

Preparation and Characterization of Cellulose-CaCO₃ Composites by an Eco-Friendly Microwave-assisted Route in a Mixed Solution of Ionic Liquid and Ethylene Glycol

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The purpose of this study was to investigate a popular reinforcing agent in the papermaking industry through a quick, environmentally friendly, microwave-assisted method. The preparation and characterization of cellulose-CaCO₃ composites through this route, in a mixed solution of an ionic liquid and ethylene glycol, can occur within a 10-min timeframe. The chemical compounds, calcium acetate and sodium carbonate, were used as reactants for the as-obtained CaCO₃ crystals. A NaOH-urea aqueous solution was used to treat the cellulose and prepare cellulose-CaCO₃ composites. It was discovered that the addition of ionic liquids favors the preparation of cellulose-CaCO₃ composites.

Keywords: CaCO₃; Composites; Cellulose; Ethylene glycol; Ionic liquid; Reinforcing agent

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INTRODUCTION

There have been reports that composites consisting of cellulose and CaCO₃ can combine the advantages of each of the individual components and produce a material that can act as an optimal candidate in the papermaking industry (Li and Wu 2009). CaCO₃ is a common biomineral in both organisms and within nature itself (Lowenstam 1981; Mann 1988), and it is widely recognized for its applications in papermaking (Kim *et al.* 2013). A surface coating of micro-sized CaCO₃ with a dipping treatment was found to further increase the water contact angle and water resistance of paper (Hu *et al.* 2009).

Cellulose constitutes the most abundant renewable polymer resource produced on the Earth (Klemm *et al.* 2005). Cellulose/CaCO₃ composites have attracted particular attention, and much effort has been expended on the synthesis of cellulose/CaCO₃ composites (Zhang *et al.* 2009a,b; Hilder and Batchelor 2010; Shen *et al.* 2010). In the literature, there are many reports on cellulose/CaCO₃ composites, such as the interactions between the cellulose and the CaCO₃ (Fimbel and Siffert 1986), the process kinetics of calcite overgrowth on a cellulose substrate (Dalas *et al.* 2000), and the co-precipitation of CaCO₃ on pulp (Subramanian *et al.* 2005). Biomimetic CaCO₃ with hierarchical ordered micro- and nanostructures was fabricated with cellulose substances as the templates (Zheng *et al.* 2007). CaCO₃/cellulose composites were prepared by the controlled reaction of CaCl₂ with dimethylcarbonate, in an alkaline medium, in the presence of cellulose fibers (Vilela *et al.* 2010). Ciobanu *et al.* (2010) prepared *in-situ* cellulose fibers loading with CaCO₃, precipitated by three methods.

The development of rapid, green, and environmentally-friendly methods for the fabrication of cellulose-CaCO₃ composites is of great importance for broadening their applications. A microwave-assisted method that combines an ionic liquid is a promising technology that explores the advantages of the microwave and of ionic liquids (Hoffmann *et al.* 2003). In the literature, there are reports on the fabrication of cellulose/carbonated hydroxyapatite using the microwave-assisted method in an ionic liquid (Ma *et al.* 2011). Moreover, the alkali extraction cellulose/CaCO₃ nanocomposites were obtained by a microwave-assisted method in ionic liquid using CaCl₂ and Na₂CO₃ as starting reactants (Ma *et al.* 2013). To date, however, there has not yet been a report on the synthesis of microcrystalline cellulose-CaCO₃ composites through a microwave-assisted method using ionic liquid as additive.

Herein, the fabrication of cellulose/CaCO₃ composites in an ionic liquid using a microwave-assisted method is reported. The influences of the ionic liquid and the heating time on the composites were also studied. The purpose of this study was to investigate a popular reinforcing agent in the papermaking industry through an environmentally friendly microwave-assisted method using ionic liquid as an additive.



