Carbohydrate Polymers 121 (2015) 163–168

Contents lists available at ScienceDirect

Carbohydrate Polymers

journal homepage: www.elsevier.com/locate/carbpol

Microwave-assisted rapid synthesis and characterization of CaF_2 particles-filled cellulose nanocomposites in ionic liquid

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ARTICLE INFO

Article history:
Received 6 November 2014
Accepted 4 December 2014
Available online 31 December 2014

Keywords:
Cellulose
Alkali earth metal fluorides
Ionic liquid
Microwave

ABSTRACT

In this article, we try to compound cellulose/alkali earth metal fluorides (MF_2, M = Ca, Mg, Sr, Ba) nanocomposites via microwave-assisted ionic liquid method, wherein cellulose/CaF_2 and cellulose/MgF_2 were successfully synthesized through this method while cellulose/SrF_2 and cellulose/BaF_2 could not be synthesized. We focused on the synthesis of cellulose/CaF_2 and investigated the influences of the different time and different temperature for the synthesis of cellulose/CaF_2 nanocomposites. The influence of different heating methods such as oil-bath heating method was also studied. Ionic liquid ([Bmim][BF_4]) was used for dissolving microcrystalline cellulose and providing the source of fluoride ionic and the alkali earth metal nitrate ($Ca(NO_3)_2$, $Mg(NO_3)_2$, $Sr(NO_3)_2$, and $Ba(NO_3)_2$) was used as the reaction initiator. They were investigated by X-ray powder diffraction (XRD), Fourier transform infrared spectrometry (FTIR), scanning electron microscopy (SEM), thermogravimetric analysis (TG), derivative thermogravimetric (DTG), and energy-dispersive X-ray spectra (EDS). The different heating modes have influence on the morphology and property. The different temperature and heating time also have a certain influence on the morphology and crystallinity of calcium fluoride.

1. Introduction

Cellulose is a kind of environment-friendly renewable biopolymer and is the most abundant and versatile carbon source on the earth, which can be used as feedstocks for the synthesis of biomaterials and biofuels due to its abundance, low weight, high strength, and biodegradability (Atsushi & Paresh, 2006; Dieter, Brigitte, Hans-Peter, & Andreas, 2005; Youssef, Luian, & Orlando, 2010). As new environment-friendly materials, cellulose-based nanocomposites were widely used as forest products and engineering materials because of their unique properties such as biodegradation and bio-renewable nature (Eichhorn et al., 2010; Robert, Ashlie, John, John, & Jeff, 2011; Xiong, Wang, Zhang, Lu, & Lan, 2014). Cellulose-based nanocomposites not only can enrich the family of materials, but may also affect the development direction of future materials. In order to acquire cellulose-based nanocomposites, the dissolution of cellulose is one of the most important steps. Among traditional solvents, alkali/urea aqueous, *N*-methylmorpholine-*N*-oxide solvent, cuprammonium solution, and DMA_C/LiCl solvent had been reported in the literatures (Cai & Zhang, 2005; Fink, Weigel, Purz, & Ganster, 2001; Jia et al., 2014), but all of these solvents performed well for the problems of high environment toxicity and/or bad dissolving efficiency (Heinze & Liebert, 2001; Henniges, Kostic, Borgards, Rosenau, & Potthast, 2011). Ionic liquids have many perfect properties such as thermal stability, environment-friendliness, high fluidity and nonflammability, which will guide the development solvents as a clean technology (Natalia & Kenneth, 2008; Robin & Kenneth, 2003). Ionic liquids including [Bmim]Cl, [Amim]Cl, and [C_4mim]Cl have been reported to dissolve cellulose and the mechanism of cellulose dissolving was also studied by researchers (Andre, Kenneth, Pang, & Mark, 2009; Bruno & Björn, 2014; Richard, Scott, John, & Robin, 2002; Zhu et al., 2006). Microwave heating has many excellent properties such as rapid volumetric heating, short reaction time, energy saving and high reaction selectivity. Microwave-assisted ionic liquid method combined the advantages of microwave and ionic liquid will be an indispensable method for the synthesis of cellulose nanocomposites.

