

Increase of Paper Strength and Bulk by Co-Flocculation of Fines and Fly Ash-based Calcium Silicate

Meiyun Zhang,^{a,*} Qiumei Li,^a Shunxi Song,^{a,b,*} Ning Hao,^a and Guodong Liu^a

Fly ash-based calcium silicate (FACS), which has a large surface area (121 m²/g) and porous structure, has the potential to be used as a filler for the production of high-bulk paper. In theory, paper with a higher bulk has a lower strength. This work explores the possibility of improving paper strength without compromising its bulk through co-flocculation of cellulosic fines and FACS. To investigate the effect of co-flocculation on paper properties, composites made with various ratios of fines to FACS were studied. Results showed that paper bulk and tensile strength increased with increasing ratio of fines to FACS, up to 0.3 at 17% filler content. To further confirm these findings, the structures of composites were studied with a light microscope and scanning electronic microscope (SEM). Images showed that the composite formed at the ratio of 0.3 exhibited a larger size and looser structure than other composites, which can be attributed to the improvement of the paper's strength and bulk. Schemes for the composite formation process and its interactions with fibers were also proposed.

Keywords: Bulk, strength; Composite; Fines; Fly ash based calcium silicate; Co-flocculation

Contact information: a: Shaanxi Province Key Laboratory of Papermaking Technology and Specialty Paper, College of Light Industry and Energy, Shaanxi University of Science & Technology, Xi'an 710021, China; b: State Key Laboratory of Pulp and Paper Engineering, South China University of Technology, Guangzhou, 510640, China; *Corresponding authors: myzhang@sust.edu.cn; songshunxi@sust.edu.cn

INTRODUCTION

Fine paper, especially printing paper, with low cost, high strength, and high bulk, is ceaselessly pursued by papermakers. For many paper grades, filler is used to decrease production costs and improve paper properties (e.g., brightness, printability). However, paper strength can be negatively affected because the filler impedes the inter-fiber hydrogen bonding. To improve the strength of filled paper, many methods have been tried, such as strength additives (Hamzeha *et al.* 2013), lumen loading (Miller and Paliwal 1985), filler pre-flocculation (Sang *et al.* 2012; Chauhan and Bhardwaj 2014), and filler modification (Yan *et al.* 2005; Zhao *et al.* 2005; Yoon and Deng 2007; Shen *et al.* 2009, 2010). Among those methods, filler pre-flocculation and modification are of great interest. In the pre-flocculation process, filler aggregates are formed by polymers. Chauhan and Bhardwaj (2014) pre-flocculated talc with cationic starch, resulting in a 7% to 15% increase in tensile index with 24% filler content. Yan *et al.* (2005) showed a significant improvement in the strength of paper filled with starch-coated clay compared with that filled with unmodified clay.

Bulk is another important paper parameter, particularly for printing, because it affects printability and runnability. For printing-grade paper, high bulk is preferred, which correlates with high stiffness. Paper with a higher stiffness can make the printers work more smoothly (Gao *et al.* 2009; Chen *et al.* 2013). Moreover, improving paper bulk is a

good way to reduce fiber amounts at a given thickness. The addition of high-yield pulp (HYP) is one of the most frequently used methods to produce high-bulk paper (Resalati 2007; Xu and Zhou 2007; Zhang *et al.* 2011). Although the bulk of paper can be improved, the thick-walled HYP fibers may affect paper surface smoothness and can cause the surface to roughen upon rewetting when printing (Danby 2002; Nesbakk and Helle 2002).

It is typically believed that paper bulk and strength are contradictory parameters. The inter-fiber hydrogen bonds, which are related to the number of free hydroxyl groups and the total area in molecular contact, provide the mechanical strength of paper (Retulainen *et al.* 1998; Mark 2002; Dongbo 2013). When the bulk of paper increases, the distance between fibers increases, which decreases paper strength. The aforementioned methods can enhance paper strength, but compromise paper bulk, or *vice versa*. Hence, it is necessary to investigate a method that improves both paper bulk and strength.

