In-situ Preparation of Nano-calcium Carbonate/Cellulose Fiber Composite and Its Application in Fluff Pulp

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ABSTRACT

Calcium carbonate/cellulose fiber composites combining natural polymers and inorganic particles are promising materials for preparing fluff pulp. In this study, calcium carbonate ($CaCO_3$) particles were in-situ precipitated on cellulose fiber surfaces to decrease the level of hydrogen bonding. The results showed that nano $CaCO_3$ particles precipitated and dispersed well on the fiber surface. The fluff pulp made from cellulose/$CaCO_3$ modified fibers exhibited high effectiveness in the dry defibration process and good adsorption capacity due to the weak hydrogen bonding. The burst index of the handsheets decreased 31% (based on the ash content of 1.48 wt. %) without compromising the adsorption capacity of the fluff pulp.

Keywords: Modified fibers, In-situ precipitation, Fluff pulp, Dry defibration, Absorption capacity

INTRODUCTION

Fluff pulp, a kind of special cellulose fiber with high adsorption capacity, has been widely used in the health field, as well as in such applications as adult incontinence articles, baby diapers, and sanitary articles [1-3]. The fluffiness and moisture absorption are two most important quality parameters of the fluff pulp. Moreover, fluff pulps with a sufficient network structure and strength of fibers are capable of carrying a large amount of the super absorbing polymers (SAPs), thus allowing a higher moisture adsorption capacity [4-5]. In order to meet or even enhance the properties above, paper boards should be subjected to dry defibration prior to the production of fluff pulp, since those key properties are highly related to the inter-fiber bonds [6-8]. In the defibration process, paper boards were fed into a hammermill to produce fluff pulp consisting of intact, single fibers. More inter-fiber bonds and higher bonding strength in the fiber matrix lead to greater energy input during the dry defibration process [9-11]. Therefore, it is imperative to minimize the high hydrogen bonds between the fibers.

In traditional processes, reducing bonds and bonding strength between fibers is accomplished by applying debonders that typically contain a large amount of positive functional groups on one side (such as nitrogen ions) and hydrophobic groups on the other side (such as a long alkyl chain). Potential hydrogen bonding sites on the fiber surface are thus inhibited due to the reactions between the hydroxyl groups on the fiber surface and the positive functional groups of the debonders [12]. However, the hydrophobic groups of the debonders exhibit detrimental effects on the water absorption of the pulp. As a result, the performance of the fluff pulp products could be improved by an alternate method of minimizing the hydrogen bonds [13].

Calcium carbonate ($CaCO_3$) is an important inorganic material and many literature have reported the synthesis of the cellulose and $CaCO_3$ composites, such as the cellulose/$CaCO_3$ nanocomposites, cellulose acetate/ calcium carbonate hybrid nanocomposites and wood powder/$CaCO_3$ composites [14-21]. For many paper grades, $CaCO_3$ can be incorporated into the paper sheets to improve paper properties or reduce costs as a filler [22-23]. To achieve the maximum filler content, in-situ precipitation of $CaCO_3$ into the lumen and in the wall of the cellulose fibers have been utilized [24-28]. For the fluff pulp, $CaCO_3$ produced by the in-situ precipitation method can used to weaken the inter-fiber bonds by occupying the potential bonding sites on the fiber surface and increasing their steric hindrances. The use of such in-situ modified fibers in fluff pulp is expected to address the issue of limited fiber absorbability by eliminating the need for the hydrophobic debonders.

In this study, in-situ precipitation of nano $CaCO_3$ on cellulose fiber surface to improve the fluffiness and adsorption properties of the modified fluff pulp was investigated. First, the cellulose fibers were modified by an in-situ precipitation method. Subsequently, the resultant cellulose/$CaCO_3$ fibers were used to prepare

the fluff pulp. The crystalline structure and microstructure of the modified fibers were determined to verify the formation of Cellulose/$CaCO_3$ composites. The fluffiness and moisture absorption capacity of the fluff pulp before and after modification were also determined.

