Microwave-assisted Synthesis and Characterization of $CaCO_3$ Particles-filled Wood Powder Nanocomposites

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The purpose of this study was to develop a rapid and green method for the synthesis of biomass-based materials. A microwave-assisted method was used for the preparation of $CaCO_3$ particles-filled wood powder nanocomposites, which involve natural cellulosic materials, $CaCO_3$, and microwave heating. Dewaxed wood powder was pretreated in the NaOH/urea solution. The urea acts as part of the CO_3^{2-} source and provides a basic condition for the synthesis of $CaCO_3$. The influences of reaction parameters such as the heating time and the addition of $(NH_4)_2SO_4$ on the products were investigated by X-ray powder diffraction (XRD), Fourier transform infrared spectrometry (FTIR), scanning electron microscopy (SEM), thermogravimetric analysis (TGA), and differential thermal analysis (DTA). The experimental results demonstrated that the heating time had an effect on the crystallinity and morphology of the nanocomposites. In addition, the presence of $(NH_4)_2SO_4$ played an important role in the morphology and dispersion of $CaCO_3$ in the nanocomposites.

Keywords: Wood powder; $CaCO_3$; Nanocomposites; Microwave

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INTRODUCTION

Since the first report of microwave-assisted synthesis in 1986 (Fimbel and Siffert 1986), microwave heating methods have received more attention and are accepted as rapid and green promising methodologies in the synthesis of materials due to their unique effects as compared with conventional processes. Advantages of microwave heating include rapid volumetric heating, higher reaction rates, shorter reaction times, enhanced reaction selectivity, environmental friendliness, and energy efficiency (Polshettiwar *et al.* 2009). The American Chemical Society monograph on green chemistry recommended that microwave radiation would minimize the energy required for a reaction to take place (Ryan and Tinnesand 2002). This has opened up the possibility of realizing fast preparation of materials. The application of microwave heating in the synthesis of nanomaterials and nanocomposites has been reported by using these advantages (Tsuji *et al.* 2005).

Previous studies have reported the synthesis of cellulose-based composites such as cellulose/hydroxyapatite nanocomposites (Ma *et al.* 2010), cellulose/silver nanocomposites (Li *et al.* 2011), cellulose/calcium silicate nanocomposites (Jia *et al.* 2011), and cellulose/F-substituted hydroxyapatite (Jia *et al.* 2012) *via* microwave heating;

however, there is no known prior report on the synthesis of $CaCO_3$ particles-filled wood powder composites by the microwave-assisted method. This novel preparation method is based on the simultaneous formation of the colloidal inorganic particles, the synthesis of regenerated cellulose, and the fabrication of cellulose-based composites.

As very promising and sustainable green materials, biomass-based composites have been extensively explored (Ashori 2008). Biomass-based composites can completely utilize the components of biomass via the dissolution of lignocelluloses in complete dissolution systems such as certain organic solvents and ionic liquids (Li *et al.* 2011; Maki-Arvela *et al.* 2010).

Researchers have discovered that the introduction of inorganic materials into the lignocellulose matrix may significantly improve the performance of a composite (Blanchard and Blanchet 2011; Mai and Militz 2004) and have a positive effect on the compression strength of lignocellulose/plastic composites. Chen *et al.* (2004) investigated the effect of temperature on the mechanical and surface properties of calcium carbonate filled bamboo fibers and polypropylene composites and discovered that the treatments improved compatibility between bamboo fibers and polypropylene matrix. Consequently, the tensile strength and modulus of the composites were increased. Moreover, the types of cellulose were found to play an important role in the microstructure and morphologies of the cellulose/$CaCO_3$ composites (Ma *et al.* 2012b).

The cellulose fibers and $CaCO_3$ particles were observed using alkali extraction cellulose; meanwhile, using microcrystalline cellulose instead of alkali extraction cellulose, a combination of cellulose particles having irregular shape along with $CaCO_3$ microspheres was obtained. The previous study included synthesizing wood powder/ $CaCO_3$ composites *via* a hydrothermal route using dewaxed wood powder (Ma *et al.* 2012a).