Previous research has found that fly ash-based calcium silicate (FACS), an environmentally friendly by-product prepared from the silicate-rich fly ash of coal-fired power plants, has the potential to produce high-bulk paper (Song *et al.* 2012; Zhang *et al.* 2013). However, the strength of FACS-filled paper was sacrificed with improvements to the bulk. In this study, the co-flocculation of FACS particles and cellulosic fines with a high-molecular weight cationic polyacrylamide (CPAM) was employed to explore the possibility of improvement to both the strength and the bulk of FACS-filled paper.

EXPERIMENTAL

Materials

Bleached softwood kraft pulp was supplied by a pulp mill in Fujian province, China. The pulp was refined to a freeness of 425 mL (Canadian Standard Freeness) with a PFI refiner following TAPPI T248 sp-00 (2000). The pulp was diluted to a consistency of 0.3% before use. FACS was obtained from a coal-fired power plant in China. CPAM with a molecular weight of approximately $(6.5 \pm 0.5) \times 10^6$ g/mol was supplied by Nalco Chemical Company, Nanjing, China. CPAM solution (0.01% (w/v)) was prepared daily with deionized water and stirred by a magnetic stirrer at room temperature for 30 min.

Fines were produced by extensively refining the bleached softwood kraft pulp to a freeness of 50 mL and separating the fraction that passed through the 200-mesh screen of a SWECO fiber classifier (Sweco division of M-I L.L.C.).

Methods

Filler and fines characterization

The morphology and particle size of the FACS were tested with a scanning electron microscope (S-4800, Hitachi Ltd., Japan) and a BT-9300H particle size analyzer (Bettersize Instruments Ltd., China). The surface area of the FACS was measured by the multi-point Brunauer Emmett Teller (BET) nitrogen adsorption method (Gemini VII2390, Micromeritics Instrument Corporation, USA). The morphology of the fines was observed by a light microscope (DMB5-223IPL-5, Motic Electric Group Co., Ltd., China).

Preparation and observation of composites

Five grams of FACS (oven-dried weight) was diluted with deionized water to 5 wt%, followed by stirring at 300 rpm for dispersion. Then, various amounts of fines (Table 1) were added to the FACS slurry, and the solution was mixed for 1 min. After that, 0.05

wt% (based on the dry weight of FACS) CPAM solution was added. The resulting mixture was stirred for another 5 min at 300 rpm to form a stable composites slurry. The structure of the composites was observed with the light microscope.

Table 1. Amounts of FACS and Fines

ID	FACS (g)	Fines (g)	Ratio of fines to FACS
1	5	0.00	0
2	5	0.75	0.15
3	5	1.50	0.3
4	5	2.25	0.45
5	5	3.00	0.5
6	5	3.75	0.75

Handsheets preparation and testing

The pulp slurry was disintegrated to a 1.2% consistency and then diluted to a concentration of 0.3%. The prepared filler-fines composite slurry was subsequently added to the pulp to make the filler content to be 17 wt%. Sheets with a target basis weight of 70 g/m² were made with a laboratory sheet former.

The wet sheets were pressed in accordance with TAPPI T205 sp-95 (1995) and then air-dried for 24 h at 25 °C at 50% relative humidity before testing. Paper bulk, tensile, and tear index were measured according to TAPPI T220 sp-01(2001). The filler content was measured following TAPPI T211 om-93(1993).

RESULTS AND DISCUSSION

Characterization of FACS and Fines

The morphology and properties of the FACS are shown in Fig. 1 and Table 2, respectively.

