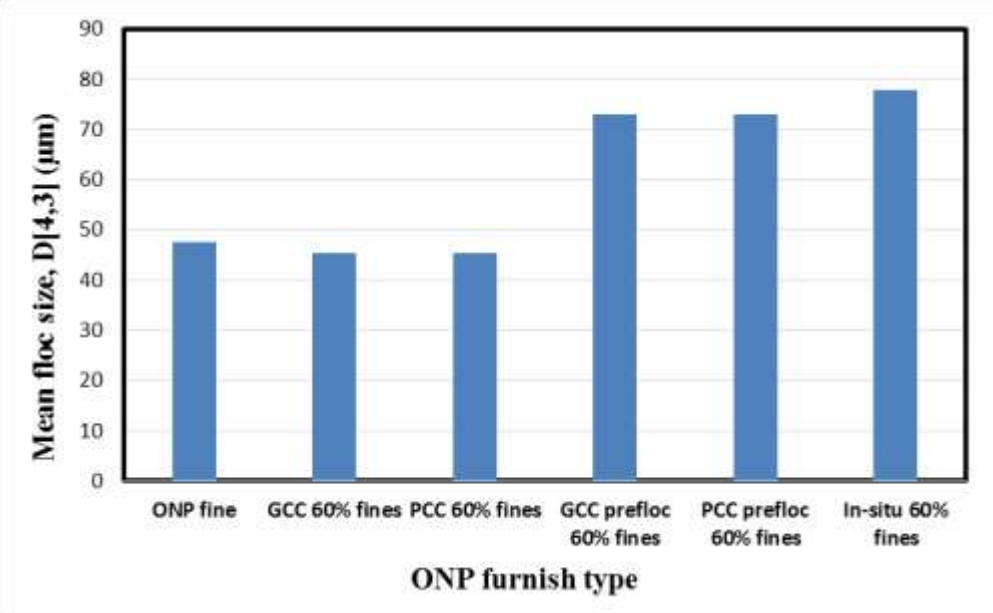

Fig. 10. Size of fractionated fines measured by FlowCAM® dynamic imaging particle analyzer

The fractionated fines from the ONP furnish with $CaCO_3$ loading after passing through a 200-mesh screen had the same weight portions and the same ash contents, as shown in Fig. 9. Figure 10 shows the size of the fractionated fines, where $CaCO_3$ pre-flocculation and *in-situ* process furnishes had similar sizes, although they were larger than those of the GCC and the PCC furnish. The pre-flocculated and in-situ $CaCO_3$ furnishes led to higher tensile strength values (Fig. 11). For the ONP furnish only case, its breaking length was 2.43 km at paper ash of 19.8%. In the mill trial, low tensile of ash-rich furnish was compensated by controlling the amount of strength agent addition without causing property and cost problems in paperboard.

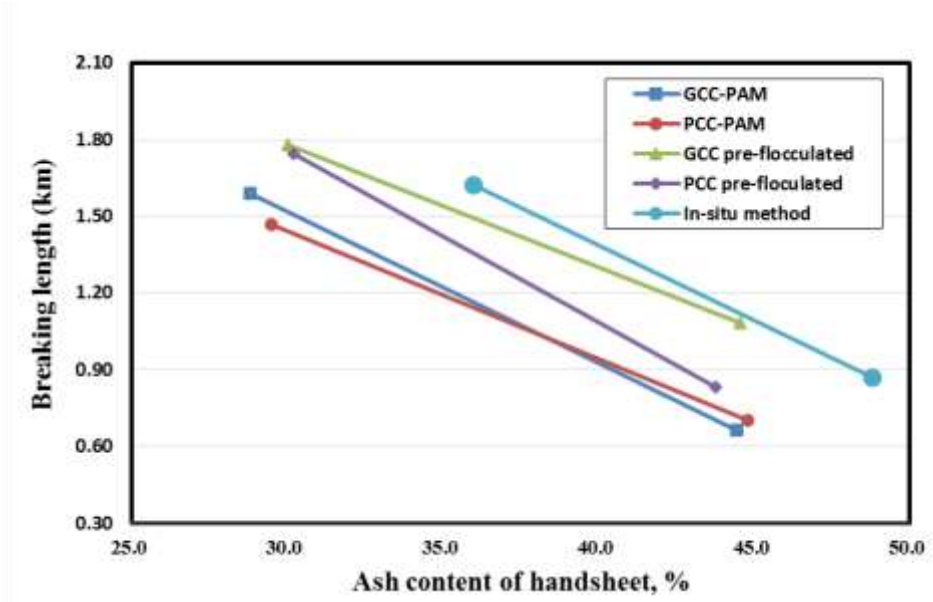

Fig. 11. Breaking lengths of handsheets from ONP furnishes with addition of $CaCO_3$

