USING CALCIUM CARBONATE WHISKERS AS PAPERMAKING FILLER

Xiaoyu Chen, Xueren Qian,* and Xianhui An

Whiskers, having large length/diameter ratio, are fiber-shaped single crystals. The technical possibility of using calcium carbonate whiskers as papermaking filler to replace conventional powder-like calcium carbonate was investigated. The results showed that it may be feasible to use calcium carbonate whisker as papermaking filler. Compared with conventional precipitated calcium carbonate, calcium carbonate whisker had higher retention efficiency. The use of calcium carbonate whisker also favorably affected the strength properties of paper sheets. A model was proposed to suggest the mechanism for paper strength improvement. The whiskers filled in paper sheets could increase the friction between fibers, thus increasing bonding strength. Moreover, the strength properties of paper were further improved because calcium carbonate whiskers were partly embedded in pulp fiber walls.

Keywords: Calcium carbonate whiskers; Fillers; Paper strength

*Contact information: Key Laboratory of Bio-based Material Science and Technology of Ministry of Education, Northeast Forestry University, Harbin, Heilongjiang Province, 150040, P. R China; *Corresponding author: qianxueren@yahoo.com.cn*

INTRODUCTION

Calcium carbonate ($CaCO_3$) has become the dominant filler in the production of wood-free uncoated paper and coating base stock (Laufmann and Forsblom 2000). Substituting part of fibers in paper stock with $CaCO_3$ fillers has been practiced for more than ten decades. Using calcium carbonate fillers has the following benefits (Zhao et al. 2005):

- It protects the environment through supplementing virgin fibers.
- It increases paper production capacity without the addition of extra pulping capacity.
- It reduces operating costs associated with paper production.
- It improves paper properties, such as brightness, opacity, gloss, porosity, and printability.
- It enhances the quality of most paper grades.

However, two problems are usually associated with the use of fillers. First, filler particles added to fibers suspended in water are not easily retained in the forming sheet, because they are often too small to be entrapped mechanically and because filler particles and fibers are negatively charged, so they repel each other. Second, filler particles can interfere with the fiber-fiber bonding; therefore the tensile strength of the filled paper suffers (Al-Mehbad 2004).The addition of $CaCO_3$ filler beyond a certain level will cause some problems, such as reduced paper strength and stiffness, increased size demand, abrasion, and dusting (Hu et al. 2009). So developing filler varieties that can overcome these problems has become a global interest.

Several approaches have been explored to increase $CaCO_3$ filler content without obvious detriment to paper quality. Gill (1991) modified the surface of precipitated calcium carbonate (PCC) filler to improve filler-fiber bonding using epichlorohydrin and polyamino-amide or polyamine. Middleton et al. (2003) loaded PCC particles into the lumens of softwood bleached kraft pulp fibers up to the level of 0.3 g filler/g fiber by pretreatment of the fibres with a cationic polyacrylamide retention aid followed by the use of elevated temperatures (75°C). The handsheet properties of pulps with lumens loaded with PCC were evaluated in terms of their potential applications in industry. Subramanian et al. (2005) prepared composites of PCC and pulp by co-precipitating calcium carbonate on pulp, and found the Scott bond strength of papers with composite filler addition was higher than that of the PCC reference paper. Zhao et al. (2005) used starch-modified PCC as papermaking filler to improve the strength of high filler content papers. Unfortunately, to date, none of these technologies have delivered a practical, broadly accepted solution for paper manufacturers.

In contrast to conventional $CaCO_3$ fillers, calcium carbonate whiskers (CCW), have a large length/diameter ratio, consisting of fiber-shaped single crystals. Some patents disclosed that needle-like calcium carbonate filler might give better properties of paper with high bulk, brightness, opacity, and strength, as well as improved retention (Fairchild and Thatcher 2000; Kazuto et al. 2001). However, detailed studies are still scarce. In a very recent study, needle-like aragonite was synthesized using calcium hydroxide and carbon dioxide as reactants in the presence of magnesium chloride, and the physical and optical properties of the paper handsheets containing these needle-like aragonite fillers were evaluated (Hu et al. 2009). The results indicated that tensile strength, *Z*-direction tensile strength, and folding endurance of the paper were improved by the needle-like aragonite crystals compared to the paper using commercial PCC as filler. In this study, the retention of CCW fillers was measured, the physical and optical properties of the CCW filled paper were evaluated, and a model was proposed based on SEM, SEM-EDX analysis to suggest the mechanism of paper strength improvement.

EXPERIMENTAL

Materials

The pulp used for making handsheets in this study was a commercial dry-lap bleached softwood kraft pulp with a beating degree of 17ºSR and an ISO brightness of 87%. Precipitated calcium carbonate (PCC) fillers with an ISO brightness of 92.88% were provided by Guilin Wuhuan Industry development Co., Ltd. (Guangxi, China). Calcium carbonate whisker (CCW) fillers with an ISO brightness of 82.65% were obtained from Lucheng Jinsheng Mineral Fiber Technology Co., Ltd. (Shanghai, China). Cationic polyacrylamide (CPAM) with a molecular weight of more than 3 million and an ISO brightness of 82.57% used as retention aid was obtained from Tianjin Yongda Chemical Reagents Development Center (Tianjin, China).