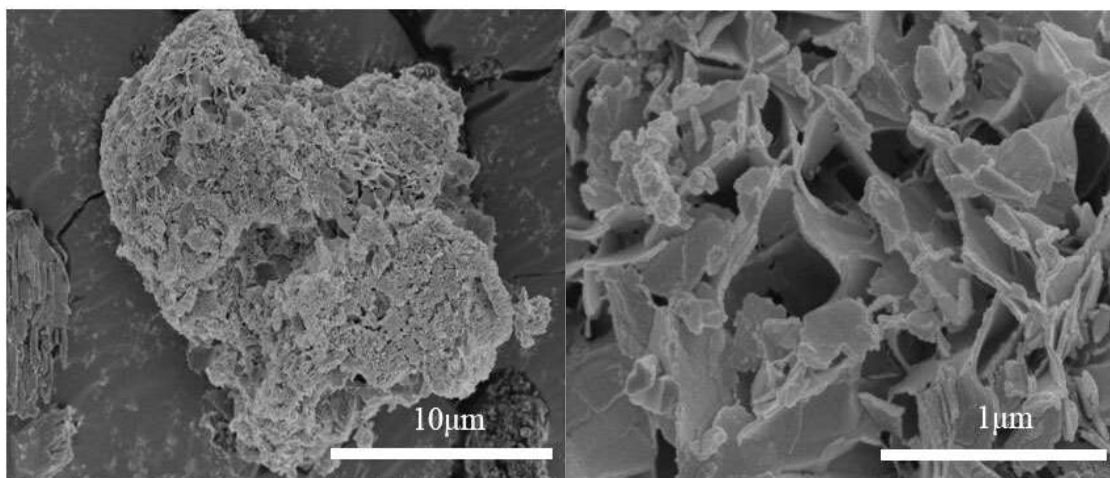


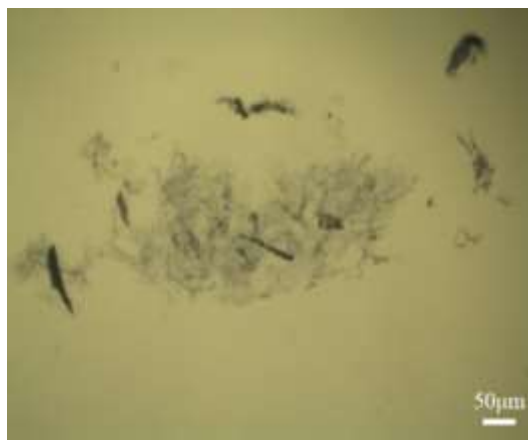
Fig. 1. Scanning electron micrographs of FACS

Table 2. Characteristics of FACS

Average particle size (μm)	22.52
Specific surface area (m^2/g)	121
Pore volume (cm^3/g)	1.63
Pore size (μm)	0.3 to 1
Ignition loss (525 °C; %)	10.5
Brightness (%ISO)	90.5

As shown in Fig. 1, FACS is formed by the accretion of lamellar structures and exhibits a wrinkled, porous surface, which gives it large specific surface area. Additionally, the air voids on the surface of FACS contribute to a lower bulk density. These properties help to produce high-bulk paper but may negatively affect paper strength.

In general, pulp fines are defined as the fraction passing through a 200-mesh screen. They are categorized into primary and secondary fines according to their shape (Lee *et al.* 2011; Hyll 2015). Primary fines (flakes) are present in pulp before refining (*e.g.*, vessel elements and ray cells). Secondary fines (fibrils) are produced in the refining process. In this study, most of the fines are secondary as a result of the extensive refining. The fines morphology is shown in Fig. 2.

**Fig. 2.** Light microscope image of fines

Morphology of Composites

The molecular weight and charge density of CPAM are $6.5 \pm 0.5 \times 10^6$ g/mol and 1015 $\mu\text{equiv/g}$, respectively. It is generally believed that CPAM, with a high molecular weight and a low charge density, flocculates fillers through a bridging mechanism (Biggs *et al.* 2000; Blanco *et al.* 2002; Rasteiro *et al.* 2008). The CPAM adsorbs on the surface of FACS particles or fines randomly, and its loops and tails extended far beyond the particle surface to interact with other particles, forming FACS-fines composites.

As shown in Fig. 3, the FACS particles were entwined with fines fibers, but the composite size and package density were different. All of the composites had larger particle sizes than the FACS flocs. At ratios of 0.15 and 0.3, all the filler and fines formed composites, and no fines or FACS particles existed alone. However, the composites formed at the ratio of 0.3 were larger in size and had a looser structure than those formed at 0.15. At a ratio of 0.75, excess amounts of fines existed alone or self-flocculated to form fines aggregates, which can improve the paper strength but decrease the paper bulk.