The stored optical images used for calculating floc sizes in the FlowCAM® dynamic imaging particle analyzer are shown in Figs. 12, 13, and 14, which are in the same magnification. The image of the PCC 60% added furnish (Fig. 12) was no different from that of the original ONP fines. However, the PCC pre-flocculated furnish gave much larger flocs than the PCC 60% furnish, as shown in Fig. 13. Finally, the *in-situ* $CaCO_3$ formation method (Fig. 14) showed an extensive attachment of organic and inorganic materials, and their attachment seemed strong because there was still high retention, even without a retention aid, as shown in Fig. 2. The GCC had the same trend as PCC, but the data are not shown to avoid redundancy.

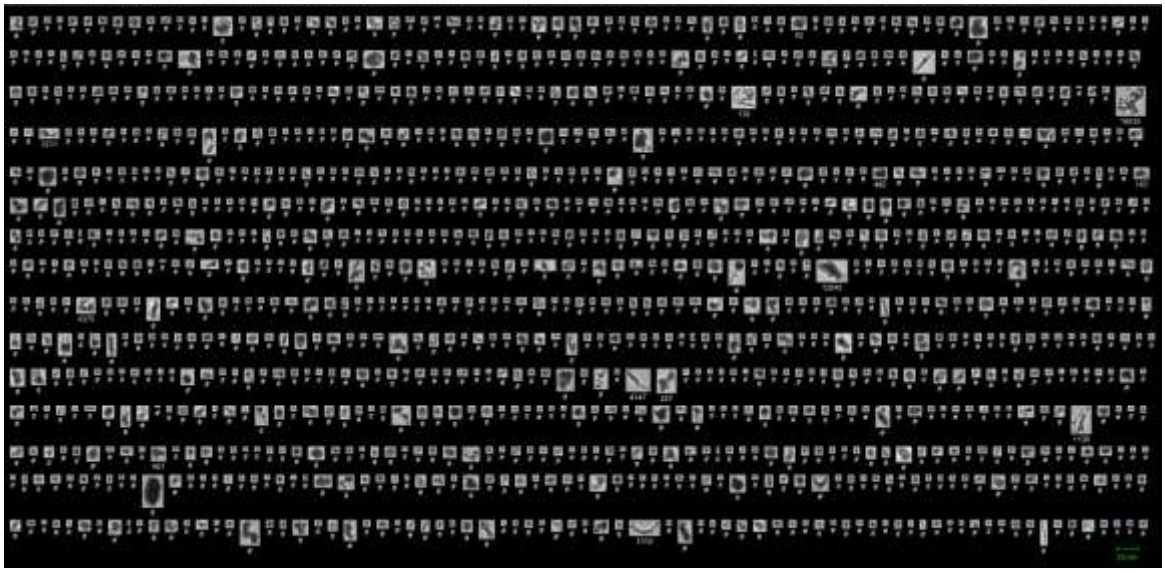

Fig. 12. Optical image of the fine fraction at PCC 60% (FlowCAM® dynamic imaging particle analyzer)