Calcium fluoride (CaF_2) is called fluorite in nature, which shows different colours with different impurities. The applications of CaF_2 have been widely investigated. For instance, CaF_2 was used for dental nanocomposites due to its low thermal conductivity, biocompatibility, and high strength, which played an important role in releasing fluoride ions for dental restoration (Hawa, Anthony,

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http://dx.doi.org/10.1016/j.carbpol.2014.12.033
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Richard, & Jennie, 2005; Hockin, Jennifer, Limin, & Laurence, 2008; Sun & Laurence, 2008). CaF_2 with better optical property was applied for glass–ceramic materials, which was considered as a major component of many glasses (Hawa et al., 2005; Namba, Yoshida, Yoshida, & Yoshida, 2005). Porous CaF_2 was prepared for a novel fluorinating reagent (Quan, Masanori, Gao, & Akira, 2002). It was reported that CaF_2 had an effect on the densification and properties of hydroxyapatite–zirconia composites (Kim, Noh, Koh, Kim, & Kim, 2002). Luminescent CaF_2:Ce^{3+}/Tb^{3+}-poly (acrylic acid) hybrid microspheres could be used as candidate in the pH-responsive drug delivery system (Dai et al., 2012). More recently, $BiVO_4$/CaF_2:Er^{3+}, Tm^{3+}, Yb^{3+} with enhanced upconversion properties was reported to be applied as near-infrared photocatalysts (Huang et al., 2014). There are a few reports about the synthesis of CaF_2 microballoon spheres in the previous literatures (Raiker, Marcus, Claus, & Anne, 2013; Yang et al., 2012; Zhang, Jiang, Chen, & Huang, 2013). However, the synthesis of CaF_2 particles-filled cellulose nanocomposites by microwave-assisted ionic liquid method has not been reported yet.

Today, we reported a simple, highly efficient, and environment-friendly method for the synthesis of cellulose/CaF_2 nanocomposites. The influences of different time and temperature were discussed. What is more, the traditional heating method for the synthesis of cellulose/CaF_2 was also compared in this article. On the other hand, we compared the study with one family of calcium, cellulose/MgF_2, cellulose/SrF_2, and cellulose/BaF_2 nanocomposites in the condition of 130 °C for 20 min through microwave-assisted ionic liquid method. But cellulose/SrF_2 and cellulose/BaF_2 nanocomposites were not successfully synthesized through this method.

2. Experimental

2.1. Materials

All chemicals were of analytical grade and used as received without further purification. All experiments were conducted under an air atmosphere. Microcrystalline cellulose (molecular weight of 34,843–38,894, degree of polymerization (DP, DP = 215–240) of a commercial reagent was purchased from Sinopharm Group Chemical Reagent Co., Ltd., Shanghai, China. Calcium nitrate ($Ca(NO_3)_2$), magnesium nitrate ($Mg(NO_3)_2$), strontium nitrate ($Sr(NO_3)_2$), and barium nitrate ($Ba(NO_3)_2$) were purchased from Beijing Chemical Works. Ionic liquid ([Bmim][BF_4]) was used in this experiment. The ionic liquid was used for dissolving microcrystalline cellulose and providing the source of fluoride ionic.

