Effects of phosphogypsum whiskers modification with calcium stearate and their impacts on properties of bleached softwood paper sheets

HAITANG LIU, XIN JIN, LIN CHEN, XIAOCHEN ZHANG, JIE LI, YONGZHEN AN, JING LIU, CHUNXIA PANG, AND YUJIE GAO

ABSTRACT: By combining the structural properties and characteristics of phosphogypsum whiskers, a preliminary study on the modification of phosphogypsum whiskers and their application in papermaking was carried out. The effects of reaction temperature, reaction time, and reaction concentration on the solubility and retention of modified phosphogypsum whiskers and the effects of phosphogypsum whiskers on the physical properties of paper under different modified conditions were explored.

The research results show that, after the phosphogypsum whiskers are modified with calcium stearate, a coating layer will be formed on the surface of the whiskers, which effectively reduces the solubility of the phosphogypsum whiskers. The best modification conditions are: the amount of calcium stearate relative to the absolute dry mass of the phosphogypsum whisker is 2.00%; the modification time is 30 min, and the modification temperature is 60°C. The use of modified phosphogypsum whiskers for paper filling will slightly reduce the whiteness, folding resistance, burst resistance, and tensile strength of the paper, but the tearing degree and retention of the filler will be increased to some extent.

Application: Phosphogypsum whiskers modified by calcium stearate have reduced solubility in water and enhanced application as a paper filler.

At present, the demand in the global paper and board market is growing at an annual rate of 1.3% and is expected to reach 490 million metric tons in 2030 [1]. In particular, there is a huge demand for paper in China, and the lack of domestic forest resources cannot meet the needs of paper production. Therefore, it is particularly important to develop a more effective papermaking filler to reduce the amount of pulp fiber and improve the performance of paper. Global emissions of phosphogypsum whiskers (PG) already exceed 150 million metric tons per year. At the same time, a large amount of phosphogypsum whisker waste is not well stored, but simply piled up in an open space, which leads to a waste of land resources, a change in soil pH value, and effects on water quality and aquatic organisms, causing serious damage to the environment [2-4]. Therefore, the effective use of phosphogypsum whisker waste is particularly important.

Phosphogypsum whiskers are widely used in many fields such as rubber, plastic, cement, and ceramics [5-7] as a reinforcing material with high strength, toughness, and high temperature resistance [8-9]. Applying phosphogypsum whiskers to the paper industry, such as making fireproof paper, can partially replace pulp fibers, greatly reducing papermaking costs and pulp pollution index, protecting both forest resources and solving the problem of phosphogypsum waste utilization.

Adding papermaking filler in the papermaking process can not only reduce the cost of fiber raw materials but also improve the optical properties and printability of the paper sheet, such as increasing the whiteness, opacity, uniformity, and smoothness of the paper sheet. At present, the commonly used fillers for paper are talc, kaolin, calcium carbonate, titanium dioxide (TiO_2), zinc sulfide, calcium sulfate, diatomite, barium sulfate, and some organic fillers. Park et al. [10] used TiO_2–silicon dioxide (SiO_2) as a filler to make tissue paper and found that the opacity of the paper was significantly improved and the oil absorption was good. He et al. [11] developed a new type of composite filler using cellulose nanofibers (CNF) to make paper sheets have better tensile strength and other characteristics. Shang et al. [12] used modified diatomaceous earth as a papermaking filler to improve physical properties of the paper sheet, such as the tensile strength and tear strength. Phosphogypsum whiskers have excellent physical properties and the adoption of it into papermaking is expected to dramatically improve the physical properties of paper.

Phosphogypsum whiskers, also commonly known as calcium sulfate ($CaSO_4$) whiskers, are prepared by essentially transforming granular $CaSO_4 \cdot 2H_2O$ into fibrous $CaSO_4 \cdot 0.5H_2O$ or $CaSO_4$ [13]. Due to the high solubility of phosphogypsum whiskers in water, it is easy to enter into the white water system and affect the normal operation of the paper machine [14]. Therefore, it is particularly important to solve the dissolution problem of phosphogypsum whiskers in water [15-16]. On the one hand, in a weak acidic environment, polyphosphate can form chelates with calcium ions. The chelate adheres to the surface of phosphogypsum whiskers and has a certain inhibitory effect on the dissolution of phosphogypsum whiskers [17]. On the other hand, macromolecular surfactants such as calcium stearate can combine with the hydroxyl groups on the surface of phosphogypsum whiskers to improve their hydrophobicity. Calcium stearate, a commonly used inorganic powder modifier, can be used to modify polar reagent phosphogypsum to enhance the interfacial compatibility between phosphogypsum whiskers and the polymer matrix, so as to inhibit the dissolution of phosphogypsum whiskers [18-21]. Solute dissolution is both a physical process and a chemical process, and the factors affecting the solubility of a substance are also multifaceted. In order to improve the compatibility and dispersion of anhydrous calcium sulfate whiskers (ACSW) in polymer composites, the treatment for surface modification was studied with aqueous solution sodium stearate (SS, $C_{17}H_{35}COONa$) at hot temperature. The surface property of modified anhydrous calcium sulfate whiskers (M-ACSW) became hydrophobic by changing the water contact angle with the calcium sulfate whisker (CSW) from 0° to 132° [22]. A hydrogel of CMC-$Al_2(SO_4)_3$ was used to encapsulate the gypsum whiskers in order to solve problems such as high solubility and low retention rate when used as filler in the papermaking process. The results showed that the coating CMC-$Al_2(SO_4)_3$ hydrogel on gypsum whiskers was effective in inhibition of the dissolution of calcium ion [23]. In the papermaking experiments, the results showed that the paper filled with the phosphorus gypsum whiskers that were modified with calcium stearate and zinc ammonium nitrate can obtain equal whiteness and physical strength (such as burst index, tear index, and tensile index). However, the whisker retention has been improved to a certain extent, from 13% and 20% to 20% and 50%, respectively [24].

In this study, the phosphogypsum whiskers were modified by calcium stearate modifier. It was expected to ultimately reduce the solubility of phosphogypsum whiskers in water and to explore the influence of calcium stearate on the solubility of modified phosphogypsum at different reaction temperatures, reaction times, and reaction concentrations, as well as the effect of modified phosphogypsum whiskers as fillers on bleached softwood paper properties.

MATERIALS AND METHODS

Materials

The materials used were as follows: bleached softwood pulp board and phosphogypsum whiskers of 92.25% ISO whiteness (Shandong Quanlin Paper Company; Liaocheng, Shandong, China); calcium stearate modifier of 92.25% ISO whiteness (Henan Liangdong Non-metallic Materials Company; Luoyang, Henan, China); potassium bromide (KBr) (spectral purity, Shenzhen Jiping Chemical Industry; Shenzhen, China); ethyl alcohol (analytically pure, Tianjin No. 1 Chemical Reagent Factory; Xiqing, Tianjin, China); and calcium stearate (Tianjin No. 1 Chemical Reagent Factory).