The synthesis of the $CaCO_3$ particles-filled wood powder nanocomposites was carried out by the microwave-assisted method using dewaxed wood powder, $CaCl_2$ solution, and Na_2CO_3 solution. The influences of reaction parameters such as the heating time and the addition of $(NH_4)_2SO_4$ on the products are discussed in detail. Compared with a previous report (Ma *et al.* 2012), this synthetic methodology for the preparation of $CaCO_3$ particles-filled wood powder nanocomposites is simpler, more rapid, and greener.

EXPERIMENTAL

Methods

All chemicals were of analytical grade and used as received without further purification. All experiments were conducted under an air atmosphere. The preparation of dewaxed wood powder solution is explained in a previous report (Ma *et al.* 2012). In a typical experimental, 7.00 g of NaOH and 12.00 g of urea were added to 81 mL of distilled water under vigorous stirring to form a NaOH-urea aqueous solution. Then, 1.00 g of dewaxed wood powder was added to the solution under vigorous stirring. The resulting solution was then cooled to -12 °C for 12 h. The obtained solution was used for the preparation of $CaCO_3$ particles-filled wood powder nanocomposites.

For the synthesis of $CaCO_3$ particles-filled wood powder nanocomposites, 10 mL of $CaCl_2$ solution (0.10 M) and 10 mL of Na_2CO_3 solution (0.10 M) were added to the above obtained solution (20 mL) under vigorous stirring. The flasks containing the solution were microwave-heated to 90 °C for 10, 30, and 60 min and then air cooled to room temperature. The microwave oven used for sample preparation was purchased from Beijing Xiang-Hu Science and Technology Development Reagent Co., Ltd. and was equipped with a magnetic stirring system and a water-cooled condenser outside the microwave cavity. The product was separated from the solution by centrifugation, washed with water and ethanol three times, and dried at 60 °C for further characterization.

For comparison, samples were also synthesized by a microwave-assisted method using $(NH_4)_2SO_4$ solution (10 mL, 0.10 M) instead of Na_2CO_3 solution (10 mL, 0.10 M) at 90 °C for 10, 30, and 60 min while keeping the other conditions the same.

Characterization

X-ray powder diffraction (XRD) was performed in the 2θ range from 10º to 70º on a Rigaku D/Max 2200-PC diffractometer with Cu Kα radiation (λ = 0.15418 nm) and a graphite monochromator at ambient temperature.

Fourier transform infrared spectroscopy (FTIR) was carried out on a FTIR spectrophotometer (Nicolet 510) using the KBr disk method.

Scanning electron microscopy (SEM) images were recorded with a Hitachi 3400 N scanning electron microscopy. All samples were Au-coated prior to examination by SEM.

Thermal behavior of the samples was tested using thermogravimetric analysis (TGA) and differential thermal analysis (DTA) on a simultaneous thermal analyzer (DTG-60, Shimadzu) at a heating rate of 10 °C min^{-1} in flowing air.

RESULTS AND DISCUSSION

Figure 1a shows the X-ray powder diffraction pattern of a typical sample prepared by microwave heating at 90 °C for 10 min. The sample consisted of mixed phases of well-crystallized calcite with a hexagonal structure (JCPDS 47-1743) and cellulose (marked with * in Fig. 1a).

No peaks from impurities such as aragonite were observed. The composites were successfully synthesized *via* the microwave-assisted route within only 10 min; however, the $CaCO_3$ particles-filled wood powder composites were obtained *via* a hydrothermal route at 160 °C for 2 h (Ma *et al.* 2012).

The samples prepared by the microwave heating at 90 °C for 30 and 60 min had similar XRD patterns (Figs. 1b and 1c) as those heated for 10 min. The slight difference was that the peak intensity of calcite increased with increasing heating time, indicating a better crystallinity of calcite.