2.2. Synthetic process of cellulose/alkali earth metal fluorides (MF_2, M = Ca, Mg, Sr, Ba) nanocomposites

A simple, rapid and environmental-friendly method was used for the synthesis of cellulose/alkali earth metal fluorides (MF_2, M = Ca, Mg, Sr, Ba) nanocomposites. Microcrystalline cellulose (0.324 g) and ionic liquid (10 mL) were added into three flasks. The mixture was heated to 130 °C for 20 min in the microwave oven under vigorous magnetic stirring aiming to dissolve microcrystalline cellulose. Then, calcium nitrate (0.236 g), magnesium nitrate (0.256 g), strontium nitrate (0.211 g), and barium nitrate (0.261 g) were directly added into above-mentioned mixed solution, respectively. For obtaining the mixed solution of calcium nitrate, this mixture was heated to 130 °C in the microwave oven for a certain time (10 min or 20 min or 40 min). For the mixed solution of magnesium nitrate, strontium nitrate and barium nitrate were heated to 130 °C for 20 min in the microwave oven. The microwave oven was using 700 W cyclic microwave radiation and was equipped with vigorous magnetic stirring. The white products were obtained by centrifugal separation and washed with deionized water followed by ethanol for three times, and dried at 60 °C for further characterization.

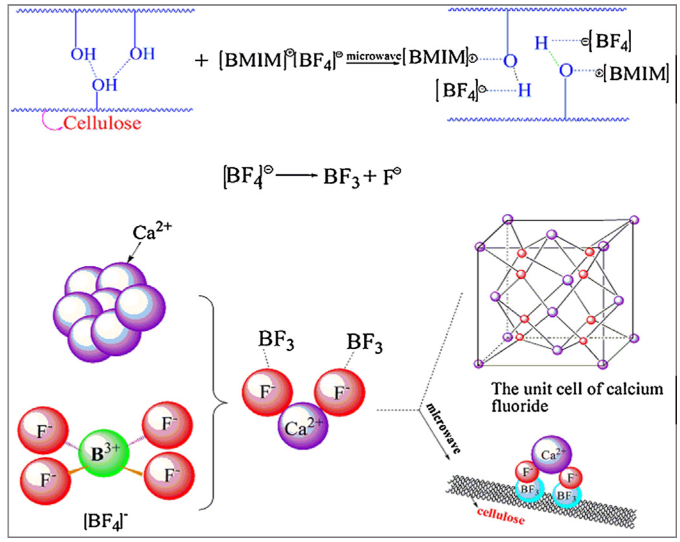

Fig. 1. Schematic image of the dissolution mechanism of cellulose in ionic liquid and the formation process of the CaF_2 particles-filled cellulose nanocomposites.

For comparison, cellulose/CaF_2 nanocomposites were also synthesized by microwave-assisted method for 20 min at a certain temperature (110 °C or 130 °C or 150 °C). What is more, the oil-bath heating method at 130 °C for 20 min was also investigated for the synthesis of cellulose/CaF_2 nanocomposites. The dosage of other reagents and the other conditions are all keeping the same. Fig. 1 visually showed the process of cellulose using ionic liquid and the combination between cellulose and calcium fluoride.

2.3. Characterization

X-ray powder diffraction (XRD) patterns were performed in the 2θ range from 10° to 70° on a Rigaku D/Max 2200-PC diffractometer with Cu Kα radiation (λ = 0.15418 nm) and a graphite monochromator at ambient temperature. Scanning electron microscopy (SEM) images were obtained with a Hitachi 3400N scanning electron microscopy. All samples were Au coated prior to examination by SEM. The energy-dispersive X-ray spectra (EDS) attached to the scanning electron microscopy was used to analyze the compositions of sample. Fourier transform infrared (FTIR) spectroscopy was carried out on Thermo Scientific Nicolet iN10 FTIR Microscope (Thermo Nicolet Corporation, Madison, WI, USA), which was equipped with a liquid nitrogen cooled MCT detector. Thermal behavior of the samples was tested using thermogravimetric (TG) and differential thermal gravity (DTG) on a simultaneous thermal analyzer (DTG-60, Shimadzu) at a heating rate of 10 °C min^{-1} in flowing air.

