Improving Recycled Fiber by Applying In-Situ Aragonite Calcium Carbonate Formation Process

Joobeom Seo¹, Jong Gyu Lee¹, Thenepalli Thriveri¹, Chul Seoung Baek² and Ji-Whan Ahn¹,*

¹Korea Institute of Geoscience and Mineral Resources (KIGAM), Gwangang-no 124, Yuseong-gu, Daejeon 305-350, Korea
²Korea Institute of Limestone and Advanced Materials (KILAM), Udeok-ri 63, Maepo-up, Danyang 395-903, Korea

Needle-shaped aragonite, a thermodynamically metastable polymorph of CaCO₃, was synthesized in a deinked old newspaper pulp (ONP) slurry, otherwise known as the in-situ aragonite formation process, in order to improve the optical properties such as the brightness and ERIC value (effective residual ink concentration) as well as to preserve the strength properties such as the breaking length of the resultant handsheet. The brightness and ERIC value of the handsheet obtained from pulp that was subjected to the in-situ aragonite formation process was improved by 20.4% (from 56.8 to 68.4%) and 55.4% (from 292.1 to 130.4 ppm), respectively, relative to a raw ONP sample. The effects of the in-situ aragonite formation process on the resultant handsheet were compared with the results obtained from a similar process in which rhombohedral-type calcite was synthesized instead of the needle-shaped aragonite. From the comparison, it can be concluded that the in-situ aragonite formation process provides better optical and strength properties to the resultant handsheet than that of calcite, and this is attributed to the needle-shaped morphology of aragonite.

(Received September 26, 2013; Accepted November 25, 2013; Published January 18, 2014)

Keywords: calcium carbonate, aragonite, calcite, old newspaper pulp, in-situ calcium carbonate formation

1. Introduction

Calcium carbonate is an important inorganic material that is widely used in different industries such as paper-making, plastics, coating technology, etc. Calcium carbonate appears in nature in three polymorphs. The most common is calcite, which is the thermodynamically most stable polymorph at ambient temperature and pressure. Calcite appears in a range of morphologies including the most common forms, rhombohedral and scalenohedral.¹⁷) Aragonite is a metastable polymorph that is characterized by a needle-shaped morphology.¹⁴) Lastly, vaterite has a spherical morphology and is thermodynamically unstable and rapidly reverts to one of the stable forms, calcite or aragonite.¹⁵)

The main sources of calcium carbonate are ground calcium carbonate (GCC) mined from calcite deposits and precipitated calcium carbonate (PCC) produced by means of a chemical reaction. PCC is an important inorganic filler material because particulate calcium carbonate parameters such as particle size, morphology, polymorphic form, and purity can be tailored by carefully controlling the reaction conditions.¹⁴-¹¹) The calcium carbonate parameters greatly influence the properties of the resultant products bearing calcium carbonate filler.¹²-¹⁵) It is therefore important to synthesize calcium carbonate with desired morphology, size, and polymorphic form.

Industrially, PCC is produced through the gas–solid–liquid carbonation route, which entails bubbling gaseous carbon dioxide (CO₂) through a concentrated aqueous slurry of calcium hydroxide (Ca(OH)₂), according to the following carbonation reaction (1):

\[
\text{Ca(OH)}_2 + \text{CO}_2 \rightarrow \text{CaCO}_3 + \text{H}_2\text{O}
\]

In the carbonation reaction, control of the calcium carbonate parameters can be achieved by modifying the reaction conditions such as reaction temperature, use of additives, CO₂ flow rate, etc.⁸-¹¹¹⁶)

Calcium carbonate is an important filler material in paper-making. It is used in paper-making to provide high bulk, high brightness, high smoothness, and high air permeability.¹⁵) It has been reported that PCC is superior to GCC in terms of the development of desired handsheet properties.¹⁷)

