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Short communication

Rapid exfoliation of rectorite in quaternized carboxymethyl chitosan

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ABSTRACT

Exfoliated quaternized carboxymethyl chitosan/rectorite (QCMC/REC) nanocomposite was prepared via microwave irradiation method for 70 min, which was performed in only water without any additional plasticizer. XRD, TEM, AFM, SEM and FTIR results revealed that when the mass ratio of QCMC to REC was no less than 4:1, the silicate layers of REC were completely exfoliated in QCMC matrix and were homogenous with QCMC, the surface of QCMC/REC nanobiocomposite was very smooth; two types of interactions of hydrogen bond and electrostatic attraction existed in the QCMC/REC nanobiocomposite. Thermal analysis indicated that QCMC/REC nanobiocomposite had higher thermal stability than only QCMC. Therefore, the microwave irradiation method appears to be a promising tool for preparing exfoliated biopolymer/layered silicate nanocomposites at a mild condition.

1. Introduction

Biopolymer/layered silicate (BPLS) nanocomposites are a new type of environmentally friendly materials with nontoxicity and biodegradability (Bitinis, Hernandez, Verdejo, Kenny, & Lopez-Manchado, 2011). These novel environmental-friendly materials open new scenarios for biodegradable polymers with potential perspectives for medicine, coatings, automotive, packaging applications, etc. (Ruiz-Hitzky, Aranda, Darder, & Ogawa, 2011; Wang, Du, Luo, Lin, & Kennedy, 2007; Wang, Pei, Du, & Li, 2008). Generally, depending on the strength of interfacial interactions between the biopolymer matrix and layered silicate (modified or not), three different types of BPLS nanocomposites are thermodynamically achievable: intercalated nanocomposites, flocculated nanocomposites and exfoliated nanocomposites (Ray & Okamoto, 2003). The exfoliation of BPLS nanocomposite is an ideal structure, in which silicate layers are completely homogenous with biopolymer. But according to the previous study, it can only be obtained in a harsh condition, for example, the exfoliated starch-based nanobiocomposite was prepared in the help of plasticizer (Chivrac, Pollett, Schmutz, & Averous, 2008) and hot-pressing (Chivrac, Pollet, Dole, & Averous, 2010). However, for some biopolymers with relatively poor thermal stability, such as chitosan, it is very difficult to obtain exfoliated nanocomposites at a mild condition.

Chitosan is one of the most abundant natural aminopolysaccharides. It has been widely used in food production, pharmaceutical areas, environment protection, etc. But the use of chitosan is limited because of its insolubility in water (Liu, Wang, Yang, & Sun, 2012). Quaternized carboxymethyl chitosan (QCMC) is an amphoteric soluble derivative of chitosan, which exhibited many potential applications (Guo, Xing, Liu, Zhong, & Li, 2008; Song, Zhou, & Chen, 2012; Xu, Xin, Li, Huang, & Zhou, 2010). In addition, in order to widen its application, we intercalated QCMC into rectorite (REC), a kind of layered silicate, but obtained only intercalated QCMC/REC nanocomposite in 2 days via conventional heating method (Wang et al., 2010). Therefore, it will be a promising way to obtain exfoliated chitosan-based layered silicate nanocomposites by a simple and fast method.

Recently, microwave irradiation technology has widely been used in chemical synthesis by the high efficiency and homogeneous heating manner (Ratanakamnuan, Atong, & Aht-Ong, 2012). In our previous study, soluble quaternized carboxymethyl chitosan was obtained rapidly by microwave irradiation (Liu et al., 2012). In this study therefore, an attempt has been made to prepare exfoliated QCMC/REC nanobiocomposite via microwave irradiation method in water without any additional plasticizer, the workflow is given in Scheme 1.