EXPERIMENTAL

Materials

Calcium oxide and sodium carbonate were of analytical grade purchased from Tianjin Chemical Reagent Co., Ltd, respectively and were used without further purification. Bleached kraft softwood pulp was purchased from Phoenix Paper Co., Ltd.

In-Situ Precipitation of Calcium Carbonate on Fiber Surface

Ten grams of CaO was mixed in deionized water at 90°C to form calcium hydroxide slurry, which was stored for 24 h prior to being used. Insoluble substances were removed via a 200 mesh screen and obtain a pure calcium hydroxide solution. The pulp fibers and calcium hydroxide solution were mixed into deionized water (deionized water, fiber and calcium ratio was 50:5:1, g/g/g). The mixture was agitated vigorously and then maintained at 25°C for 10 minutes. After that, an overdose of Na_2CO_3 was added to the mixture to precipitate the $CaCO_3$ when calcium hydroxide penetrated into the fibers. The fibers were subsequently washed thoroughly with running tap water over a 60 mesh screen until a clear filtrate was obtained.

Handsheets were prepared using the in-situ modified softwood pulp fibers. The fluff pulp sheets with basis weights of 650 ± 10 g/m^2 were first prepared via a sheet former, and then pressed at 350 kPa for 1 minute. Finally, the samples were dried in a vacuum oven at 105°C to obtain the handsheets with solid concentration of 93 wt. percent. A schematic of the handsheet production process is presented in *Figure 1*.

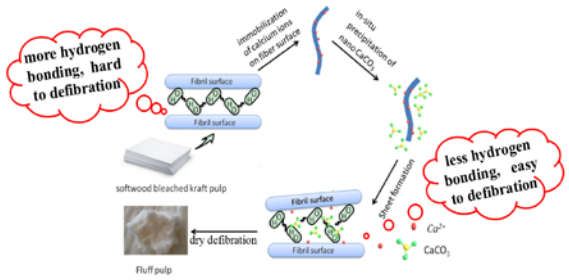

FIGURE 1. Schematic of the concept of preparing the cellulose/$CaCO_3$ modified fibers for enhanced the defibration process of fluff pulp.

Analytical Methods

The X-ray diffraction (XRD) spectra of the samples were obtained using a D/max 2200PC X-ray diffractometer (40 kV, 20mA) with a Cu Kα anode (λ=0.1542nm) from 10° to 70° of 2θ with a 0.025°/s speed at the ambient temperature.

The fluff pulp samples made from modified fibers were analyzed using a scanning electron microscopy (SEM) at 20 kV (Hitachi S-4800). The sample was prepared as a paper sheet with dimensions of 2mm×2mm and all the samples were coated with Au prior to the examination.

The burst index of handsheets was determined using the DCP-NPY5600 bursting strength tester (China) according to the standard of ISO 2759: 2014. The ash content of the handsheets was tested according to the TAPPI T221-om 02 method.

The absorption capacity of the fluff pulp was measured according to GB/T 21331-2008. The procedures detail as follows: 3.0 g of well-dispersed fluff pulp was put into a tube of 50 mm diameter, and 500 g of weight was loaded on fluff pulp pad lightly for 30 s. An open water container was subsequently placed under the pulp and the pad absorbed water for 3 min. Then the open water container was removed. After 30 s, the weight was removed. The weight of wet fluff pulp after absorbing the water was measured. The absorption capacity can be calculated as,

$$Absorption\ capacity = m_1\text{-}m_0/m_0 \qquad (1)$$

Where m_0 is the weight of fluff pulp; m_1 is the weight of fluff pulp with absorbing water.

The morphology characteristics of the fibers were measured by using Morfi Compact. The concentration of each test sample was set as 1% (g/g). This equipment is equipped with a high-resolution camera that can perform dynamic analysis of the pulp fiber and shives. The fiber properties tested include length, width, curl, kink and coarseness of the fiber, as well as shives and fines analysis. Samples were tested in the Morfi equipment, using a population of fibers of about 5000 units for obtaining the parameters of fibers.

