Surface Modifications of Organic Fillers to Improve the Strength of Paperboard

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In a previous study the authors determined that non-woody materials including brewers' grain (BG) and oil palm frond (OPF) could be alternatives to wood powder as organic fillers. However, they have the disadvantage of deteriorating the strength of paperboard. If the strength of paperboard could be improved, then one would expect more production cost reductions and bulk improvements by increasing the addition of organic fillers. In this study, surface modification of organic fillers was used as a method to improve paperboard strength. The goal was to find the most effective condition for surface modifications. Surface modifications of BG and OPF fillers were carried out using cationic and oxidized starches, and the strengths and reductions in the drying energies of the sheets were measured. The zeta potentials of the modified organic fillers showed that the surface modifications were performed properly. Surface modification with starches improved the bulk and strength of the sheets simultaneously, and modification with the addition of a large amount of cationic starch was more effective in improving the strengths and the reductions in drying energies of the sheets than using cationic and oxidized starches together.

Keywords: Paperboard; Organic filler; Surface modification; Bulk; Strength; Drying energy

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INTRODUCTION

Wood powder (WP) organic filler has been widely used in the Korean duplex board industry. Many studies (Lee *et al*. 2014a,b; Sung *et al*. 2014) claim that bio-based organic fillers made of WP and other materials can reduce the production cost due to an increase in the bulk and a decrease in the steam consumption of paperboard. In particular, unlike for inorganic fillers, mills can add organic filler powders to a mixing or machine chest directly without passing it through pulping and refining processes, and they can control particle size distribution to obtain the desired improvement of bulk and drying energy reduction (Lee *et al*. 2009).

A previous study showed that the organic fillers made of brewers' grain (BG) and oil palm frond (OPF) could be alternatives to wood powder (Lee *et al*. 2014a). However, BG, OPF, and wood powder organic fillers deteriorate the strength of paperboard (Lee *et al*. 2014b). The loss in strength limits the use of organic fillers, so attempts to improve the strength of paperboard containing organic fillers are necessary to generate the desired reductions in production costs and paperboard qualities.

Fillers are usually embedded in the paper sheet, resulting in increased thickness, increased light scattering, and a loss of strength (Krogerus 1997). Many studies, including those using a starch-modified calcium carbonate filler (Zhao *et al*. 2005), a calcium

carbonate composite filler (Subramanian *et al*. 2005; Kumar *et al*. 2009), pre-flocculation (Gerischer *et al*. 1996; Goto and Pelton 2000; Lee *et al*. 2006), layer-by layer surface treatment (Brynda and Housksa 1996; Decher 1997; Lojou and Bianco 2004; Zhang *et al*. 2007; Ryu *et al*. 2008), and filler surface modification (Ahn *et al*. 2012; Lee *et al*. 2013) have been carried out to overcome the strength losses caused by fillers. These approaches all were based on surface modifications of materials, so in the present work surface modifications of organic fillers were carried out with starches to provide them with the ability to form hydrogen bonds with cellulosic fibers.

The authors have also reported that surface modifications of BG and OPF organic fillers with cationic and oxidized starches could be carried out effectively by identifying the zeta potentials and observing confocal laser scanning microscopy (CLSM) images of organic filler particles (Lee *et al*. 2013). This study considers the effect of surface modifications of organic fillers made of BG and OPF with cationic and oxidized starches on the strengths and reductions in drying energies of paperboards.

EXPERIMENTAL

Materials

Brewers' grain and oil palm frond were provided by Hitejinro Co. LTD. (South Korea) and Daeyoung Powertech Co. LTD. (South Korea), respectively. To modify the surfaces of the BG and OPF fillers, cationic and oxidized starches were obtained from Samyan Genex Co. LTD. (South Korea) and Dasesang Co. LTD (South Korea). Korean old corrugated container (KOCC) pulp was used to prepare the laboratory handsheets. To retain small particles of the organic fillers in the wet web, cationic PAM (or Percol 175) supplied from Ciba (South Korea) was used as a retention aid.

