Papermaking of mineral fiber composites

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Mineral and hardwood fiber composites were assessed by various factors (folding degree, tensile strength, elongation, tearing strength and tear factor). Performance of wollastonite or sepiolite composites is found higher than that of the same percentage fillers (calcium carbonate, talc) due to interwoven structure between mineral fibers and hardwood fibers. Composites of wollastonite and sepiolite (1:1) can significantly improve performance of composite fibers due to combined effect of mineral fibers.

Keywords: Composites, Mineral fibers, Papermaking, Sepiolite, Wollastonite

Introduction

Paper is composed of cellulosic fibers and considerable amounts of other substances¹⁻⁵. Mineral substances that have long been used in papermaking⁶⁻⁸ include precipitated calcium carbonate (PCC) fillers with bagasse pulp fibers⁷, PCC with kaolin clay particles¹⁰ and sericite and talc powders¹¹. Wollastonite is chemically inert, sometimes prevents cellulosic fiber-to-fiber contact and thus reduces paper strength. In order to overcome such problems, it is sometimes recommended to coat mineral surface with other materials before their addition to the paper¹²⁻¹⁷.

In present study, for papermaking, composite fibers of wollastonite and sepiolite (1:1) were assessed by various factors (folding degree, tensile strength, elongation, tearing strength and tear factor) and surface morphology of wollastonite was investigated using SEM.

Experimental

Materials

Hardwood fibers were provided by Chinese Pulp and Paper Research Institute. Wollastonite particles were selected from Jiangxi province and sepiolite from Henan province. Chemical composition of wollastonite is as follows: SiO₂, 51.07; TiO₂, 0.02; Al₂O₃, 0.48; Fe₂O₃, 0.027; FeO, 0.24; MnO, 0.034; CaO, 45.36; MgO, 1.10; K₂O, 0.17; Na₂O, 0.057; and loss, 0.32%. Chemical composition of sepiolite is as follows: SiO₂, 44.87; MgO, 21.01; CaO, 15.61; Al₂O₃, 0.25; K₂O, 0.03; MnO, 0.03; TiO₂, 0.01; Fe₂O₃, 0.23; loss, 17.98%.

Process of Composite Paper

Hardwood fibers were beaten into slurry (Fig. 1), and then mixed with mineral fibers (wollastonite, sepiolite) and calcium carbonate (CaCO₃) / talc as control. Hardwood fibers were immersed in water for one day, and beaten with J23 type beater for 5 h to get slurry (conc., 2%; SR, 23°). For preparation of cationic polyacrylamide (CPAM) modified wollastonite, CPAM (0.5 g) was added into distilled water (500 ml). Then, wollastonite (50 g) was added into CPAM solution, and stirred for 4 h in water bath at 50°C. After centrifuge dewatering and drying, modified wollastonite (1 mg/l) was dispersed evenly in ultrasonic devices to measure ζ potential value. An appropriate amount of hardwood slurry was mixed with mineral fiber composites including sepiolite and CPAM modified wollastonite. Composite fibers were tested on ZQJ1-B paper test machine.

Characterizations

Zeta potentials were determined by measuring electrophoresis mobility of materials with a zeta potential analyzer (Zeta, BI-90Plus, USA). Paper was tested on J23-type beater, and ZQJ1-B-type paper test machine.
Power structure of materials was characterized by X-ray diffractometry (X Pert PRO DY2198, Holland) using monochromatized X-ray beam from Cu K\textsubscript{α} radiation. Morphologies and particle sizes of samples were observed by Nikon YS100 microscope and scanning electron microscope (SEM, JSM -35CF, Japan). All measurements were performed at RT under ambient conditions.

**Results and Discussion**

**X-Ray Diffraction and Morphology Analysis of Wollastonite and Sepiolite**

Chemical compositions of wollastonite particles (Fig. 2) and that of sepiolite particles (Fig. 3) were measured by X-ray diffractometry. From XRD image, wollastonite particles have diffraction peaks at 7.6752, 5.4535, 3.8373, 3.5147, 3.3238, 3.0911, 2.9781, 2.7218, 2.5573, 2.4794, 2.3341, 2.3042, 2.1672, 1.9812, 1.9133, 1.8762, 1.8568, 1.8309, 1.8084, 1.7584, 1.7251, 1.7191, 1.5354, 1.4593 and 1.3620. Quartz particles have diffraction peaks at 4.2509, 3.3410, 2.4558, 2.2340, 2.1253, 1.6050 and 1.3743. Calcite particles have diffraction peaks at 3.0335, 2.0924, 1.9133 and 1.5079. From XRD image, sepiolite particles have diffraction peaks at 12.099, 7.4811, 6.7426, 5.0237, 4.5028, 3.7387, 3.0335, 2.5602, 2.2817 and 1.1903. Tale particles have diffraction peaks at 9.3612, 4.6748, 3.1207, 3.4927 and 2.2489. Dolomite particles have diffraction peaks at 2.8878, 2.6947 and 1.8125.

**ζ Potential of Wollastonite and Modified Wollastonite**

ζ potential was measured under different pH value to evaluate pH effect of wollastonite and modified wollastonite. At different pH, ζ potentials for
wollastonite and modified wollastonite, respectively, were found as follows: 1, 2.8, 15.5; 2.1, -0.5, 11.2; 3.4, -1.2, 6.5; 4.7, -5.5, 2.9; 5.9, -10.8, -0.3; 7.2, -13.6, -2.9; 8.4, -15.2, -5.9; 9.5, -18.9, -8.7; 11.3, -25.8, -10.1; and 12.7, -30.4, -16.9 \( \zeta \) potential/mV. It is observed that absolute potential value of negative charged wollastonite is gradually increased with a gradual increase in pH value. Isoelectric point of CPAM modified wollastonite shifts from 1.9 to 6.0. When pH value is adjusted below 6.0, negative-charged hardwood fiber can electrostatically adsorb on the surface of CPAM modified wollastonite particles with positive charges, and form a uniform distribution between mineral and hardwood fibers. Moreover, CPAM modified wollastonite in paper-making process has a certain intensity to enhance effectiveness of the paper, so that CPAM is selected to modify wollastonite in the experiment.