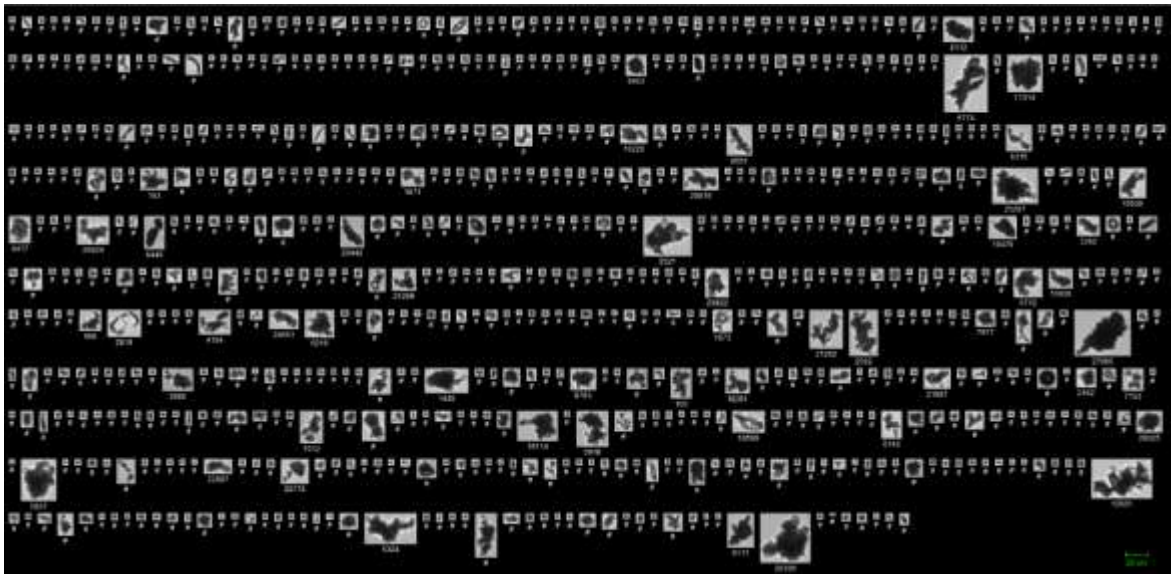

Fig. 13. Optical image of the fine fraction at PCC pre-flocculation 60% (FlowCAM® dynamic imaging particle analyzer)

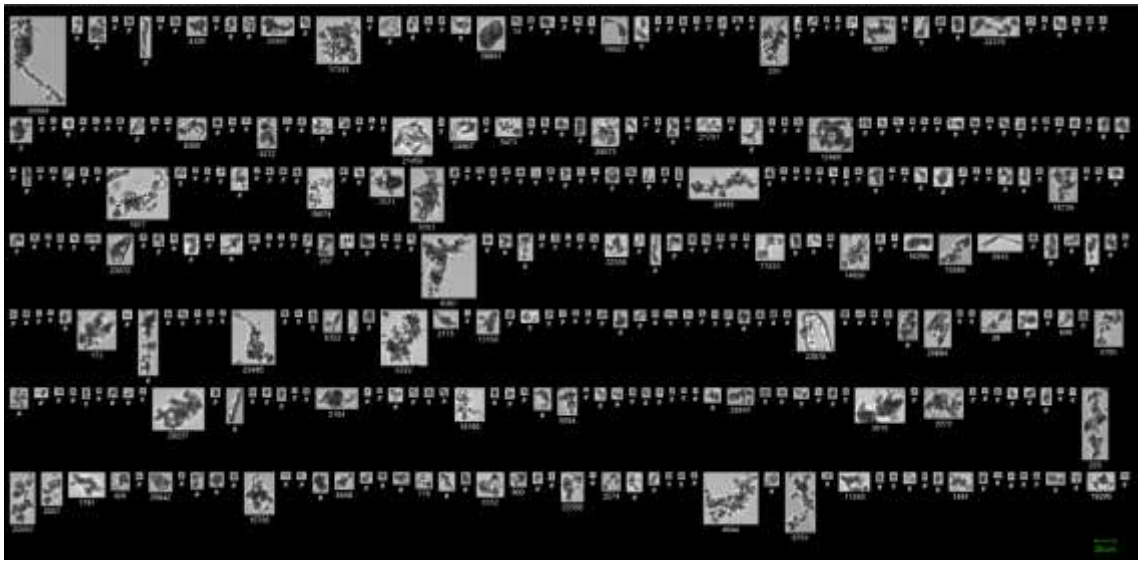

Fig. 14. Optical image of the fine fraction at *in-situ* $CaCO_3$ 60% (FlowCAM® dynamic imaging particle analyzer)

The SEM micrographs in Fig. 15 show the morphology of fines after fractionation with a 200-mesh screen. The *in-situ* $CaCO_3$ formation method was compared to PCC addition. With the *in-situ* $CaCO_3$ (Fig. 15d), nano-size $CaCO_3$ particles were aggregated to form micron-size particles. A magnified micrograph of the *in-situ* $CaCO_3$ is shown in Fig. 15e, where $CaCO_3$ particles of 300 to 600 nm size were aggregated together. The PCC addition by pre-flocculation (Fig. 15c) did not yield a different in morphology from that with a retention aid (Fig. 15b). The PCC shape, which was assumed to be scalenohedral, was not clearly detected because of the ash present in the ONP (A and B in Figs. 15a and b).

CONCLUSIONS

1. During *in-situ* $CaCO_3$ formation on the ONP furnish, the ERIC value and macro sticky area of the furnish were decreased greatly.
2. No measureable colored impurities were left in the liquid phase of the ONP when it was processed by *in-situ* $CaCO_3$ formation method with up to 60% ash level (initially 23.8%).
3. The mechanism of lowering the ERIC value by the *in-situ* $CaCO_3$ formation method seemed to be that the colored and sticky materials acted as nuclei for the $CaCO_3$ formation to make small-size filler materials, which aggregated on the ONP furnish to form micron-size $CaCO_3$ fillers.
4. The ONP fines were found to be heavily covered with newly formed PCC in the *in-situ* $CaCO_3$ method, and the attachment of newly formed PCC to the fines seemed to be strong enough to render unnecessary the use of a retention aid.
5. The decrease in breaking length with the addition of the $CaCO_3$ in the *in-situ* formation method was equivalent to or slightly lower than that of the $CaCO_3$ pre-flocculation method, which is a method that is known to lead to high strength properties at a given filler content.