Increasing the use of recycled pulp in paper-making is highly encouraged because it helps to reduce greenhouse gases by less cutting of trees, provides energy savings through reduction of the amount of chemical pulping, and reduces production costs. However, due to low brightness and the presence of numerous dark specks, recycled pulp is not acceptable for use as a fiber source. Because PCC can improve the optical properties such as brightness and effective residual ink concentration (ERIC) value, that indicates the amount of the remained ink residues in the recycled paper, of the resultant handsheets, it can be used for the recycling of waste pulp, and the resultant recycled pulp can be used as a fiber source owing to the increased optical properties.¹⁸)

PCC can be added in the pulp slurry via two methods: conventional loading and in-situ formation of PCC on pulp fibers. In the conventional loading process, PCC is added into the pulp slurry with a retention aid to increase PCC attachment on the fiber surface. On the other hand, in the in-situ formation process, PCC is synthesized by a carbonation reaction (1) in the pulp slurry.¹⁸-²⁰) Compared to the conventional loading process, PCC synthesized via the in-situ formation process is strongly attached on the fiber surface because calcium carbonate crystals are grown on the fiber surface in the carbonation reaction, thus indicating that the use of a retention aid is not necessary.¹⁹) In addition, the in-situ formation process can increase paper opacity by increasing the scattering coefficient compared to the conventional loading of PCC on fiber furnish.¹⁸,²⁰) Most research on the in-situ formation process has focused on the synthesis...
of calcite in the pulp slurry.\textsuperscript{18-20} Because the characteristics of calcium carbonate are affected by its morphology,\textsuperscript{13,15,21} controlling the structure and morphology of calcium carbonate is an important research subject.

Aragonite has several advantages compared to calcite due to its needle-shaped morphology.\textsuperscript{10,14,22,23} It has been reported that aragonite endows improved physical and mechanical properties to the resultant products. Plastic, polyvinyl, and polypropylene composites with aragonite filler present improved tensile strength, impact strength, glass transition temperature, and decomposition temperature.\textsuperscript{10} It has been also reported that aragonite containing paper coating offers benefits such as improved brightness, opacity, strength, and printability.\textsuperscript{14} Despite that aragonite presents improved properties, to the best of our knowledge the \textit{in-situ} formation of aragonite through a carbonation reaction in a pulp slurry has not yet been reported.

The synthesis of aragonite through a carbonation reaction is favored at elevated temperature (generally 353 K is recommended) to obtain aragonite with an increased aspect ratio, that is, the ratio between the height and width of the particle.\textsuperscript{29} It is also necessary to employ magnesium ions as an additive for the synthesis of aragonite with a molar ratio of magnesium-to-calcium greater than 3.\textsuperscript{8}

In this study, we investigated the \textit{in-situ} formation of aragonite in a deinked old newspaper pulp (ONP) slurry, the pulp slurry obtained from the recycling of the newspaper, by employing magnesium ions at a low temperature (318 K) that is close to the working temperature at a paper mill. The improvement of the optical and mechanical properties of the resultant handsheets was also evaluated. For comparison, \textit{in-situ} calcite formation in a deinked ONP slurry was also carried out.

2. Experimental Procedure

2.1 Process and materials

The recycled old newspaper pulp (ONP) used in this study was kindly supplied by the H. paper mill, located in Daejeon, Korea. The ONP pulp used in the research was supplied after completing the deinking process and the handsheet properties (no refining applied) are summarized in Table 1.

Ca(OH)\textsubscript{2} (Sigma-Aldrich, GR, 95%) and MgCl\textsubscript{2} (Junsei, EP, 97%) were analytically pure and used without further purification. Powder X-ray diffraction (XRD; Rigaku Xpert MPD equipped with Cu K\textsubscript{α} radiation) and scanning electron microscopy (SEM, JSM-6380 LA, JEOL) were used for characterization of the resultant handsheets.