Experimental methods

Determination of the solubility of phosphogypsum whiskers

Two grams of phosphogypsum whiskers of absolute dry weight was weighed in a clean beaker, diluted with distilled water to a concentration of 1%, and dissolved at room temperature for more than 6 h. After filtration, a clean and constant weight weighing bottle was used to take part of the filtrate and put it into a constant temperature drying box for more than 12 h (105°C). Finally, it was transferred to a desiccator for 30 min and weighed. The solubility of phosphogypsum whiskers was calculated according to the following formula:

$$s = \frac{m_3 - m_1}{m_2 - m_3} \times 100$$

where:

m_1 = mass of weighing bottle, g

m_2 = total mass of whisker and weighing bottle before constant temperature drying, g

m_3 = total mass of filtrate and weighing bottle after constant temperature drying, g

Modification of phosphogypsum whiskers

The phosphogypsum whiskers with an absolute dry mass of 36 g was poured with distilled water to prepare a suspension with a concentration of 7.2% and heated to 60°C in a water bath, after which the calcium stearate modifier was added. The phosphogypsum whisker suspension was filtered at hot conditions. The filter cake was transferred to a petri dish and placed in a constant temperature drying oven (105 ± 2°C) for 6 h. After cooled at room temperature, the whiskers were dispersed by mechanical external force to obtain modified phosphorus gypsum whiskers.

Infrared spectrum analysis of phosphogypsum whiskers

The samples of phosphogypsum whiskers and potassium bromide were put in a constant temperature drying

oven (105 ± 2°C), dried at a constant temperature for more than 4 h until they were completely dry, and then transferred to a desiccator for 30 min. A proper amount of phosphogypsum whiskers was mixed with potassium bromide and ground evenly for 5 min. The tablet was pressed under the conditions of 10 MPa pressure and 1 min tablet pressing time, and then placed in a Vector 22 Fourier transform infrared (FTIR) spectrometer (Bruker; Billerica, MA, USA) for analysis.

Scanning electron microscope of phosphogypsum whiskers

The surface morphology of phosphogypsum whiskers was observed using scanning electron microscope (SEM, JSM-IT300LV, JEOL; Tokyo, Japan).

Defibering and beating

The bleached softwood paddle board was soaked in water and torn into 25 mm × 25 mm sized pieces. The pulp was defibered in a 970154 slurry high frequency dehydrator (Asea Brown Boveri; Zurich, Switzerland) for 30 min and then beaten in the ZQS2-23L Valley beater (Machinery Factory of Shanxi University of Science & Technology; Shanxi, China) until the beating degree was 30°SR, which was measured by ZDJ-100 beating degree tester (Yibin Paper Co. Ltd.; Yibin, Sichuan, China). Then, the beaten pulp was put in a plastic bag for 24 h and the moisture value was measured.

Papermaking

Thirty-percent phosphogypsum whiskers and modified phosphogypsum whiskers were added to the bleached softwood pulp with a beating degree of 30°SR to prepare handsheets with a basis weight of 80 g/m² with an NO.7047.S standard sheet former (Elof Hansson; Gothenburg, Sweden). An NO. 2571-I press (Kumagai Riki Kogyo Co. Ltd.; Tokyo, Japan) was used to press handsheets, and an RK-2A-KWT type PTI dryer (Elof Hansson) was used for drying handsheets.

Detection of physical properties of paper

According to the Chinese National Standard GB/T 10739-1989 "Paper, board and pulps — Conditioning of samples and testing atmospheres," the handsheets were treated with constant temperature and humidity for 4 h, and then the grammage of handsheets was determined according to the method of GB/T 451.2-2002 "Paper and board — Determination of grammage." Five handsheets of similar quality were selected for physical properties. Other handsheet tests for physical properties included:

- Whiteness: GB/T 7974-2002 "Paper, board and pulp — Measurement of brightness — Diff/Geometry" using Model 970894 (Lorentzen & Wettre; Kista, Sweden).
- Folding resistance: GB/T 457-2008 "Paper and board — Determination of folding endurance" using a TD908-1 folding resistance degree tester (Tinius Olsen; Redhill, UK).
- Tear strength: GB/T 455-2002 "Paper and board determination of tearing resistance" using an SE099 tear tester (Lorentzen & Wettre).
- Tensile strength: GB/T 12914-2008 "Paper and board — Determination of tensile properties" using an SE062 tensile strength tester (Lorentzen & Wettre).
- Bursting strength: GB/T 454-2002 "Paper — Determination of bursting strength" [25] using a 969920 burst tester (Lorentzen & Wettre).

Determination of phosphogypsum whisker retention

The retention (R) of the filler is calculated by measuring the ash content of the handsheet. First, dry the handsheet at 105°C, put it into a crucible that is pre-fired to a constant mass, move it into a muffle furnace with a burning temperature of 575°C, and burn it until the mass is constant. The calculation formula of retention rate is:

$$R(\%) = \frac{M(X_1 - X_2)}{c(1-d)} \times 100$$

$$d(\%) = \frac{m_1 - m_2}{m_1} \times 100$$

where M is the quality of the filled paper sample before burning (g); X_1 is the ash content of paper (%); X_2 is the ash content of blank sample (%); d is the ignition loss rate of CSW at 575°C (%); m_1 is the weight of CSW before burning (g); and m_2 is the weight of CSW after burning.

RESULTS AND DISCUSSION

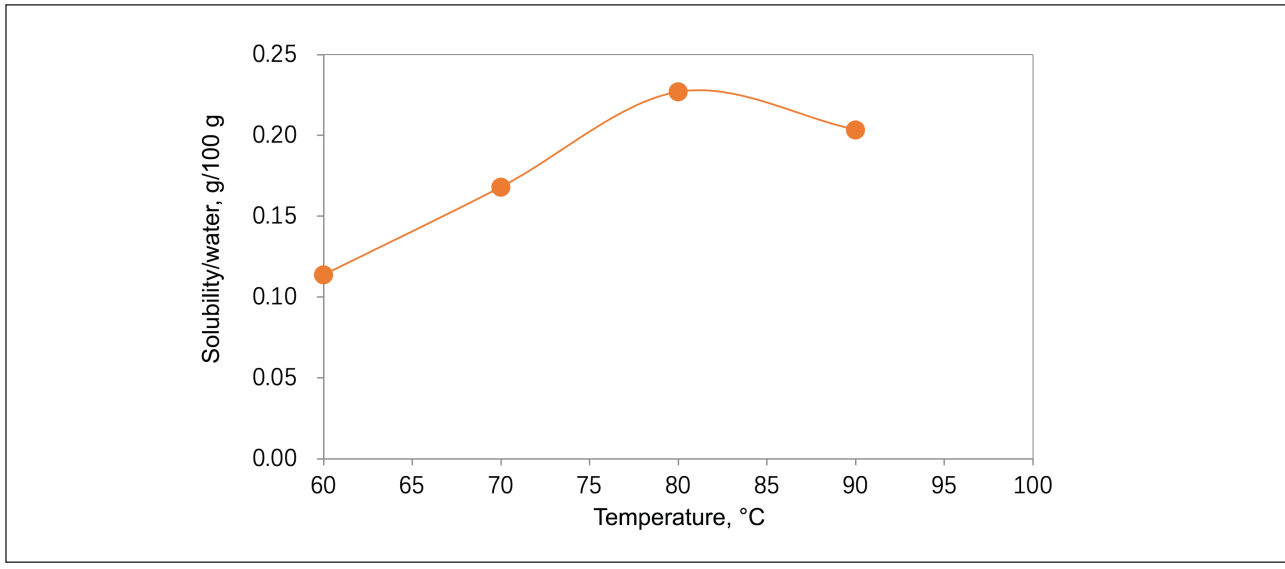
Effect of calcium stearate modifier on solubility of phosphogypsum whiskers

The effects of different reaction temperature, reaction time, and the amount of calcium stearate on the solubility of modified phosphogypsum whiskers in water during the modification process were discussed.

