WOOD RESEARCH doi.org/10.37763/wr.1336-4561/67.3.511518
e-ISSN 2729-8906
67(3): 2022 511-518 pp.

SHORT NOTES

A RESEARCH ON THE APPLICATION OF INDUSTRIAL BY-PRODUCT CALCIUM SULFATE WHISKERS IN PAPER FILLING

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(RECEIVED OCTOBER 2021)

ABSTRACT

The basic properties of calcium sulfate whiskers were studied and compared with commercial ground calcium carbonate (GCC) fillers. The modified whiskers were used for paper filling and compared with a commercial precipitated calcium carbonate (PCC). As a result, it shows that when the unmodified calcium sulfate whisker is used to fill the paper, the ash content of the handmade sheet is low because of its dissolution problem. The ash content of the paper increased obviously when the modified calcium sulfate whisker was added, which reached the ash level of PCC filling. In addition, the paper strength increased greatly, but the light scattering coefficient decreased. In addition, the strength property of the modified calcium sulfate whisker filling paper is basically the same as that of the PCC filling paper with 14.99% ash content when the ash content of the modified calcium sulfate whisker filling paper is 21.95%.

KEYWORDS: Calcium sulfate whisker, modification, filler, strength, ash.

INTRODUCTION

Cellulose fibers and minerals are commonly used as fillers in papermaking process (Chauhan et al. 2014). By filling fillers, some paper properties can be improved and cost can be reduced (Dong et al. 2008), which can significantly improve the efficiency and economy of papermaking process. The cost of mineral fillers is much lower than that of cellulose fibers (Shen et al. 2009), and it has certain advantages in improving the properties of paper (whiteness, opacity, etc.) (Huang et al. 2014). However, the introduction of too many fillers will prevent the formation of hydrogen bonds, which is detrimental to the strength of paper (Koivunen et al. 2010).

At present, most paper filling materials in China comes from ground calcium carbonate (GCC) and precipitated calcium carbonate (PCC) (Chauhan et al. 2013). Although China is rich

in calcium carbonate resources, many mines with abundant reserves have been depleted because the calcium carbonate resources producing GCC or PCC are non-renewable resources (Wang et al. 2002), and serious damage has been caused by vegetation and natural environment in mining areas (Gong et al. 2019).

Calcium sulfate whisker also known as gypsum whisker (Tian et al. 2006), the international trade name is ONODA-GPF. It is a novel synthetic inorganic microfiber (Feng et al. 2015) between plant fiber and traditional filler. It is a high-quality mineral material with excellent performance and low price (Liu et al. 2009, Wang et al. 2008). Calcium sulfate whisker combines the advantages of ultra-fine inorganic materials and reinforced fibers such as good dimensional stability, heat resistance, chemical resistance, flame retardancy and electrical insulation (Song et al. 2006, Shen et al. 2009) and has good prospects for development as paper reinforcement materials (Wang et al. 2013, Louren et al. 2013, Peng 2017).

Research on calcium sulfate whiskers has been increasing in recent years, mainly due to the treatment of flue gas or waste acid by some industrial enterprises (Song et al. 2017). At present, most of the desulfurization processes in China for the conversion of sulfur dioxide in industrial flue gas use calcium-based compounds (lime) as absorbents, and the by-products obtained are mainly desulfurization gypsum (Zhou et al. 2020). The utilization of a large number of desulfurization gypsum waste has become an urgent problem in related industries (Wang et al. 2014). In addition, the metallurgical industry in a large number of waste acid (mainly sulfuric acid) can also be synthesized by a specific chemical reaction of calcium sulfate whiskers (Shi et al. 2010, Puurtinen 2004). It is of great significance to protect natural mineral resources, save plant fiber resources and reduce environmental pollution if calcium sulfate whisker can be fully used as papermaking functional filler to replace or partially replace non-renewable calcium carbonate resources as filler (Lin et al. 2011, Chen et al. 2012, Kumar et al. 2012).

