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Effect of activated carbon on the properties of carboxymethylcellulose/activated carbon hybrid hydrogels synthesized by γ-radiation technique

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Abstract

Activated carbon (AC) was incorporated into carboxymethylcellulose (CMC) to form CMC/AC hybrid hydrogels with excellent elasticity and flexibility by radiation crosslinking. The effect of AC on the formation, properties and structure of CMC/AC hybrid hydrogels was discussed in terms of gel fraction, gel strength, gel swelling, TGA, FTIR spectra and SEM image. Compared with pure CMC hydrogel, the gel fraction, gel strength and thermal stability were improved obviously after incorporating AC into CMC hydrogels, and similar swelling ability were maintained up to the hybrid of 5%AC. FTIR and TGA spectra of the prepared gels after extracting sol revealed two findings: (1) radiation crosslinking reaction of CMC occurs in side chain of CMC molecules due to the presence of –OH and $–CH_2$ groups; (2) AC enhanced the radiation crosslinking of CMC because AC was binding to CMC through physical adsorption and hydrogen bond as well as other interactions. From SEM images, it was found that AC particles were embedded in the network of CMC gels to form a uniform structure.

Keywords: Hybrid hydrogel; Radiation; Strength; Carboxymethylcellulose; Activated carbon

1. Introduction

Hybrid hydrogels have attracted more and more attention in the past several years because besides properties of its parent polymers, novel properties can be introduced into the hybrid systems via the cooperative effects and some specific interactions (Li, Wang, Chen, Liu, & Gao, 2003; Morimoto, Endo, Iwasaki, & Akiyoshi, 2005; Shi et al.; Wang, Kopecek, & Stewart, 2001; Zhang, Sun, & Chu, 2004). For example, multiwalled carbon nanotube (MWCT) and poly (vinyl alcohol) (PVA) hybrid hydrogel showed reversible bending behavior as well as other novel properties made them good candidate as actuator.

CMC, the most popular and cheapest cellulose ether, is an anionic linear polymer in which original H atoms of cellulose hydroxyl groups are replaced by carboxymethyl substituent, $–CH_2COO^-$. Due to its good biocompatibility, high water absorption ability, good degradability, innoxious and low cost, CMC hydrogel was widely used in many fields (Fujimoto & Petri, 2001; Sannino et al., 2004). CMC was also the first polysaccharide which was successfully crosslinked by radiation method. The effect of degree of substitution (DS) and molecular weight on its radiation crosslinking was investigated and the results turned out to play significantly role on the investigation of radiation synthesis of polysaccharide hydrogels (Fei, Wach, Mitomo, Yoshii, & Kume, 2000; Liu, Zhai, Li, Peng, & Wu, 2002; Wach, Mitomo, Yoshii, & Kume, 2001; Wach, Mitomo, Nagasawa, & Yoshii, 2003). Moreover, CMC hydrogel

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shows pH sensitivity in aqueous solution: at about pH >8 or pH <5, the swelling ratio of the hydrogel decreases obviously.

However, CMC hydrogels in the swollen state have very poor mechanical strength, which limits their applications. In this work, we aimed to improve the properties of CMC hydrogels by incorporating inorganic component into CMC hydrogels, i.e., activated carbon (AC), which has been used as the inorganic functional component in many organic-inorganic hybrid materials and found that it is an ideal candidate for developing new functional materials with excellent mechanical strength. For example, AC hybrid membranes with good mechanical properties have shown higher efficiency for CO_2 absorption (Anson, Marchese, Garis, Ochoa, & Pagliero, 2004; Ballinas, Torras, Fierro, & Garcia-Valls, 2004) and waste water treatment (Thiruvenkatachari, Shim, Lee, Aim, &Moon, Moon).

Although the improvement of mechanical strength of the hydrogels via incorporating of inorganic compositions was seldom reported, it is reasonable to expect that incorporation of AC would not only overcome the poor mechanical strength of CMC hydrogels, but also extend the applications of CMC hydrogels as a new kind of functional material.

2. Experimental

2.1. Materials

CMC in form of sodium salt with DS 1.89 was purchased from Daicel Co. Ltd., Japan. Molecular weight was 1.5×10^5, which was determined by viscometer.

AC with purity of chemical reagent was supplied by Tianjin Chemical Plant.