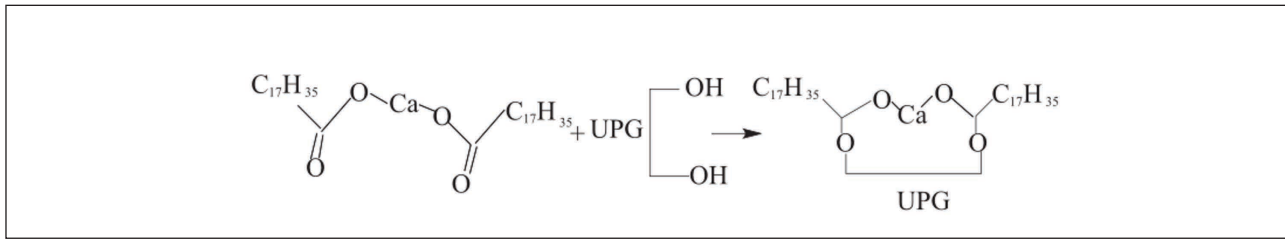
Effect of reaction temperature on solubility of modified phosphogypsum whiskers

Because calcium stearate is not soluble in cold water, the reaction temperatures of phosphogypsum whiskers were set at 60°C, 70°C, 80°C, and 90°C, respectively. When the dosage of phosphogypsum whiskers was 36 g, the dosage of calcium stearate modifier was 0.72 g and the reaction time was 30 min. **Figure 1** shows the experimental results.

The solubility of phosphogypsum whiskers in 100 g water was 0.33 g at room temperature. It could be seen from Fig. 1 that the solubility of phosphogypsum whiskers modified with calcium stearate was between 0.11–0.23 g/100 g water, which



1. Effect of reaction temperature on solubility of whiskers.



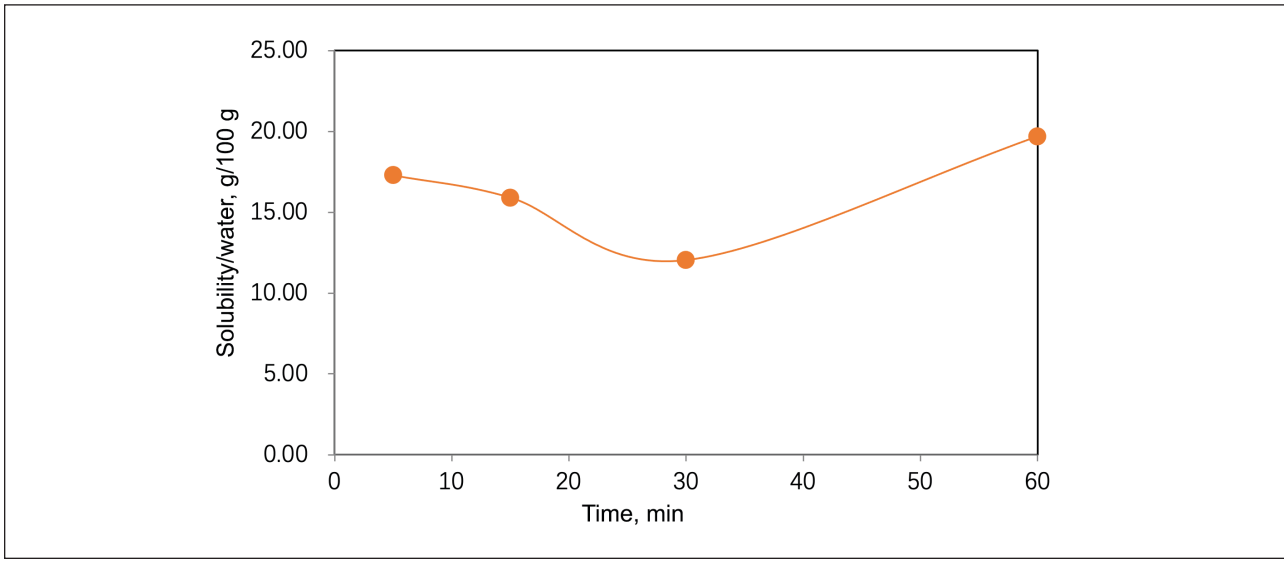
2. Action mechanism of calcium stearate-modified ultrafine phosphogypsum.

was much lower than the original gypsum whiskers. This was because the carbonyl group in the calcium stearate undergoes a condensation reaction with the hydroxyl group on the PG, so that the calcium stearate is adsorbed on the surface of the PG through chemical bonds [26]. Moreover, there were long hydrophobic chains in the calcium stearate molecule. These hydrophobic chains were adsorbed on the surface of the phosphogypsum whiskers under the modified action, thereby greatly improving the hydrophobicity of the phosphogypsum whiskers. The reaction mechanism is shown in **Fig. 2**. Therefore, the calcium stearate modifier played a significant role in suppressing the dissolution of the phosphogypsum whiskers. As can be seen from Fig. 1, with the increase in the reaction temperature, the solubility of the modified phosphogypsum whiskers first increased and then decreased. Normally, the solubility of phosphogypsum increases with increasing temperature [27], while the high temperature of 90°C could make the phosphogypsum modified by calcium stearate more hydrophobic [18], so that the solubility at 90°C was lower than that at 80°C; this result was consistent with Zheng's finding [18].

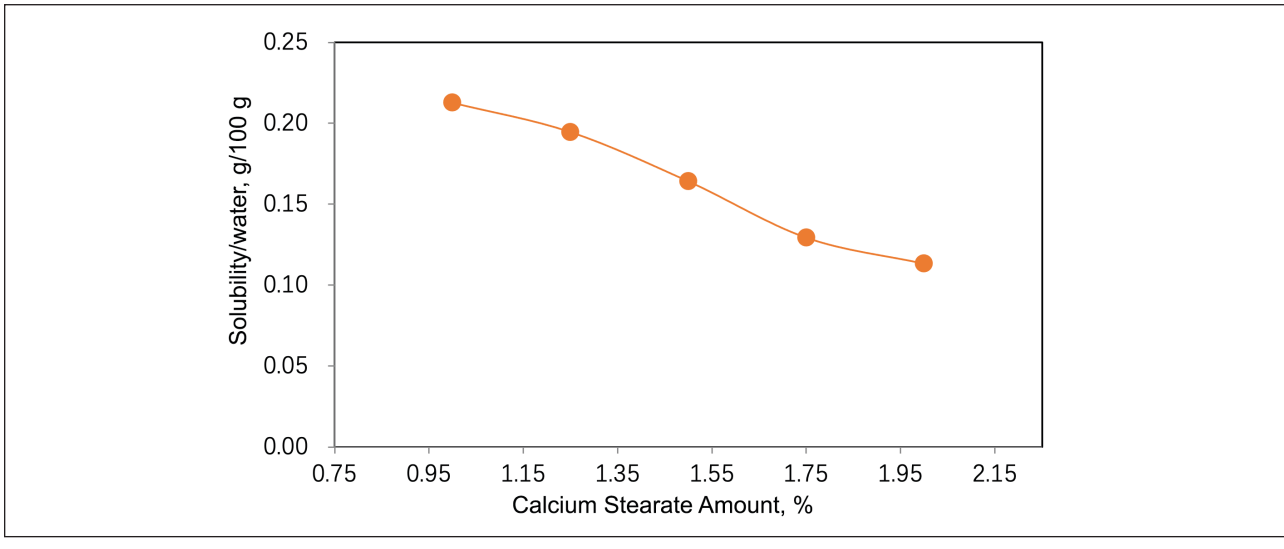
Effect of reaction time on solubility of modified phosphogypsum whiskers