Methods

Manufacturing organic fillers and preparation of starch solutions

As Brewers' grain and oil palm frond were supplied in the form of wet powders, they were dried in a dry oven (WOF-155, DAIHAN Scientific; Korea) at 105 °C for 48 h. The grinding process was carried out to make the BG and OPF organic fillers using a Wonder Blender (WB-01, Sanplantec; Japan) at 25,000 rpm for 20 s. The ground organic fillers were placed in a vibratory sieve shaker (J-VSS, Jisico; Korea) equipped with 60-mesh screens to remove the particles that could not pass through, following a Korean patent (Lee *et al*. 2009). The average particle size of the organic fillers was measured using a particle size analyzer (1090, Cilas; France).

Cationic and oxidized starches were cooked at 90 to 95 °C for 30 min. After cooking, the starch solutions were cooled rapidly to room temperature, and viscosity and charge density were determined. The Brookfield viscosity for the 0.5% solution was measured at 25 °C, and the charge density for the 0.1% solution was detected using a streaming current detector (PCD, BTG; Germany). Table 1 shows the viscosities and charge densities of the starches.

Surface modification of organic fillers using starch solutions

The conditions of the surface modifications are shown in Table 2, and Fig. 1 shows the flow diagram of the surface modifications. Brewers' grain and oil palm frond organic

fillers were diluted to 0.1% consistencies using distilled water. The addition levels of the cationic starch were 1.5, 2.0, and 2.5% of oven-dried organic fillers, and those of the oxidized starch were 0.5 and 1.0% of oven-dried organic fillers, according to the zeta potential experiments of the previous study (Lee *et al*. 2013). As the BG and OPF organic filler particles had a negative charge when they were suspended in the distilled water (Lee *et al*. 2013), the cationic starch was first added to the organic filler suspension and mixed at 600 rpm for 20 min. In cases 1 through 3, the organic filler slurries were carried to the next step, and in cases 4 and 5, the oxidized starch was added to the organic filler suspension and mixed at 600 rpm for 20 min. One layer of cationic starch was applied in cases 1 through 3 and two layers of the cationic and oxidized starches were applied in cases 4 and 5 on the surface of the organic filler particles. After the addition of the starch solutions to the organic filler suspensions, the BG and OPF organic filler powders were collected using a rotary evaporator (N-1110SW, EYELA; Japan). To determine whether the surface modifications were carried out properly, the zeta potentials of the organic fillers were measured using a Zeta-potential analyzer (Nano ZS, Malvern; UK).

Table 1. Viscosities and Charge Densities of the Cationic and Oxidized Starches

Starch type	Viscosity (cPs at 0.5%, 25 °C)	Charge density (meq/g)
Cationic starch	111.4	+ 0.75
Oxidized starch	7.0	-0.68

Table 2. Surface Modification Conditions Based on Addition Levels of Starches

Case No.	Cationic starch addition level (% on oven dried) organic fillers)	Oxidized starch addition level (% on oven dried organic fillers)
1	1.5	0.0
2	2.0	0.0
3	2.5	0.0
4	1.5	0.5
5	1.5	1.0

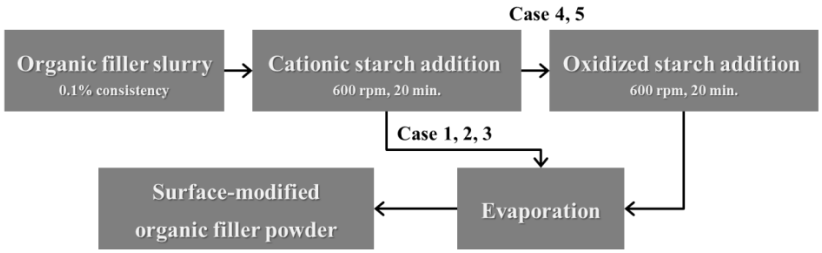

Fig. 1. Flow diagram of the surface modifications of the organic fillers

Preparation of handsheets and measurement of their physical properties

After the KOCC was soaked for 18 h, disintegration was carried out at 10% consistency for 30 min using a standard disintegrator. The disintegration time was determined by identifying whether all the individual fibers were separated. After disintegration, the KOCC was diluted to a 0.5% consistency for handsheet preparation.