In this study, the existing calcium sulfate whisker products in China were used to systematically study the main problems when they were used as paper filler, and the calcium sulfate whiskers were modified accordingly. The modified samples were subjected to paper filling test, and the test results were comprehensively evaluated.

MATERIAL AND METHODS

Materials and testing equipment

Chemical bleached hardwood pulp (Silver Star Company, Chile), chemical bleached softwood pulp (Ostrand Company, Sweden) and wheat straw pulp (Xinya Paper Group, China) were used in this study. Calcium sulfate whisker, commercial GCC and PCC were obtained from Datang Corporation (China), alkylkeetene dimer from Jinhao Company (China) and cationic polyacrylamide from Basf Company (Germany) .

Main equipment includes Laser particle size distribution tester (Bettersize3000Plus, Malvern, UK); abrasion tester (Tribovac2000, HEIDON, Japan); Kaiser rapid sheet papermaking apparatus (BBS, Estanit, Germany); whiteness color tester (YQ-Z-48B, Qingtong instrument Company, China); tensile strength tester (YQ-Z-1, Changjiang Company, China); paper bursting tester (B0660005, Linda company, Sweden); water bath pot and electric stove.

Testing method

Determination of solubility of calcium sulfate whisker by gravimetric method was according to JISK 1423: 1970(1991) (Japanese industrial standard for calcium sulfate). In this test, take 3 g dry calcium sulfate (solid content of 0.5%) dissolved in 100 ml water bath heated to 40°C, and stirred at this temperature for 30 min to completely dissolve (stirring speed 1500 rev $\cdot$ min^{-1}). After that, filtration of mixed solution and drying at 105°C for three hours. Gravimetric method was used to determine the solubility according to Eq. 1:

$$S = (M_0\text{-}M_1)/M_0 \quad (g \cdot ml^{-1}) \tag{1}$$

where: M_0 - the quality of the original calcium sulfate whisker in the dispersion (g), M_1 – the weight of the calcium sulfate whisker obtained after filtration and drying (g).

Filler performance test

The whiteness, particle size, oil absorption value and particle morphology of calcium sulfate whisker and commercial GCC were determined according to QB/T 2811: 2006 testing methods (National standard for GCC for papermaking in China).

Papermaking

Take 20 g of prepared pulp beating and defibering scattered in 1980 ml water, and adds different proportion of calcium sulfate whisker or calcium carbonate (the filling amount is relative to the absolute dry pulp), and adds 0.3% AKD (relative to the absolute dry pulp) and 0.05% cationic polyacrylamide (CPAM), respectively in the stirring state. The configured pulp is used for paper copying on the laboratory film copier.

Paper performance test

The whiteness, opacity, tensile strength, bursting strength and ash content of the paper were determined according to the standard TAPPI method after 24 hours of moisture balance.

RESULTS AND DISCUSSION

Basic properties of calcium sulfate whisker

The performance comparison between calcium sulfate whisker and papermaking filler GCC is shown in Tab. 1. Compared with GCC, calcium sulfate whisker has obvious whiteness advantage, and the shape of fibrous particles is helpful to reduce the decline in strength caused by papermaking filling. However, calcium sulfate whisker has the problems of low pH value and high electrical conductivity (Mao et al. 2005). At present, the papermaking process is mostly alkaline papermaking (Chen 2011). If the filler itself is acidic, it will seriously affect the efficiency of other papermaking auxiliaries. The high conductivity may be caused by the high-water solubility of calcium sulfate whisker (Gong et al. 2019).

In addition, the test cannot be carried out because of its fast sedimentation rate in aqueous dispersion when determining the particle size and wear of calcium sulfate whisker.

Tab. 1: Comparison of properties between calcium sulfate whisker and papermaking filler GCC.