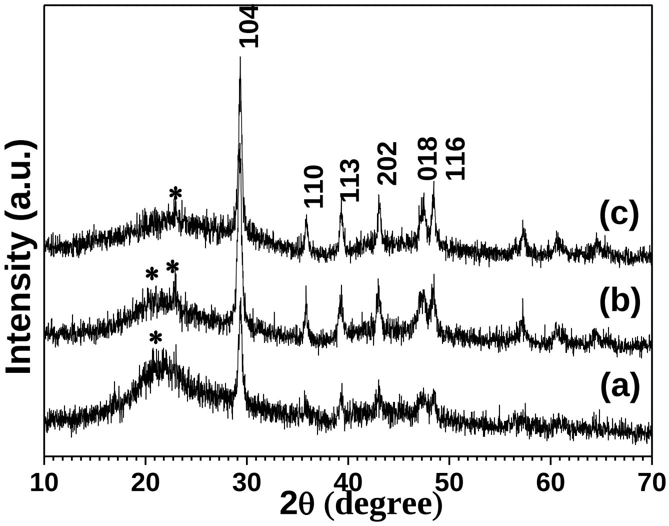

Fig. 1. XRD patterns of the $CaCO_3$ particles-filled wood powder nanocomposites prepared by microwave heating at 90 °C for different times: (a) 10 min; (b) 30 min; and (c) 60 min

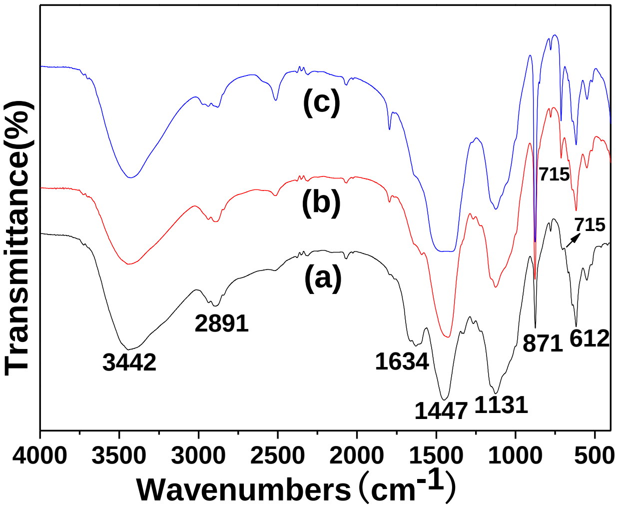

Fig. 2. FTIR spectra of the $CaCO_3$ particles-filled wood powder nanocomposites: (a) 10 min; (b) 30 min; and (c) 60 min

The crystal structure and phase of the nanocomposites were further examined by FTIR analysis (Fig. 2). The band at 1131 cm^{-1} can be assigned to the C-O of cellulose. The band at 1447 cm^{-1} is characteristic of $\nu_{3\text{-}3}$ CO_3^{2-} and $\nu_{3\text{-}4}$ CO_3^{2-} (Nelson and Featherstone 1982). The band at 871 cm^{-1} is characteristic of calcite (Donners *et al.* 2000). There were differences among the FTIR spectra of all the samples. One can see that only a shoulder was observed at 715 cm^{-1}, which was also characteristic of calcite, when the heating time was 10 min (Fig. 2a). When the heating time was increased to 30 min, a peak at 715 cm^{-1} appeared (Fig. 2b). When the heating time was increased to 60 min, the peak intensity at 715 cm^{-1} increased (Fig. 2c). From Fig. 2, one can see the peak intensity at 715 cm^{-1} increased with increasing heating time, demonstrating the increasing crystallinity of calcite. These results were in accordance with the XRD results.

The morphology of the samples was investigated with SEM, as shown in Fig. 3. When the heating time was 10 min, some of the $CaCO_3$ congregates grew on wood powder as substrate (Fig. 3a). The magnified micrograph of the $CaCO_3$ congregates is shown in Fig. 3b, from which one can see the $CaCO_3$ with a rice-like shape. This result was different from a previous report (Ma *et al.* 2012), in which $CaCO_3$ with a six-side-like shape was dispersed on the surface of the wood powder. When the heating time was increased to 30 min, $CaCO_3$ congregates and particles were also observed on the substrate of wood powder (Fig. 3c).

