Preparation and Characterization of Superfine Calcium Carbonate In-situ Modification of Ramie Fiber

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Abstract. In order to solve the composite interface problem caused by the hydrophobic groups of the natural fiber and hydrophobic property of the polymer, an ionic solution reaction to in-situ deposit calcium carbonate (CaCO\textsubscript{3}) particles was applied onto ramie fibers. The influence of reaction temperature, concentration of ions in solution, reaction time and dosage of dispersants EDTA-2Na were studied. The surface morphology and structure of modified ramie fiber were characterized by scanning electron microscopy, infrared spectroscopy and tensile test. The results show that the optimal reaction time is 30min, and the extension of the reaction time has no effect on the test results. The optimization process of orthogonal test for the other three factors is as follows: the temperature is 40 degrees, the concentration of ion solution is 0.5mol/L, and the amount of dispersant EDTA-2Na is 4g/L.

1. Introduction
Ramie fiber is a kind of natural plant fiber with high strength and modulus, good wear resistance and corrosion resistance. It has been used in clothing, medical, automotive, construction, transportation and many other fields. In China, there are varieties of ramie fibers. The resources of it are abundant and yield is high. As reinforced composite is an important part of the ramie fiber industry application [1]. However, because of the composite interface problem caused by the hydrophobic groups of the natural fiber and hydrophobic property of the polymer, the combination of the two is poor. Mechanical properties of composite materials have been greatly affected. Changed ramie fiber’s surface morphology, wetting and mechanical properties by surface modification method have been a hotspot of ramie fiber reinforced composites. Calcium carbonate as a kind of inorganic filler is commonly used in papermaking, rubber, resin and other industries. Adding it to the plant fiber surface can achieve the toughening effect. It can also solve interface problems between ramie fibers and polymers through changing the ramie fiber’s surface morphology, covering the hydrophilic group [2, 3].

At present, no matter in the field of papermaking or composite materials, there are two main methods of adding calcium carbonate to the modified plant fiber: Cell cavity/Wall filling method and in-situ precipitation method[4]. Calcium carbonate particles are attached to the surface of the fiber when the porous, gully growth, and the fiber under the stress of the original weak link-pore load is transferred to the attached to the calcium carbonate particles, can effectively prevent these weak links caused by the fiber fracture, thereby improving fiber strength.(Li \textit{et al}, 2013). With the increase of the preparation temperature, the particle size of calcium carbonate particles increases and the distribution becomes wider, the adsorption quantity increases firstly and then decreases, and the maximum value is reached at 40 °C [5]. This shows that calcium carbonate on the fiber surface adsorption is not the more
the better. Calcium carbonate modified fiber with small particle size, uniform distribution and certain adsorption quantity is the modified fiber with ideal effect. (Feng, 2010).

The objective of this study was to investigate the effect of reaction temperature, concentration of ions in solution, reaction time and dosage of dispersants EDTA - 2 Na on the levels of Superfine Calcium Carbonate In-situ Modification of Ramie Fibers.

2. Experimental

2.1. Materials
Ramie fiber was purchased from LiangLiang Textile Co. Ltd. Anhydrous calcium chloride, anhydrous sodium carbonate, sodium hydrate and acetic acid were obtained from Sinopharm Group Chemical Reagent Co. Ltd. EDTA Disodium was purchased from Tianjin ZhiYuan Chemical Reagent Co. Ltd. All the chemicals used in this study were of analytical grade and were used without further purification.

2.2. Alkaline pretreatment of ramie fiber
The sodium hydroxide aqueous solution of 3%, 5% and 7% of the mass concentration was prepared respectively. The ramie fiber after degumming is immersed in the sodium hydroxide aqueous solution of different concentration by Bath ratio 1:150, after soaking for 3 hours in 40 °C water bath, after washing with the acetic acid solution with a mass concentration of 0.5%, rinse with deionized water to neutral, dry and prepare the alkali treated ramie fiber [6]. According to the same procedure, the reactor is placed in an ultrasonic cleaner to prepare alkaline treated ramie fiber under ultrasonic conditions. Ultrasonic frequency 20KHz, power 100W.