When the amount of phosphogypsum whiskers was 36 g, the amount of calcium stearate modifier was 0.72 g, the reaction temperature was 60°C, and the reaction time of the modification process was set to 5 min, 15 min, 30 min, and 60 min. The modification results are shown in **Fig. 3**.

It can be seen from Fig. 3 that the solubility of the modified phosphogypsum whiskers first decreased and then increased with the increase in reaction time. With the increase in dissolution time, the solubility of phosphogypsum increased, and the surface modification of phosphogypsum by calcium stearate became more and more sufficient from the beginning of the reaction. The hydrophobicity of the modified phosphogypsum particles continuously increased, and the increase in hydrophobicity of phosphogypsum was greater than the increase in hydrophilic solubility [28]. When the reaction time was 30 min, the solubility of the modified phosphogypsum whiskers was the smallest, which was 0.11 g/100 g. At this time, the surface coating of calcium sulfate was almost completed, and the particle hydrophobicity had reached the maximum value. At the same time, calcium stearate had fully reacted. When the reaction continued, the absolute decrease in solubility brought about by the modified phosphogypsum was less than the absolute increase in solubility of the phosphogypsum itself. At 60 min, the modification effect decreased, so the optimal modification time of calcium stearate modifier for whiskers was 30 min.



3. Effect of reaction time on solubility of whiskers.



4. Effect of calcium stearate dosage on solubility of whiskers.

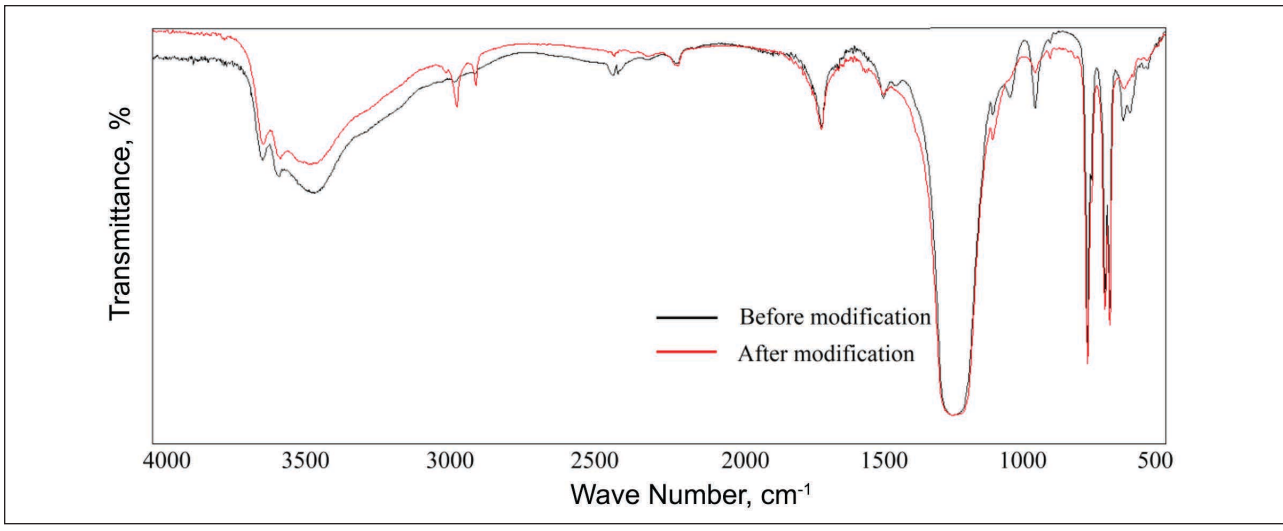
Effect of calcium stearate dosage on solubility of modified phosphogypsum whiskers

When the absolute amount of phosphogypsum whiskers was 36 g, the reaction temperature was 60°C, the reaction time was 30 min, and the modification amount of calcium stearate on phosphogypsum whiskers was 0.36 g, 0.45 g, 0.54 g, 0.63 g, and 0.72 g; that is, the percentage of calcium stearate relative to absolute dry amount of phosphogypsum whiskers was 1.00%, 1.25%, 1.50%, 1.75%, and 2.00%, respectively. The modification results are shown in **Fig. 4**.

It can be seen from Fig. 4 that the solubility of the modified phosphogypsum whiskers gradually decreased when the amount of calcium stearate was increased, and the solubility of the modified phosphogypsum whiskers reached the lowest value of 0.11 g when the calcium stearate was 0.72 g, which was 2% of the phosphogypsum mass. When the amount of modifier was increased from 1% to 2%, more and more modifiers were coated on the surface of phosphogypsum whiskers. The hydrophobicity of the surface of the modified phosphogypsum whiskers was increased due to the hydrophobic long chain of calcium stearate, and it was difficult for water to contact the surface of the phosphogypsum whiskers directly. Zheng et al. [18] used calcium stearate to modify ultrafine phosphogypsum, and it was concluded that the oil absorption value of the modified ultra-fine phosphogypsum decreased and the contact angle increased as the amount of calcium stearate added to the modifier increased from 0.5% to 2%. Also, when the amount of modifier was 2%, the hydrophobicity was the highest.

Surface properties of modified phosphogypsum whiskers

In order to study the surface properties of the modified phosphogypsum whiskers and to understand the modifica-



5. Infrared spectroscopy comparison of whiskers before and after modification.

tion mechanism, infrared spectroscopy and SEM analysis were performed on the phosphogypsum whiskers.

Infrared spectrum analysis of modified phosphogypsum whiskers

Figure 5 gives a comparison of infrared spectra of phosphogypsum whiskers before and after modification. From Fig. 5, it can be seen that the phosphogypsum whiskers showed the stretching vibration peaks of hydroxyl groups at 3423.03 cm^{-1} before and after the modification. It was considered that this was due to the hydroxylation of calcium ions on the surface of the phosphogypsum whiskers and that the association between them formed hydrogen bonds: asymmetric stretching vibration peaks of hydroxyl groups appeared at 1621.84 cm^{-1}; and there were very sharp absorption peaks at 1159.91 cm^{-1}, 674.96 cm^{-1}, 613.25 cm^{-1}, and 595.90 cm^{-1}. These absorption peaks were generated by the vibration of S—O and S = O covalent bonds in sulfate ions [27]. It could be established from this analysis that the surface of the phosphogypsum whiskers contained -OH and $-SO_4^{2-}$ groups and that the quality of the phosphogypsum whiskers was relatively pure before modification. The modified whiskers showed absorption peaks at 2915.84 cm^{-1} and 2848.35 cm^{-1}. The analysis suggested that the absorption peak should be a saturated carbon-hydrogen bond stretching vibration in $-CH_3$ and $-CH_2$. Therefore, it could be considered that the organic groups in the calcium stearate modifier were successfully adsorbed on the surface of the whiskers, and a bond occurred with the phosphogypsum whiskers [29]. The surface properties of the whiskers were changed, and the water solubility of the whiskers was effectively reduced, thereby achieving the effect of improving its retention.