Handsheets Preparation

First of all, a certain amount of commercial bleached softwood kraft pulpboard was soaked with water and beaten in a Valley beater to about 37°SR. Then, a pulp suspension was made by mixing beaten pulp with water. Next, a selected amount of filler (CCW or PCC) was added to the pulp suspension. Then 0.03% of CPAM (based on the total mass of oven-dry pulp and filler) was added to papermaking furnishes while continuing to stir. Finally, a handsheet with a pre-determined basis weight of 60g/m^2 was made using tap water.

Measurement of Filler Retention

The filler retention (R) was determined by measuring the ash content of the handsheet. The determination of ash content was conducted in a muffle furnace at 575$\pm$25°C. The filler retention (R) was calculated as follows,

$$R\,(\%) = [\,(A - B)\,/\{C\times(1 - D)\}]\times 100 \quad (1)$$

where, A is the ash content of handsheet (%); B is the ash content of control handsheet (i.e. pulp fiber) (%); C is the amount of filler added (%); and D is the ignition loss of filler (%).

Measurement of the Physical Properties of Handsheets

The tensile and burst strengths of handsheets were measured according to the Chinese National Standards GB/T 453-2002 and GB/T 454-2002, respectively. The zero and short span (0.4 mm) tensile measurements of dry and wet strips were carried out using Pulmac's Z-Span 1000 according to TAPPI Test Methods T 231, T 273, T 276, and T 279, respectively. The brightness and opacity of handsheets were measured according to the Chinese National Standards GB/T 7974-2002 and GB/T 1543-2005 respectively. The air permeability of handsheets was measured according to the Chinese National Standard GB/T458-1989.

SEM and SEM-EDX Analysis

Scanning electron microscopy (SEM) and scanning electron microscope/energy-dispersive X-ray analysis (SEM-EDXA) was done with a FEI Quanta-200 environmental scanning electronic microscope. The specimens were coated with gold before observation and analysis.

RESULTS AND DISCUSSION

Filler Retention

Figure 1 shows the variation of the retention of CCW and PCC fillers in paper sheets with increasing addition of filler. From Fig. 1 it is apparent that the retention of CCW was significantly higher than that of PCC at the same addition level, regardless of whether or not CPAM was being used as a retention aid. CPAM could obviously improve the retention of CCW and PCC, but was more effective for CCW. The retention of CCW and PCC increased with increasing the amount of filler added when CPAM was used as a retention aid. The peak values occurred when the fillers addition was equal to 20%. The values showed a decreasing trend beyond 20% filler addition.

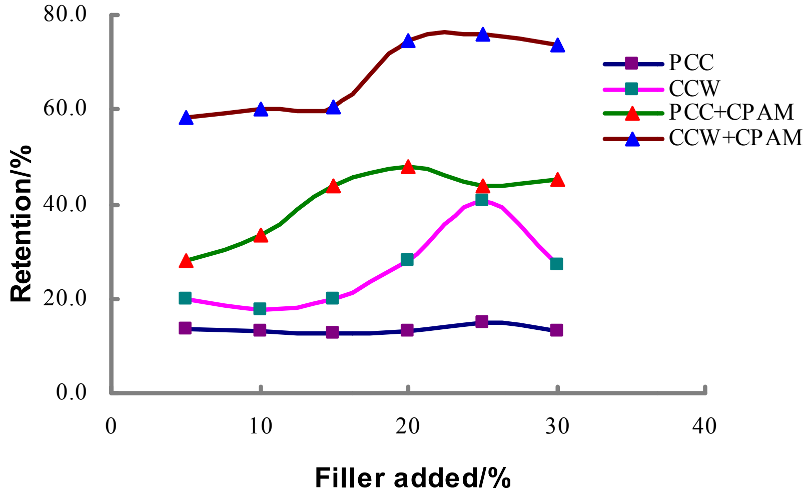
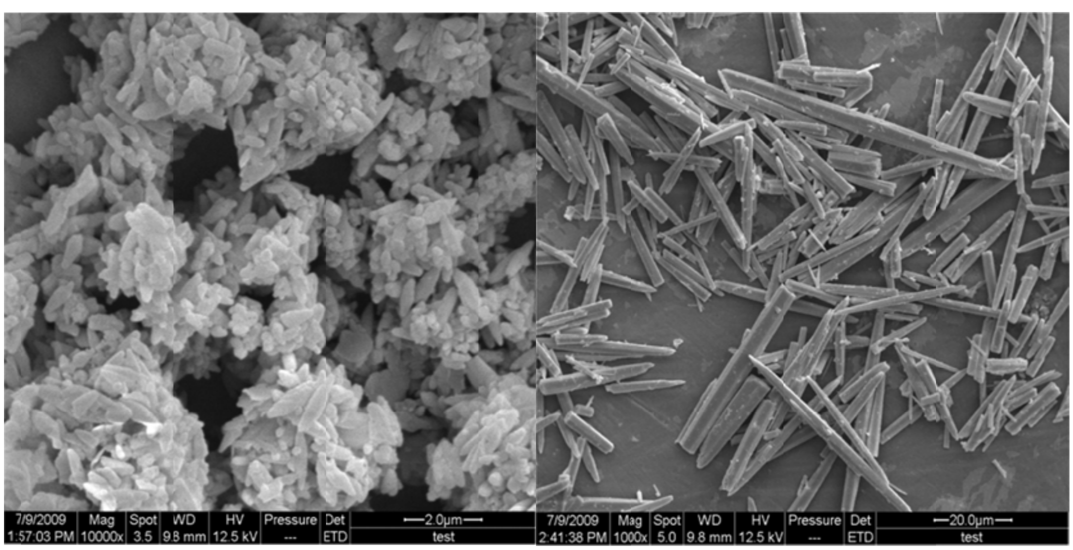