Handsheets with grammages of 100 ± 4 g/m^2 were produced by adding surface-modified BG and OPF organic fillers according to the TAPPI standard T205 sp-06 (2006). After the organic fillers were added to the pulp suspension and mixed for 1 min, cationic PAM was added and mixed for 1 min at 600 rpm. Then, handsheets with grammages of 100 g/m^2 were prepared.

The handsheets were wet-pressed at 3.5 kg$_f$/cm^2 for 5 min and dried at 120 °C using a laboratory wet press and a cylinder dryer, respectively. The dried handsheets were conditioned at 23 °C and at 50% RH to control the moisture content of the handsheets at 8%. The physical properties of the handsheets, including the bulks (TAPPI T411 2010), breaking lengths (TAPPI T494 2006), burst indices (TAPPI T403 2010), and compressive strengths (TAPPI T818 2007), were measured.

The sheets were analyzed for increased bulk using a scanning electron microscope operating at an accelerating voltage of 15 kV.

Evaluation of the reductions in the drying energies of handsheets

The moisture content of the wet web was created by sheet forming and wet pressing (the after-pressing moisture content), and was selected as a measure to indicate the potential drying energy requirement. It is expected that a lower after-press moisture content, indicating a lower amount of water that has to be removed from the drying sections, means a lower drying energy requirement; Peel (1999) reported that an increase of 1% sheet dryness reduces the heating requirement in the dryer section by about 4%. Therefore, the increase in dryness after wet pressing was defined as the reduction in drying energy and computed, as shown in Eq. 1. Handsheets for these measurements were prepared and pressed in the same manner as those for physical testing. After wet-pressing, the moisture contents of the handsheets were measured using a dry oven (WiseVen, Daihan Scientific; Korea).

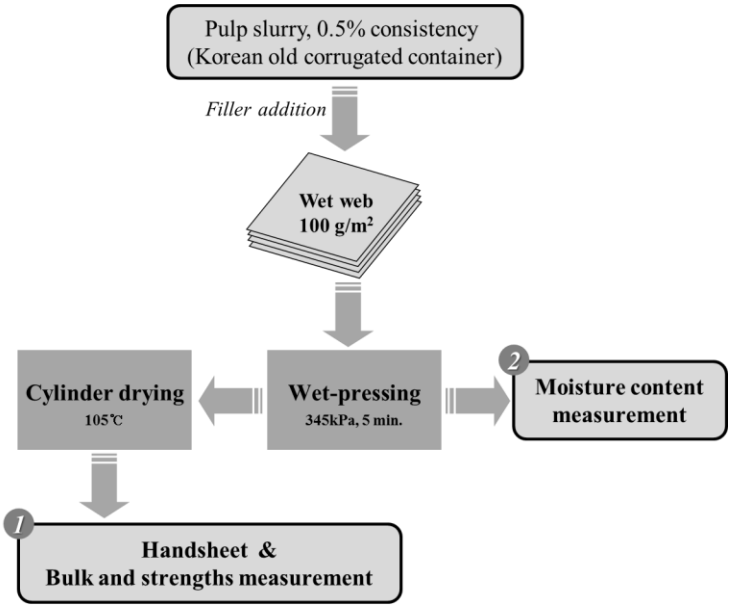

Fig. 2. Flow diagram of the experimental regimen

Figure 2 summarizes the experimental regimen of handsheet preparation and the evaluation of dryness,

$$\text{Increase in dryness after pressing} = \frac{MC_{control} - MC_{addition}}{MC_{control}} \times 100 \quad (1)$$

where $MC_{control}$ is the after-pressing moisture content of a sheet containing no organic filler, and $MC_{addition}$ is the after-pressing and the moisture content of a sheet containing an organic filler.

RESULTS AND DISCUSSION

Zeta Potentials and Appearances of the Surface-modified Organic Fillers

Because BG and OPF, which contain 41% and 29% of lignin, respectively, are lignocellulosic materials, they have negative charges in water (Hubbe and Rojas 2008); their negative zeta potentials were determined, as shown in Table 3. When the addition of cationic starch increased from 0% to 1.5%, the zeta potentials of BG and OPF increased to positive values.

