**ABSTRACT**

Cellulose/carbonated hydroxyapatite (CHA) nanocomposites were successfully prepared in ionic liquid by microwave-assisted method and were characterized by X-ray powder diffraction, thermogravimetric analysis, Fourier transform infrared spectrometry and scanning electron microscopy. Ionic liquid acts simultaneously as a solvent and a microwave absorber for the synthesis of cellulose/CHA nanocomposites. The cellulose in nanocomposites displayed cellulose type II crystalline structure. The XRD and FTIR results confirmed the products as cellulose/CHA nanocomposites. The SEM and TEM results indicated that the aggregated CHA nanorods were observed in the cellulose matrix. The effects of cellulose concentrations and heating methods on the products were also investigated. The density of nanocomposites was increased with higher cellulose concentration. Cellulose/CHA nanocomposites with rough surface were formed in ionic liquid by microwave-assisted method, in contrast to the cellulose/HA nanocomposites with flake-like cellulose and rod-like HA prepared in N,N-dimethylacetamide by the microwave heating. A good example of combining green chemistry and functional materials, the microwave-assisted ionic liquid method for the synthesis of cellulose/CHA nanocomposites is capable to achieve the full product within 30 min. This method is fast, environmentally friendly and suitable for the large-scale production of cellulose-based nanocomposites with minimal environmental impact. This nanocomposite is a very promising candidate in application of bioactive materials.

**INTRODUCTION**

Recently, as important high-value-added applications of cellulose, cellulose-based nanocomposites have attracted great attention [1-4]. Cellulose is the most abundant renewable polysaccharide on earth, which consists of $\beta$(1$\rightarrow$4) -linked glucose repeating units. However, it is difficult for the dissolution of cellulose in water and common organic solvents due to its strong inter- and intra-molecular hydrogen bonding. The solvents which dissolve cellulose include LiCl/DMAc [5,6], N-methylmorpholine-N-oxide monohydrate [7,8], NaOH/urea [9,10], NaOH/H$_2$O [11], LiOH/urea [12,13], NaOH/(NH$_2$)$_2$CS/H$_2$O [14,15], NaOH/urea/(NH$_2$)$_2$CS [16,17] and ionic liquids [18-21]. Among these solvents, ionic liquid is well known...
as the solvent for cellulose due to its high fluidity, low melting temperature, low toxicity, non-flammability, high ionic conductivity and important of all no measurable vapour pressure [22-24].

There have been a few reports on the synthesis of cellulose-based composites using ionic liquid [25-31]. Composites of cellulose and a polystyrene-type polymeric ionic liquid were prepared in imidazolium-type polymerizable ionic liquid [25]. Cellulose-starch composite gel from an ionic liquid solution (BMIMCl) was synthesized at room temperature for several days [26]. Cellulose/HA composite tissue engineering scaffolds were fabricated by a particulate leaching technique with poly(methyl methacrylate) particles as the porogen from 1-butyl-3-methylimidazolium chloride (BMIMCl) solution [27]. Single-walled carbon nanotubes (SWCNTs)/cellulose composite with excellent biocompatibility have been prepared by the treatment of SWCNTs with a cellulose solution in an ionic liquid such as 1-butyl-3-methylimidazolium bromide [28]. It is worth pointing out that the main problem associated with making effective nanocomposites from inorganic materials is to produce a homogeneous dispersion within a cellulose matrix. Therefore, to develop new synthetic methods to control dispersion are of great importance for extensive applications of cellulose-based nanocomposites.

Herein, we report a microwave-assisted ionic liquid method for the fabrication of cellulose/carbonated hydroxyapatite (CHA) nanocomposites using microcrystalline cellulose, Ca(NO₃)₂·4H₂O, and NH₄H₂PO₄. Ionic liquid is a very good medium for absorbing microwaves, leading to a very high heating rate, and increasing the rate and yield of reactions due to the presence of large organic positive ions with high polarizability [32]. We fabricated cellulose/HA nanocomposites in N,N-dimethylacetamide, cellulose/CHA nanocomposites in NaOH/urea aqueous solution, and cellulose/calcium silicate nanocomposites using ionic liquid as an additive in ethylene glycol by a microwave-assisted method [33-35]. Compared to the previous reports, an ionic liquid acts simultaneously as a solvent and a microwave absorber for the synthesis of cellulose/CHA nanocomposites; thus no additional solvent is needed. Microwave-assisted method is an environmentally friendly technology for the fabrication of nanocomposites due to its rapid volumetric heating, fast reaction rate, short reaction time and energy saving. Therefore, the new microwave-assisted ionic liquid method is more environmentally friendly green for the synthesis of cellulose/CHA nanocomposites by combining the advantages of ionic liquid, microwave heating and cellulose.