2.3. Preparation of ultrafine calcium carbonate modified ramie fiber
In this study, the superfine calcium carbonate modified Ramie fiber was prepared by in situ precipitation method. The ramie fiber after degumming is cut into a short fiber to be immersed in a certain molar concentration of calcium chloride aqueous solution, and the mixture is stirred for a certain amount of time after adding a certain mass of dispersant EDTA-2Na, then adding the same amount of the same molar concentration of sodium carbonate solution, mixing and stirring for a certain time to remove 100 Mesh filter in deionized water to clean to no obvious white particles, drying. The modified fibers were prepared by changing the test temperature, molar concentration of ionic solution, reaction time and dispersant EDTA-2Na dosage.

2.4. Characterization of modified ramie fibers

2.4.1. Determination of Calcium Carbonate Adhesion on Fiber Surface. Take a certain quality of the fiber in the pre-burning and weighing crucible, drying in a dry box to the constant weight, recording the weight of the fiber at this time is dry weight. In advance, add a certain amount of magnesium acetate ethanol solution to the fiber-filled crucible, the crucible is placed on the electric stove for a period of time and then moved into the muffle furnace after the high-temperature carbonation out, in the room temperature cooling 10 minutes later moved to the dryer to cool to room temperature, weighing. Ash content (X) calculated according to the following formula:

\[ X = \frac{m_2 - m_1}{m} \times 100\% \]  

(1)

Where X is ash content(%), m is fiber dry weight(g), m_1 is the weight of the crucible after burning(g) and m_2 is the weight of a crucible containing residue after burning(g).

2.4.2. SEM Microscopy. First, the fiber samples were fixed to conductive double faced adhesive tape and sputtered with gold nanoparticles. Then the longitudinal surface was observed on a Sirion200 scanning electron microscope at scanning voltage of 3 kv, temperature of 20 °C, and relative humidity of 65%.
2.4.3. FT-IR Spectroscopy. Through the method of KBr pellets, the FT-IR spectra were acquired on a Nicolette iS50 FT-IR spectrophotometer at resolution of 4cm⁻¹, 128 times scanned.

2.4.4. Breaking Strength Measurements. Breaking strength measurements of bamboo pule fabrics were performed at an Instron YG (B)026D-250 electronic fabric strength tester according to ISO 13934-1. Test length was 30cm, and speed was 200mm/min, the tensile strength of the fabric was measured as the mean of 6 individual fabrics.

3. Results and Discussion

3.1. Effect of different conditions on the adhesion of calcium carbonate

The changes of calcium carbonate adhesion on the surface of modified fiber under the condition of different temperature, concentration, reaction time and EDTA-2Na dosage are shown in Figure 1. Figure 1(a) shows that the temperature from 30 °C to 70 °C process, the surface of the modified fiber calcium carbonate rise firstly and then decline. At the temperature of 40 °C to reach the highest was 4.89%. This is because with the increase of temperature, Ca²⁺ and CO₃²⁻ in ionic solution under the action of super saturation, the rate of crystallization and growth speed are accelerated, the number of calcium carbonate crystals produced in the same time increased, volume increased, calcium carbonate adhesion on the surface of modified fiber increased[7-9].

It is denoted in Figure 1(b) that the concentration of calcium carbonate is the largest in 0.5mol/l, reaching 6.45%. This is because the concentration of ionic solution increases the concentration of Ca²⁺ and CO₃²⁻ in the solution, the number increases and the collision probability increases. The combination of the two with the power of over saturation increases, so the calcium carbonate is increased, the crystal growth speed increases, and the content of calcium carbonate on the surface of the modified fiber increases. But when the concentration is too high, it will make the growth of calcium carbonate too fast, the formation of larger crystal size, it is difficult to attach to the surface of the fiber, resulting in the modification of fiber calcium carbonate adhesion decreased.

Meanwhile, Figure 1(c) shows that the adhesion of calcium carbonate on the surface of modified fibers increased firstly and then tended to unchanged with the increase of reaction time. On the one hand, the ionic solution in the stirring infiltration process will penetrate the fiber pores, ravines and even the fiber cell wall, the synthesis of calcium carbonate in these positions will form a stable growth and adhesion fastness of calcium carbonate crystals [10]. On the other hand, a supersaturated ionic solution takes a certain amount of time to precipitate calcium carbonate and crystal growth [11]. When the time is extended to adequate fiber for good infiltration, calcium carbonate can be uniformly stable growth; the growth of reaction time on the modified effect is not too much impact.
EDTA-2Na is a surface modifier of fatty acid sodium salts, in which the fatty acid root ion RCOO-binds with calcium ions around the outer surface of calcium carbonate particles to produce insoluble salts. These insoluble salts are covered on the surface of calcium carbonate crystals, effectively preventing the growth and agglomeration of crystals, thus achieving the refinement of calcium carbonate particle size. The more EDTA-2Na dosage, the smaller the formation of calcium carbonate particles, the more easily attached to the fiber surface, the modified fiber surface calcium carbonate adhesion is higher.