When we added more than 1.5% of the cationic starch, the zeta potentials of BG and OPF increased linearly. On the other hand, when 0.5% of the oxidized starch was added to the BG and OPF containing 1.5% of the cationic starch, the zeta potentials changed to negative values.

When the addition of oxidized starch increased, the zeta potentials of BG and OPF decreased linearly. Positive zeta potentials indicated the adsorption of the cationic starch by the BG and OPF fillers, and the negative charges after the addition of the oxidized starch indicated the formation of an oxidized starch layer on the cationic starch layer. Therefore, it was concluded that the surface modifications were carried out properly by identifying the zeta potentials of BG and OPF.

Figures 3 and 4 show the images of the original BG and OPF fillers, as well as those of the modified BG and OPF fillers. No significant changes were observed in the appearances and colors caused by surface modifications, so it was proposed that the modified BG and OPF fillers could be used as alternative organic fillers in place of the original ones.

Table 3. Zeta Potentials of the Original and Modified BG and OPF Fillers

Case No.	BG fillers (mV at pH 6.0 - 7.0)	OPF (mV at pH 6.0 – 7.0)
Control	- 9.0	- 20.5
1	+ 4.5	+ 2.3
2	+ 4.7	+ 3.2
3	+ 5.0	+ 4.2
4	- 2.8	- 3.8
5	- 4.0	- 4.9

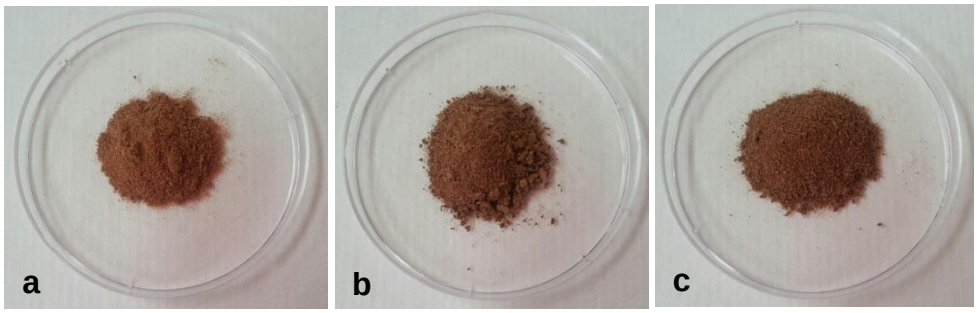

Fig. 3. Images of the (a) original BG, (b) modified BG with 1.5% cationic starch, and (c) modified BG with 1.5% cationic starch and 1.0% oxidized starch

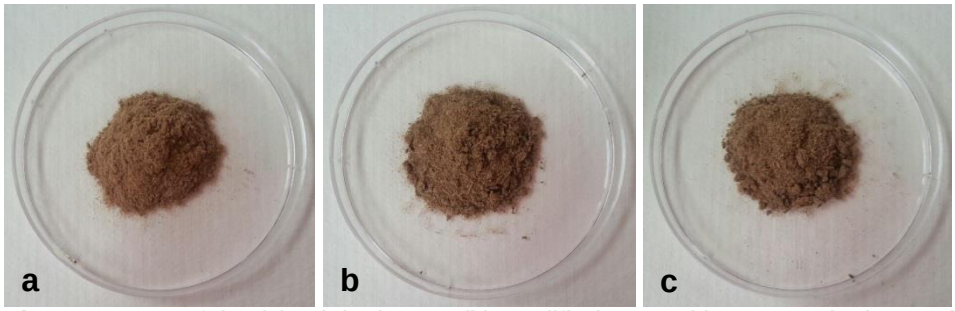

Fig. 4. Images of the (a) original OPF, (b) modified OPF with 1.5% cationic starch, and (c) modified OPF with 1.5% cationic starch and 1.0% oxidized starch

Effects of Surface-modified Organic Fillers on Physical Properties of Handsheets

Figure 5 shows the effects of the original and modified BG and OPF fillers on the bulks of the handsheets. Both of the original organic fillers increased the bulks of the handsheets. The original OPF showed higher handsheet bulks than the original BG because the OPF fillers were larger than the BG fillers, as shown in Table 4. It was concluded that the organic fillers improved bulk. The modified BG and OPF fillers improved the bulk more than the unmodified BG and OPF fillers due to the increase of particle size. The third condition that contained only 2.5% of the cationic starch showed the greatest bulk among the conditions of the surface modifications. The surface modifications caused the flocculation of the organic fillers, so the surface-modified organic fillers improved the bulk more than the unmodified ones.