Scanning analysis of modified phosphogypsum whiskers

Figure 6 shows an SEM image of phosphogypsum whiskers before and after modification. It can be seen from Fig. 6a that the shape of phosphogypsum whiskers before modification was regular, generally in the shape of needle or rod; the size was relatively uniform; and the surface was smooth without attachments. Moreover, its surface was smooth and free of attachments, and there were no obvious crystal defects such as cracks on the surface. After modification with the calcium stearate modifier, a large number of distributed coatings uniformly appear on the surface of the whiskers in Fig. 6b. The surface state of the whiskers had been changed, which had a good effect on reducing the solubility of the whiskers. It can be seen from the figure that the mechanical stirring force during the modification process made the volume of phosphogypsum whisker particles smaller.

Effect of different phosphogypsum whisker modification reaction conditions on paper properties and filler retention.

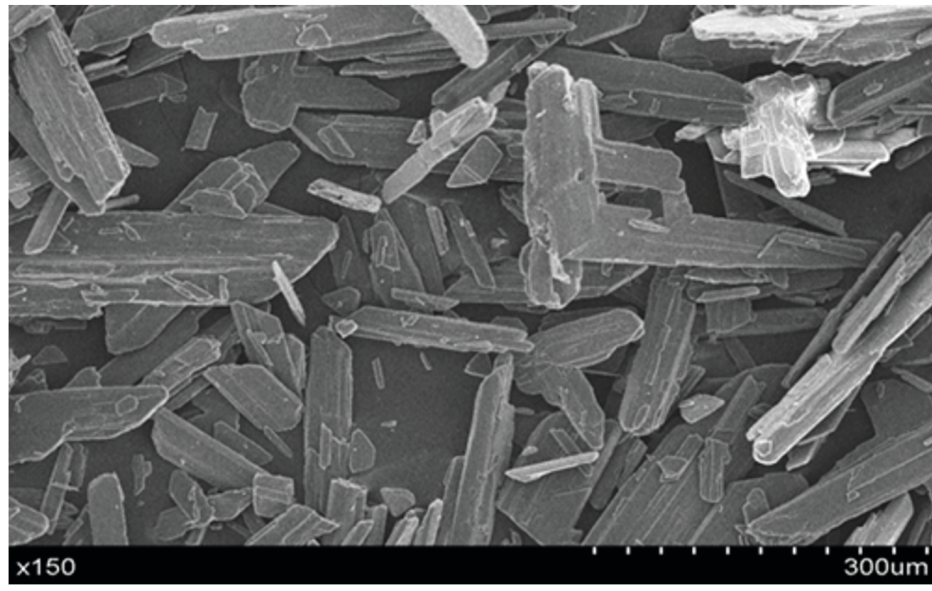
By making handsheets with the basis weight of 80 g/m^2, the effects of calcium stearate phosphate gypsum whisker filling on the properties of papermaking paper under different modification conditions were investigated.

Effect of phosphogypsum whisker modification reaction temperature on physical properties and filler retention of paper

The effects of the addition of phosphogypsum whiskers with different modification reaction temperatures on the optical properties, physical strength properties, and filler retention of paper were investigated when the amount of calcium stearate modifier was 0.72 g and the reaction time was 30 min.

According to **Table I**, the whiteness of the paper with the original whiskers was 80.96%. The modified phosphogypsum whiskers reduced the whiteness of the paper. This was because the light scattering coefficient of the phosphogypsum whiskers modified by calcium stearate was lower than that of the original whiskers, which made the whiteness of modified whiskers become lower. The whiteness of the paper filled with modified whiskers at 80°C

a.



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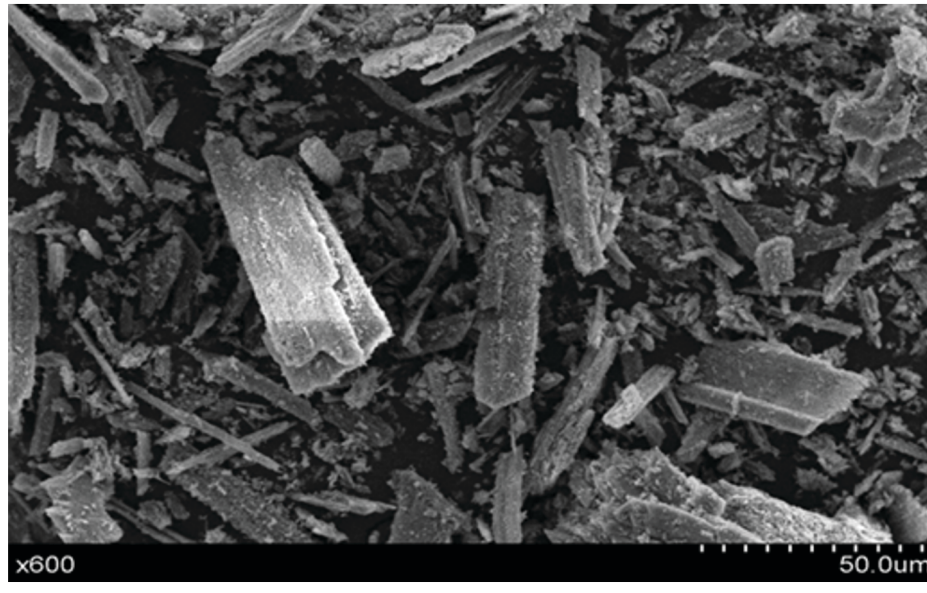
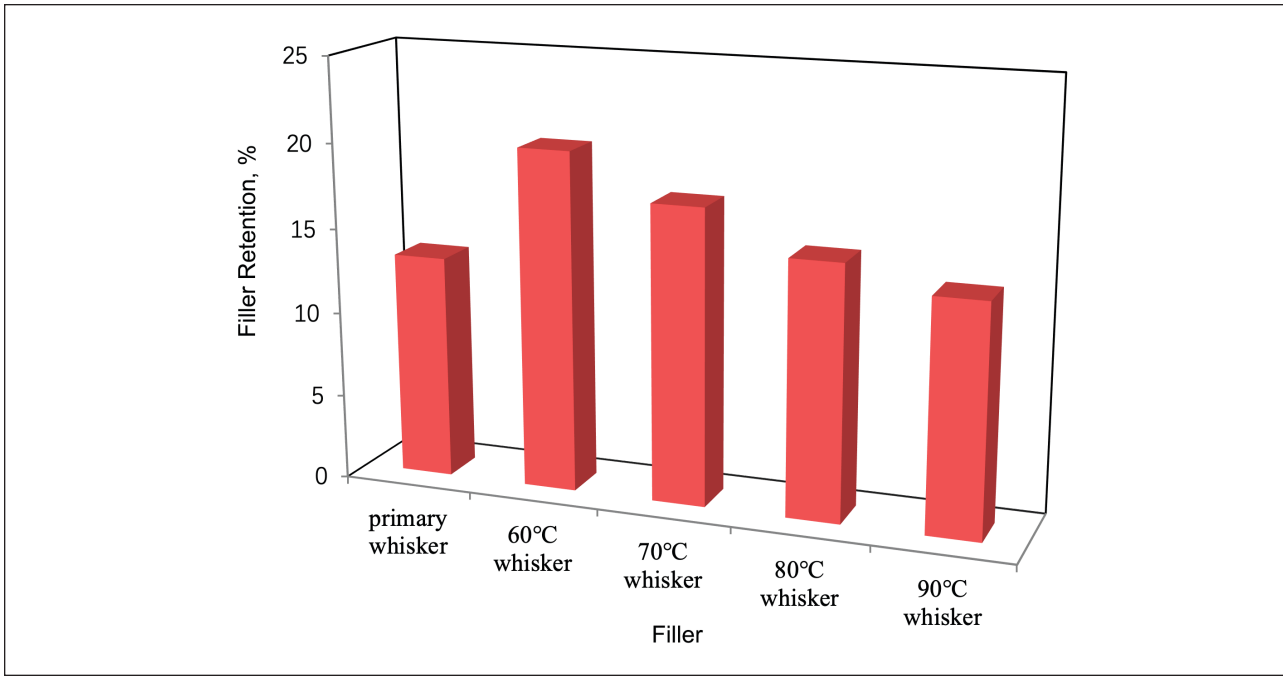