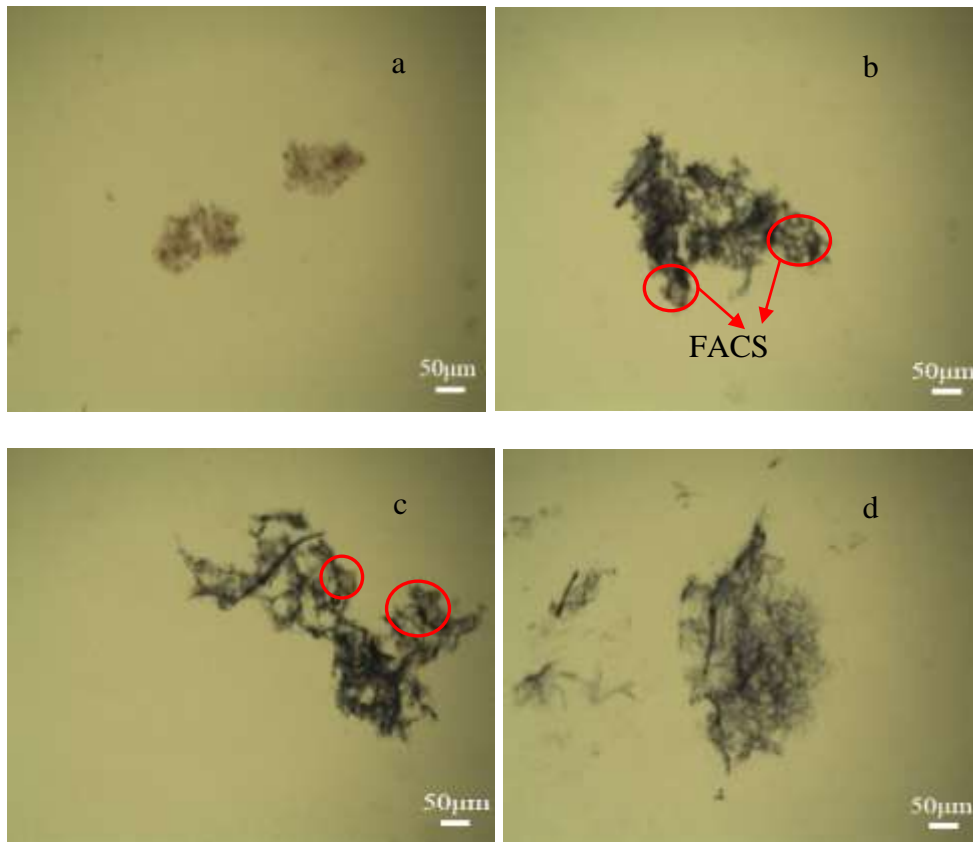


Fig. 3. Light microscope images of composites formed at various ratios: (a) 0, (b) 0.15, (c) 0.3, and (d) 0.75

Paper Properties

Paper bulk is an important property that influences printing performance. The paper basis weight will decrease if the bulk increases at a constant thickness, which reduces the amount of fibers and production cost. Figure 4 shows that when increasing the ratio of fines to FACS to 0.3, the value of paper bulk increased by 6% in comparison with the control sample (no fines). This is contrary to the popular theory that paper bulk decreases when fines content increases (Sirviö and Nurminen 2004). When the ratio was larger than 0.3, paper bulk decreased (the filler content of all paper samples was $17\pm 0.5\%$).

The particle size and structure of the filler are responsible for paper bulk (Brown 1998). Large particles can create greater inter-fiber spaces in the fiber-fiber bonding domain, which helps to improve bulk (Hubbe and Gill 2004). Additionally, composites with a loose structure can result in more air voids, which also creates more bulk.

As shown in Fig. 3, compared with FACS flocs, composites formed at a ratio of 0.15 exhibited larger particle sizes, which improved the bulk. However, the composite formed at a ratio of 0.3 was bigger and had a looser structure than that formed at 0.15, which resulted in continued improvements to paper bulk. When the ratio was greater than 0.3, although the particle size of composite is larger than FACS, the excess amount of fines filled the voids in the bonds and placed the fibers closer to each other. This resulted in a decreased paper bulk.