Figures 6 through 8 show the effects of the BG and OPF fillers on the breaking lengths, burst indices, and compressive strengths of the handsheets. All of the strengths of the handsheets containing the organic fillers decreased as the amounts of their additions increased. The increased bulks resulted in decreases in sheet strengths because the organic fillers were located between fibers and interfere with the fiber bonds, as shown in Fig. 9 (arrow). However, the surface-modified organic fillers showed improved strengths of the handsheets compared to the unmodified organic fillers. The graph of the breaking lengths showed that cases 3 or 5 resulted in higher breaking lengths than other cases. The graphs of the burst indices and compressive strengths also showed that cases 3 or 5 resulted in higher strengths than other cases. In case 3, 2.5% of the cationic starch was applied to the organic fillers. In case 5, 1.5% of the cationic starch and 1.0% of the oxidized starch were subsequently applied to the organic fillers. Therefore, for both conditions 3 and 5, the total amount of the starches was 2.5%.

The purpose of the surface modifications was to acquire the greatest strengths with the greatest bulks of the handsheets. To determine the best conditions for surface modifications, the relationship between bulk and strength was analyzed. Figure 10 shows the relationship between bulk and breaking length, and Fig. 11 shows the relationship between bulk and burst index. Bulk showed a reciprocal relationship with strength. The unmodified BG and OPF showed the lowest strengths with the lowest bulks. The surface modifications with cationic starch showed higher strengths than with cationic and oxidized starches together. In particular, the strengths of the sheets with 2.5% of the cationic starch showed the highest values among the conditions of the surface modifications. Therefore, surface modifications with a sufficient amount of cationic starch are judged to be the most effective for improving the strengths of paperboards that contain organic fillers.

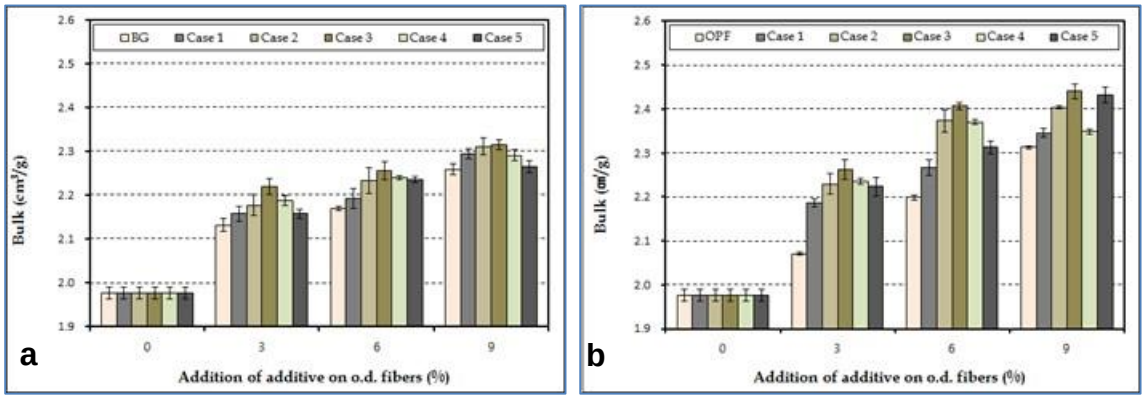

Fig. 5. The effect of surface modifications of (a) BG and (b) OPF fillers on the bulk of sheets. Data presented as the average ± standard deviation

Table 4. Average Particle Sizes of Original Organic Fillers

Organic filler		Average particle size (μm)
BG filler	Original	65
	Case 3	87
	Case 5	75
OPF filler	Original	150