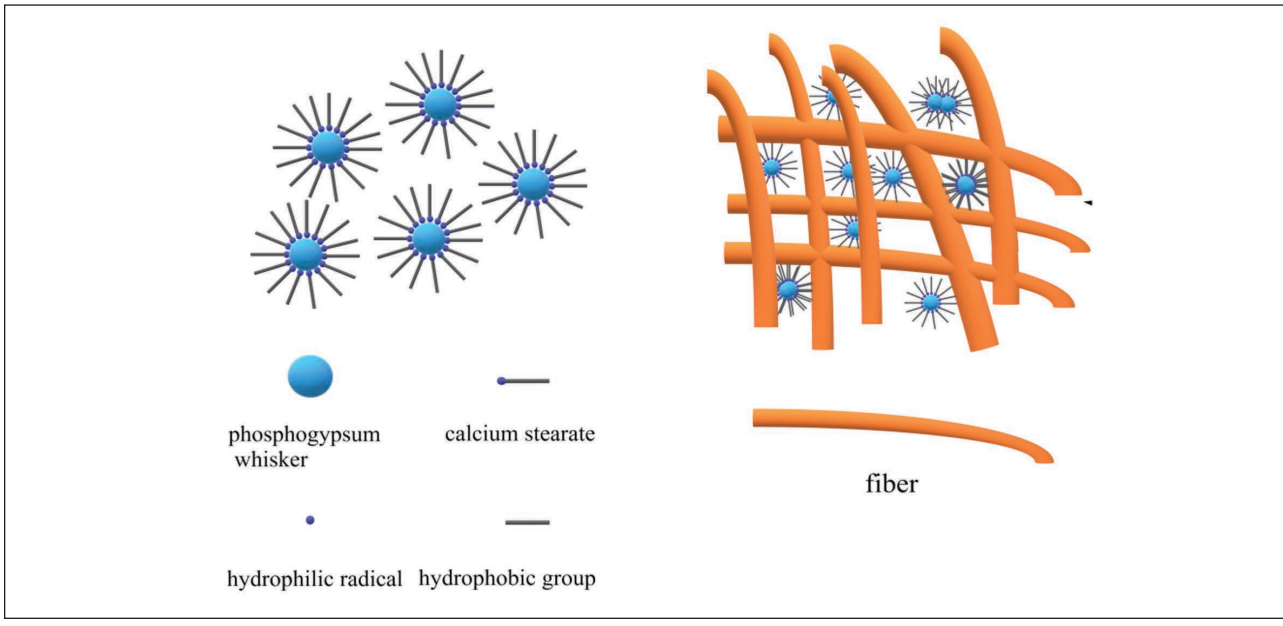
6. Scanning electron microscope (SEM) image comparison of whiskers before (a) and after (b) modification.

Filler	Whiteness, %	Tensile Index, $N \cdot m \cdot g^{-1}$	Tear Index, $mN \cdot m^2 \cdot g^{-1}$	Burst Index, $kPa \cdot m^2 \cdot g^{-1}$	Folding Resistance, times	Retention, %
Primary whisker	80.96	40.1	7.54	2.52	83	13.16
60°C modified whiskers	80.16	36.4	8.69	2.43	77	20.01
70°C modified whiskers	80.65	37.9	8.57	2.46	78	17.41
80°C modified whiskers	80.68	39.9	8.49	2.50	94	14.97
90°C modified whiskers	80.53	38.6	8.37	2.47	92	13.58

I. Effect of reaction temperature on paper properties.



7. Effect of reaction temperature on the retention of whiskers.



8. Whiskers and fibers intertwine into a paper sheet.

was 80.68% ISO, which was higher than the whiteness of paper modified at other temperatures. Because the solubility of the modified whiskers was up to 0.23 g/100 g (Fig. 1), the corresponding paper retention was low (**Fig. 7**); the whiskers and fibers were intertwined to form a handsheet (**Fig. 8**); the binding between paper fibers was stronger than that at other modified temperatures, which can reduce the light wave absorption in the visible light range; and the reflection at 457 nm was increased, so that the whiteness of the paper was significant at this time [30]. Under these conditions, the physical strength of the handsheets was relatively good, and the tensile index, burst index, and folding endurance had all reached the maximum compared with those at the other modification temperatures. It can be seen from Fig. 7 that the filler retention was significantly improved when the calcium stearate-modified phosphogypsum whiskers were used as fillers added to the paper, to a certain extent. The filler retention of modified whiskers was the highest when the reaction temperature was 60°C, which increased from 13.16% (original whiskers) to 20.01%. As the modification reaction temperature increased from 60°C to 90°C, the filler retention

Filler	Whiteness, %	Tensile Index, $N \cdot m \cdot g^{-1}$	Tear Index, $mN \cdot m^2 \cdot g^{-1}$	Burst Index, $kPa \cdot m^2 \cdot g^{-1}$	Folding Resistance, times	Retention, %
Primary whisker	80.96	40.1	7.54	2.52	83	13.16
5 min modified whiskers	80.37	37.4	8.44	2.48	83	16.09
15 min modified whiskers	79.14	37.1	8.44	2.45	81	16.58
30 min modified whiskers	78.58	36.2	8.52	2.43	79	19.09
60 min modified whiskers	80.01	38.1	8.21	2.51	80	15.88