Fig. 1. Relationship between filler retention and the amount of filler added

The retention of filler particles in the paper web is traditionally considered to be due to a combination of adsorption, filtration, sedimentation, and flocculation (Eklund and Lindstrom 1991). The filtration mechanism can partly explain the observed high retention of CCW. Figure 2, parts (a) and (b), shows the SEM images of PCC and CCW, respectively. The rice grain- or spindle-shaped scalenohedral PCC exhibited a major diameter of 1.5 to 1.8μm and a minor diameter of 0.2 to 0.5μm, while the needle- or rod-shaped CCW had an aspect ratio of 15 to 40 with a diameter of 0.5 to 3.0μm. Therefore, it seems reasonable that CCW showed higher retention efficiency than PCC.

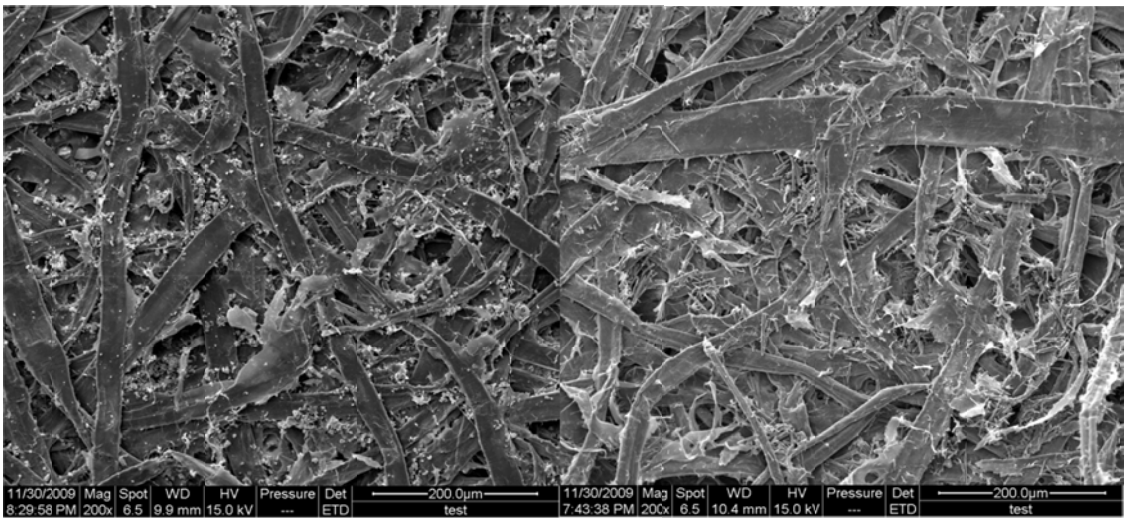


(a) **(b)**

Fig. 2. SEM images of PCC (a) and CCW (b)

Filler Distribution

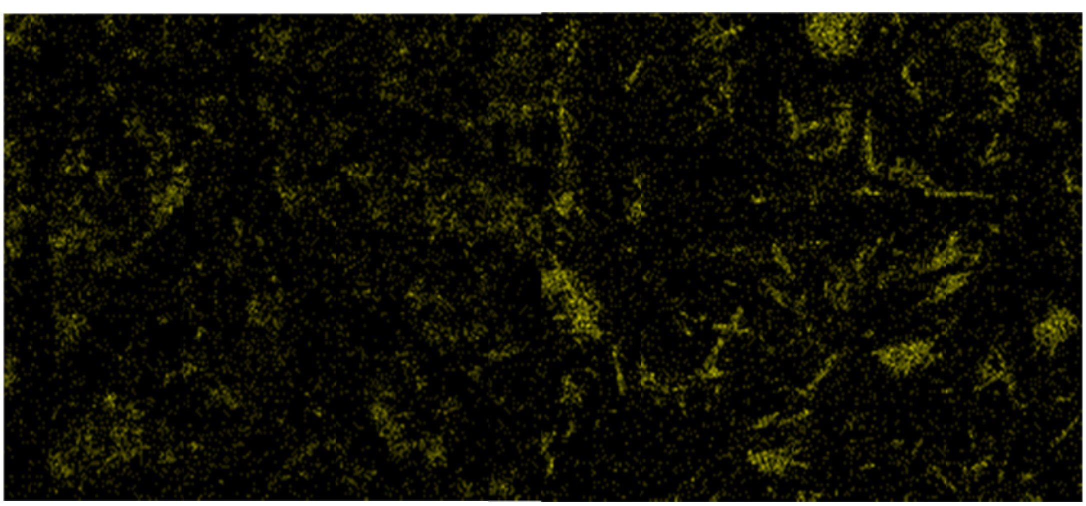
Figure 3, parts (a) and (b), shows the SEM images of PCC and CCW in paper samples, respectively. From Fig. 3(a) it is apparent that the PCC particles in the paper sample were nearly round in shape, and they were distributed on the pulp fiber surface or filled into the gaps between pulp fibers. On the other hand, from Fig. 3(b) one can see that the CCW in the paper sample appeared as short, fine fibers, and they were distributed on the fiber surface or filled into the gap between pulp fibers or partly embedded into pulp fiber walls.