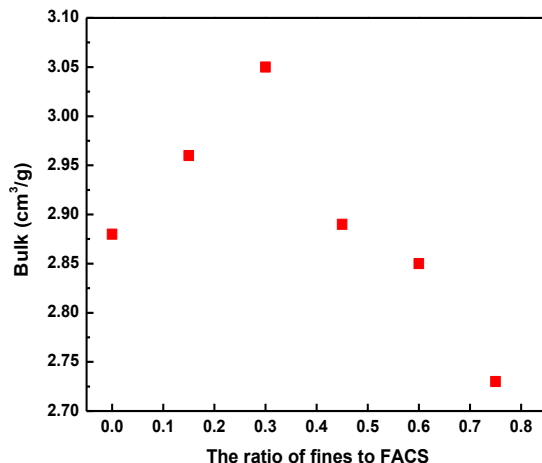


Fig. 4. Effect of the ratio of fines to FACS on paper bulk

The tensile strength of paper is influenced by hydrogen bonding. Compared with fibers, fines have a larger surface area and more surface hydroxyl groups per unit mass, which favors the formation of hydrogen bonds. Thus, fines can be regarded as strengthening agents (Xu and Pelton 2005). On the other hand, the composites have larger sized particles than FACS aggregates, as shown in Fig. 3, which helps to decrease the number of particles at the same filler content. Hence, the inter-fiber bonding is affected to a lesser extent. This explains why the paper tensile index increased when fines increased. Fiber average length and hydrogen bonding are critical for tear strength (Liu *et al.* 2012). Hydrogen bonding and fiber average length are two contradictory parameters with the ratio increase. When the amount of fines increased, the hydroxyl bonding increased and the average length of fibers decreased. Hence, there should be an equilibrium ratio at which the tear strength reaches its maximum. In this work, that ratio is 0.3.

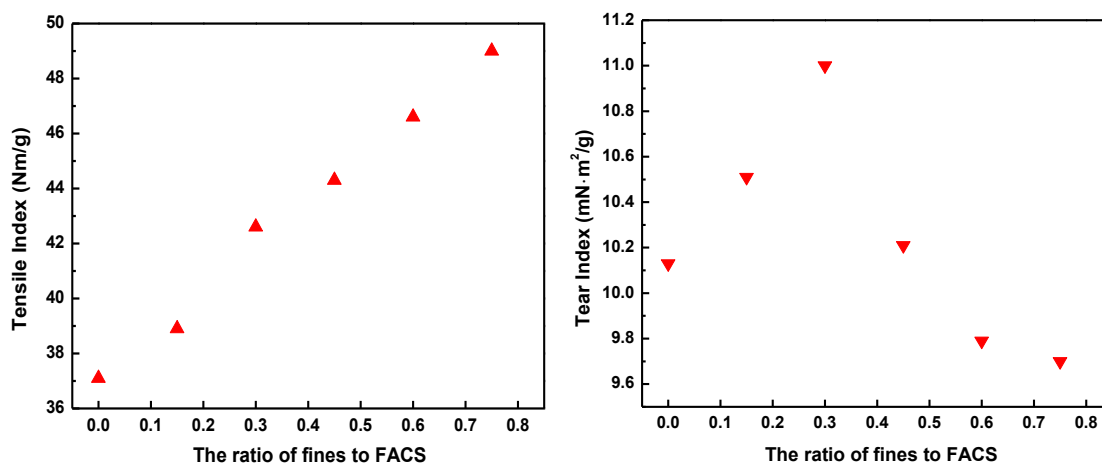


Fig. 5. Effect of the ratio of fines to FACS on paper tensile and tear strengths

To confirm the formation of filler-fines composites in paper, the paper morphology was observed by SEM. As shown in Fig. 6, the fines were coated on the surface of the FACS, playing the role of a bridge linking the FACS and fibers, which mitigated the destruction of hydrogen bonds between fibers.

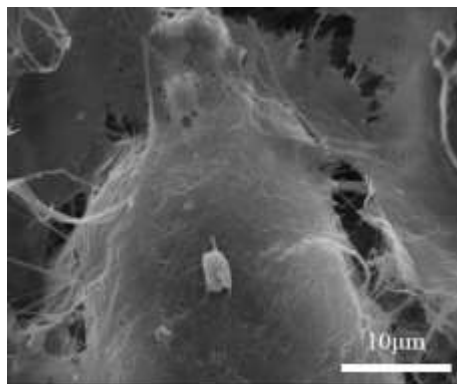


Fig. 6. Scanning electron micrograph of composites in paper sheet

Proposed Mechanism Models

Some possible mechanisms of the composite formation process are shown in Fig. 7. The FACS and fines slurry is homogeneously dispersed until the addition of CPAM. The chains of CPAM extend its loops and tails, which attach to the filler particles or fines randomly and interact with other particles to form open-structure composites. Without fines, FACS particles flocculate together to form filler flocs. At ratios of 0.15 and 0.3, all the filler and fines form composites, and no fines or FACS particles exist alone. Moreover, the composite formed at a ratio of 0.3 has larger size and looser structure than that formed at 0.15. However, with an increased ratio, excess fines exist or flocculate to flocs, which fill the voids in fiber networks and cause fibers to be closer to each other, resulting in a decreased paper bulk.