Fig. 1. Schematic image of the synthesis of cellulose@CaCO₃ composites using a microwave-assisted route

EXPERIMENTAL

Materials and Methods

Microcrystalline cellulose was purchased from Sinopharm Group Chemical Reagent Co., Ltd., Shanghai, China. Urea was purchased from GuangZhou XiLong Chemical Co., Ltd. The chemicals NaOH, Ca(CH₃COO)₂·3H₂O, and Na₂CO₃ were purchased from Beijing Chemical Works. In a typical synthesis, a NaOH-urea aqueous solution was formed using a mixture containing 81 mL of distilled water, 7.00 g of

NaOH, and 12.00 g of urea. Then, 3.24 g of microcrystalline cellulose was added to the solution under vigorous stirring. The as-obtained solution was cooled to $-12\text{ }^{\circ}\text{C}$ for 12 h. Then, 5 mL of the cellulose solution was mixed with 20 mL of ethylene glycol (EG) in a flask under magnetic stirring. Finally, 1.00 g of 1-butyl-3-methylimidazolium chloride, 2 mL of $\text{Ca}(\text{CH}_3\text{COO})_2 \cdot 3\text{H}_2\text{O}$ solution (0.75 M), and 2 mL of Na_2CO_3 solution (0.75 M) were added to the solution under vigorous stirring. The flask containing the solution was heated to $100\text{ }^{\circ}\text{C}$ for 20 min through the use of microwave heating and then air-cooled naturally to room temperature. The microwave oven was purchased from Beijing Xiang-Hu Science and Technology Development Reagent Co., Ltd., and is equipped with a magnetic stirring system and a water-cooled condenser outside the microwave cavity. The as-prepared samples were separated from the solution by centrifugation, washed with water and absolute ethanol several times, and air-dried at $60\text{ }^{\circ}\text{C}$. The experimental method details are shown in Fig. 1 and Table 1.

Table 1. Detailed Experimental Parameters for the Synthesis of some Typical Samples

Sample	Temperature	Time	Reaction system
1	$100\text{ }^{\circ}\text{C}$	10 min	0.75 M $\text{Ca}(\text{CH}_3\text{COO})_2 \cdot 3\text{H}_2\text{O}$ + 0.75 M Na_2CO_3 + 1.00 g ionic liquid + 5 mL cellulose solution + 20 mL EG
2	$100\text{ }^{\circ}\text{C}$	20 min	0.75 M $\text{Ca}(\text{CH}_3\text{COO})_2 \cdot 3\text{H}_2\text{O}$ + 0.75 M Na_2CO_3 + 1.00 g ionic liquid + 5 mL cellulose solution + 20 mL EG
3	$100\text{ }^{\circ}\text{C}$	30 min	0.75 M $\text{Ca}(\text{CH}_3\text{COO})_2 \cdot 3\text{H}_2\text{O}$ + 0.75 M Na_2CO_3 + 1.00 g ionic liquid + 5 mL cellulose solution + 20 mL EG
4	$100\text{ }^{\circ}\text{C}$	20 min	0.75 M $\text{Ca}(\text{CH}_3\text{COO})_2 \cdot 3\text{H}_2\text{O}$ + 1.00 g ionic liquid + 5 mL cellulose solution + 20 mL EG
5	$100\text{ }^{\circ}\text{C}$	20 min	0.75 M $\text{Ca}(\text{CH}_3\text{COO})_2 \cdot 3\text{H}_2\text{O}$ + 0.75 M Na_2CO_3 + 5 mL cellulose solution + 20 mL EG

To investigate the formation mechanism of calcium carbonate nanocrystals, the samples were prepared at $100\text{ }^{\circ}\text{C}$ for 10 min and 30 min, respectively, while other reaction conditions were the same. Moreover, the samples were prepared without the Na_2CO_3 solution and the ionic liquid at $100\text{ }^{\circ}\text{C}$ for 20 min, respectively, while other reaction conditions were the same.

Characterization

X-ray powder diffraction (XRD) was carried out on a Rigaku D/Max 2200-PC diffractometer with Cu $K\alpha$ radiation ($\lambda = 0.15418\text{ nm}$, Rigaku Corporation, Japan) and a graphite monochromator under ambient temperature. Fourier transform infrared spectroscopy (FTIR) was performed on an FTIR spectrophotometer (Nicolet 510, Thermo Nicolet Corporation, USA) in a wavenumber range from 4000 to 400 cm^{-1} , using the KBr disk method. Scanning electron microscopy (SEM) images were acquired with a Hitachi 3400 N scanning electron microscope (Hitachi Limited Corporation, Japan). All samples were coated with Au prior to SEM examination (MC1000, SU8010, Hitachi Limited Corporation, Japan). The thermal behavior of the samples was tested using thermogravimetric analysis (TGA) and differential thermal analysis (DTA) on a simultaneous thermal analyzer (DTG-60, Shimadzu Corporation, Japan), by heating the samples from room temperature to $600\text{ }^{\circ}\text{C}$ at a heating rate of $10\text{ }^{\circ}\text{C}/\text{min}^{-1}$ in flowing air.