2.1.1 \textit{In-situ} aragonite formation

The \textit{in-situ} aragonite formation was carried out in a 2 L reactor, which was surrounded by an open water bath to keep the reaction temperature at 318 K, with a two-wing paddle-type impeller rotating at 400 rpm (Fig. 1). Ca(OH)\textsubscript{2} slurry (0.40 M, 1.00 L) was added to a MgCl\textsubscript{2} (3.00 M, 0.375 L) solution with mechanical agitation (400 rpm). ONP furnish (5 mass%, 300 g) was added to the reaction mixture and additional distilled water was then added to maintain the reaction volume of 2 L. Gaseous CO\textsubscript{2} (99.9%) was injected to the reaction mixture for 3 h through porous glass with a flow rate of 50 mL/min to precipitate aragonite. The pH of the slurry after addition of Ca(OH)\textsubscript{2} is 12 and then decreases to 8–9 by the addition of MgCl\textsubscript{2}. The pH decreased to about 6 after the gaseous CO\textsubscript{2} injection for three hours.

2.1.2 \textit{In-situ} calcite formation

The \textit{in-situ} calcite formation was performed according to the method applied for \textit{in-situ} aragonite formation except for the use of MgCl\textsubscript{2} and a reaction temperature of 298 K. Ca(OH)\textsubscript{2} slurry (0.40 M, 1.00 L) was added to the ONP furnish (5 mass%, 300 g). Additional distilled water was added to maintain the reaction volume of 2 L. Gaseous CO\textsubscript{2} (99.9%) was injected through porous glass with a flow rate of 50 mL/min to the reaction mixture. The reaction was finished when the pH of the reaction mixture decreased to about 7.

2.1.3 Handsheet analysis

The handsheet of the pulp resulting from the \textit{in-situ} calcium carbonate formation was prepared using the standard sheet machine of TAPPI (Technical Association of the Pulp and Paper Industry) with a basis weight of 60 g/m\textsuperscript{2}. Ash contents (TAPPI 413 om-93), brightness (ISO 2407), ERIC values (ISO 2275), and the breaking length (km) of the handsheets prepared from the pulp furnish after the \textit{in-situ} calcium carbonate formation process were measured by international standards.

3. Results and Discussions

3.1 \textit{In-situ} aragonite formation

The carbonation method was employed for the \textit{in-situ} aragonite formation process in this study. Raw ONP furnish

<table>
<thead>
<tr>
<th>Brightness (%)</th>
<th>ERIC (ppm)</th>
<th>Breaking length (km)</th>
<th>Ash (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>56.8</td>
<td>292.1</td>
<td>3.28</td>
<td>6.4</td>
</tr>
</tbody>
</table>

Table 1 Properties of the deinked old newspaper (ONP) furnish.
was added to a mixture of 0.40 M Ca(OH)$_2$ slurry and 3.00 M MgCl$_2$ with a magnesium-to-calcium molar ratio of 2.8. Gaseous CO$_2$ (99.9\%) was injected with a flow rate of 50 mL/min to the mixture through porous glass for three hours. The resultant pulp (pulp-aragonite) was treated to obtain handsheets (handsheet-aragonite) to analyze ash content (TAPPI 413 om-93), brightness (ISO 2407), ERIC values (ISO 2275), and breaking length (km). The calcium carbonate formed in the reaction was analyzed by PXRD to confirm the polymorph and phase purity.

The SEM images of handsheet-aragonite in Fig. 2 show that needle-shaped aragonite particles with a particle size in a range of about 2–7 µm were synthesized. In addition, it is also confirmed by the SEM images that particles were synthesized on the fiber surface. The needle-shaped morphology does not appear to disturb the interactions between the fibers (Fig. 2). The aragonite particles appear to be synthesized on the fiber surface and some are located between the fibers with the aid of micro-fibers (Fig. 2(b)).

The comparison of the PXRD patterns of handsheet-aragonite and the handsheet resulting from the raw ONP furnish (ONP handsheet) clearly show the formation of aragonite in the reaction (Fig. 3).