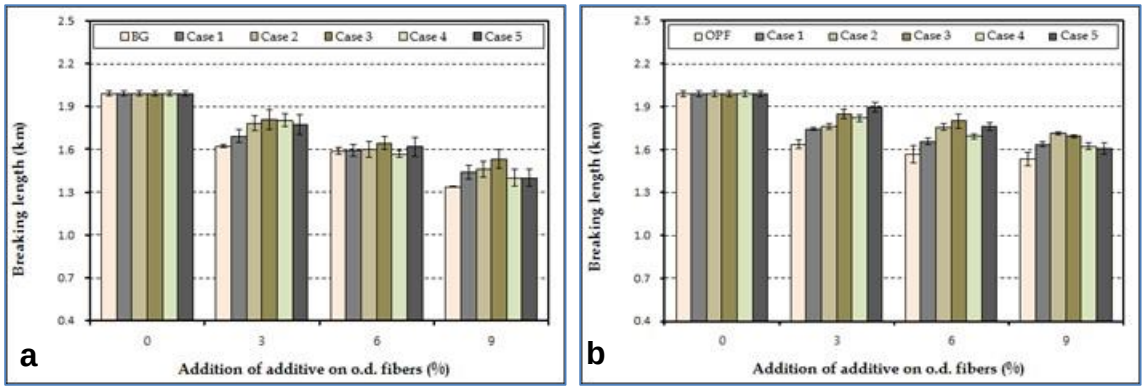

Fig. 6. The effects of the (a) BG and (b) OPF fillers on the breaking lengths of the sheets. Data presented as the average ± standard deviation

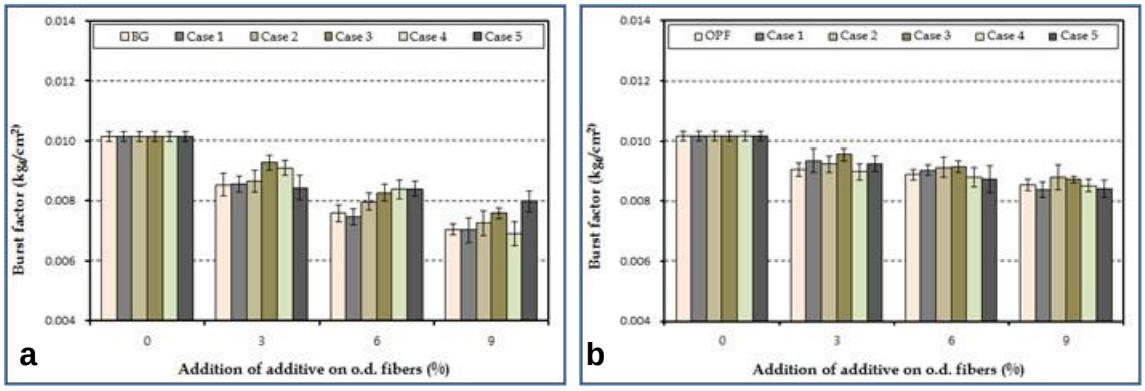

Fig. 7. The effects of the surface modifications of the (a) BG and (b) OPF fillers on the burst indices of the sheets. Data presented as the average ± standard deviation

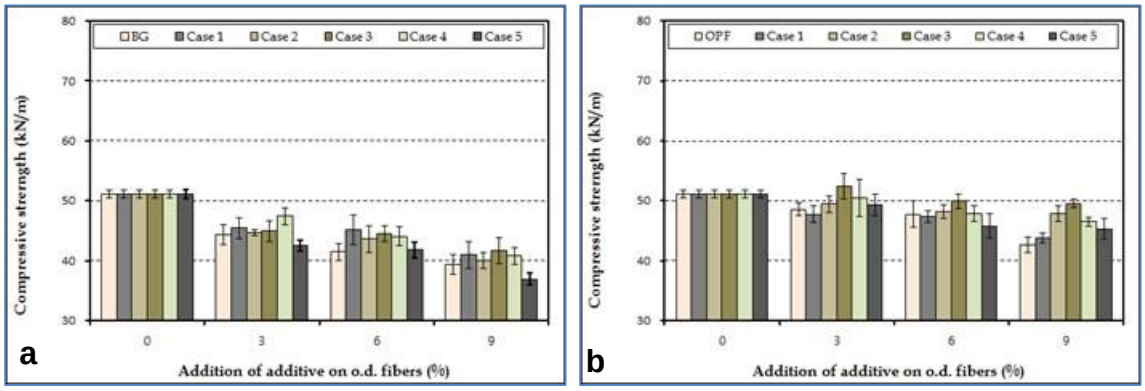

Fig. 8. The effects of the surface modifications of the (a) BG and (b) OPF fillers on the compressive strengths of the sheets. Data presented as the average ± standard deviation