3. Results and discussion

In recent years, the microwave-assisted ionic liquid method has been accepted as a promising green methodology for the preparation of nanomaterials and nanocomposites by complying with the major green chemistry principles (Ma, Deng, & Yao, 2014; Zhu & Chen, 2014). Fig. 2a–c shows the XRD patterns of cellulose nanocomposites prepared by microwave-assisted ionic liquid method at 130 °C for 10, 20, and 40 min, respectively. One can clearly see the characteristic peaks of CaF_2 and cellulose (marked with *). The peaks intensities such as the planes of (1 1 1), (2 2 0),

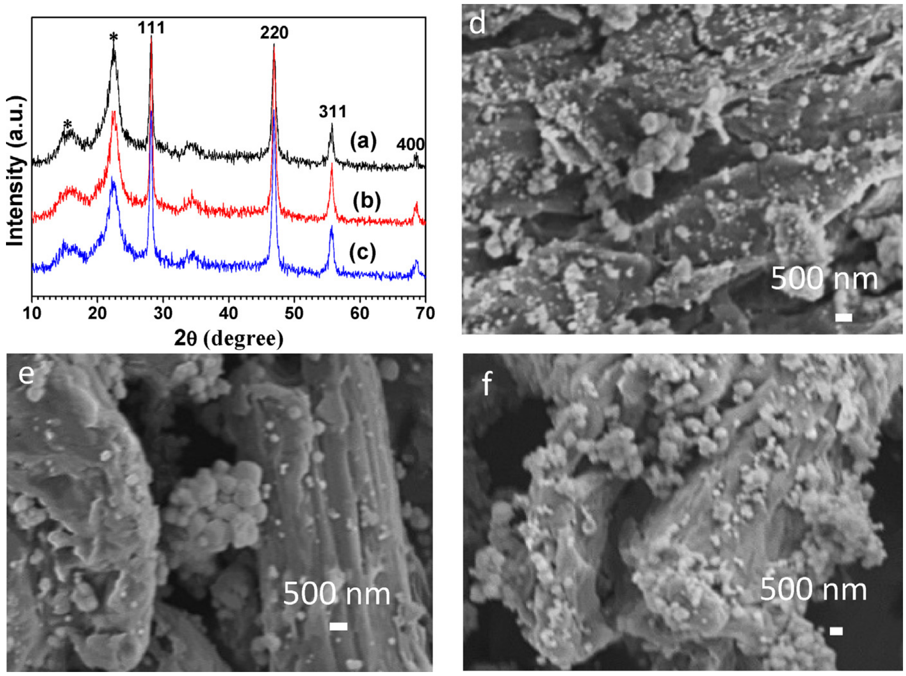

Fig. 2. XRD patterns (a–c) and SEM images (d–f) of the CaF_2 particles-filled cellulose nanocomposites prepared via microwave-assisted ionic liquid method at 130 °C for (a and d) 10 min, (b and e) 20 min, (c and f) 40 min.

(3 1 1), and (4 0 0) of CaF_2 increased with the increasing time, implying the increased crystallinity of CaF_2. One can conclude that the heating time can enhance the crystallinity of CaF_2. In the literature, microwave-assisted ionic liquid solvothermal method was applied to rapid synthesis of hollow microspheres of alkaline earth metal fluorides (MF_2, M = Mg, Ca, Sr) (Xu & Zhu, 2012). Fig. 2d–f showed the corresponding SEM micrographs of CaF_2 particles-filled cellulose nanocomposites synthesized by microwave-assisted ionic liquid method at 130 °C for 10, 20, and 40 min, respectively. One can observe amounts of spherical CaF_2 particles grew on cellulose substrate. When the heating time was increased to 40 min, the size and quantities of CaF_2 particles increased (Fig. 2f), indicating that long heating time preferably favors the growth of CaF_2 particles. Obviously, this morphology of CaF_2 in the cellulose matrix is completely different from the reported results (Xu & Zhu, 2012), in which CaF_2 double-shelled hollow microspheres were obtained using $Ca(NO_3)_2{\cdot}4H_2O$ and $NaH_2PO_4{\cdot}2H_2O$ in the ionic liquid ([Bmim][BF_4]) at 120 °C for 10 min.