RESULTS AND DISCUSSION

X-ray diffraction was used to characterize the phases of the composites, as shown in Fig. 2.

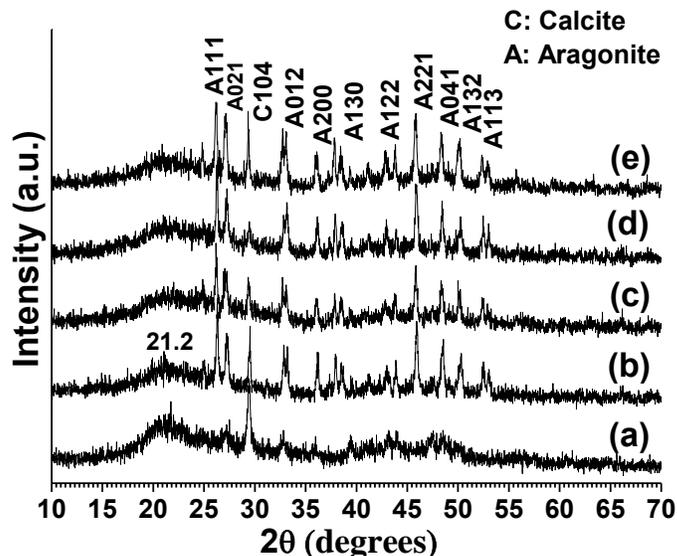


Fig. 2. XRD patterns of cellulose- CaCO_3 composites formed in a mixed solution of ionic liquid and ethylene glycol via a microwave-assisted route at $100\text{ }^\circ\text{C}$: (a) without the Na_2CO_3 solution for 20 min; (b) without the ionic liquid for 20 min; (c-e) with 1.00 g of ionic liquid for 10 min, 20 min, and 30 min, respectively

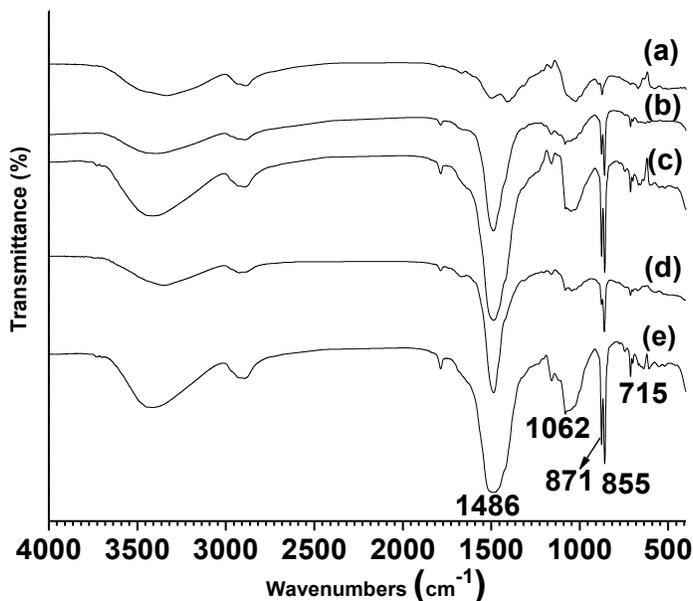


Fig. 3. FTIR spectra of cellulose@ CaCO_3 composites formed in a mixed solution of ionic liquid and ethylene glycol via a microwave-assisted route at $100\text{ }^\circ\text{C}$: (a) without Na_2CO_3 solution for 20 min; (b) without ionic liquid for 20 min; (c-e) with 1.00 g of ionic liquid for 10 min, 20 min, and 30 min, respectively