2.2. Preparation of CMC/AC hybrid hydrogels

CMC and AC were dissolved or dispersed in distilled water. According to literature report (Wach et al., 2001), the sample was stored for about 7 days to obtain homogeneous mixture. Then the samples were irradiated with γ-rays from ^{60}Co source (Peking University) to get CMC/AC hybrid hydrogels. Pure CMC hydrogel was also prepared using the above method.

2.3. Gel fraction

CMC/AC hybrid hydrogels were cut into small pieces and immersed into distilled water at room temperature for 24 h to remove the sol part. Gel fraction was calculated according to Eq. (1):

$$\text{Gel fraction}(\%) = \frac{G_d}{G_i} \times 100 \tag{1}$$

where G_i is the initial dried weight of the sample and G_d is the mass of dried gel after extraction.

The AC particles were embedded in the network of CMC hydrogel and could not be removed completely by the above method. To investigate that whether there is interaction between CMC and AC under irradiation, gel fraction of the hybrid hydrogels was corrected according to Eq. (2). The correction was carried out by subtracting AC's content from gel fraction (g) of the hydrogel calculated according to Eq. (1).

$$g' = \frac{m \times (A + 20\%) \times g - m \times A}{20\% \times m} = \frac{(A + 20\%) \times g - A}{20\%} \tag{2}$$

where g' and g are gel fractions after and before the correction, respectively; m is the weight of the hydrogel sample; 20% and A are contents of CMC and AC in the initial mixture, respectively.

2.4. Gel strength of the hybrid hydrogel

Gel strength of CMC/AC hybrid hydrogels was measured according to the method described in our previous work (Zhang & Ha, 2001; Liu, Yi, Zhai, & Ha, 2006). The hydrogel was cut into cylinder with 10 mm height and 10 mm diameter. Gel strength of different samples was evaluated by determining the relative change in height of the hydrogel cylinders under a 50 g weight. The compression ratio (CR) of the hydrogel was calculated as following:

$$CR = \frac{L}{L_0} \tag{3}$$

where L_0 is the initial height of the sample, and L is the height under the pressure.

2.5. Swelling behavior

The hydrogel samples with certain weight were immersed into distilled water and taken out at desired time to weight. Swelling degree was calculated as following:

$$\text{Swelling degree}(\%) = \frac{G_s}{G_d} \times 100 \tag{4}$$

where G_s is weight of the hydrogel in swollen state and G_d is the weight of dried gel after extraction.

After the equilibrium state of swelling was reached, equilibrium degree of swelling (EDS) was also calculated according to Eq. (4), and here G_s is mass of the hydrogel in equilibrium state of swelling.

2.6. TGA analyses of the gel portion

Thermogravimetry (TG) analyses of the dried gels (5 mg) were carried out in Dupont TA instrument (model 1090B) from 25 °C to 500 °C at a heating rate of 10 °C · min^{-1} under nitrogen flow (20 ml · min^{-1}).

2.7. Micro-FTIR analyses of the gel portion

The gel samples after extracting the sol part were immersed into liquid nitrogen and lyophilized at −20 °C. Dried samples were taken for micro-FTIR analysis. IR spectra with a resolution of 4 cm^{-1} were recorded by Nicolet (Magna-IR 750) spectrometer in absorbance mode.

2.8. Morphologies of gel structure

Morphologies of the gels were observed according to the method described by others (Wach, Mitomo, Yoshii, & Kume, 2002). Structures of the gels in equilibrium swollen state were observed using S530 (Hitachi, Japan) scanning electron microscope (SEM). To preserve the network structure after drying, the hydrogels in equilibrium state were immersed into liquid nitrogen and then lyophilized in vacuum at −20 °C. The dried samples were coated with gold using an ion coater prior to observation. The cross-sectional morphology of gel was then photographed.

3. Results and discussion

3.1. Gel formation

The effect of AC's content on gel formation in terms of gel fraction was illustrated in Fig. 1, while some characteristic parameters, such as gelation dose (D_g) and p_0/q_0 were calculated from Charlesby-Pinner equation and listed in Table 1. It was found that the addition of AC increased the tendency of crosslinking of CMC according to the higher gel fraction, lower p_0/q_0 and lower D_g of the CMC/AC hybrid hydrogel.