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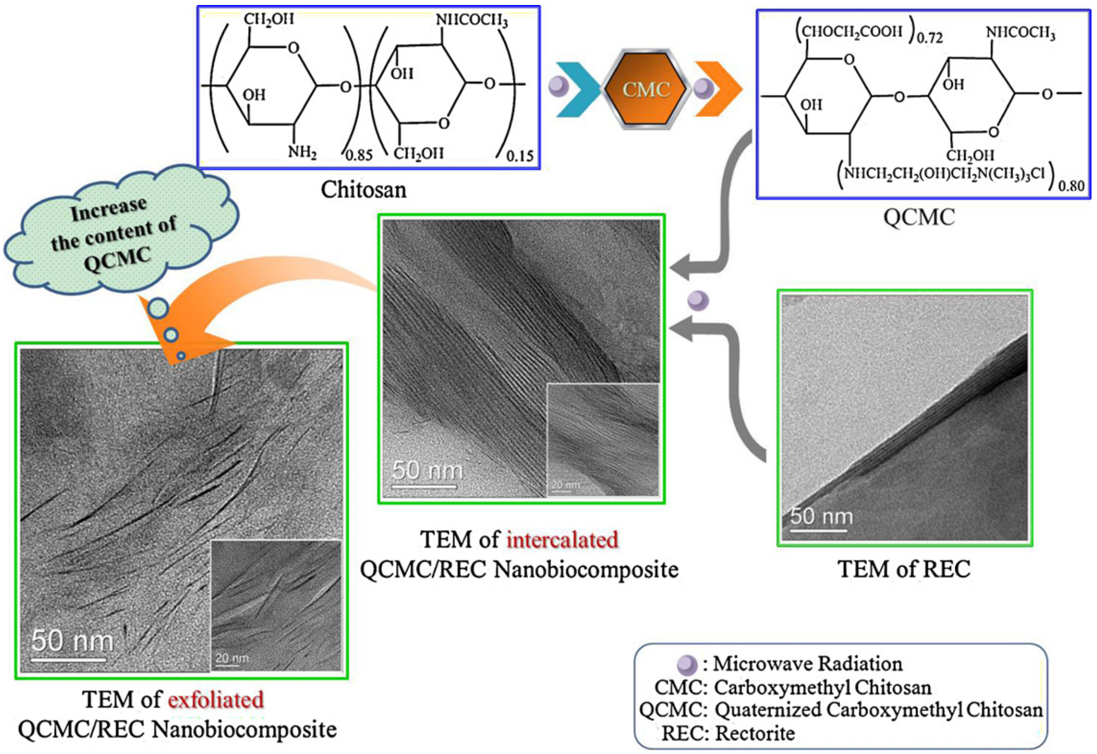

Scheme 1. The exfoliation course of REC in QCMC matrix.

2. Materials and methods

2.1. Materials

Chitosan was purchased from Jinan Haidebei Marine Bioengineering Co. Ltd (Shandong, China). The molecular weight (*Mw*) of chitosan is 2.0×10^5 and the degree of deacetylation is 85%. Calcium rectorite (REC) refined from the clay minerals was provided by Hubei Mingliu Inc., Co. (Wuhan, China). All other chemicals were of analytical grade. A XH-100B microwave synthesis system was obtained from Beijing XiangHu Sci.-Tech. Dept. Co. Ltd (Beijing, China).

2.2. Preparation of QCMC and QCMC/REC nanocomposites

QCMC was prepared under microwave irradiation by using chloroacetic acid and 2,3-epoxypropyltrimethyl ammoniumchloride (ETA) as modification agent according to our previous study (Liu et al., 2012). Briefly, the carboxylmethylation of chitosan was performed at 500 W and 70 °C for 25 min, after which carboxylmethyl chitosan was quaternized at 400 W and 75 °C for 70 min. The molar ratio of chloroacetic acid to amino groups of chitosan was 4:1, and that of ETA to amino groups of chitosan was 6:1. The reaction mixture was purified by acetone, dialyzed, and finally freeze-dried at −45 °C to obtain QCMC. The *Mw* of QCMC was 8.28×10^4 which was determined by the gel permeation chromatography method and the degree of substitution of carboxymethyl groups and quaternary ammonium groups were respectively 0.72 and 0.80 which were determined by potentiometry (Muzzarelli & Giacomelli, 1987; Muzzarelli, Tanfanim, & Emanuelli, 1984).