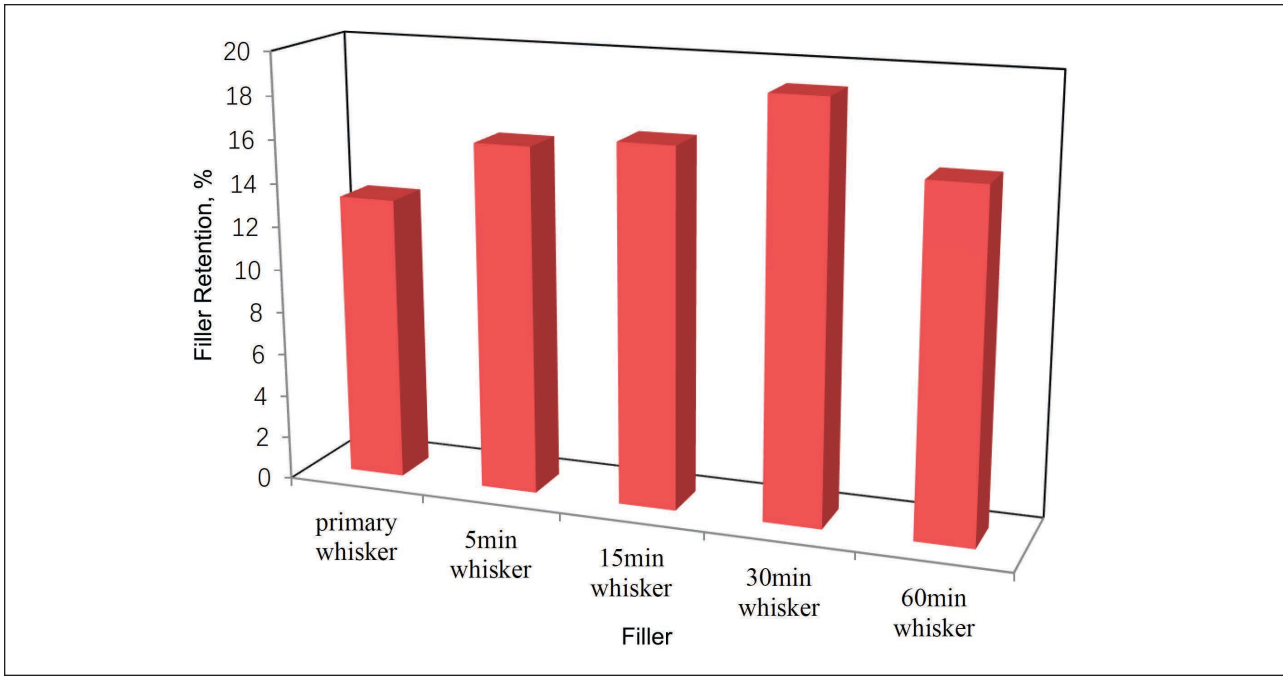
II. Effect of reaction time on paper properties.

of modified whiskers decreased accordingly, which corresponded to the effect of reaction temperature on the solubility of whiskers. That is to say, the higher the solubility of modified phosphogypsum, the lower the retention of filler is. On the contrary, the lower the solubility, the higher the retention of filler. After modification, the tensile index and the burst index of the handsheets were both reduced to a certain extent, but the tear index was increased. The tear index of the filled paper was mainly related to the fiber length and the effective fiber bonding area [31]; the SEM image in Fig. 6 shows that the volume of the modified phosphogypsum particles became smaller, which induced the fiber bonding area to become larger per unit mass, thus increasing the handsheet tearing index. The folding resistance of the handsheets with the corresponding modified whiskers was lower than that of the handsheets with the original whiskers when the reaction temperature of the modified phosphogypsum whiskers was lower than 80°C. The folding resistance of the handsheets with the corresponding modified whiskers was higher than that of the handsheets with the original whiskers when the reaction temperature of the modified phosphogypsum whiskers exceeded 80°C; this may be caused by the partial thermal oxygen decomposition of calcium stearate at higher temperatures [32], which caused the hydrophobic long-chain adsorbed on the surface of phosphogypsum whiskers to partially break. This was beneficial for the good distribution of the modified phosphogypsum whiskers in the handsheets, and there was a better binding force between the fibers of the handsheets after the filler was added, so that the folding resistance of the handsheets was improved.

Effect of modification reaction time of phosphogypsum whiskers on physical properties and filler retention of paper

When the amount of calcium stearate modifier was 0.72 g and the reaction temperature was 60°C, the effects of phosphogypsum whiskers on the optical properties, physical strength properties, and filler retention of the handsheets under different modification reaction times were investigated.

As can be seen from **Table II**, compared with the original filler whiskers, the whiteness, tensile strength, and fracture index of the handsheets can be reduced to some extent under this condition by the modified whiskers, but the tearing degree was increased to some extent. With the increase of the reaction time, the whiteness, tensile index, burst index, and folding endurance of the paper with the corresponding modified whiskers all showed a trend of decreasing first and then increasing, while the tear index and retention (**Fig. 9**) showed a trend of rising first and then decreasing. The whiteness of handsheets filled with modified whiskers for 30 min was 78.58% ISO, which was lower than the whiteness of other modified-time whiskers. At this time, the solubility of the modified whiskers was at least 0.11 g (Fig. 3), and the corresponding paper retention was 19.09% (Fig. 9), which increased 45.06%, compared with 13.16% for the original whiskers. The principle was that the binding between the fibers was weaker than for other papers with different reaction times, which could increase the absorption in the visible light range and reduce the reflection at 457 nm so that the whiteness of the handsheet was small at this time [31]. Under these conditions, the physical strength tensile index of the paper sheet was 36.2 $N \cdot m \cdot g^{-1}$ and the burst resistance index was 2.43 $kPa \cdot m2 \cdot g^{-1}$, both of which reached the lowest values compared with other modification times; the tear index of 8.52 $mN \cdot m2 \cdot g^{-1}$ was the highest value under different reaction time conditions. Combining the solubility of phosphogypsum at 30 min reaction time, it can be known that the surface of the modified phosphogypsum whiskers was well covered with fully reacted calcium stearate, which had good hydrophobicity and low solubility. Most of them remain well on the fiber, so the tensile index and bursting index were reduced, but the particle volume became smaller, enhancing the fiber bonding area, so the tear index was increased [32]. It can be seen from Table II that the change in reaction time had little effect on the folding resistance, and because the reaction temperature was 60°C at this time, there was no partial thermal oxygen decomposition of calcium stearate. At 90°C, the hydrophobic long chain part adsorbed on the surface of the phosphogypsum whiskers was partially broken, which in turn affected the phenomenon of folding resistance.