The influences of heating method and heating temperature on the phases and crystallinity of CaF_2 particles-filled cellulose nanocomposites were also investigated. The corresponding XRD patterns of nanocomposites were shown in Fig. 3a–c. CaF_2 particles-filled cellulose nanocomposites with better crystallinity were successfully synthesized in all these conditions. Using oil-heating method (Fig. 3a), all the peaks were obviously decreased, compare with the peaks in Fig. 3b and c. The result illustrated the microwave-assisted ionic liquid method can improve the crystallinity of CaF_2. When the temperature increased from 110 to 150 °C, the characteristic peaks of CaF_2 slightly increased (Fig. 3c), indicating that the heating temperature had a slight effect on the crystallinity of CaF_2.

The microstructures and dispersion of the as-prepared nanocomposites were also investigated by SEM. The micrographs of CaF_2 particles-filled cellulose nanocomposites synthesized by microwave-assisted ionic liquid method for 20 min at 110 and 150 °C were presented. One can see that CaF_2 particles-filled cellulose nanocomposites were successfully synthesized. Compared with oil heating method (Fig. 3d) and microwave heating method (Fig. 2e) at the same condition, the size of CaF_2 obviously increased using microwave-assisted ionic liquid method, indicating that microwave can urge CaF_2 particles to happen to nucleation and then form the big spheroid crystals. Plentiful of spherical CaF_2 grew on cellulose substrate; the CaF_2 particles-filled cellulose nanocomposites synthesized by oil heating method had the better dispersity. Fig. 3e and f showed the SEM micrographs of CaF_2 particles-filled cellulose nanocomposites synthesized at different temperature, the shape and size of CaF_2 particles had not obviously changed and the CaF_2 crystals displayed the spherical shape. But the quantity of the CaF_2 particles dramatically increased, manifesting that high temperature can promote the combination of CaF_2 and cellulose. One can see that CaF_2 particles-filled cellulose nanocomposites with better shape and dispersity were successfully synthesized at these conditions.

The EDS spectrum displayed that the samples consisted of C, O, F and Ca, the right compositions of cellulose/CaF_2 nanocomposites (Fig. 4). Compare with Fig. 4a, the peaks intensities of Ca and F increased using microwave ionic liquid heating method (Fig. 4b), implying the more CaF_2 existed in nanocomposites.

The thermal behavior of the CaF_2 particles-filled cellulose nanocomposites was also investigated by TG and DTG. The total weight losses of the CaF_2 particles-filled cellulose nanocomposites were 78.6%, 71.4%, 70.9%, and 71.9%, respectively. Compared with Fig. 5a, the cellulose/CaF_2 nanocomposites synthesized by microwave-assisted ionic liquid method performed the less weight loss (Fig. 5c), indicating that the microwave heating method can improve the combining capacity between cellulose and CaF_2. The cellulose/CaF_2 nanocomposites synthesized at different temperatures showed the similar weight loss (Fig. 5b–d), indicating that the temperature had less influence on the thermal stability of the cellulose/CaF_2 nanocomposites. Seeing from TG curves, the small weight loss around 25–100 °C contributed to the desorption of water, accompanied by endothermic peak at about 87 °C in DTG curves. Mainly the weight loss from 290 to 470 °C is due to the thermal degradation of cellulose in composites, according with the endothermic peaks located at 338 °C.