Five QCMC/REC nanocomposites were prepared as follows: REC was dispersed in distilled water by using a magnetic stirrer at 500 rpm for 24 h. An aliquot of QCMC solution was dropped slowly into clay suspension and reacted under microwave irradiation for 600 W and 80 °C for 70 min. Finally the QCMC/REC nanobiocomposites were freeze-dried at −45 °C and ground to powder. The initial mass ratios of QCMC to REC were 1:2, 1:1, 2:1, 4:1 and 8:1, respectively, and the nanocomposites were labeled as QR-1, QR-2, QR-3, QR-4 and QR-5, respectively.

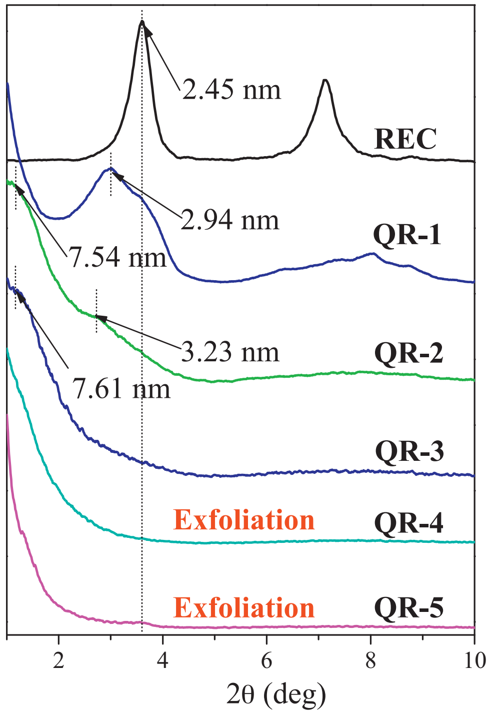

Fig. 1. XRD patterns of REC and QCMC/REC nanobiocomposites.