Physical and chemical properties		$CaSO_4$	GCC
Whiteness (%)		95.6	89.6
Chromaticity (%)	L	98.93	95.93
	a	-0.75	-0.53
	b	1.57	1.59
Particle size distribution	< 10 μm	The settlement is too fast to be determined.	44
	< 5 μm		24
	< 2 μm		10
	< 1 μm		5
	Average (μm)		11.0
Wear value 2000 times (mg)		The blockage of the pipeline has not been detected.	41.8
Oil absorption value (mL· 100g)		86.6	24.6
pH (20%)		3.38	7.66
Zeta potential (5%) (mV)		-3.2	-67.8
Electrical conductivity ($ms \cdot cm^{-1}$)		1.013	0.462
Moisture (powder 105°C) (%)		13.77	0.02
Particle morphology		Fibrous	Cube

Filling test of unmodified calcium sulfate

The filling test was carried out with calcium sulfate whisker recovered from the factory and compared with a commercial GCC to investigate the problems of calcium sulfate whisker used in paper filling. The comparison of paper properties between GCC and calcium sulfate whiskers is shown in Tab. 2. The retention rate of calcium sulfate in the paper is low (only 12.25%, while GCC is 50.64%), so that there is a big difference between paper ash and GCC filling, with GCC of 15.54% and calcium sulfate whisker filling of 3.56%. Consequently, it is considered that the paper properties listed in Tab. 2 are not comparable.

Tab. 2: Properties of GCC and calcium sulfate whisker filling paper.

Types of fillers		GCC	$CaSO_4$
Filling amount (%)		30	30
Quantitative analysis ($g \cdot m^{-2}$)		70.4	69.6
Tightness ($g \cdot cm^{-3}$)		0.67	0.74
Whiteness (front / reverse) (%)		97.2/96.6	96.5/95.8
Chromaticity (front /reverse)	L	94.0/94.0	93.3/93.2
	a	6.3/6.1	7.3/7.0
	b	-8.6/-8.0	-9.7/-9.4
Opacity (%)		79.3	78.1
Smoothness (front / reverse) (S)		3.0/2.6	4.3/4.6
Tensile index (N·m·g)		64.4	69.2
Folding endurance		282	675
Burst index ($kPa \cdot m^2 \cdot g^{-1}$)		3.7	5.0
Tear index ($mN \cdot m^2 \cdot g^{-1}$)		6.55	5.92
K&N value (front / reverse) (%)		42.6/44.8	40.0/37.8
Ash (525°C) (%)		15.54	3.56
Filler retention (%)		50.64	12.25

The main problem leading to the low retention rate of calcium sulfate is its solubility in water. Combined with the papermaking process, it is not difficult to find that if the online concentration of the paper material is 0.5% and the filling amount is calculated according to 30%, the concentration of calcium sulfate whisker in the paper material is only 0.15%. However, the its solubility is usually about 0.2% (more than 0.15%). In theory, all the calcium sulfate whiskers added to the slurry may be dissolved if the conditions are suitable.

It can also be found that more fine fractions can be observed, and part of the whiskers are broken after the dissolution test (Fig. 2). Therefore, most of the calcium sulfate is lost with the papermaking white water when the calcium sulfate whisker is directly used for papermaking filling, resulting in a lower ash content in the paper. It is necessary to reduce the water solubility of calcium sulfate whiskers and slow down or eliminate the problem of fragmentation to successfully realize the filling of calcium sulfate whiskers in papermaking. Consequently, in view of this phenomenon, calcium sulfate whiskers were modified under laboratory conditions, and the modified samples were used to fill the paper.

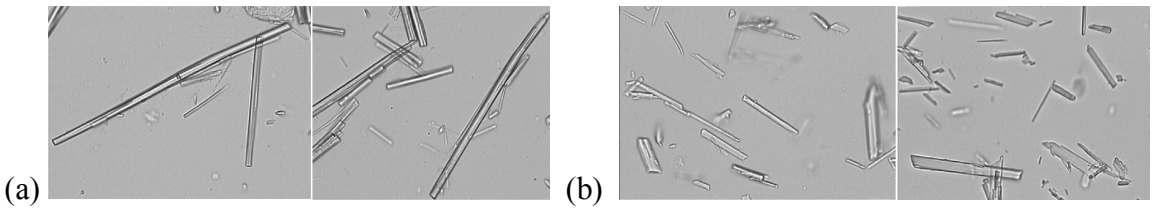

Fig. 2: Particle morphology of calcium sulfate: (a) original particles, (b) after dissolution test.