Performance Testing of a Single Hardwood Fiber, Mineral Fillers, and Mineral Fiber Composites

A single hardwood fiber, CaCO\(_3\) (or talc) fillers (20%), and mineral fibers and their composites were tested to find effect of fiber composition on paper performance.

(1) A Single Hardwood Fiber

A single broad-leaved forest hardwood fiber gave paper performance indicators as follows: whiteness, 74.8%; folding degree, 16; tensile strength, 1740 kN/m; elongation, 4.2%; tearing strength, 1747.0 mN; and tear factor, 21.9, mN⋅m\(^2\)/g.

(2) Mineral Fillers Blended with Hardwood Fibers

A composite [CaCO\(_3\) (20%) or talc fillers (20%)] added with hardwood fibers (80%)] gave paper performance indicators for CaCO\(_3\) and talc composites, respectively, as follows: whiteness, 75.2, 75.4%; folding degree, 8, 9; tensile strength, 1566, 1560 kN/m; elongation, 4.6, 4.4%; tearing strength, 1285.6, 1217.3 mN; and tear factor, 15.5, 15.9 mN⋅m\(^2\)/g. Thus, paper sheets filled with CaCO\(_3\) or talc suffered loss in mechanical properties with respect to single hardwood fibers blank sheets. Folding degree was significantly decreased (44-50%) when 20% fillers were added. Tearing strength and tear factor were decreased (26-30%). Tensile strength also reduced (10%). Retained amount of fillers was sufficient to prevent fiber-to-fiber bonding of hardwood fibers.

(3) Wollastonite Mineral Fibers Blended with Hardwood Fibers

Modified wollastonite (20%, 30%, 40%) was mixed with hardwood fiber (80%, 70%, 60%), respectively (Table 1). Paper performance of wollastonite (20%) fiber composite is higher than that of fillers (CaCO\(_3\) 20%,..
When wollastonite reaches 30% in fiber composite, paper performance is still higher than that of filler (20%) except elongation. While comparing modified wollastonite (40%) fiber composites with filler (20%) composites, performance of former was improved in tearing strength and tear factor, and decreased slightly in tensile strength and elongation. Results showed that paper performance with addition of wollastonite was better than that with adding CaCO$_3$ and talc filler. Addition of wollastonite fibers does not act as a general fill material, but plays the role of mineral fibers. Addition of modified wollastonite significantly improved retention value of mineral fibers, so that it is possible to add modified wollastonite (40%) to fiber composites. Use of surface treated wollastonite allows papermaker to increase mineral fiber content of the paper.

(4) Sepiolite Mineral Fibers Blended with Hardwood Fibers

Sepiolite (20%, 30%, 40%) was mixed with hardwood fiber (80%, 70%, 60%), respectively (Table 1). Performance of sepiolite (20%) fiber composites, compared with wollastonite (20%) fiber composites, has been found improved in tearing strength, decreased in tensile strength and elongation. Thus it is possible to add wollastonite and sepiolite mineral fibers simultaneously.

(5) Composites of Wollastonite and Sepiolite Blended with Hardwood Fibers

Wollastonite / sepiolite (1:1) (20%, 30%, 40%) was mixed with hardwood fiber (80%, 70%, 60%), respectively (Table 1). Sepiolite / modified wollastonite (1:1) composite mineral fibers significantly improved performance of composite fibers, having combined advantage of sepiolite in tearing strength and wollastonite in tensile strength. When composite of mineral fibers reached 30%, tearing strength and tear factor were significantly higher than those supplemented with filler (CaCO$_3$ 20%, talc 20%).

Morphology Analysis of Hardwood and Mineral Fiber Composites

A single hardwood fiber (Fig. 4) is thick and has smooth surface. Needle columnar wollastonite (Fig. 5) has: average length L, 16.24 µm; average diameter D, 1.36 µm; and aspect ratio L/D, 11.94. Morphology of sepiolite fibers (Fig. 6) showed that sepiolite is single-scattered. Image of hardwood fibers added with composites of wollastonite and sepiolite (Fig. 7) showed that coarse and short wollastonite fibers stayed with thin and long sepiolite fibers, and intertwined with hardwood fibers. Hardwood and mineral composite fibers formed interwoven structure with good mineral fibers intertwined with hardwood fibers. Intertwined structure improved paper performance with a relatively high value.

Table 1—Performance of wollastonite, sepiolite and sepiolite/ modified wollastonite

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<th>Material</th>
<th>Whiteness %</th>
<th>Folding degree Times</th>
<th>Tensile strength kN/m</th>
<th>Elongation %</th>
<th>Tearing strength mN</th>
<th>Tear factor mN/m$^2$/g</th>
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Conclusions

Paper performance of wollastonite or sepiolite composite was found higher than that of same percentage fillers (CaCO$_3$, talc). Addition of wollastonite and sepiolite does not act as a general fill material, but plays the role of mineral fibers. Sepiolite / modified wollastonite (1:1) were added with hardwood fibers for papermaking. Composites of wollastonite and sepiolite (1:1) integrate advantage of sepiolite in tearing strength and wollastonite in tensile strength. Performance of composite fibers was significantly improved due to combined effect of mineral fiber. Surface morphology of composite fibers showed that mineral fibers not only stayed on paper surface, but formed interwoven structure with hardwood fibers.

Acknowledgments

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