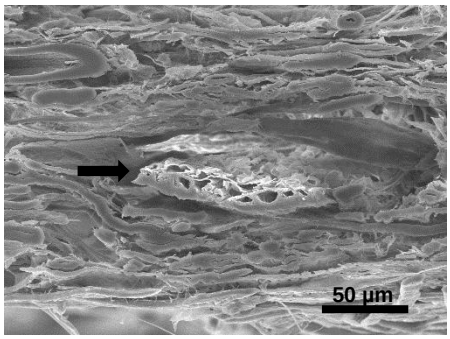

Fig. 9. Scanning electron micrograph of BG organic filler particle located between fibers

Effects of Surface-modified Organic Fillers on After-press Moisture and on Reductions in Drying Energies

To simplify the effect of a reduction in drying energy consumption in this study, the concept of reductions in drying energies was developed and calculated with the final after-press moistures of the sheets with and without organic fillers. Figure 11 shows the moisture content and the reductions in the drying energies of the sheets as a function of BG

addition. The control indicates the after-press moisture content of a sheet containing no organic fillers.

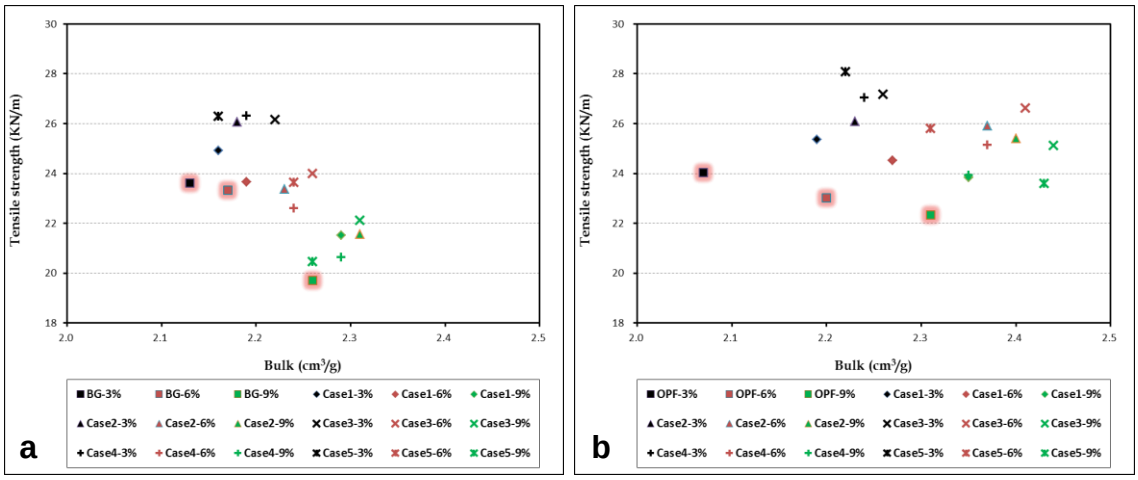

Fig. 10. The relationship between the bulks and tensile strengths of the handsheets containing surface-modified (a) BG and (b) OPF. Data presented as the average ± standard deviation

As BG fillers were added to the handsheets, the after-press moisture content decreased. The BG fillers increased the bulk and decreased the after-press moisture content simultaneously by increasing the gap between fibers and the amount of more hydrophobic organic fillers than OCC in the sheets relative to the amount in the sheets containing no BG fillers.

With the introduction of the surface modifications, the after-press moisture content decreased dramatically. In particular, case 3 showed the lowest moisture content. The calculated reduction in the drying energy of case 3 also increased dramatically, as the addition of the surface modified BG increased to 9%.

Figure 12 shows the moisture contents and the reductions in the drying energies of the sheets as a function of the OPF addition. The OPF also decreased the after-press moisture contents of the sheets, and condition 3 showed the lowest moisture content and the highest reduction in drying energy. The reduction in the drying energies of the BG fillers was higher than that of the OPF fillers.