Microwave-assisted ionic liquid method was also applied for the synthesis of cellulose/alkali earth metal fluorides (MF_2, M = Mg, Sr,

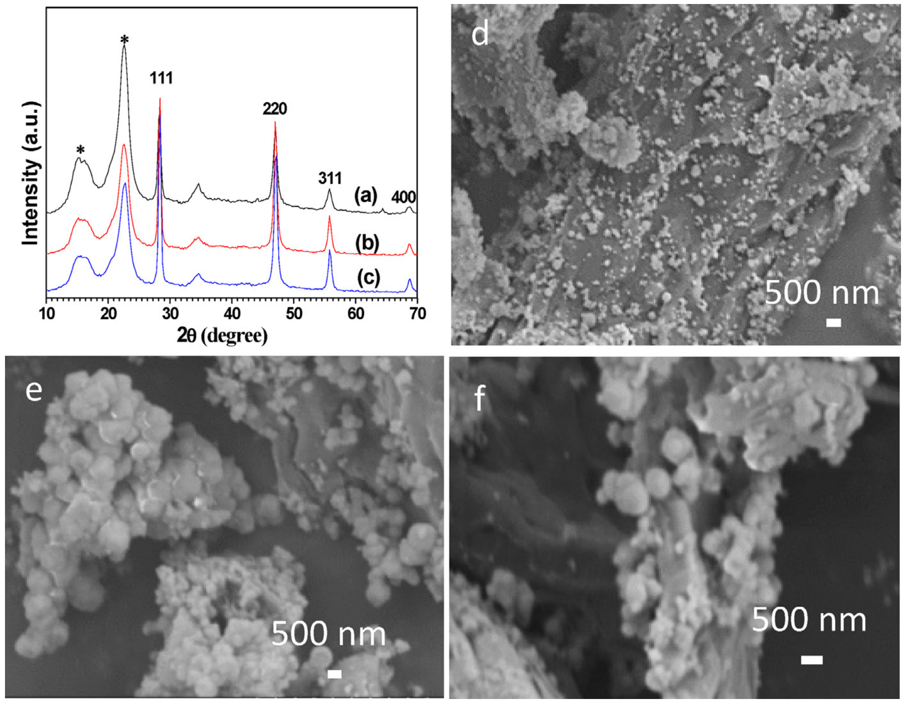

Fig. 3. XRD patterns (a–c) and SEM images (d–f) of the CaF_2 particles-filled cellulose nanocomposites prepared via (a and d) oil-heating method at 130 °C for 20 min and microwave ionic liquid method for 20 min at (b and e) 110 °C and (c and f) 150 °C.

Ba) nanocomposites by microwave-assisted ionic liquid method at 130 °C for 20 min. One can see that cellulose/MgF_2 nanocomposites with low crystalline were successfully synthesized (Fig. 6a). However, cellulose/SrF_2 and cellulose/BaF_2 nanocomposites were not successfully synthesized through this similar method and only the characteristic peaks of cellulose were observed (marked with *, Fig. 6b and c). Xu and Zhu (2012) reported that the microwave-assisted ionic liquid solvothermal method could also be extended to prepare hollow microspheres of MgF_2 and SrF_2. However, in this article, cellulose/MgF_2 nanocomposites were obtained, and cellulose/SrF_2 and cellulose/BaF_2 nanocomposites were not synthesized in the existence of cellulose. Therefore, one can conclude that cellulose played an important role in the phase of alkali earth metal fluorides in the nanocomposites. This is due to the restrain effect of cellulose. In the previous study, it was found the restrain effect of cellulose during the synthesis of inorganic materials (Ma, Zhu, Zhu, & Sun, 2014). On the other hand, the effect of the ionic radius may result in the failure synthetic. One can guess the bigger ionic radius will restrain the formation of cellulose nanocomposites using ionic liquid. Of course the intrinsic and detailed formation mechanism needs to be further explored in the near future. Fig. 6d–f displayed the corresponding SEM micrographs of the samples. Few spherical MgF_2 particles were observed on cellulose substrate in the cellulose/MgF_2 nanocomposites (Fig. 6d). However, SrF_2 and BaF_2 particles were not observed and only cellulose with fiber-like shape was obtained (Fig. 6e and f). These results are consistent with the conclusion in XRD patterns. The atomic radius may affect the synthesis of alkali earth metal fluorides.