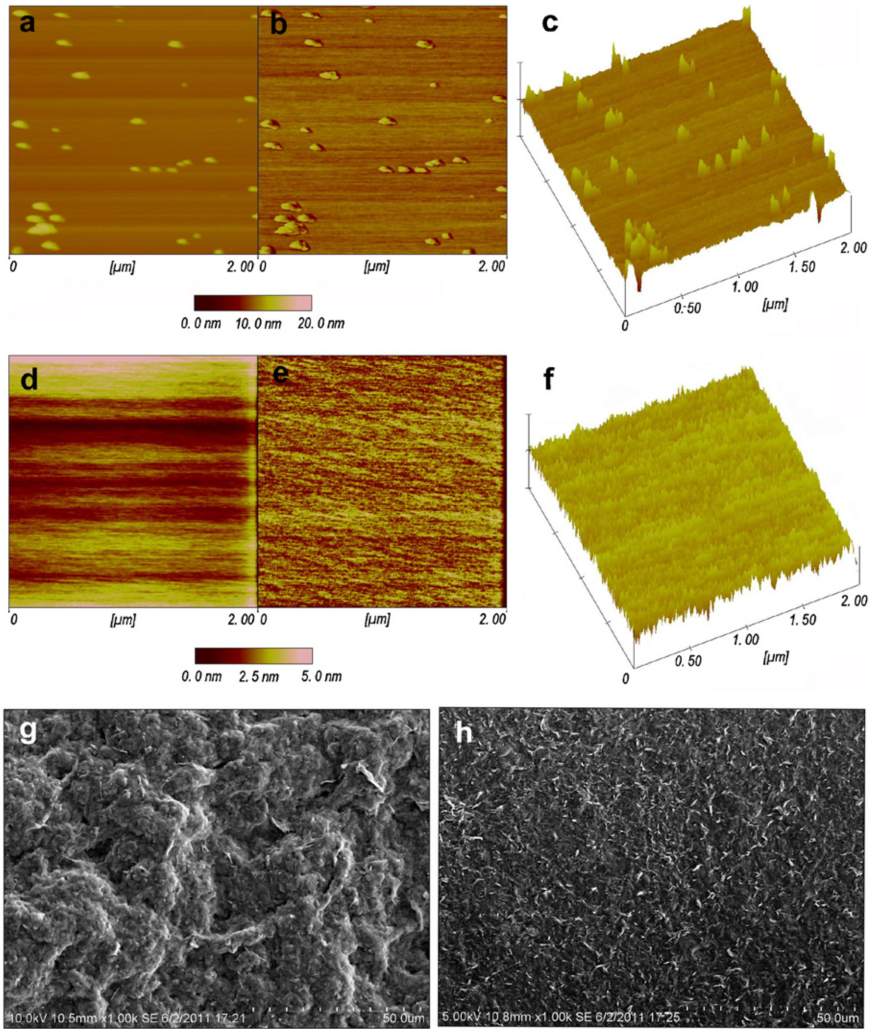

Fig. 2. AFM images of REC (scale bar = 2 μm): (a) height image, (b) phase image, and (c) three-dimensional phase image. AFM images of QR-4 nanobiocomposite (scan size = 2 μm): (d) height image, (e) phase image and (f) three-dimensional phase image. SEM images of (g) REC and (h) QR-4 nanobiocomposite.

2.3. *Characterization*

Fourier transform infrared (FT-IR) spectra were recorded on a Nicolet FT-IR 5700 spectrophotometer (Madison, USA) using KBr pellets method. X-ray diffraction (XRD) patterns were obtained using a D8 advance X-ray diffractometer (Bruker, Germany) with a Cu Kα radiation. A JEM-2010HR transmission electron microscopy (TEM) (JEOL, Japan), atomic force microscope (AFM) (Veeco Metrology Group, USA) and scanning electron microscope (SEM) (Hitachi, Japan) were used to investigate the microstructural and surface morphology of REC and the nanocomposite. Thermogravimetric analysis (TGA) was carried out on a TGA Q500 (TA, USA).

3. Results and discussion

Fig. 1 exhibits typical XRD patterns of pristine REC and the prepared QCMC/REC nanobiocomposites. Compared to REC, the (0 0 1) diffraction angles of QR-1, QR-2 and QR-3 significantly shifted to lower angle, which suggests that QCMC intercalated into the interlayer of REC (Wang et al., 2010; Wang, Pei, et al., 2008). Their interlayer distance can be calculated by the Bragg's law ($n\lambda = 2d \sin\theta$) according to the (0 0 1) diffraction angles, which is an evidence for the formation of intercalated nanobiocomposites. Noteworthily, the interlayer distances of QR-4 and QR-5 cannot be obtained because no obvious diffraction peaks were observed in their XRD patterns, indicating complete exfoliation of the silicate layers (Chivrac et al., 2010). Besides, the direct confirmation of the intercalation or exfoliation can be observed from TEM images in Scheme 1. All TEM images extensively displayed typical layered structure of layered silicates and biopolymer/layered silicate nanocomposite. The dark entities are the cross section of REC layers and the gray areas are the biopolymer matrix. Compared to TEM image of REC, the enlarged interlayer of the nanocomposites can be seen clearly, furthermore, the exfoliated layers were observed with the increase of the QCMC content, which well coincides with the XRD results. In addition, Scheme 1 shows that REC layers were arranged well in the QCMC matrix at a nanometer scale, confirming very high affinity between QCMC and clay layers. These above results demonstrated that the mass ratios of QCMC to REC played an important role in the formation of intercalated or exfoliated nanobiocomposite, and the high content of QCMC strengthened the interaction between polymer chains and the REC, as well as promoted the capability of intercalation to exfoliation (Meng, Wang, Du, Wang, & Tang, 2009).

Fig. 2 gives the surface morphology of REC and exfoliated QR-4 nanobiocomposite. Contrast the height micrographs of REC (Fig. 2a) with QR-4 nanobiocomposite (Fig. 2d), REC had some obvious protuberances in 5–15 nm nanoscale, but QR-4 nanobiocomposite was flat in even smaller bar (5 nm), the excellent agreement was confirmed by SEM images of Fig. 2g and Fig. 2h, in which QR-4