Although CMC is one of the polysaccharides which were able to form hydrogel by radiation crosslinking in so-called "paste-like" status (Fei et al., 2000), considering the rather high p_0/q_0 and slow increment of gel fraction in the dose range of 5–20 kGy, we can conclude that chain scission took a significant role during gel formation procedure. In our previous work (Wang et al., in revision), D_g of CMC solution with lower concentration (10%CMC) was even higher (25 kGy). In addition, the maximum gel fractions of pure CMC hydrogel in all the above mention cases were reported to be ca. 40–50% and the gel strength was rather weak. To improve the gel properties to meet the demands for many practical applications, AC which was used as inorganic filler of many polymer materials was chosen to modify the gel strength of CMC hydrogel. The results showed that gel fraction of CMC/AC hybrid hydrogel was much higher than that of pure CMC hydrogel and the gel fraction increased remarkable with increasing absorbed dose at the early stage of gel formation (i.e., shortly after D_g). Further calculation by Charlesby–Pinner equation also proved that the crosslinking tendency increased by the addition of AC and this tendency increased with increasing amount of AC.

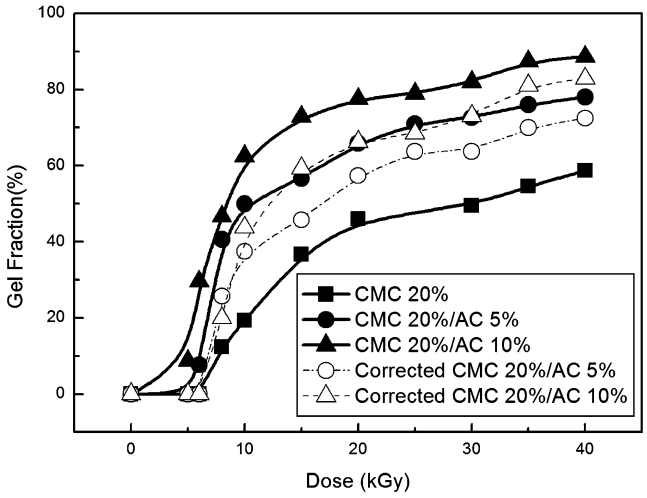

Fig. 1. Gel fraction and corrected gel fraction of CMC/AC hybrid hydrogels.

Table 1
p_0/q_0 and D_g of different CMC/AC hybrid hydrogels

	20%CMC	20%CMC/5%AC	20%CMC/10%AC
p_0/q_0[a]	0.91	0.51	0.29
D_g (kGy)	6.88	5.15	4.48
p_0'/q_0'	0.91	0.66	0.39
D_g' (kGy)	6.88	5.80	6.23

[a] p_0 is the ratio of main chain scissions per unit dose to chain units, q_0 is the proportion of chain units crosslinked per unit dose.

The AC particles were embedded in the network of CMC hydrogel and could not be removed by the above method. To investigate that whether there is interaction between CMC and AC under irradiation, gel fraction of the hybrid hydrogels was corrected. The correction was carried out by subtracting AC's content from the gel fraction (g) calculated according to Eq. (1). The corrected gel fraction was also shown in Fig. 1 as open point. The difference between gel fraction and corrected gel fraction was caused by the removing of AC from the hydrogel during extracting procedure. The difference was higher in the case of low absorbed dose due to the weak gel strength, and the slightly higher difference in 20%CMC/10%AC hydrogels was assumed to be caused by the lower embedment fraction of AC in hydrogel. However, the difference was decreased to ca. 5% when the absorbed dose was higher than 35 kGy, which revealed that most of AC was embedded when the crosslinking density of the hydrogel was high enough.

Being inorganic material, AC was unable to crosslink itself. The fact that it can accelerate the gel formation of CMC implied that there are some specific binding interactions between AC and CMC. It is reported that AC was usually characterized into three main zones: the carbon basal planes, heterogeneous surface groups (mainly oxygen-containing groups), and inorganic ash so that it is capable to adsorb a large variety kinds of substance through physical adsorption, hydrogen bonding as well

as many other interactions. The oxygen-containing groups such as carbonyl group, carboxylic group can serve as hydrogen bond acceptor and hydroxyl group can serve as hydrogen bond donor (Franzl, Arafat, & Pinto, 2000). CMC is a kind of cellulose derivative and there are plenty of hydroxyl group in its main chain which can serve as hydrogen bond donor at the same time, its carboxyl substitution can serve as hydrogen bond acceptor so that CMC is easy to form complex with other chemicals through hydrogen bonding. Thus, AC and CMC bound to each other by hydrogen bonding as well as physical absorption and probably other interactions, leading to higher tendency of crosslinking.