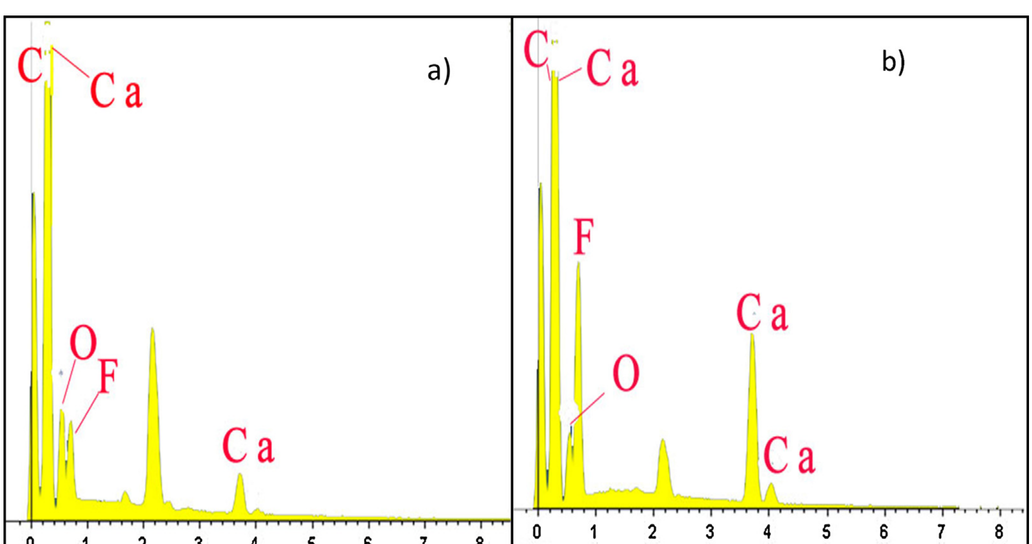

Fig. 4. EDS spectrum of CaF_2 particles-filled cellulose nanocomposites synthesized via (a) oil-heating method and (b) microwave ionic liquid heating method.