(a) (b)

Fig. 3. SEM images of PCC-filled sample (a) and CCW sample (b)

Figures 4(a) and 4(b) show the calcium cartographies of PCC- and CCW-filled paper samples, respectively. From Fig. 4, it is apparent that the PCC filler particles were granular, while CCW were short, fibrous and had a higher length/diameter ratio.



(a) (b)

Fig. 4. Calcium mapping of PCC- (a) and CCW-filled (b) samples

However, from Fig. 4 it is also clear that the distributions of two fillers in the paper sheets were not very uniform, and some aggregated filler clusters were observed, especially in the case of CCW. The presence of such clusters was attributed to the use of a static sheet former. The dispersion of CCW will be further researched.

Table 1 shows the energy spectrum results of PCC- and CCW-filled paper sheets. Table 1 shows that the weight and atomic fractions of calcium element in the PCC-filled paper sheet were 8.02% and 2.90% respectively, while the weight and atomic fractions of calcium element in the CCW-filled paper sheet were 8.92% and 3.25%, respectively, and the values were higher than those in PCC-filled paper sheet. This was in agreement with the observed fact that the retention of CCW was higher than that of PCC.

Table 1. Energy Spectrum Results of PCC- and CCW-filled Samples

Element	PCC-filled paper		CCW-filler paper	
	Wt%	At%	Wt%	At%
CK	45.77	55.24	44.75	54.44
OK	46.20	41.86	46.33	42.31
CaK	8.02	2.90	8.92	3.25

Strength Properties

Tensile index and burst index

Figures 5 and 6 show the relationships between tensile index, burst index, and the percentage of filler in paper respectively. Both the tensile index and burst index first increased and then decreased with increasing the percentage of filler in paper. When adding a small amount of fillers, the fillers could be more evenly distributed in the fiber network, and they have little effect on the formation of hydrogen bonds between fibers. When the paper sheet is under tension, the fillers increase entanglement friction between fibers, which is beneficial for paper strength properties. However, adding large amounts of fillers will reduce the paper strength properties due to the decrease of contact area between the fibers.

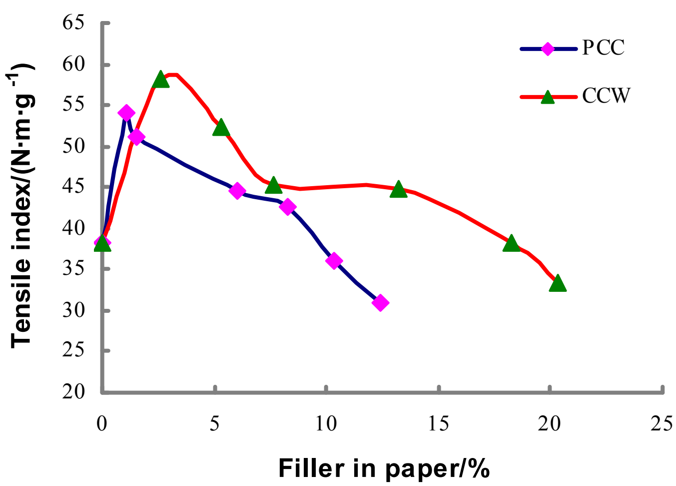


Fig. 5. Relationship between tensile index and percentage of filler in paper

The tensile index and burst index of CCW-filled paper were higher than those of PCC-filled paper at the same filling level. This means that more CCW fillers may be loaded while retaining the same strength level, compared with PCC fillers. The particle size and shape of fillers are important factors in determining the strength properties of the filled paper. In general, the smaller the filler particles, the greater their negative effect on strength (Bown 1998). Smaller particles are able to prevent inter-fiber contact over a larger fraction of the available surface area (Hubbe 2004).

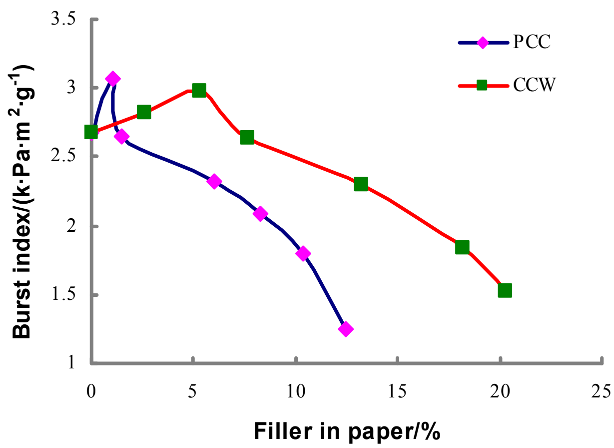


Fig. 6. Relationship between burst index and percentage of filler in paper

Fiber bonding number and fiber strength number

The zero/short span tensile tests of dry and wet strips were measured according to the TAPPI Test Method. This is a fast and economical method for assessing the strength of various types of papermaking pulp (Cowan 1995; Somboon and Paulapuro 2009). According to these data, the fiber bonding number and the fiber strength number were calculated with the following equations:

$$Fiber\ bonding\ number\ (\%) = \frac{Avg.of\ wet\ short\ spans}{Avg.of\ dry\ short\ spans} \times 100 \quad (2)$$

$$Fiber\ strengh\ number\ (\frac{N}{cm}) = \frac{Avg.of\ wet\ zero\ span \times (actual\ basis\ weight)}{target\ basis\ weight} \quad (3)$$