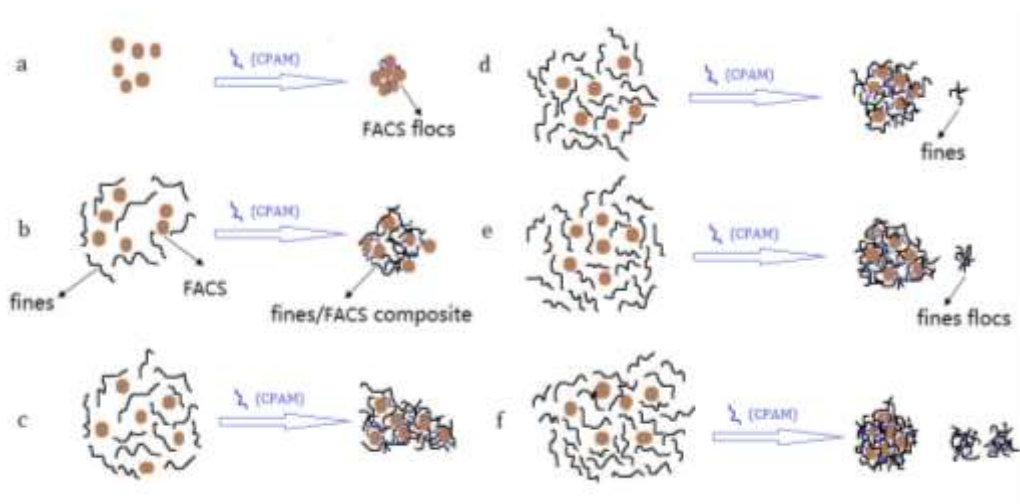


Fig. 7. Scheme of fines and FACS co-flocculation by CPAM at various fines to FACS ratios: (a) 0, (b) 0.15, (c) 0.3, (d) 0.45, (e) 0.6, and (f) 0.75

The mechanism model demonstrates the interaction between fibers and composites (Fig. 8). In the traditional filling method, some fillers exist on the surface of fibers and disturb the fiber-fiber hydrogen bonding. In contrast, in the co-flocculation filling method, FACS are enfolded and entwined by fines, which decrease the direct contact between fillers and fibers. Fines bridge the interaction between fibers and fillers and bring fibers closer together, which increases paper strength and decreases bulk. However, the formed composites have a larger particle size than FACS flocs, which compensates for the decrease

in bulk to some extent. This may be the reason that paper strength and bulk both increased within a certain ratio range.

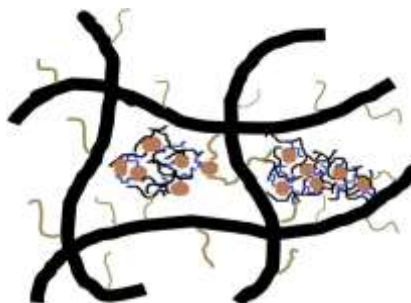


Fig. 8. Scheme of the interaction mechanism between composites and fibers

CONCLUSIONS

1. Composites were formed by the co-flocculation method. The ratio of fines to FACS has an influence on the composite structure. The composites formed at the ratio of 0.3 exhibited larger particle size and looser structure compared with other composites.
2. The co-flocculation of fines and FACS prior to pulping can improve paper strength without a loss in bulk within a certain ratio range. When the ratio is below 0.3, paper bulk and strength can be improved. This demonstrates the potential for the production of high-bulk and high-strength paper.
3. Possible mechanisms of interaction between filler and fines were proposed to explain the improvements in paper bulk and strength. Fines improved the inter-fiber bonding ability, and composites with large size and loose structure were responsible for improvements in paper bulk.