ERIC values (Effective Residual Ink Concentration, measured at 950 nm) of ONP handsheet and handsheet-aragonite were evaluated (Fig. 4). The ERIC value of ONP handsheet is 292.1 ppm whereas the ERIC value of handsheet-aragonite decreased to 130.4 ppm. Higher ERIC values indicate lower paper quality. It therefore can be suggested that the quality of the paper is improved by applying the in-situ aragonite formation process. As the ERIC value decreased by applying the in-situ aragonite formation process, brightness was also increased, from 56.8\% for ONP handsheet to 68.4\% for handsheet-aragonite (Fig. 4). The ash contents, evaluated to confirm the amount of inorganic filler content in the pulp, was increased from
6.37% for the raw ONP furnish to 35.25% for pulp-aragonite (Fig. 4).

3.2 In-situ calcite formation

The in-situ calcite formation process was carried out through the carbonation method wherein gaseous CO$_2$ (99.9%) is injected for the synthesis of calcium carbonate. The raw ONP furnish was added to Ca(OH)$_2$ slurry (0.40 M, 1.00 L). Gaseous CO$_2$ (99.9%) was then injected through porous glass with a flow rate of 50 mL/min to the reaction mixture with mechanical agitation (400 rpm) at room temperature. The pH of the mixture was monitored to confirm the reaction. After injection of CO$_2$ for about 20 min, the pH of the reaction mixture decreased to about 7.

The SEM images of handsheet-calcite indicate that rhombohedral-type calcite was synthesized in the reaction. The particle size of the synthesized calcite ranges from 0.8 to 2.1 µm (Fig. 5). The calcite particles appear to be synthesized on the fiber surface and some are located between the fibers with the aid of micro-fibers.

The PXRD pattern of the resultant handsheets (handsheet-calcite) from the pulp with application of the in-situ calcite formation process (pulp-calcite) clearly shows that calcite is synthesized in the reaction (Fig. 3).

The optical properties of handsheet-calcite were measured. The ERIC value of handsheet-calcite decreased to 115.0 ppm from 292.1 ppm for ONP handsheet; with the decreased ERIC value, brightness was improved from 56.8% for ONP handsheet to 72.8% for handsheet-calcite (Fig. 4).

3.3 Comparison of the results from in-situ aragonite and calcite formation processes

The in-situ formation of calcium carbonate (aragonite or calcite) in the deinked ONP slurry improved the optical properties of the resultant handsheets. The SEM images of the resultant handsheets (handsheet-aragonite and handsheet-calcite) clearly show that needle-shaped aragonite and rhombohedral-type calcite are formed on the fiber surface by the reactions. The ERIC values of the handsheets decreased from 292.1 ppm for ONP handsheet to 130.4 ppm for handsheet-aragonite and 115.0 ppm for handsheet-calcite. The brightness was also improved to 68.4% for handsheet-aragonite and 72.8% for handsheet-calcite from 56.8% for ONP handsheet. To compare the improvement in the optical properties according to the morphology and polymorph of the in-situ formed calcium carbonate, ash contents of the resultant handsheets was compared. This comparison is carried out because the optical properties of the handsheet are related to the amount of loaded calcium carbonate filler. The amount of ash was 35.3% for handsheet-aragonite and 58.0% for handsheet-calcite. The small amount of loaded aragonite relative to that of the calcite is likely related to the needle-shape of aragonite. As the amount of mineral filler has a direct relationship with the optical properties of the resultant handsheet, the optical properties were compared according to ash contents (Fig. 4). The brightness of handsheet-aragonite was 68.4% at ash contents of 35.3%. On the other hand, the brightness of the handsheet-calcite was 72.8% at ash contents of 58.0%. The improvement in brightness of the handsheets bearing calcium carbonate filler is induced by diffused reflection of visible rays. It has been reported that the scattering efficiency of a paper coating depends on the size, shape, packing density, and refractive index of inorganic pigments. In the in-situ calcium carbonate formation process, crystals of calcium carbonate grown on the fiber surface and remain attached in the resultant handsheet. This results in less exposure of the dirty fiber surface of ONP and consequently improves the optical properties. Even though the ash contents of handsheet-calcite and handsheet-aragonite show a large difference, the brightness of the two handsheets is comparable. This is likely due to the characteristics of aragonite and calcite and the crystal size.