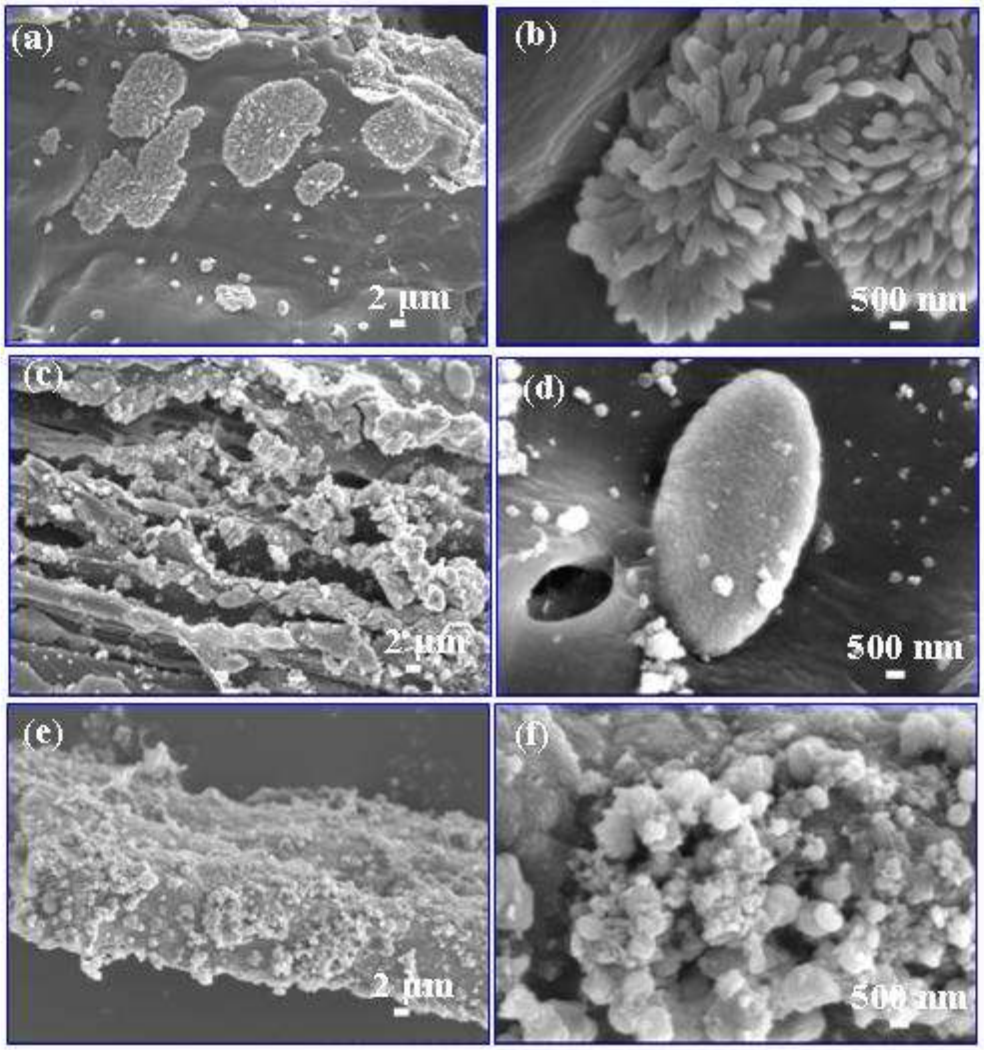

Fig. 3. SEM images of the $CaCO_3$ particles-filled wood powder nanocomposites: (a, b) 10 min; (c, d) 30 min; and (e, f) 60 min

The sizes of $CaCO_3$ congregates were larger, as shown in Fig. 3d, compared with those in Fig. 3b. When the heating time was increased to 60 min, wood powder fibers loading with $CaCO_3$ congregates and particles were observed (Fig. 3e). From the magnified micrograph, one can see that the size of $CaCO_3$ congregates decreased, while the size of $CaCO_3$ particles increased (Fig. 3f), compared with Figs. 3a-d. Furthermore, one can clearly see that the number of $CaCO_3$ particles increased with increasing heating time. When the heating time was 10 min, $CaCO_3$ particles of relatively small size were obtained. When the heating time was increased to 60 min, $CaCO_3$ particles were dispersed on the surface of the wood powder fibers and embedded in the wood powder fibers. These results demonstrated that the heating time played an important role in the morphology and dispersion of $CaCO_3$ in the nanocomposites. From Fig. 3, one can observe that the $CaCO_3$ shape changed from rice-like to congregate/particles to individualized particles with increasing heating time.