Figures 7 and 8 show the relationships between fiber bonding number, fiber strength number, and the percentage of filler in paper, respectively. From Figs. 7 and 8 it is apparent that the fiber bonding number of CCW- and PCC-filled papers had a similar variation trend, and both first decreased and then increased with increasing the amount of filler. The fiber bonding number of CCW-filled paper was slightly higher than that of PCC-filled paper. However, both of them were lower than the fiber bonding number of blank paper samples. The fiber strength number of CCW- and PCC-filled papers also had a similar variation trend, and both decreased with increasing the amount of filler. The fiber strength number of CCW-filled paper was also higher than that of PCC-filled paper. So we can conclude that the adverse influence of CCW on the fiber bonding number and the fiber strength number was lower than that of PCC. This is accordance to the tensile and burst strength results.

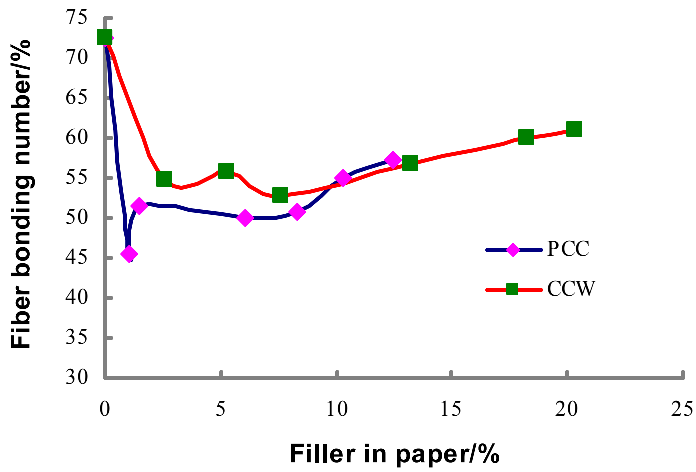


Fig. 7. Relationship between fiber bonding number and percentage of filler in paper

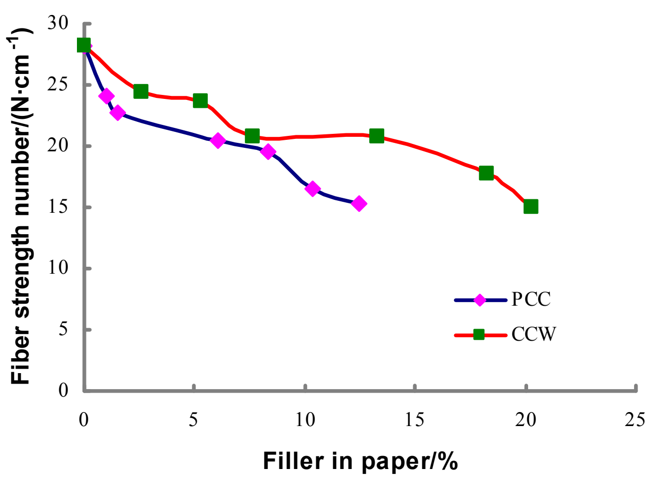
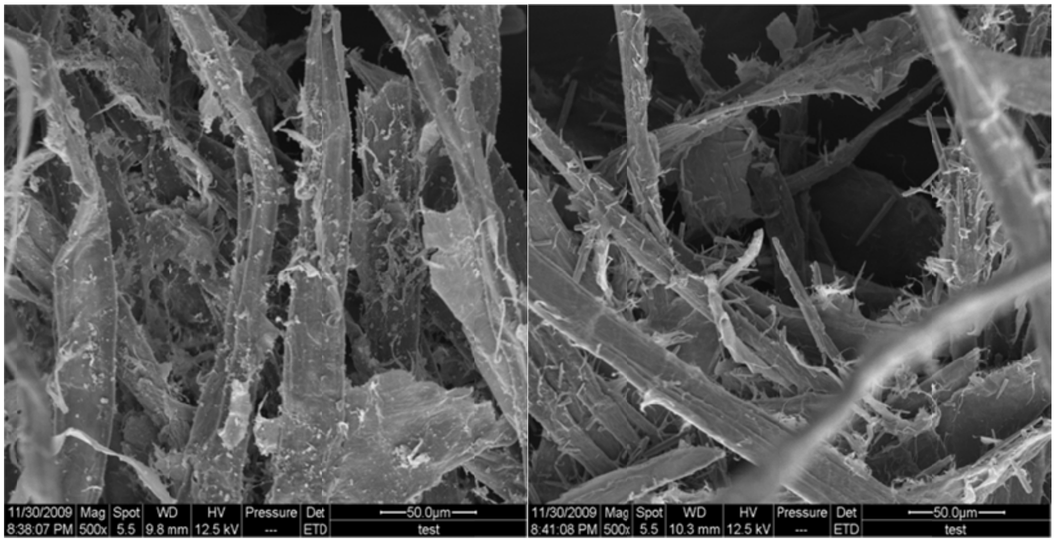