Strength properties such as breaking length are one of the important parameters that should be considered in research on paper-making, because the strength properties of handsheets bearing an inorganic filler have a direct relationship with the amount of loaded filler. Hydrogen bonding between celluloses, which makes the handsheet mechanically stronger, can be destroyed by the presence of inorganic filler particles between pulp fibers. Breaking lengths of handsheet-aragonite and handsheet-calcite are 1.43 and 0.63 km, respectively, and 3.28 km for the raw ONP, indicating that the strength properties are decreased by the presence of aragonite or calcite (Fig. 6). The breaking length is also related to the morphology and size of the inorganic filler. The ash content of handsheet-aragonite and handsheet-calcite is 35.3 and 58.0%, respectively. Even though the ash contents of handsheet-aragonite is almost two-thirds that of handsheet-calcite, the breaking length of handsheet-aragonite
(1.43 km) is much higher than that of handsheet-calcite (0.63 km) (Fig. 6). These results indicate that aragonite provides better mechanical properties to the resultant handsheet than calcite, which is due to the needle-shaped morphology of aragonite.

4. Conclusion

Needle-shaped aragonite and rhombohedral type calcite were synthesized in a deinked ONP slurry by a carbonation method to increase the optical properties. From the results obtained in this research, the following conclusions can be derived:

1. Aragonite was synthesized in a deinked ONP slurry at 318 K by employing magnesium ions as an additive for the growth of aragonite. Needle-shaped aragonite with crystal size in a range of 2–7 µm were synthesized on the fiber surface.

2. Calcite was formed in the deinked ONP slurry at room temperature. The reaction was finished when the pH decreased to about 7. The SEM images show that about 1–2 µm size rhombohedral-type calcite was synthesized on the fiber surface.

3. The in-situ synthesized aragonite and calcite improved the optical properties of the resultant handsheets. The ERIC values of handsheet-aragonite and handsheet-calcite decreased to 130.4 and 115.0 ppm, respectively, from 292.1 ppm for the ONP handsheet. As the ERIC value decreased, the brightness increased to 68.4% for handsheet-aragonite and 72.8% for handsheet-calcite from 56.8% for ONP handsheet.

4. The changes in polymorph, morphology, and crystal size of the in-situ synthesized calcium carbonate resulted in large differences in the optical and strength properties of the resultant handsheets. The optical properties (ERIC value, brightness) and the strength property (breaking length) were compared based on the ash contents of the resultant handsheets. In the case of handsheet-aragonite, despite that the amount of loaded calcium carbonate is less than that of handsheet-calcite, the optical properties were enhanced to a level similar to those of handsheet-calcite. In addition, the breaking length of handsheet-aragonite is longer than that predicted from handsheet-calcite due to the needle-shaped morphology of aragonite.

The results show that in-situ calcium carbonate formation can improve the optical properties of the resultant handsheet because calcium carbonate crystals are grown on the fiber surface. However, the calcium carbonate filler disturbs the interactions between the pulp fibers, and consequently the strength properties are decreased. The degree of reduction in the strength properties of the handsheet is related to characteristics of the calcium carbonate crystals. The in-situ aragonite formation resulted in greater improvement of the optical properties while preserving the strength properties of the resultant handsheet compared to in-situ calcite formation.

Acknowledgments

This research was supported by a grant (2012) from the Energy Technology Development Program (2010201010093B) funded by the Ministry of Knowledge Economy of the Korean government.

REFERENCES