An investigation was conducted into the effect of the addition of $(NH_4)_2SO_4$ on the $CaCO_3$ particles-filled wood powder nanocomposites. The samples were synthesized using $(NH_4)_2SO_4$ instead of Na_2CO_3. The XRD patterns indicated that the samples consisted of the mixed phases of calcite and cellulose (Fig. 4A); however, the peak intensity of calcite increased with increasing heating time. All the samples had similar FTIR spectra, compared with Fig. 2. The peak intensity at 1447 cm^{-1} increased with increasing heating time, which was characteristic of $\nu_{3\text{-}3}$ CO_3^{2-} and $\nu_{3\text{-}4}$ CO_3^{2-}. The peak intensity at 1124 cm^{-1} decreased with increasing heating time. Moreover, a shoulder at 715 cm^{-1} was observed (Fig. 4B (a and b)). When the heating time was increased to 60 min, the peak at 715 cm^{-1} was observed (Fig. 4B (c)). These results indicated that the peak intensity of $CaCO_3$ increased, while the peak intensity of wood powder decreased with increasing heating time.

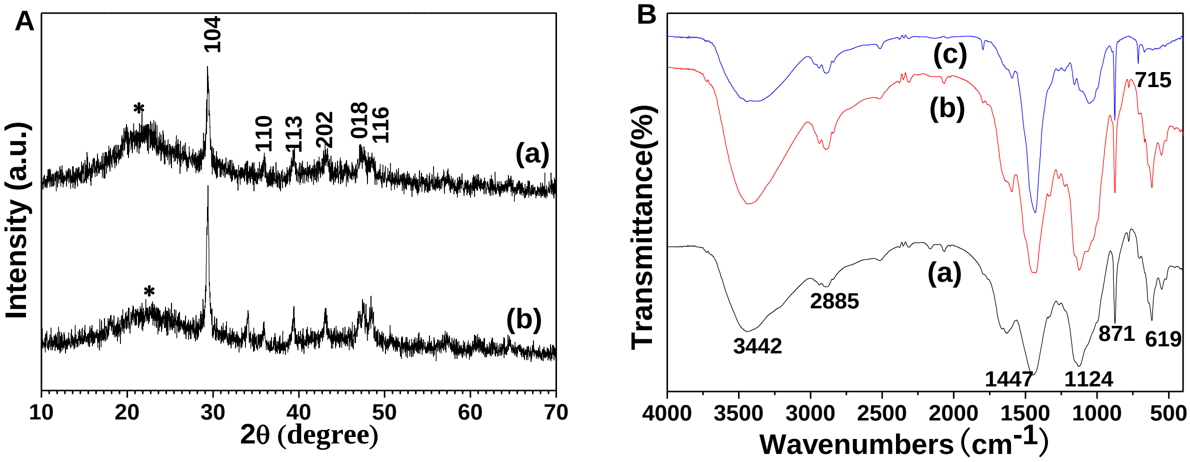

Fig. 4. (A) XRD patterns and (B) FTIR spectra of the $CaCO_3$ particles-filled wood powder nanocomposites in the presence of $(NH_4)_2SO_4$ at 90 °C for different times: (a) 10 min; (b) 30 min; and (c) 60 min

The morphology and dispersion of the $CaCO_3$ particles-filled wood powder nanocomposites are displayed in Fig. 5. These specimens were prepared by microwave heating in the presence of $(NH_4)_2SO_4$ at 90 °C for 10, 30, and 60 min. When heating time was 10 min, the $CaCO_3$ particles were dispersed on the surface of the wood powder fibers (Fig. 5a). The magnified micrograph of the sample is shown in Fig. 5b, from which one can see the $CaCO_3$ with a cube-like shape. Increasing the heating time to 30 min, the $CaCO_3$ particles and $CaCO_3$ congregates were dispersed on the surface of the wood powder fibers (Figs. 5c and 5d). When the heating time was increased to 60 min, serious $CaCO_3$ aggregation of the cube-shaped particles was observed, as shown in Fig. 5e and f. From Fig. 5, one can conclude that the degree of the $CaCO_3$ agglomeration increased with increasing heating time and that better dispersion of $CaCO_3$ in the wood powder matrix was obtained by using a short heating time.