3.2. SEM analysis

The longitudinal surfaces of the modified and unmodified ramie fiber were morphologically observed by SEM. Many long and narrow stripes were displayed on the surface of ramie fiber after alkali pretreatment as shown in Figure 2. Figure 2a denoted that the surface of ramie fiber without any treatment is smooth and flat, there are a few shallow transverse cracks, which may be caused by the process of fiber growth or ramie fiber degumming. The fiber surface is still smooth and has a small amount of transverse fissures, as shown in Figure 2b. But the surface appears to have a certain depth of longitudinal cracks and ravines. This is caused by the damage of fiber after NaOH treatment.

Meanwhile, Figure 2a and 2b compared with the Figure 2c and 2d, fiber after calcium carbonate modified surface obviously have more granular attachment, the calcium carbonate modified after the fiber surface calcium carbonate crystal adhesion, and a large number of small particle size. Besides, the fiber with modified NaOH alkali treatment is more attached to the surface calcium carbonate than alkali treatment. It can be concluded that the fiber's adhesion to the surface of the fiber is advantageous to the NaOH alkali treatment before modification. This is because the fibers are etched on the surface.
by NaOH alkali, resulting in many ravines and fissures, which provide a growing point for calcium carbonate crystals and are therefore more easily attached to the fiber surface [13-14].

![Figure 2](image.png)

**Figure 2.** Electron microscopy of (a) unmodified before alkali pretreatment, (b) unmodified after alkali pretreatment, (c) modified before alkali pretreatment, and (d) modified after alkali pretreatment ramie fiber.

### 3.3. FT-IR analysis
The modified fibers showed new absorption peaks at 1417.43 cm\(^{-1}\), 874.58 cm\(^{-1}\), and 724.6 cm\(^{-1}\) respectively as shown in Figure 3b. Among them, the V3 absorption peaks of calcite-type calcium carbonate crystals are attributed to the asymmetric 1417.43 cm\(^{-1}\) of C-O in carbonate roots, and the 874.58 cm\(^{-1}\) absorption peaks of calcite-type calcium carbonate crystals at V2 are attributed to the surface deformation and vibration of carbonate roots; The V4 absorption peaks of 724.6 cm\(^{-1}\) calcium carbonate crystals are attributed to the O-C-O deformation vibration in the plane [15]. After modification, the infrared spectra of ramie fiber have added the characteristic peak of calcium carbonate on the basis of the original cellulose characteristic peak, which shows that the surface of ramie fiber has calcium carbonate crystal adhesion and the crystal type is not single after modified treatment[16].
3.4. Breaking strength analysis

Compared with the Figure 4a and 4b curves, the fracture strength of the ramie fiber modified by calcium carbonate was increased and the maximum of 9.85% was increased. At the same time, the surface deposition of calcium carbonate may cover the hydrophilic groups on the surface of ramie fiber, improve the interfacial properties of the fiber/resin, and improve the strength properties of the composites.

4. Summary

The aim of this investigation was to explore the optimum technological conditions of superfine calcium carbonate modified ramie fiber. All experimental fibers were well characterized by FT-IR and SEM. The amount of calcium carbonate on the modified fiber under different reaction conditions was evaluated. It was observed that ramie fiber with superfine calcium carbonate by in-situ deposition can obtain the modified fiber with more calcium carbonate adhesion, smaller particle size and better adhesion effect. With an ionic solution concentration of 0.5mol/L at 40 °C, EDTA-2Na dosage 4g/l is chosen as the optimal condition. The scanning electron microscope showed that the surface of ramie
fiber before modification was smooth, and here were obvious longitudinal cracks after alkali treatment. The modified Ramie fiber has obvious granular attachment on the surface, more particles, smaller particle size and uniform distribution. The infrared spectra showed that the characteristic absorption peaks of calcium carbonate newly appeared in the modified fibers at 1417.43 cm\(^{-1}\), 874.58 cm\(^{-1}\) and 724.6 cm\(^{-1}\). The surface of the modified fiber has calcium carbonate adhesion.

5. References

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