Fig. 8. Relationship between fiber strength number and percentage of filler in paper

Tensile fracture morphology

The fracture SEM images of PCC- and CCW-filled samples were examined as shown in Fig. 9(a) and 9(b). From Fig. 9(a) it is apparent that some whole fibers were pulled out from the PCC-filled paper matrix, while fractured fibers were not observed. This indicated that the fracture of paper was mainly due to the rupture of fiber-to-fiber bonds, not mainly due to the rupture of fiber itself. PCC may reduce the friction between fibers. From Fig. 9(b), we could see some CCW were entangled with the paper fibers, or embedded in the paper fibers. This indicated that the entanglement between CCW and paper fibers could increase the friction and bonding between fibers.



(a) (b)

Fig. 9. Fracture of PCC-filled sample (a) and CCW-filled sample (b)

From the above results it can be concluded that PCC would significantly reduce the paper tensile and burst strength because PCC particles in handsheets interfere with the fiber-fiber bonding. Although CCW also interferes with the formation of hydrogen bonds between fibers, resulting in decreasing strength, the rate of decline in paper strength is slower for the following reasons: (1) the size of CCW is larger than that of PCC, so the number of the isolated points generated among the fibers is greatly reduced; (2) CCW having needle-like structure can twine the paper fibers together. Like the mullite needle-like crystals of cement, this twining structure will improve strength of the materials (Hu et al. 2009).

Optical Properties

The relationship between paper brightness and the percentage of filler in paper is shown in Fig. 10.

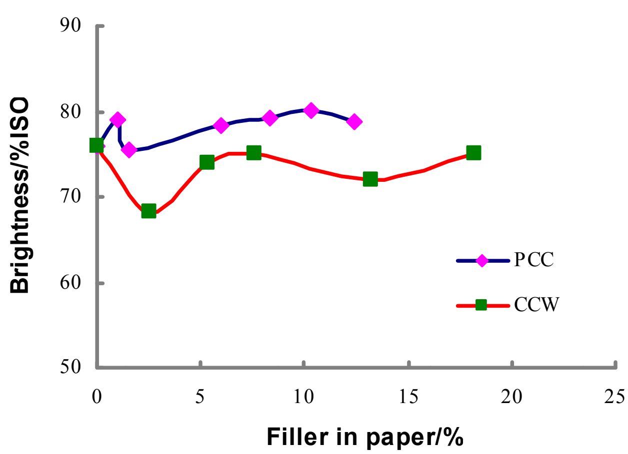


Fig. 10. Relationship between brightness and percentage of filler in paper

Obviously, the brightness of PCC-filled paper was higher than that of CCW-filled paper. This was because the brightness of CCW was 82.65% ISO, much lower than that of PCC (92.88% ISO). The lower brightness of the CCW used in this study might be related to the production method and process. The addition of the CCW used in this study had an adverse effect on the brightness of paper.

The relationship between paper opacity and the percentage of filler in paper is shown in Fig. 11. The opacity of paper increased slowly with increasing the percentage of filler in paper, and the opacity of CCW-filled paper was a little bit lower than that of PCC-filled paper.

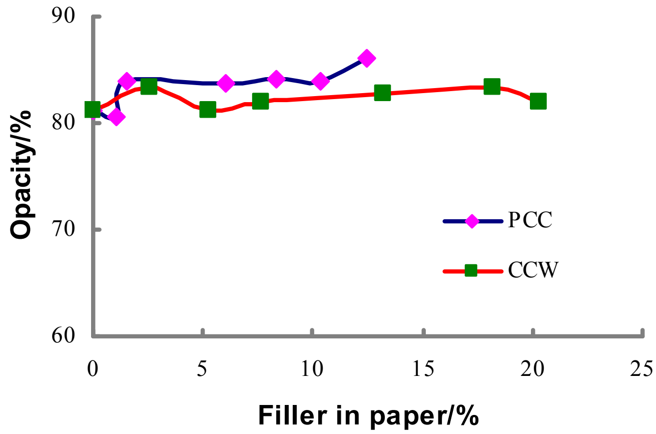


Fig. 11. Relationship between opacity and percentage of filler in paper

Air Permeability

Figure 12 shows the relationship between air permeability of handsheets and percentage of filler in paper.