RESULTS AND DISCUSSION

In-Situ Precipitation of Nano $Caco_3$ on Cellulose Fiber for Improving the Defibration Process and Fluffiness of Fluff Pulp

As shown in *Figure 1*, the hypothesis of the present study is that, for the native cellulose fiber without the presence of the nano $CaCO_3$ on the fiber surface, hydrogen bonds are extensively formed, due to the large amount of hydroxyl groups that are present in the cellulose fibers. In this way, the fluff pulp made from the native cellulose fiber has more inter-fiber hydrogen bonds, which make the defibration process much harder. In contrast, for the in-situ modified fiber, less amount of hydroxyl groups are available for the formation of inter-fiber hydrogen bonds due to the fact that the nano $CaCO_3$ precipitated and dispersed uniformly on the fiber surface, and thus occupied a proportion of potential hydrogen bonding sites through steric hindrance. In the literature, Subramanian et al have investigated the effect of $CaCO_3$ on uncoated cellulose fiber and the results showed that the addition of $CaCO_3$ can interfere with fiber-to-fiber bonding [29]. As a result, fluff pulp made from the modified fiber has less inter-fiber hydrogen bonds, which makes the defibration process much easier.

Microstructure of the Cellulose/$CaCO_3$ Fibers

The microstructures of the cellulose/$CaCO_3$ fibers were observed using SEM. As shown in *Figure 2a*, $CaCO_3$ dispersed well on the surface of the cellulose fiber. Thanks to the in-situ precipitation method, the size of the formed $CaCO_3$ particles is nano-scale, around 300-600 nm. Additionally, those nano $CaCO_3$ particles were firmly and effectively adhered and bonded to the fiber surface. *Figure 2b* shows a magnified micrograph of the composite. These crystals seemed to be entrapped in the cellulose network structure. Stoica-Guzun et al. [21] reported that cellulose fibers with porous structures can be used as substrates for calcium carbonate deposition. Moreover, cellulose fibers could provide nucleation sites to mineralize $CaCO_3$ particulates. The nucleation process was described as heterogeneous [30]. Therefore, based on the SEM results, it can be concluded that in this case the cellulose fibers provided a large amount of sites on their surfaces for the nucleation of the nano $CaCO_3$ particles.

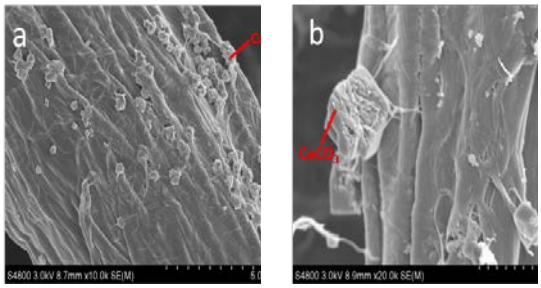

FIGURE 2. The SEM images of the cellulose/$CaCO_3$ fibers.

The Crystalline Structure of the Cellulose/$Caco_3$ Fibers

Shown in *Figure 3* are the XRD patterns of the native fibers (spectrum a) and cellulose/$CaCO_3$ modified fibers (spectrum b). Both of the samples had the similar diffraction peaks at 2θ of 16.8°, 22.8°, those of which are characterized as the (101) and the (002) plane of the crystalline cellulose I, respectively. The results above revealed that the in-situ modification did not change the crystalline lattice of the modified fibers. Interestingly, only a diffraction peak at 2θ of 29.4º, which assigned to the (104) plane of calcite ($CaCO_3$) [31], can be observed in the spectrum of modified fibers, indicating that the $CaCO_3$ particles are immobilized on the cellulose fibers. Based on the results of the SEM images (shown in *Figure 2*) and XRD patterns (shown in *Figure 3*), It can be concluded that a number of nano $CaCO_3$ particles have immobilized and dispersed well on the fiber surface via the in-situ precipitation method.

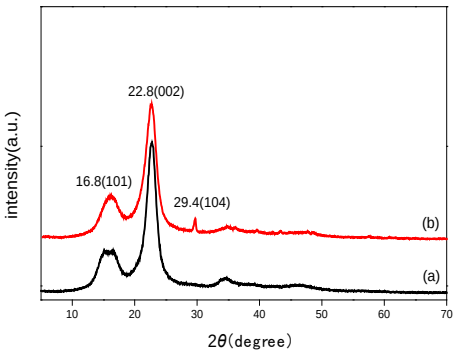

FIGURE 3. XRD patterns of (a) native softwood chemical pulp fiber, (b) cellulose/$CaCO_3$ modified fiber.