All of the as-prepared samples consisted of mixed phases of cellulose at $2\theta = 21.2^\circ$ and CaCO_3 (Figs. 2(c-e)). For comparison, Fig. 2(a) also shows the XRD pattern of the sample synthesized without the Na_2CO_3 solution; the peak intensity of CaCO_3 dramatically decreased, compared to that in Figs. 2(c-e). There is also the possibility to obtain the CaCO_3 sample without using the Na_2CO_3 solution, because of the existence of urea. Moreover, the as-synthesized sample that did not use the ionic liquid had an XRD pattern, as seen in Fig. 2(b), similar to that in Figs. 2(c-e). This result indicates that the addition of an ionic liquid has little influence on the phases of the composites. Figure 3 shows the corresponding FTIR spectra of the composites. The results show the typical bands of cellulose at 1062 cm^{-1} (the C-O in cellulose) and CaCO_3 at approximately 1486 cm^{-1} ($\nu_{3-3}\text{ CO}_3^{2-}$ and $\nu_{3-4}\text{ CO}_3^{2-}$) (Nelson and Featherstone 1982). More importantly, the characteristic peaks of calcite are observed at 715 and 871 cm^{-1} (Nelson and Featherstone 1982), while the typical band of aragonite near 855 cm^{-1} is also observed (Naka *et al.* 2000). These results further indicate the mixed phases of calcite and aragonite that existed in the composites, which is consistent with the XRD results.

The morphologies of the cellulose- CaCO_3 composites were also investigated with SEM, as shown in Fig. 4. The cellulose- CaCO_3 composites with CaCO_3 particles were dispersed within the cellulose matrix. Figures 4b, d, and f display magnified micrographs of the cellulose- CaCO_3 composites. A polyhedral morphology for the CaCO_3 sample is observed.

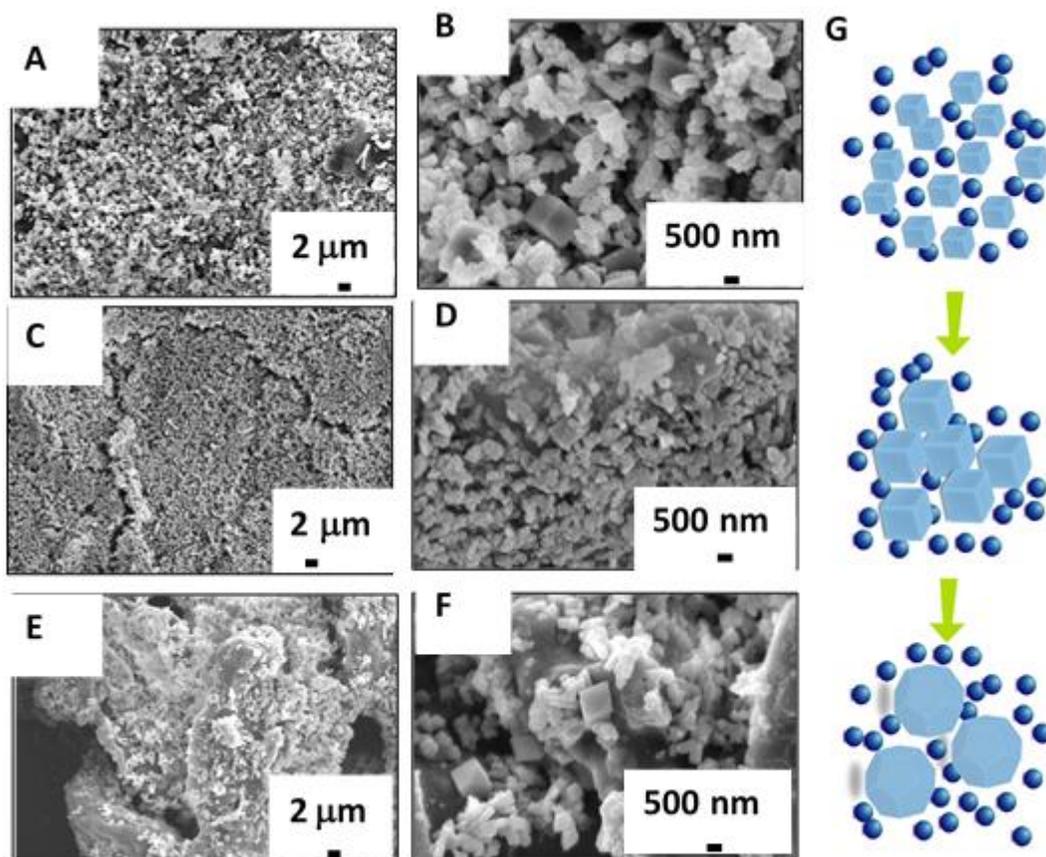


Fig. 4. SEM images of samples formed in a mixed solution of ionic liquid and ethylene glycol *via* a microwave-assisted route at $100\text{ }^\circ\text{C}$ for various times: (a, b) 10 min; (c, d) 20 min; and (e, f) 30 min; and (g) schematic image of the shape transformation of CaCO_3 with increasing heating time