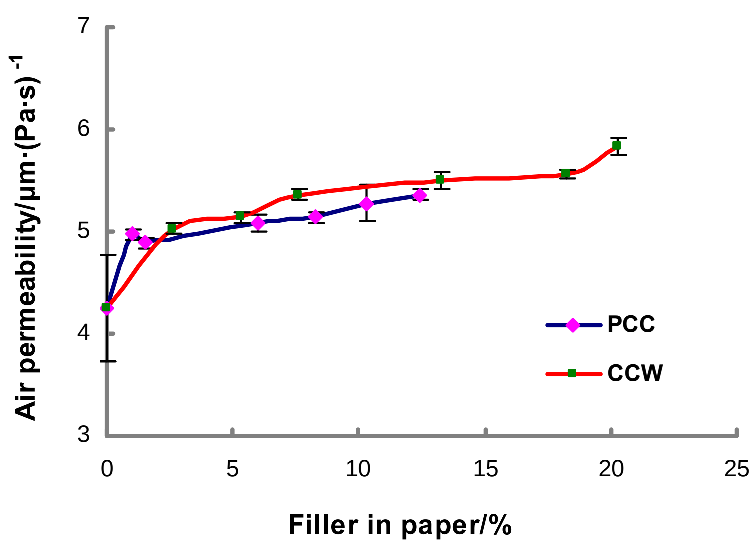


Fig. 12. Relationship between air permeability and percentage of filler in paper

From the figure it appears that the air permeability of handsheets increased with increasing the amount of filler, and the air permeability of CCW-filled handsheets was higher than that of PCC-filled handsheets. Two possible reasons to explain these observations are as follows:

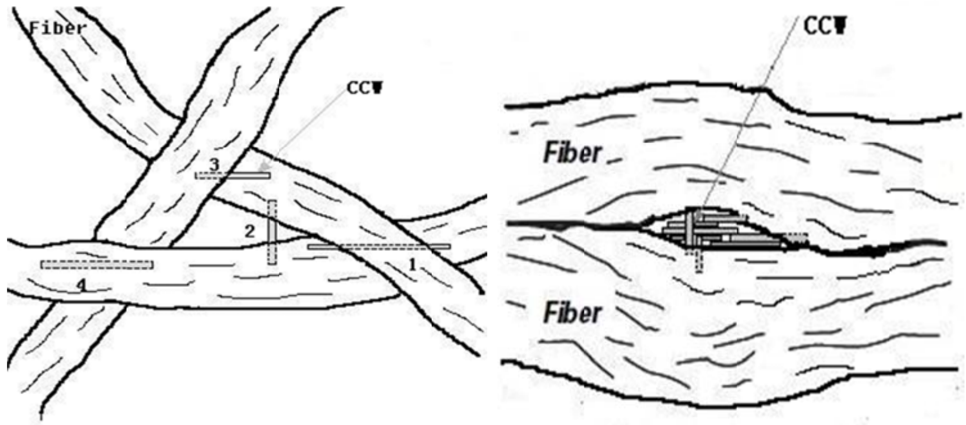
- With increasing the amount of CCW, handsheets were "supported" by whisker fillers, and became "fluffy". However, the fact which the bulk of CCW-filled handsheets was lower than that of PCC-filled handsheets negated this viewpoint.
- Owing to the special construction of CCW, with large length/diameter ratio, more voids among cellulose fibers were created.

Mechanism Model

A model was proposed to suggest the mechanism of paper strength improvement, as shown in Figs. 13 and 14. The bonding forces between CCW, PCC, and paper fibers both belong to intermolecular absorption, but there are four types of orientation between CCW and fibers as shown in Fig. 13(a): (1) CCW is distributed among fibers, (2) one end of CCW is embedded in one fiber, the other end is embedded in another fiber, (3) one end of CCW is embedded in one fiber, the other end is distributed among fibers, and (4) CCW is entirely embedded in a fiber. Although the retention of CCW in handsheets was higher than that of PCC, the strength of CCW-filled handsheet was higher than that of PCC-filled handsheets. This indicates that the strength still increased without the formation of new chemical bonds, so we can conclude that some physical effects such as friction and entanglement, different from hydrogen bonding, must exist between CCW and fibers.

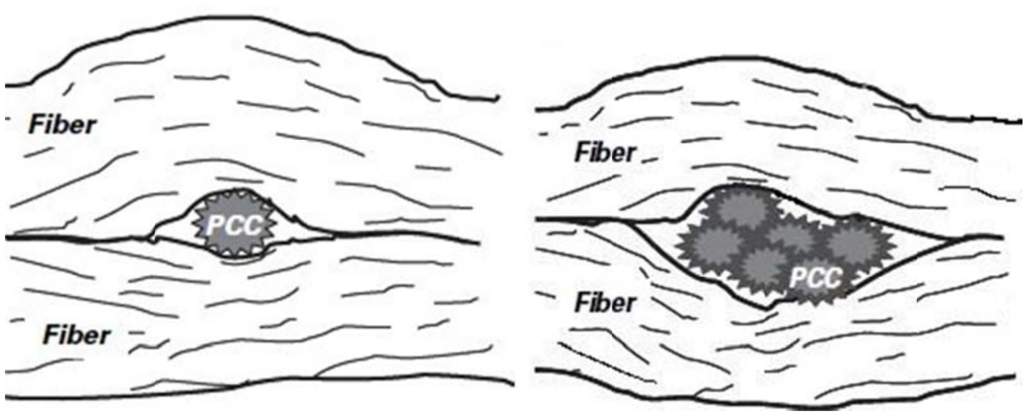
In the absence of fillers, when paper was subjected to sufficient tensile force, the bonding force of fibers was overcome, and the paper ruptured. When the CCW-filled paper was likewise subjected to tensile force, the bonding force of fibers decreased, but the strength of paper increased due to the friction between fibers and the entanglement between fibers and CCW fillers. In contrast to CCW, PCC with nearly round shape hindered fiber-fiber bonding (Xu et al. 2005; de Oliveira et al. 2009) and decreased fiber-fiber contact area, as shown in Fig. 14(a). Moreover, the flocculation of PCC led to smaller fiber-fiber contact area, as shown in Fig. 14(b). When the paper was subjected to sufficient tensile force, the friction between PCC fillers and fibers was far lower than that between CCW and fibers.