9. Effect of reaction time on the retention of whiskers.

Filler	Whiteness, %	Tensile Index, $N \cdot m \cdot g^{-1}$	Tear Index, $mN \cdot m^2 \cdot g^{-1}$	Burst Index, $kPa \cdot m^2 \cdot g^{-1}$	Folding Resistance, times	Retention, %
Primary whiskers	80.96	40.1	7.54	2.52	83	13.16
0.36 g modified whiskers	78.39	37.4	8.14	2.45	73	13.44
0.45 g modified whiskers	80.19	37.4	8.31	2.44	71	16.19
0.54 g modified whiskers	80.97	35.9	8.47	2.35	71	16.19
0.63 g modified whiskers	80.94	34.5	8.36	2.30	63	17.76
0.72 g modified whiskers	80.16	34.0	8.52	2.23	56	20.38

III. Effect of calcium stearate dosage on paper strength.

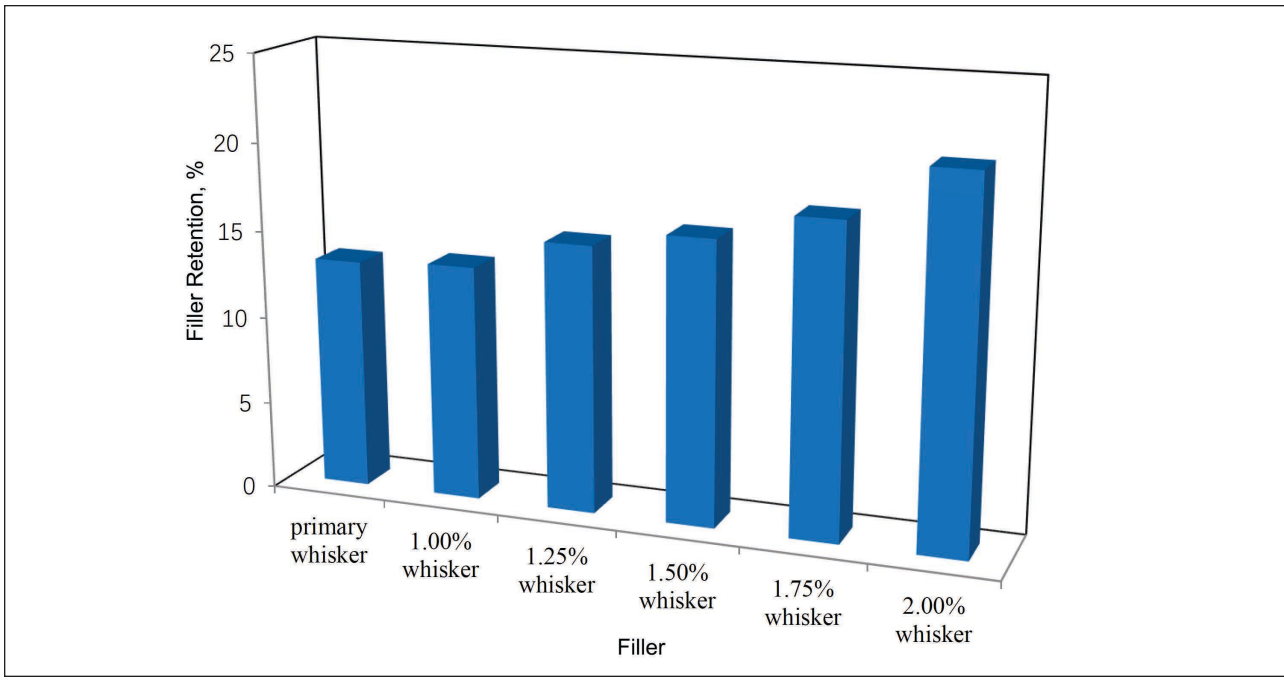
Effect of modifier amount of phosphogypsum whiskers on physical properties and filler retention of paper

When the modification reaction temperature was constant at 60°C and the reaction time was 30 min, as can be seen from **Table III**, the phosphogypsum whiskers were modified with different amounts of calcium stearate. As the amount of calcium stearate increased from 1% to 2%, the light scattering coefficient of the modified whiskers became smaller, so the whiteness became larger. At the same time, the retention increased from 13.44% to 20.38% (**Fig. 10**). This was because the solubility of the modified phosphogypsum was continuously decreasing, so more hydrophobic modified phosphogypsum was attached to the fibers, which reduced the binding ability between the fibers. Therefore, the tensile index, burst index, and folding resistance were reduced, but the modification process made the particle volume smaller (Fig. 6) and increased the fiber bonding area, so the tear index increased.

CONCLUSIONS

Key findings from this study include:

1. The solubility of phosphogypsum whiskers was inhibited by modification. In terms of solubility, the optimal conditions of modification treatment are as follows: dosage of calcium stearate at 2.00%; modification temperature of 60C°; and modification time of 20 min. Under these conditions, the solubility of phosphogypsum whiskers after modification can be reduced from 0.33 g/100 g to 0.11 g/100 g.



10. Effect of calcium stearate dosage on the retention of whiskers.

2. Modification of phosphogypsum whiskers for paper fillers has the following effects: slight reduction in the whiteness of the paper, but with little impact; reduction in the folding resistance, bursting index and tensile index of the paper; improved tear index of the paper; and increased filler retention of whiskers, to a certain extent. When the modification temperature is 60°C, the modification time is 30 min, and the amount of modifier is 2.00%, the retention of modified whiskers can be increased from about 13% to about 20%. This result is consistent with the results of the effect of reaction conditions on solubility. Based on this, it can be considered that the solubility of phosphogypsum whiskers has an important effect on retention in papermaking.
3. The modification mechanism is that the organic groups in the calcium stearate modifier adsorb on the surface of the whiskers and form a coating on the surface of the whiskers, which improves the hydrophobicity of the whiskers and reduces their solubility in water. **TJ**

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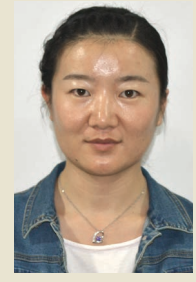
ABOUT THE AUTHORS

We studied this topic because it is directly related to renewable resource utilization for purposes of partially replacing traditional paper filler products. For the first time, a method for modifying phosphogypsum whiskers with calcium stearate to reduce its dissolving properties was used to fill bleached softwood pulp and make paper sheets.

This study gives proper modification conditions for production of a new filler from phosphogypsum whiskers. Different modification conditions, such as the amount of calcium stearate and modification of time and temperature were analyzed. It was very interesting to discover that the solubility of phosphogypsum whiskers was inhibited by modification.

Based on this study, the industry can consider that the solubility of phosphogypsum whiskers has an important effect on retention in papermaking. Hopefully, this work will help reduce dependency on non-renewable materials and help to clear and reuse phosphogypsum waste from the chemical industry.

H. Liu is associate professor; Jin is a Master's student; Chen is a Master's student; Zhang is a Master's student; Li is a Master's student; An is a Master's student; J. Liu is a Master's student; Pang is a Master's student; and Gao is professor at Tianjin Key Laboratory of Pulp and Paper, Tianjin University of Science & Technology, Tianjin, China. Email H. Liu at liuhaitang@tust.edu.cn.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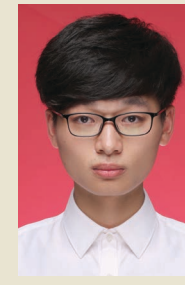
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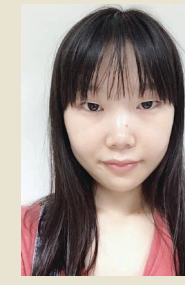
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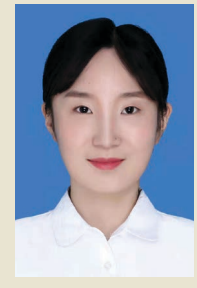
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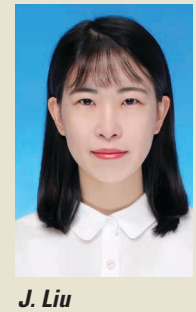
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