EXPERIMENTAL

Materials

All chemical materials and solvents used in the experiments were analytical grade reagents and were used without further purification. Microcrystalline cellulose (molecular weight of 34, 843-38, 894, with a degree of polymerization of 215-240) was obtained from Sinopharm Group Chemical Reagent Co., Ltd., Shanghai, China. 1-Butyl-3-methylimidazolium chloride (C₈H₁₅ClN₂, BMIMCl, molecular weight of 174.67, 98.0%) was purchased from Chemer Organics Chemical Reagent Co., Ltd., Hangzhou, China.

Synthetic Process of Cellulose/Carbonated Hydroxyapatite Nanocomposites

A typical synthetic experiment for the synthesis of cellulose/carbonated hydroxyapatite (CHA) nanocomposites was carried out as follows: 0.162 g microcrystalline cellulose (5% by weight) was added into BMIMCl (3.240 g) under vigorous stirring at 130°C for 30 min by microwave heating to obtain a homogeneous cellulose solution. Then, 0.472 g Ca(NO₃)₂·4H₂O and 0.138 g NH₄H₂PO₄ were added into the above cellulose solution under vigorous magnetic stirring. The resulting precipitate was separated from the solution by centrifugation, washed by water and ethanol several times and dried at 60°C for further characterization.
Measurements

Structures of the products were studied using X-ray powder diffraction (XRD) on a Rigaku D/Max 2200-PC diffractometer with CuKα radiation (λ = 0.15418 nm) and graphite monochromator at ambient temperature. Scanning electron microscopy (SEM) images were recorded with a Hitachi 3400 N type instrument. Transmission electron microscopy (TEM) images were acquired on an H-7500 electron microscope with accelerating voltage of 120 kV. Fourier transform infrared (FTIR) spectroscopy was carried out on an FTIR spectrophotometer (Nicolet 510) using the KBr disk method. Thermal behaviour of the samples was performed using thermogravimetric analysis (TGA) on a simultaneous thermal analyzer (DTG-60, Shimadzu) at a heating rate of 10°C.min⁻¹ in flowing air.

RESULTS AND DISCUSSION

The phase of the product was investigated by X-ray powder diffraction. Figure 1a shows an XRD pattern of the regenerated cellulose prepared using microcrystalline cellulose by microwave heating in ionic liquid at 130°C for 30 min, from which one can see the existence of diffraction peaks at 2θ = 20-25° of cellulose type II [36]. Compared with the XRD pattern of micro-crystalline cellulose, the XRD result indicated the conversion of cellulose I into cellulose II [37]. The samples were fabricated in ionic liquid by microwave heating of Ca(NO₃)₂.4H₂O and NH₄H₂PO₄ using 2% and 5% (by weights) microcrystalline cellulose at 130°C for 30 min, respectively. One can see that samples have all similar diffraction peaks in XRD patterns (Figures 1b and 1c). The diffraction peaks were assigned to well-crystallized HA with a cubic structure (JCPDS 31-1238). No peaks from impurities were observed. The diffraction peak of regenerated cellulose cannot clearly be observed due to the strong intensity peaks of HA. However, the cellulose/HA nanocomposites with the strong peaks of cellulose and the weak peaks of HA were observed in N,N-dimethylacetamide solvent by a microwave-assisted method [33]. Based on the above results of XRD, one can conclude that all the nanocomposites consisted of the mixed phase of the regenerated cellulose and HA.

The effect of the heating method on the samples was also investigated. The samples were fabricated in ionic liquid of Ca(NO₃)₂.4H₂O and NH₄H₂PO₄ and 2%, 4% and 5% (all by weights) microcrystalline cellulose at 130°C for 24 h, using oil bath. One can see that all diffraction peaks of the samples in XRD patterns were assigned to HA (Figure 2).