As shown in Fig. 13(b), owing to the oblate and short fiberous shape, even though CCW was flocculated, the influence on fiber-fiber contact area was far less than that of the flocculated PCC. In addition, the four orientations between CCW and fibers may still occur when CCW is flocculated. In such a case, friction exists not only between fiber and filler, but also between filler and filler when paper was subjected to the tensile force, which can counteract the negative effect of CCW flocculation. So the influence of CCW flocculation on paper strength is not serious. However, the dispersion of CCW should further be investigated.



(a) (b)

Fig. 13. Orientation of CCW (a) and CCW flocculated (b) in sheet



(a) (b)

Fig. 14. Orientation PCC (a) and PCC flocculated (b) in sheet

In addition, as previously discussed, usually larger particles are less detrimental to strength. Here the whisker filler displays larger particle size and therefore this aspect should not be ignored.

CONCLUSIONS

From our observations we can conclude that the retention of calcium carbonate whiskers with large length/diameter ratio (CCW) in a sheet can offer a great improvement compared to conventional powder-like precipitated calcium carbonate (PCC) fillers. The properties of CCW-filled handsheets, including tensile, burst, and air permeability, are better than those of PCC-filled handsheets. A model was proposed to suggest the mechanism of paper strength improvement based on experimental data and mechanism analysis. Both the friction and entanglement effects are responsible for the strength improvement of CCW-filled paper.

REFERENCES CITED

Al-Mehbad, N. Y. (2004). "Improving paper properties," *Polymer-Plastics Technol. Eng.* 43(3), 963-979.

Bown, R. (1998). "Particle size, shape and structure of paper fillers and their effect on paper properties," *Paper Technology* 39(2), 44-48.

Cowan, W. F. (1995). "Explaining handsheet tensile and tear in terms of fibre-quality numbers," *Tappi J*. 78(1), 101-106.

de Oliveira, M. H., Tejado, A., and van de Ven, T. G. M. (2009). "Effects of fillers on the wet web strength of paper," *Nordic Pulp Paper Res. J*. 24(2), 141-146.

Eklund, D., and Lindstrom, T. (1991). *Paper Chemistry: An Introduction*, DT Paper Science Publications, Grankulla, Finland.

Fairchild, G. H., and Thatcher, R. L. (2000). "Acicular calcite and aragonite calcium carbonate," *US Patent* 6,071,336.

Gill, R. A. (1991). "Cationic polymer-modified filler material, process for its preparation and method for its use in papermaking," *Canada Patent* 2,037,525.

Hu, Z., Shao, M., Cai, Q., Ding, S., Zhong, C., Wei, X., and Deng, Y. (2009). "Synthesis of needle-like aragonite from limestone in the presence of magnesium chloride," *J. Mater. Processing Tech.* 209(3), 1607-1611.

Hu, Z., Shao, M., Li, H.,Cai, Q., Zhong, C., Zhang, X., and Deng, Y. (2009). "Synthesis of needle-like aragonite crystals in the presence of magnesium chloride and their application in papermaking," *Advanced Composite Materials*18(4), 315-326.

Hubbe, M. A. (2004) "Filler particle shape vs. paper properties -A review," *TAPPI Spring Technical Conference*, 1-10.

Kazuto, T., Kiyoshi, K., Yasunori, N., and Yashuhiro, O. (2001). "Process for preparing calcium carbonate," *US Patent* 6,190,633.

Laufmann, M., and Forsblom, M. (2000). "GCC vs. PCC as the primary filler for uncoated and coated wood-free paper," *Tappi J*. 76(5), 1-13.

Middleton, S. R., Desmeules, J., and Scallan, A. M. (2003). "Lumen loading with calcium carbonate fillers," *J. Pulp Paper Sci.* 29(7), 241-246.

Somboon, P., and Paulapuro, H. (2009). "Determination of wet fiber strength," *Tappi J*. 8(5), 4-7.

Subramanian, R., Maloney, T., and Paulapuro, H. (2005). "Calcium carbonate composite fillers," *Tappi J*. 4(7), 23-27.

Xu, Y., Chen, X., and Pelton, R. (2005). "How polymers strengthen filled papers," *Tappi J*. 4(11), 8-12.

Zhao, Y. L., Hu, Z. S., Ragauskas A., and Deng, Y. L. (2005). "Improvement of paper properties using starch-modified precipitated calcium carbonate filler," *Tappi J*. 4(2), 3-7.

Article submitted: March 14, 2011; Peer review completed: April 20, 2011; Revised version received and accepted: May 5, 2011; Published: May 7, 2011.