The influence of the heating time on the morphology of the composites was also investigated. Among the three samples, the sample synthesized in the ionic liquid by microwave-assisted route at 100 °C for 20 min has a uniform size, as can be seen from Figs. 4(c) and (d). When the heating time increased to 30 min, the CaCO₃ polyhedrals and particles were observed, as shown in Figs. 4(e) and (f), moreover, the CaCO₃ sample had an increased size. When the heating time decreased to 10 min, there were no large differences in the shape of the composites, as can be seen in Figs. 4(a) and (b). Figure 4(g) displays the shape transformation of CaCO₃ in the composites with increasing amount of heating time. In this synthetic system, the mixed phases of aragonite and calcite were obtained. It is well known that calcite is the thermodynamically stable phase of CaCO₃, while aragonite is the metastable phase of CaCO₃. Long heating time induced the conversion from the metastable aragonite to the thermodynamically stable calcite. Based on the SEM results, it is safe to assume that an appropriate heating time is important for the formation of cellulose-CaCO₃ composites.

For comparison, the shapes of the samples synthesized by the microwave-assisted method at 100 °C for 20 min without the ionic liquid and without the Na₂CO₃ solution, respectively, were investigated. When the composites were fabricated in the absence of the ionic liquid, CaCO₃ aggregates were observed, as shown in Figs. 5(a) and (b). This result implies that the addition of an ionic liquid is favorable for the formation of cellulose-CaCO₃ composites with uniform shapes, sizes, and dispersions. When the composites were fabricated in the absence of the Na₂CO₃ solution, irregular particles were dispersed within the cellulose matrix, as shown in Figs. 5(c) and (d). In this synthetic system, cellulose was dissolved in NaOH-urea solution. With the high heating temperature, urea provided CO₃²⁻ and basic conditions for the synthesis of calcite. However, the sample was obtained in the absence of the Na₂CO₃ solution. There was not enough CO₃²⁻ for the synthesis of CaCO₃, inducing the as-obtained irregular particles.

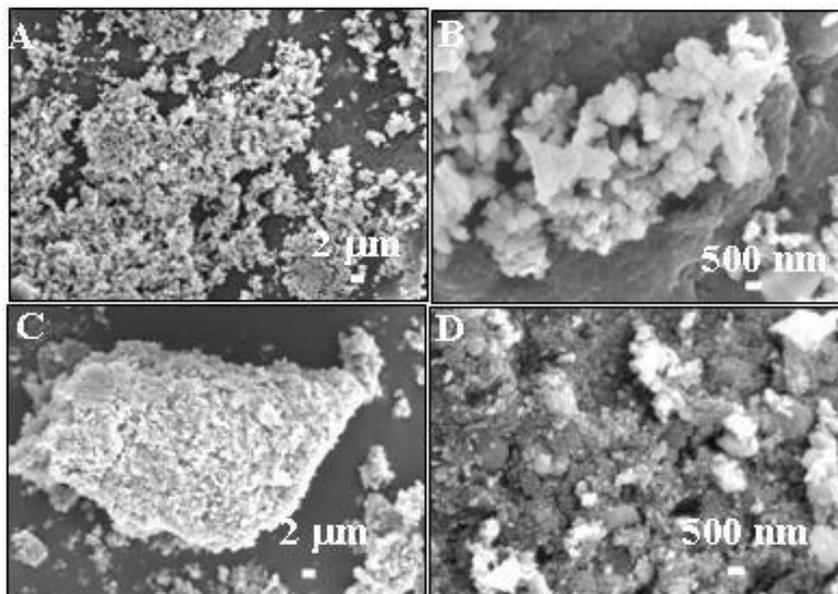


Fig. 5. SEM images of samples formed in a mixed solution of ionic liquid and ethylene glycol *via* a microwave-assisted route at 100 °C for 20 min: (a, b) without the ionic liquid; (c, d) without the Na₂CO₃ solution