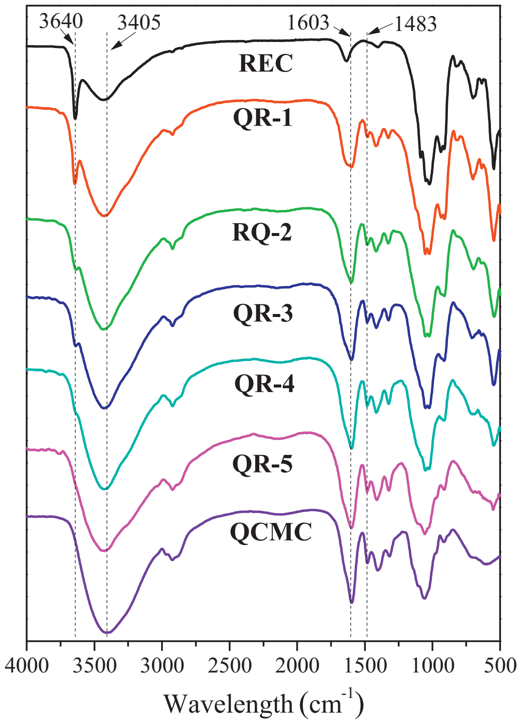

Fig. 3. FTIR spectra of QCMC, REC and QCMC/REC nanobiocomposites.

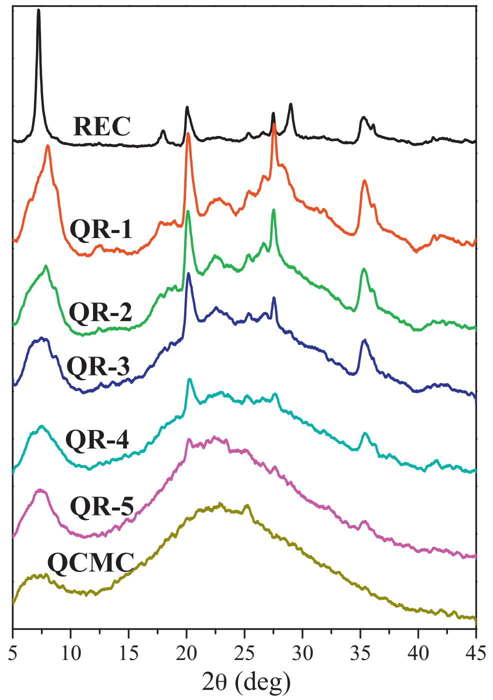

Fig. 4. XRD patterns of QCMC, REC and QCMC/REC nanobiocomposites.

nanobiocomposite had a smoother surface than REC. Fig. 2b and Fig. 2e is the corresponding phase signal of Fig. 2a and Fig. 2d, Fig. 2c and Fig. 2f is the corresponding three-dimensional phase images, respectively. Compared to REC, the flat phase image of QR-4 nanobiocomposite showed that REC layers were homogenous with QCMC matrix. Moreover, exfoliation means the nanoplatelets with a thickness of about 2 nm were oriented in all possible directions to one another in the matrix as confirmation of the XRD peak disappearance (Wang, Wang, et al., 2008). The results further confirmed that the exfoliated QCMC/REC nanobiocomposite was obtained.

Microwave radiation heating is an intramolecular heating method generated by electromagnetic wave; it can speed up the reaction rate by energy penetration, and thus change reaction kinetics to accelerate the reaction process (Zhang & Xu, 2007). As compared to the intercalation using convention heating, QCMC with many polar groups can absorb more energy from microwave irradiation, which may make more polar QCMC molecules enter into the layer space of REC by molecule's thermal motion. In consequence, in our previous study, the preparation of intercalated QCMC/REC nanobiocomposite consumed 48 h by conventional heating method (Wang et al., 2010), and the largest d_{001} spacing was only 3.27 nm. In this study, the intercalated QCMC/REC nanobiocomposite with d_{001} spacing of 7.54 nm or even exfoliated nanobiocomposite were obtained via microwave irradiation heating method in 70 min, which did not need any plasticizer and high pressing, and QCMC was homogenous with REC in the exfoliated QCMC/REC nanobiocomposite.

Fig. 3 shows the FTIR spectra of REC, QCMC and five different nanobiocomposites. Obviously, all the spectra of the nanobiocomposites exhibited the combination peaks of REC with QCMC spectrum. Differently, from QR-1 to QR-5, the peak of stretching vibration of N—H bonded to O—H in QCMC at 3405 cm^{-1} was wider and shifted to lower wavenumber, indicating that hydrogen bond interactions existed at the external surface of REC with the adsorbed QCMC (Kabiri, Mirzadeh, & Zohuriaan-Mehr, 2010). The phenomena were also found in the convention heating method (Wang et al., 2010). As a result, microwave irradiation showed the same or better effect to convention heating on the preparation of QCMC/REC nanobiocomposite.