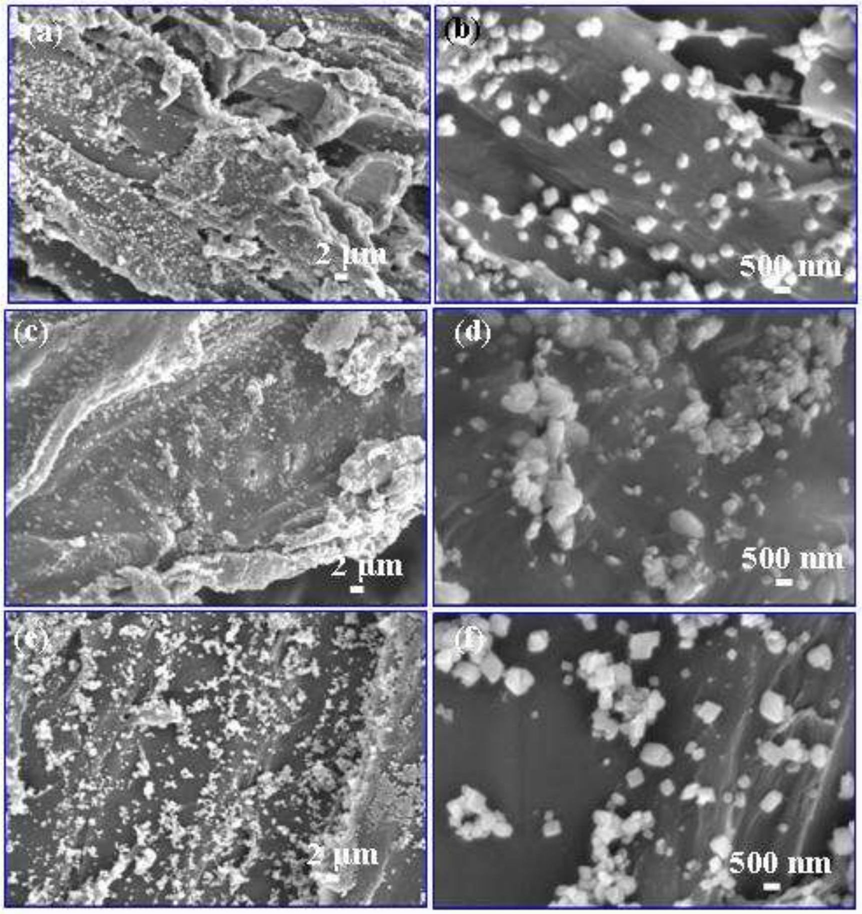

Fig. 5. SEM images of the $CaCO_3$ particles filled wood powder nanocomposites in the presence of $(NH_4)_2SO_4$ at 90 °C for different times: (a, b) 10 min; (c, d) 30 min; and (e, f) 60 min.

In view of the XRD, FTIR, and SEM results, differences clearly existed in the samples prepared by varied reactants between Na_2CO_3 and $(NH_4)_2SO_4$. When the sample was synthesized in the presence of Na_2CO_3, Na_2CO_3 was used as the CO_3^{2-} source for the synthesis of $CaCO_3$. Moreover, the urea also acts as part of the CO_3^{2-} source for the synthesis of $CaCO_3$ and provides a basic condition by decomposing with increasing heating time; however, when using $(NH_4)_2SO_4$ instead of Na_2CO_3, the urea acts as the only CO_3^{2-} source for the synthesis of $CaCO_3$. Both the urea and $(NH_4)_2SO_4$ provide a basic condition. Therefore, the variety of the CO_3^{2-} source and base source induced the difference of phase, microstructure, and morphology in the nanocomposites.