ACKNOWLEDGMENTS

We acknowledge financial support from the State Key Laboratory of Pulp and Paper Engineering (201506), Doctoral Scientific Research Foundation of Shaanxi University of Science & Technology (BJ15-12), National Science Foundation of China (Grant No.31170560) and Graduate Innovation Fund of Shaanxi University of Science and Technology.

REFERENCES CITED

- Biggs, S., Habgood, M., Jameson, G. J., and Yan, Y. (2000). "Aggregate structures formed *via* a bridging flocculation mechanism," *Chem. Eng. J.* 80(1), 13-22. DOI: 10.1016/S1383-5866(00)00072-1
- Blanco, A., Fuente, E., Negro, C., and Tijero, J. (2002). "Flocculation monitoring: Focused beam reflectance measurement as a measurement tool," *Can. J. Chem. Eng.* 80(4), 1-7. DOI: 10.1002/cjce.5450800403

- Brown, R. (1998). "Particle size, shape and structure of paper fillers and their effect on paper properties," *Pap. Technol.* 39(2), 44-48.
- Chauhan, V. S., and Bhardwaj, N. K. (2014). "Cationic starch preflocculated filler for improvement in filler bondability and composite tensile index of paper," *Ind. Eng. Chem. Res.* 53(29), 11622-11628. DOI: 10.1021/ie502008d
- Chen, J., Zhang, M., Yuan, Z., and Wang, J. (2013). "Improved high-yielded pulp network and paper properties by the addition of fines," *BioResources* 8(4), 6309-6322. DOI: 10.15376/biores.8.4.6309-6322
- Danby, R. (2002). "SC print quality influenced by fibre length, fabric structures, and machine drainage characteristics," *TAPPI J.* 1(9), 3-9.
- Gao, Y., Huang, F., Rajbhandari, V., Li K., and Zhou Y. (2009). "Effect of separate refining and co-refining of BCTMP/KP on paper properties," *Pulp Pap.-Canada* 110(6), 28-33.
- Hamzaha, Y., Ashori, A., Khorasani, Z., Abdulkhani, A., and Abyaz, A. (2013). "Pre-extraction of hemicelluloses from bagasse fibers: Effects of dry-strength additives on paper properties," *Ind. Crops Prod.* 43, 365-371. DOI: 10.1016/j.indcrop.2012.07.047
- Hubbe, M. A., and Gill, R. (2004). "Filler particle shape vs. paper properties - A review," in: *2004 TAPPI Paper Summit - Spring Technical and International Environmental Conference*, Atlanta, GA, pp. 141-150.
- Hyll, K. (2015). "Size and shape characterization of fines and fillers-a review," *Nord. Pulp Pap. Res. J.* 30(3), 466-487. DOI: 10.3183/NPPRJ-2015-30-03-p466-487
- Lee, H., Nam, W. S., Sohn, S. D., and Paik, K. H. (2011). "Effect of different types of fines on the properties of recycled chemical pulp," *J. Ind. Eng. Chem.* 17(1), 100-104. DOI: 10.1016/j.jiec.2010.12.004
- Liu, H., Chen, Y., Zhang, H., Yuan, Z., Zou, X., Zhou, Y., and Ni, Y. (2012). "Increasing the use of high-yield pulp in coated high-quality wood-free papers: From laboratory demonstration to mill trials," *Ind. Eng. Chem. Res.* 51(11), 4240-4246. DOI: 10.1021/ie2029514
- Mark, R. E. (2002). "Determination of fiber-fiber bond properties," in: *Handbook of Physical Testing of Paper*, R. E. Mark, C. C. Habeger Jr, J. Borch, and M. B., Lyne (eds.), Marcel Dekker, New York, NY, pp. 873-900.
- Miller, M. L., and Paliwal, D. C. (1985). "The effects of lumen-loading on strength and optical properties of paper" *J. Pulp Pap. Sci.* 11(3), 84-88.
- Nesbakk, T., and Helle, T. (2002). "The influence of the pulp fibre properties on supercalendered mechanical pulp handsheets," *J. Pulp Pap. Sci.* 28(12), 406-409.
- Rasteiro, M. G., Garcia, F. A. P., Ferreira, P., Blanco, A., Negro, C., and Antunes, E. (2008). "The use of LDS as a tool to evaluate flocculation mechanisms," *Chem. Eng. Process.* 47(8), 1323-1332. DOI: 10.1016/j.cep.2007.04.009
- Resalati, H. (2007). "The effect of APMP process variables on poplar pulp yields and properties," *International Mechanical Pulping Conference 2007*, Minneapolis, MN, pp. 834-838.
- Retulainen, E., Niskanen, K., and Nilsen, N. (1998). *Fibers and Bonds. Paper Physics*, Fapet Oy, Helsinki, Finland.
- Sang, Y., McQuaid, M., and Englezos, P. (2012). "Pre-flocculation of precipitated calcium carbonate filler by cationic starch for highly filled mechanical grade paper," *BioResources* 7(1), 354-373. DOI: 10.15376/biores.7.1.354-393