![Figure 1. XRD Patterns of cellulose/CHA nanocomposites prepared in ionic liquid by microwave heating using different cellulose concentrations at 130°C for 30 min: (a) without HA, (b) 2% and (c) 5% (by weights).](image)

![Figure 2. XRD Patterns of cellulose/CHA nanocomposites prepared in ionic liquid by oil bath using different cellulose concentrations at 130°C for 24 h.](image)
intensity of the peaks in both Figures 1 and 2 are the same. Microwave heating is a highly effective heating method due to its rapid volumetric heating characteristics. It is agreed that the microwave effects including thermal effects and non-thermal effects exist in microwave heating reactions [38]. As a result, microwave heating has an advantage in shortening the reaction time. With the help of microwave heating, Ca\(^+\) reacted rapidly with H\(_2\)PO\(_4\)- to form HA nuclei. These results indicated that the microwave heating is favourable for the rapid synthesis of cellulose/CHA nanocomposites.

Figures 3b and 3c show the FTIR spectra of the cellulose/CHA nanocomposites prepared in ionic liquid by microwave heating. For comparison, the FTIR spectrum of the regenerated cellulose is also displayed in Figure 3a, which exhibits the characteristic absorptions of regenerated cellulose and ionic liquid. The peak at \(~1049\) cm\(^{-1}\) is indicative of C-O-C pyranose ring skeletal vibration of regenerated cellulose. The intensity of the peak was dramatically decreased, compared to microcrystalline cellulose, further indicating the conversion of cellulose I into cellulose II [37]. Moreover, the bands due to ionic liquid were observed at \(~1605\) and 1717 cm\(^{-1}\). When the product was prepared in ionic liquid by microwave heating using 2\% and 5\% microcrystalline cellulose at 130°C for 30 min, the corresponding FTIR spectra exhibited the characteristic absorptions of regenerated cellulose, ionic liquid and HA, suggesting that the product is a composite consisting of cellulose and HA (Figures 3b and 3c). The intense bands at 606 and 565 cm\(^{-1}\) belong to the PO\(_4^{3-}\) [39]. The characteristic absorption of the PO\(_4^{3-}\) in HA is located at \(~1049\) cm\(^{-1}\), overlapped with the peak from the C-O-C pyranose ring skeletal vibration in regenerated cellulose. The bands at \(~1605\) and 1717 cm\(^{-1}\) can clearly be observed. The weak peak at 1456 cm\(^{-1}\) is assigned to the appearance of carbonate groups [40], indicating the synthesis of cellulose/CHA nanocomposites.

FTIR Spectra of the cellulose/HA nanocomposites prepared by oil bath are shown in Figure 4. All samples demonstrate similar characteristic absorptions, compared to Figures 3b and 3c. However, the intensity of peak at 1643 cm\(^{-1}\) has dropped with increased cellulose concentrations from 2\% to 5\% (by weights). Moreover, the peaks at 1451, 1387 and 893 cm\(^{-1}\) assigned to carbonate groups [40] are indicative of cellulose/CHA nanocomposites formation.

The morphologies of the samples were investigated by SEM. Figure 5a shows the SEM micrograph of
the regenerated cellulose. The particles were loosely dispersed in cellulose matrix. When 2% (by weight) cellulose was used the aggregated CHA particles were observed in the cellulose matrix, as shown in Figure 5b. When the cellulose concentration was increased to 5% (by weight), cellulose/CHA nanocomposites with rough surface were developed (Figure 5c). A magnified micrograph of the cellulose/CHA nanocomposites is shown in Figure 5d, indicating the existence of CHA particles with irregular morphologies. No cellulose with flake-like morphology was observed. The morphologies of the samples were further investigated by TEM. When 2% (by weight) cellulose was used irregular nanorods were observed (Figure 6a). When the cellulose concentration was increased to 5% (by weight), nanorods with the diameters of about 20 nm and the lengths of about 100 nm were observed and the size of nanorods increased (Figure 6b). The morphologies of cellulose/CHA nanocomposites prepared in ionic liquid by microwave heating were different from the previous reports [33,34], in which the flake-like cellulose and HA nanostructures were observed, implying that the ionic liquid had an effect on the morphologies of cellulose/HA nanocomposites and favoured the synthesis of cellulose-based nanocomposites with uniform size cellulose.