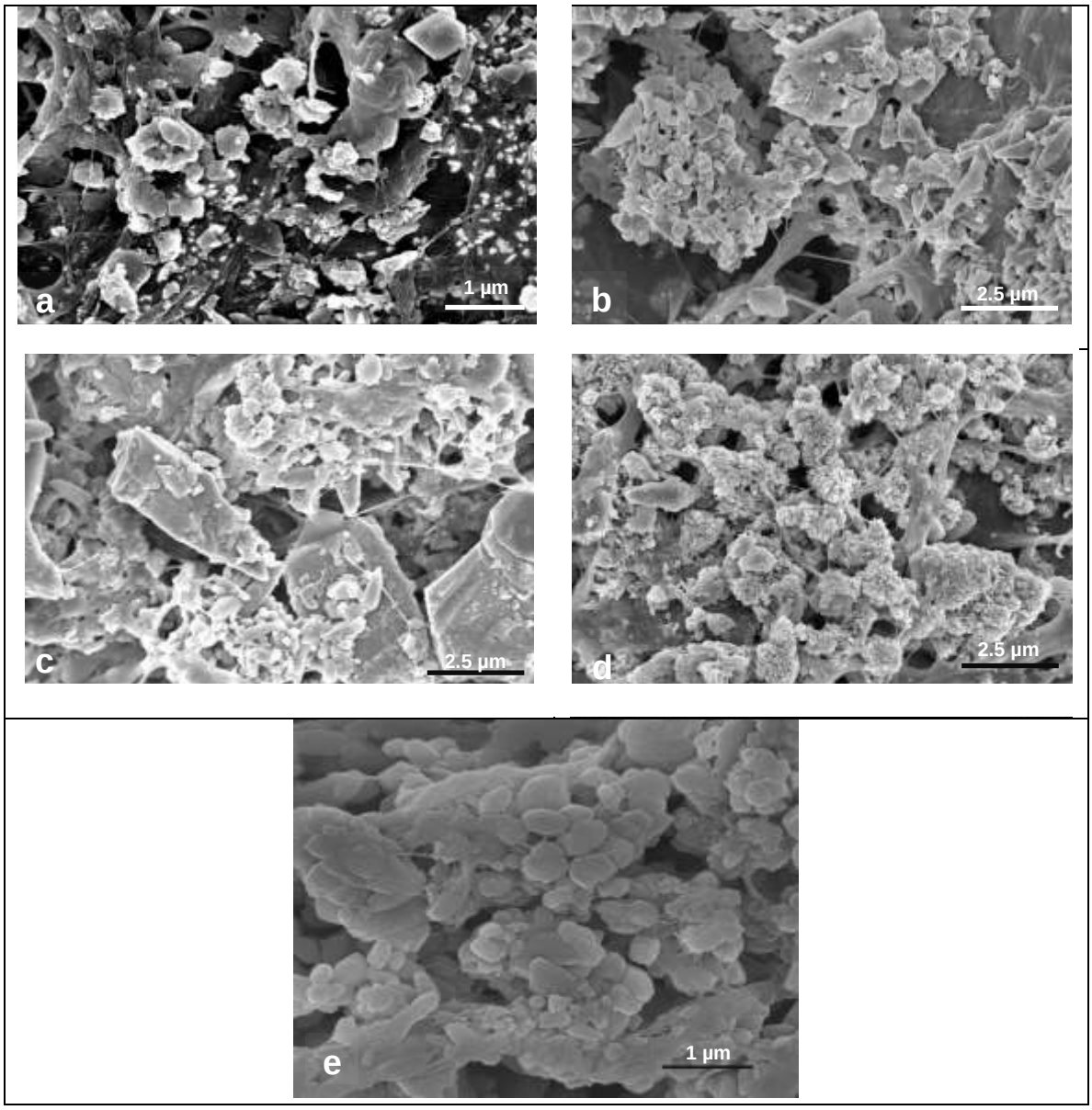

Fig. 15. SEM micrographs of ONP fractionated fines. (a) No $CaCO_3$ added, (b) PCC added, (c) pre-flocculated PCC, (d) *in-situ* $CaCO_3$, and (e) magnified image of the *in-situ* $CaCO_3$

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