Fig. 4 shows the X-ray diffraction patterns of QCMC, REC and QCMC/REC nanobiocomposites which give the crystallinity behavior. Neat QCMC showed two major characteristic crystalline peaks at around 7.3° and 22°, while the diffraction pattern of REC consists of six main crystalline peaks at 7.2°, 18.2°, 19.8°, 27.4°, 29.1°, and 35.3°. Interestingly, the XRD patterns of QCMC/REC nanobiocomposites did not show their own crystal regions, but a good combination of crystallinity peaks of QCMC with REC, this was

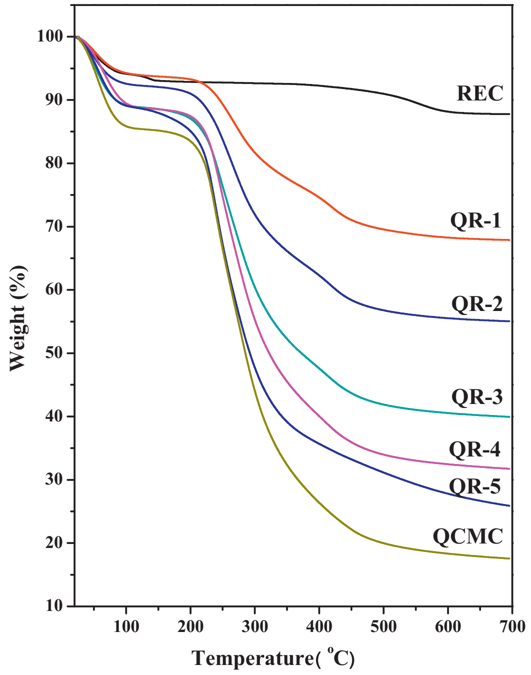

Fig. 5. Thermogravimetric curves of REC, QCMC and QCMC/REC nanocomposites.

strong proof of the interaction between QCMC and REC (Wang, Pei, et al., 2008), which agrees with the above FTIR results.

Thermal stabilities of QCMC, REC and five nanobiocomposites were investigated by thermogravimetric analysis (TGA) (Fig. 5). The $T_{\max}$ (the temperature when the rate of weight loss reaches a maximum) of QCMC was observed to be at about 235.7 °C, in contrast, $T_{\max}$ of QR nanocomposites were higher, which were at 269.6 °C, 257.4 °C, 246.1 °C, 240.9 °C, and 239.8 °C for QR-1 to QR-5 nanocomposite, respectively. Moreover, the remaining weight of QCMC at 700 °C was only 17.5%, but those were 67.8%, 55.3%, 39.9%, 31.8% and 25.9% for QR-1 nanocomposite to QR-5 nanocomposite, respectively. These results revealed that all the nanobiocomposites showed more excellent thermally stability than QCMC, which were positively related to the content of REC. It can be explained as follows, on one hand, the REC loading level was increased, leading to the enhancement of the electrostatic and hydrogen bond interaction as well as the stronger barrier action of REC (Han, Lee, Choi, & Park, 2010); on the other hand, the electrostatic and hydrogen bond interactions resulted in poor mobility of QCMC chains (Wang et al., 2007). What is more, the result of the thermal stability of these obtained nanobiocomposites was consistent with that from convention heating method (Wang et al., 2010), implying comparability of microwave radiation process.

4. Conclusions

Compared to convention heating method, larger d_{001}-spacing intercalated or exfoliated QCMC/REC nanobiocomposites were obtained by microwave irradiation heating method in water for a shorter time. Nevertheless, similar results were still obtained that QCMC molecules were connected with the silicate layers of REC via hydrogen bonds interaction, as a result, the thermal stability of the nanobiocomposites significantly improved compared to that of QCMC. In conclusion, rapid exfoliation of biopolymer/layered silicate nanocomposite can be performed via microwave radiation at a mild condition.

Acknowledgements

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