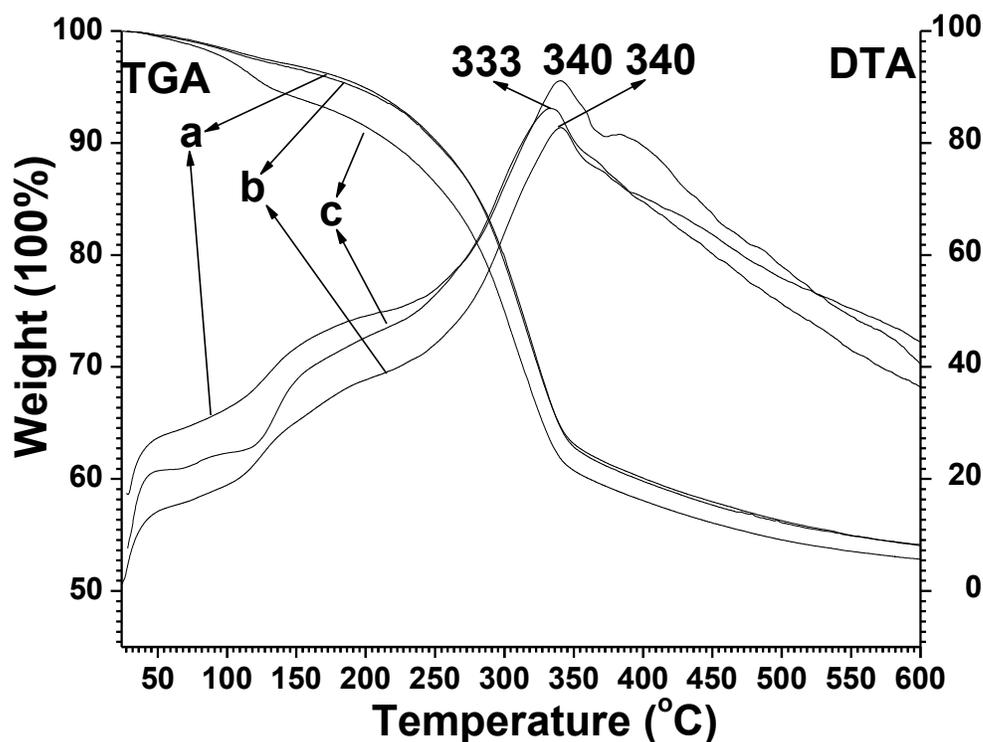


Fig. 6. TGA and DTA curves of samples formed in a mixed solution of ionic liquid and ethylene glycol via a microwave-assisted route at 100 °C for various times: (a) 10 min; (b) 20 min; and (c) 30 min

The thermal stability of the cellulose-CaCO₃ composites was also investigated by thermogravimetric analysis (TGA) and differential thermal analysis (DTA), as shown in Fig. 6. The TGA and DTA curves are shown in Figs. 6(a)-(c) for the composites prepared at 100 °C for 10, 20, and 30 min, respectively. From the TGA curves it is clear that the weight loss takes place at one stage, caused by the thermal degradation of the cellulose and the decomposition of the CaCO₃. The weight losses of the cellulose-CaCO₃ composites prepared at 100 °C for 10, 20, and 30 min were approximately 45.8%, 45.8%, and 47.2%, respectively. The corresponding exothermic peaks can be clearly seen at approximately 340, 340, and 333 °C in the DTA curves. The DTA results are in good agreement with the TGA results. However, there are exothermic peak can be clearly seen for the cellulose-CaCO₃ composites without ionic liquid (Fu *et al.* 2013). These results indicated that the functional group absorbed on the surface of the cellulose-CaCO₃ composites, inducing the different thermal stability. In the literature, there is a report on the formation mechanism of composites from lignocelluloses and CaCO₃ in ionic liquid (Fu *et al.* 2014).

CONCLUSIONS

1. A rapid and green microwave-assisted route was used for the synthesis of cellulose-CaCO₃ composites.
2. A mixed solution of an ionic liquid and ethylene glycol was used for this method, which has an effect on the cellulose-CaCO₃ composites.
3. A NaOH-urea aqueous solution treated the cellulose to prepare the cellulose-CaCO₃ composites. This pretreatment favored the synthesis of composites between cellulose and CaCO₃.
4. Both aragonite and calcite are major phases of the calcium carbonate evaluated in this work, which are different from the reports in the literature. These results favored the understanding of CaCO₃ deeply.
5. The influence of the heating time on the cellulose-CaCO₃ composites was investigated. The shape of CaCO₃ changed with increasing heating time.
6. The thermal stability of the cellulose-CaCO₃ composites was explored, which favored the understanding of the functional group in the cellulose-CaCO₃ composites.

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