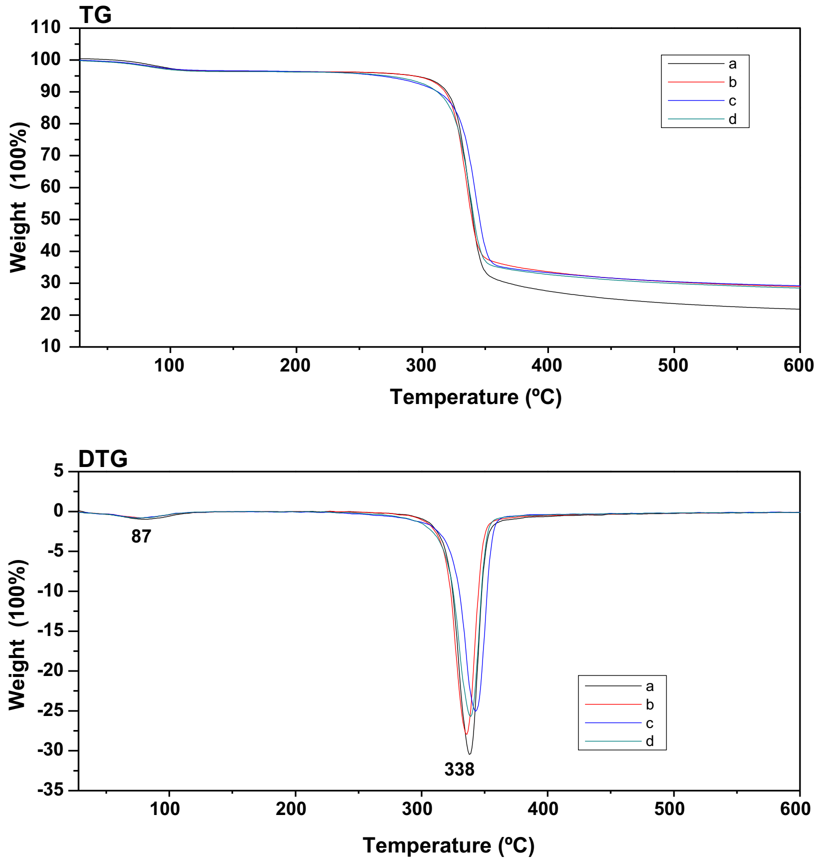

Fig. 5. TG and DTG curves of the CaF_2 particles-filled cellulose nanocomposites prepared via (a) oil-heating method at 130 °C for 20 min and (b–d) microwave-assisted ionic liquid method for 20 min at (b) 110 °C, (c) 130 °C, and (d) 150 °C.

4. Conclusions

In summary, CaF_2 particles-filled cellulose nanocomposites were successfully synthesized via this simple and rapid microwave ionic liquid method. The heating time and temperature played important roles in the crystallinity and morphology of CaF_2. This method can be extended to compound cellulose/MgF_2 nanocomposites, while cellulose/SrF_2 and

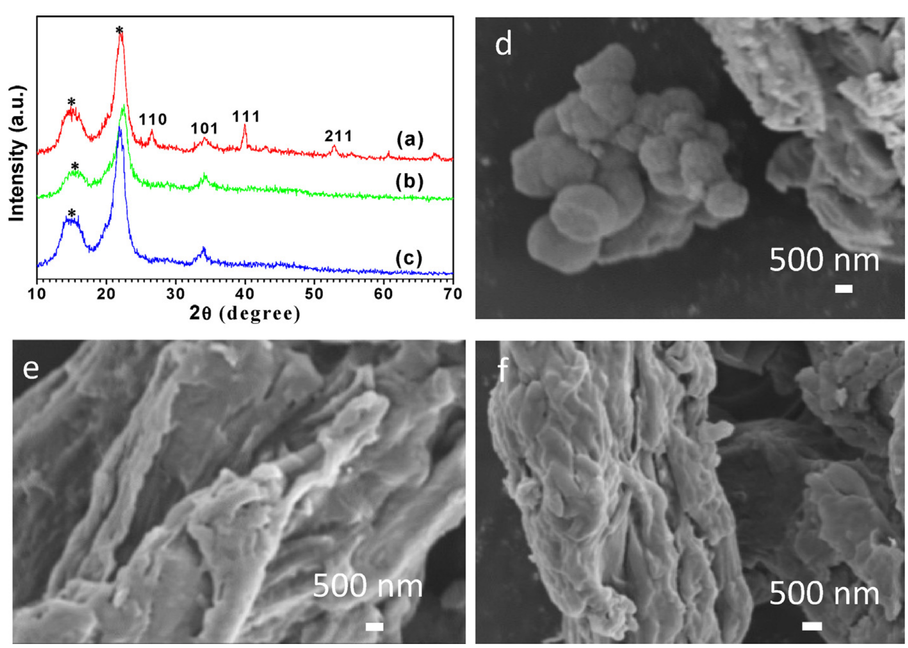

Fig. 6. XRD patterns (a–c) and SEM images (d–f) of the cellulose/alkali earth metal fluorides (MF_2, M = Mg, Sr, Ba) nanocomposites prepared via microwave ionic liquid heating method at 130 °C for 20 min: (a and d) cellulose/MgF_2; (b and e) cellulose/SrF_2; and (c and f) cellulose/BaF_2.

cellulose/BaF_2 nanocomposites cannot be obtained through this method.

Acknowledgments

Financial support from the Fundamental Research Funds for the Central Universities (No. TD2011-11), Beijing Nova Program (Z121103002512030), and the Program for New Century Excellent Talents in University (NCET-11-0586) is gratefully acknowledged.

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