- Shen, J., Song, Z., Qian X., and Liu, W. (2009). "Modification of papermaking grade fillers: A brief review," *BioResources* 4(3), 1190-1209. DOI: 10.15376/biores.4.3.1190-1209
- Shen, J., Song, Z., Qian X., and Yang, F. (2010). "Carboxymethyl cellulose/alum modified precipitated calcium carbonate fillers: Preparation and their use in papermaking," *Carbohydr. Polym.* 81(3), 545-553. DOI: 10.1016/j.carbpol.2010.03.012
- Sirviö, J., and Nurminen, I. (2004). "Systematic changes in paper properties caused by fines," *Pulp Pap.-Canada* 105(8), 39-42.
- Song, S. X., Zhang, M. Y., He, Z. B., Li, J. Z., and Ni, Y. H. (2012). "Investigation on a novel fly ash based calcium silicate filler: effect of particle size on paper properties," *Ind. Eng. Chem. Res.* 51(50), 16377-16384. DOI: 10.1021/ie3028813
- Xu, E. C., and Zhou, Y. J. (2007). "Synergistic effects between chemical mechanical pulps and chemical pulps from hardwoods," *International Mechanical Pulping Conference 2007*, Minneapolis, MN, pp.1045-1050.
- Xu, Y., and Pelton, R. (2005). "A new look at how fines influence the strength of filled papers," *J. Pulp. Pap. Sci.* 31(3), 147-152.
- Yan, Z., Liu, Q. J., Deng, Y. L., and Ragauskas, A. (2005). "Improvement of paper strength with starch modified clay," *J. Appl. Polym. Sci.* 97(1), 44-50. DOI: 10.1002/app.21727
- Yoon, S. Y., and Deng, Y. (2007). "Experimental and modeling study of the strength properties of clay-starch composite filled papers," *Ind. Eng. Chem. Res.* 46(14), 4883-4890. DOI: 10.1021/ie0613523
- Zhang, H. J., He, Z. B., and Ni, Y. H. (2011). "Improvement of high-yield pulp properties by using a small amount of bleached wheat straw pulp," *Bioresour. Technol.* 102(3), 2829-2833. DOI: 10.1016/j.biortech.2010.10.053
- Zhang, M. Y., Song, S. X., Wang, J., Sun, J. M., Li, J. Z., Ni, Y. H., and Wei, X. F. (2013). "Using a novel fly ash based calcium silicate as a potential paper filler," *BioResources* 8(2), 2768-2779. DOI: 10.15376/biores.8.2.2768-2779
- Zhao, Y., Hu, Z., Ragauskas, A. J., and Deng, Y. (2005). "Improvement of paper properties using starch-modified precipitated calcium carbonate filler," *TAPPI J.* 4(2), 3-7.
- TAPPI T248 sp-00 (2000). "Standard test method for laboratory beating of pulp," Technical Association of the Pulp and Paper Industry, Atlanta, Georgia.
- TAPPI T205 sp-95 (1995). "Standard test method for forming handsheets for physical tests of pulp," Technical Association of the Pulp and Paper Industry, Atlanta, Georgia.
- TAPPI T220 sp-01(2001). "Standard test method for physical testing of pulp handsheets," Technical Association of the Pulp and Paper Industry, Atlanta, Georgia.
- TAPPI T211 om-93(1993). "Standard test method for forming handsheets for physical tests of pulp," Technical Association of the Pulp and Paper Industry, Atlanta, Georgia.

Article submitted: March 24, 2016; Peer review completed: May 22, 2016; Revised version received and accepted: May 28, 2016; Published: July 18, 2016.

DOI: 10.15376/biores.11.3.7406-7415