To investigate the effect of heating method on the morphology of composites, the cellulose/CHA nanocomposites were fabricated by oil heating at 130°C for 24 h. When the cellulose concentration was 2% (by weight), some loose particles were covered on the cellulose (Figure 7a). When cellulose concentration was increased to 4% (by weight), the
Figure 6. TEM Micrographs of the cellulose/CHA nanocomposites prepared in ionic liquid by microwave heating using different cellulose concentrations at 130°C for 30 min: (a) 2% and (b) 5% (by weights).

The density of the sample was increased, although some individual particles were still observed (Figure 7b). No individual particles existed and some pore structures were observed using 5% (by weight), cellulose (Figure 7c). Therefore, the cellulose concentration had an effect on the dispersion of CHA particles and the morphology of nanocomposites. Moreover, the heating methods also played an important role on the microstructure of CHA in nanocomposites compared to Figures 5b and 5d.

Figure 7. SEM Micrographs of the cellulose/CHA nanocomposites prepared in ionic liquid by oil heating using different cellulose concentrations at 130°C for 24 h: (a) 2%, (b) 4% and (c) 5% (all by weights).

The thermal stability of the cellulose/CHA nanocomposites is very important for their application, and was also investigated by TGA. TGA
Figure 8. TGA Curves of the cellulose/CHA nanocomposites prepared in ionic liquid by microwave heating using different cellulose concentrations at 130°C for 30 min: (a) without HA, (b) 2% and (c) 5% (by weights).

Thermogram for the regenerated cellulose is shown in Figure 8a. The weight loss of regenerated cellulose was ~69.12% below 600°C in the TGA curve. This was due to the thermal degradation of cellulose and the loss of ionic liquid molecules, whereas those of standard cellulose and regenerated cellulose show weight losses starting below 400°C [37]. The difference in the thermal degradation temperatures indicated the absorbance of ionic liquid molecules on the regenerated cellulose in nanocomposites. The weight loss of cellulose/CHA nanocomposites with 2% (by weight), and 5% (by weight), microcrystalline cellulose were ~20.27% and 35.89% below 600°C in the TGA curves (Figures 8b and 8c), respectively, which were less than that of regenerated cellulose, further indicating the existence of CHA and the successful synthesis of cellulose/CHA nanocomposites. The TGA results also implied that the weight loss increased with microcrystalline cellulose concentration. The SEM results indicated that the aggregated CHA nanostructures were embedded in the cellulose matrix. The CHA nanostructures led to an improvement of the thermal stability of cellulose. A similar phenomenon that the existence of inorganic materials could induce changes in thermal stability of cellulose/HA nanocomposites was reported in 2010 [33], cellulose/calcium silicate nanocomposites in 2010 [37], and α-Fe₂O₃/poly(methyl methacrylate) nanocomposites in 2008 [41]. The strong interaction became evident between the groups of cellulose and inorganic materials through hydrogen bonding [37,42]. Certainly, the intrinsic interaction mechanism needs to be further explored.

For comparison, the TGA curves of the cellulose/CHA nanocomposites prepared in ionic liquid by oil heating are also shown in Figure 9. The weight losses of cellulose/CHA nanocomposites with 2%, 4% and 5% (all by weights), microcrystalline cellulose were ~26.05%, 23.30% and 14.16% below 600°C in the TGA curves (Figure 9), respectively. The TGA results indicated that the weight loss decreased with increased cellulose concentration. Moreover, the weight losses were observed at two stages, which were different from the results of the samples synthesized by microwave heating, depicted in Figures 8b and 8c.

CONCLUSION

In summary, we report a simple and reliable microwave-assisted ionic liquid route for fabrication of the cellulose/CHA nanocomposites. The heating methods and ionic liquid played an important role on the crystallinity, microstructure and thermal stability of cellulose/CHA nanocomposites. Ionic liquid
favoured the cellulose/CHA nanocomposites with uniform-size cellulose.

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