The Performance of the Fluff Pulp Before and After Modification

The fiber length, width, coarseness, kink and cur, are listed in *Table I*. The morphology characteristics of modified fibers are similar to those of the native fiber, indicating that there was no influence on the morphology of cellulose fibers during the in-situ precipitation of nano $CaCO_3$. Therefore, the in-situ precipitation modification is a mild reaction and suitable method for surface modification of the fluff pulp.

TABLE I. The morphology characteristics of fiber via Morfi Compact

	Arithm in length/mm	Weighted in length/mm	Coarseness/mg/100m	Width/μm
Native fiber	0.957	1.432	19.82	12.2
Modified fiber	1	1.458	19.48	12.4
	Kink angle/°	Kinked fibers/%	Broken Ends/%	Curl/%
Native fiber	127	53.1	11.72	15.2
Modified fiber	128	55	11.25	15.6

As shown in *Figure 4*, the burst index of the modified handsheets increased by 31 percent. The amount of the in-situ precipitated calcium carbonate can be confirmed by the increased ash content of the modified fluff pulp handsheets. An indirect way of characterizing the dry defibration behavior of the pulp is by measuring the burst strength of the pulp sheets. The more calcium carbonate particles precipitated on fiber surface, the easier fluff pulp handsheets separated in the dry defibration process. Nano $CaCO_3$ precipitated and dispersed well on the fiber surface, which improved the steric hindrance of the modified fiber. Less hydroxyl groups were available for the formation of inter-fiber hydrogen bonds due to the presence of the nano $CaCO_3$. Weaker bonds within the sheet means less energy will be required during defibration [32-34].

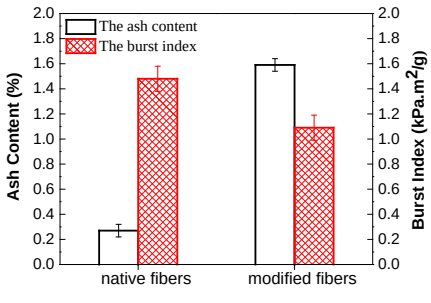

FIGURE 4. The burst index of the pulp.

Shown in *Figure 5* is the absorption capacity of the fluff pulp. There was no adverse impact on the absorption capacity of pulp made from $CaCO_3$/cellulose fiber composites. Unlike debonders, $CaCO_3$/cellulose fiber composites did not shield hydroxyl groups. The water absorption capacity of modified fiber was similar to native fiber, which indicated that the fluff pulp made from $CaCO_3$/cellulose fiber composites can meet the demands of fluff pulp. In view of the above results, it can be concluded that the cellulose/$CaCO_3$ modified fibers are good building blocks for the manufacture of fluff pulp with excellent properties.

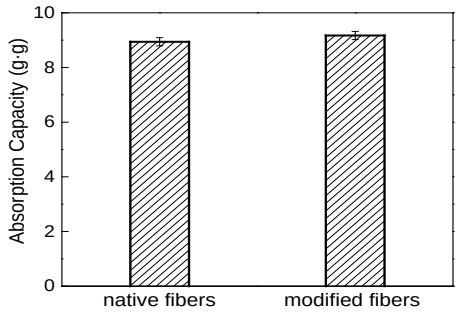

FIGURE 5. The absorption capacity of the pulp.

CONCLUSION

The cellulose fiber/$CaCO_3$ particles were synthesized in the way that Ca^{2+} and CO_3^{2-} underwent an in-situ reaction on the fiber surface. Nano $CaCO_3$ particles (300-600 nm) were in-situ precipitated on the cellulose matrix. The burst index of fluff pulp handsheet made from cellulose fiber/$CaCO_3$ composite increased 31 percent and moisture adsorption was equal to that of fluff pulp made from unmodified cellulose fibers.

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