It was concluded that a surface modification with 2.5% of the cationic starch was the most effective way to improve the strengths and the consumptions of drying energy, as well as to increase the bulk of paperboard.

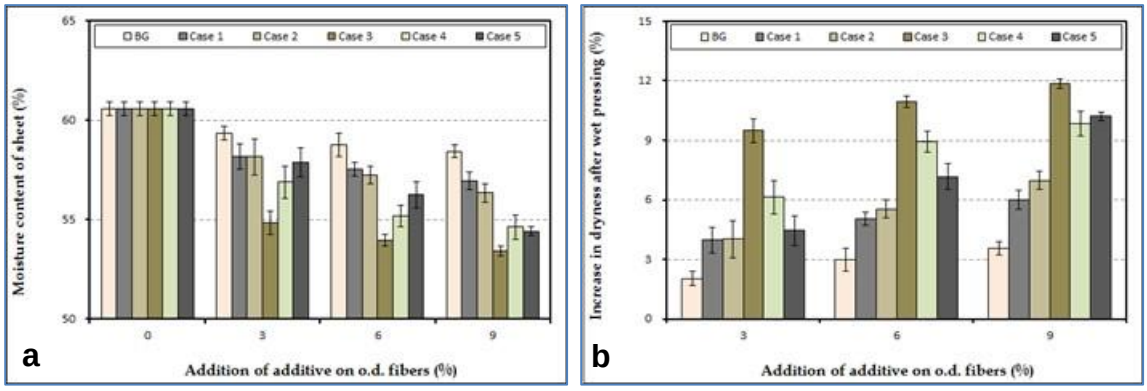

Fig. 11. The effects of the BG fillers on (a) the moisture contents of the sheets after wet pressing and (b) increase in dryness after wet pressing. Data presented as the average ± standard deviation

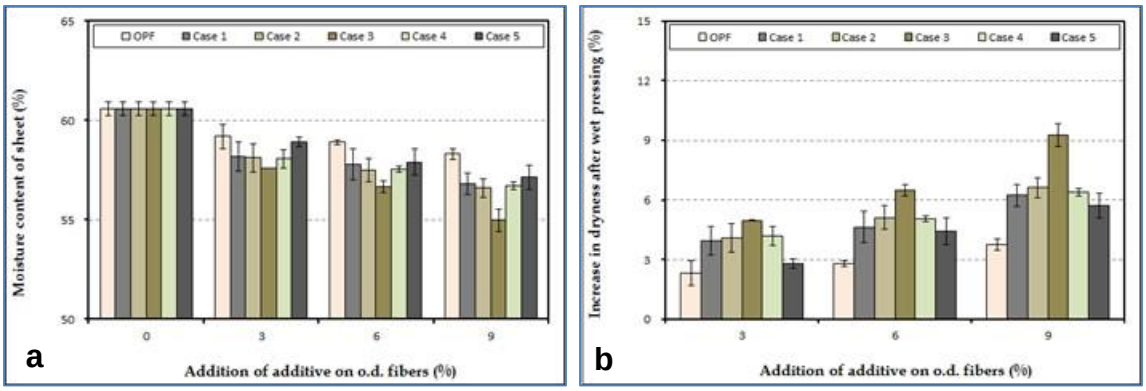

Fig. 12. The effects of the OPF fillers on (a) the moisture contents of the sheets after wet pressing and (b) increase in dryness after wet pressing. Data presented as the average ± standard deviation

CONCLUSIONS

Organic fillers were surface-modified as a method to improve paperboard strengths. The goal was to determine the most effective conditions for surface modifications. The following conclusions were drawn from the results:

1. The surface modifications of the organic fillers with starches were effective in improving the bulks and strengths of the sheets simultaneously, as well as in decreasing the after-pressing moisture content. Particularly, a sufficient amount of cationic starch is beneficial to improving bulk, strength, and reductions in drying energy.

2. Among the many cases of surface modifications, those with 2.5% cationic starch were the most effective in improving the strengths and the drying energy reduction of the sheets.

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