Filling test of modified calcium sulfate

The calcium sulfate whisker taken from the factory was modified under laboratory conditions to solve the dissolution problem of calcium sulfate whisker used in paper filling, and the modified sample was used for paper filling. The specific pulp formula is shown in Tab. 3, in which the beating degree of hardwood pulp is 35°SR, AKD solid content is 18%, which is taken from a paper mill; CPAM from Ciba; the quantitative amount of handmade sheet is 60 $g \cdot m^{-2}$, and the paper performance test results are shown in Tab. 4.

Tab. 3: Number of components in paper material.

Serial number	PCC (%)	Modification $CaSO_4$ (%)	Modification $CaSO_4$ (%)	AKD (%)	P47 (%)
1#	25	-	-	0.2	0.04
2#	-	25	-	0.2	0.04
3#	-	-	40	0.2	0.04

Note: the dosage in the table is for dry LBKP pulp.

As a result, it shows that the ash content of the handmade sheet reaches 15.07% after the calcium sulfate whisker is modified, which is basically the same as that of the PCC filled paper. The tensile index and burst index of calcium sulfate whisker filled paper were much higher than those of calcium carbonate filled paper at the same filling amount, which increased from 25.37 $N \cdot m \cdot g^{-1}$ and 1.4 $kPa \cdot m^2 \cdot g^{-1}$ to 30.88 $N \cdot m \cdot g^{-1}$ and 1.8 $kPa \cdot m^2 \cdot g^{-1}$, respectively. It indicated that calcium sulfate whisker was very beneficial to improve paper strength. In addition, the

whiteness and light scattering coefficient of calcium sulfate filled paper decreased. The analysis shows that the decrease of the light scattering coefficient of the handmade sheet is closely related to the fibrous particle morphology of the whisker itself, and the translucency of the whisker the ash content of the paper is 21.95% when the filling amount of calcium sulfate whisker is increased to 40%.

The above experimental results fully illustrate, the whiteness and strength properties of the paper are basically the same as those of the calcium carbonate filling sample with ash content of 14.99%. However, the light scattering coefficient is lower. This shows that compared with the selected PCC filling, the modified calcium sulfate whisker filling can obviously increase the ash content of the paper on the premise of maintaining the paper strength.

Tab. 4: Paper performance.

Serial number	1#	2#	3#
Quantitative ($g \cdot m^{-2}$)	61.4	60.7	59.2
Whiteness (%)	87.78	85.24	87.76
Opacity (%)	86.37	83.30	84.04
Light scattering coefficient ($m^2 \cdot kg^{-1}$)	60.92	51.63	57.48
Loose thickness ($cm^3 \cdot g^{-1}$)	1.99	1.93	1.94
Tensile index ($N \cdot m \cdot g^{-1}$)	25.37	30.88	25.66
Burst index ($kPa \cdot m^2 \cdot g^{-1}$)	1.4	1.8	1.3
Ash (%) (525°C)	14.99	15.07	21.95
Filler ablation rate (%) (525°C)	2.433	2.193	
Filler retention (%)	59.67	59.85	54.99

CONCLUSIONS

Calcium sulfate whisker is rarely used as filler in papermaking. The dissolution of calcium sulfate whisker is the main reason for its low ash content when used in paper filling. In this experiment, the paper was filled after improving the dissolution rate of calcium sulfate whisker, and compared with PCC and GCC. The results showed that the tensile index and burst index of paper filled with modified calcium sulfate whisker were higher than those of PCC and GCC under the same filling amount, but the whiteness and light scattering coefficient of paper filled with modified calcium sulfate whisker decreased. With the further increase of filling amount (40%), the performance of calcium sulfate whisker filled paper with ash content of 21.95% is basically the same as that of calcium carbonate filled paper with ash content of 14.99%. That is to say, while maintaining the strength of paper, paper ash content increased significantly.

ACKNOWLEDGEMENTS

Acknowledgements. The authors are grateful for the financial support by Inner Mongolia Natural Science Foundation (2020LH05001).

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