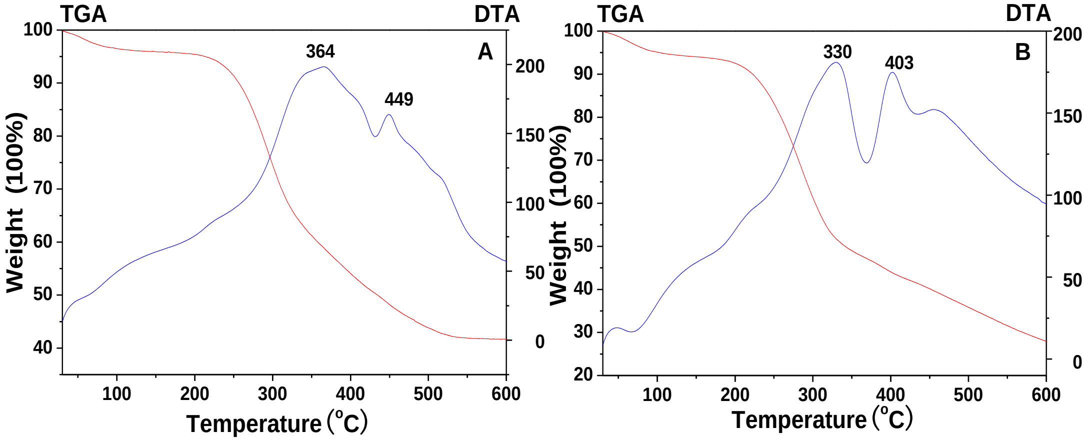

Fig. 6. TGA and DTA curves of the $CaCO_3$ particles-filled wood powder nanocomposites in the presence of (A) Na_2CO_3 and (B) $(NH_4)_2SO_4$ at 90 °C for 30 min.

The thermal stability of the $CaCO_3$ particles-filled wood powder nanocomposites was also investigated by TGA and DTA. TGA and DTA curves for the samples synthesized in the presence of Na_2CO_3 and $(NH_4)_2SO_4$ at 90 °C for 30 min are shown in Fig. 6. The TGA curve of the sample exhibited two stages of weight loss in the presence of Na_2CO_3; these weight losses were accompanied by endothermic peaks at about 364 °C and 449 °C in the DTA curve (Fig. 6A). The peak around 364 °C was caused by thermal degradation of the wood powder, while the other peak at around 449 °C resulted from the complete decomposition of the wood powder in the nanocomposites (Zheng *et al.* 2002). The total weight loss of the sample was ~58.5 %. On the other hand, the sample that was synthesized in the presence of $(NH_4)_2SO_4$ displayed two stages of weight loss at about 330 °C and 403 °C (Fig. 6B). The total weight loss of the sample was ~72.0 %. From Fig. 6, one can see that the thermal degradation temperature of the sample synthesized in the presence of $(NH_4)_2SO_4$ decreased, compared with that of the sample synthesized in the presence of Na_2CO_3. If the total weight loss was assigned to the complete decomposition of wood powder, the residual amount (41.5 %) of $CaCO_3$ in the sample prepared by using Na_2CO_3 was more than that (28.0 %) of the sample synthesized by using $(NH_4)_2SO_4$. As mentioned, both Na_2CO_3 and urea were used as the CO_3^{2-} source for the formation of $CaCO_3$ when the sample was prepared in the presence of Na_2CO_3, while only urea was used as the CO_3^{2-} source for the synthesis of $CaCO_3$ in the presence of $(NH_4)_2SO_4$. This might lead to the production of different amounts of $CaCO_3$ in the two composites.

CONCLUSIONS

1. A rapid and green microwave-assisted route was used for the synthesis of the $CaCO_3$ particles-filled wood powder nanocomposites.

2. Both Na_2CO_3 and urea were used as the CO_3^{2-} source for the synthesis of $CaCO_3$. XRD patterns showed increasing peak intensity of $CaCO_3$ with increasing heating time, indicating a higher crystallinity of calcite.
3. The heating time played an important role in the morphology and dispersion of $CaCO_3$ in the nanocomposites. The $CaCO_3$ shape changed from rice-like to congregate/particles to particles with increasing heating time.
4. Using $(NH_4)_2SO_4$ instead of Na_2CO_3, the peak intensity of $CaCO_3$ in XRD patterns increased with increasing heating time; meanwhile, the peak intensity of $CaCO_3$ increased and the peak intensity of wood powder decreased with increasing heating time in FTIR spectra. The total weight losses of the samples synthesized using Na_2CO_3 and $(NH_4)_2SO_4$ were ~58.5 % and ~72.0 %, respectively.
5. This synthetic strategy reported in this study opens a new window to the manufacture of wood-based composites as well as high value-added applications of wood powder.
6. These nanocomposites utilized the main valid components of lignocelluloses and could be a candidate for the biomedical applications.

ACKNOWLEDGMENTS

Financial support from Beijing Nova Program (Z121103002512030) and the Program for New Century Excellent Talents in University (NCET-11-0586) is gratefully acknowledged.

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Article submitted: January 15, 2014; Peer review completed: April 23, 2014; Revised version received and accepted: May 6, 2014; Published: May 12, 2014.