Generally gel fraction reflected the gel strength of the hydrogel. The effects of the AC's content and absorbed dose on gel strength of CMC/AC hydrogels were shown in Fig. 2. The gel strength improved obviously with addition of AC and increased with increasing AC content. Instead of the poor gel strength of CMC hydrogel, CMC/AC hydrogel showed excellent elasticity and flexibility, implying its potential applications as medical materials, absorbent etc.

3.2. Swelling behavior

One of the most important advantages of CMC hydrogel is its high water absorption rate and capacity. Fig. 3 exhibited swelling rate of the CMC/AC hybrid hydrogel, showing that although gel fraction of the hybrid hydrogel was significantly improved, its high swelling rate and EDS was maintained with the addition of 5%AC and the EDS of 20%CMC/10%AC hybrid hydrogel was slightly decreased. The swelling rates of all the samples were found to be very high, more than 95% of the water absorption was finished in the first 50 min and EDS of the hydrogel was reached at ca. 3 h. EDS of CMC/AC hybrid hydrogel was showed in Fig. 4 and showed good correlation with the swelling kinetic results, i.e., the addition 5%AC did not interfere the water absorption ability of CMC while the addition of 10%AC decreased the EDS of the hydrogel. The EDS of the hydrogel was the highest just after the dose oversteps the gelation point, rapidly decreased with the increase of dose at the early stage of gel formation and leveled off after ca. 25 kGy. In gel formation section, it was found that the gel fraction and gel strength increased with the absorbed dose and leveled off after ca. 25–30 kGy, which implied the significantly increasing of crosslinking density after D_g, thus leading to a compacter network of the hydrogel and lower EDS of hydrogel. The addition of 5%AC without decrement the water absorption ability of the hydrogel can be attributed to the compensation of hydrophilicity of the hydrogel by the hydrogen bonding between CMC and AC. The lower EDS of 20%CMC/10%AC hydrogel was partly caused by its higher crosslinking density, while the other reason is that probably some portion of AC was not binding to CMC and aggregated inside the hydrogel which led to lower EDS.

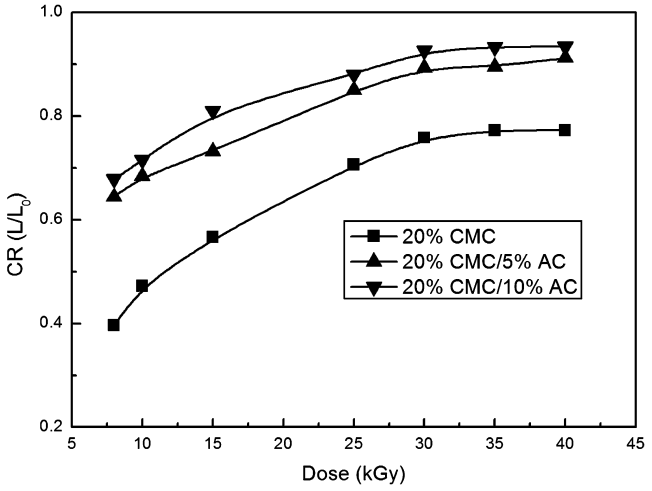

Fig. 2. Gel strength of the CMC/AC hybrid hydrogels.

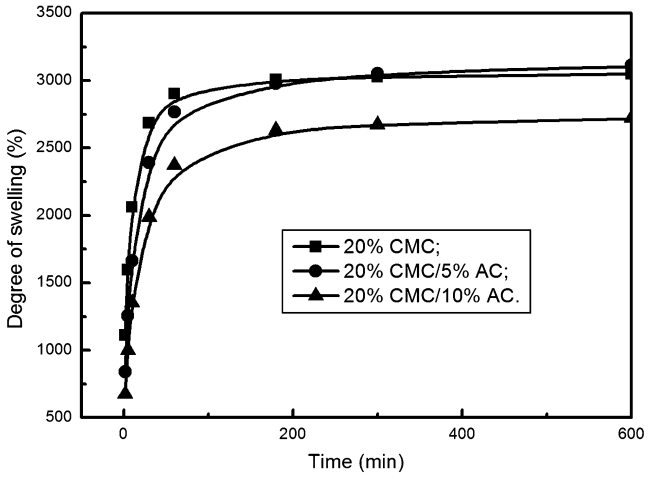

Fig. 3. Swelling dynamics of CMC/AC hybrid hydrogels. All hydrogels were irradiated at 25 kGy.

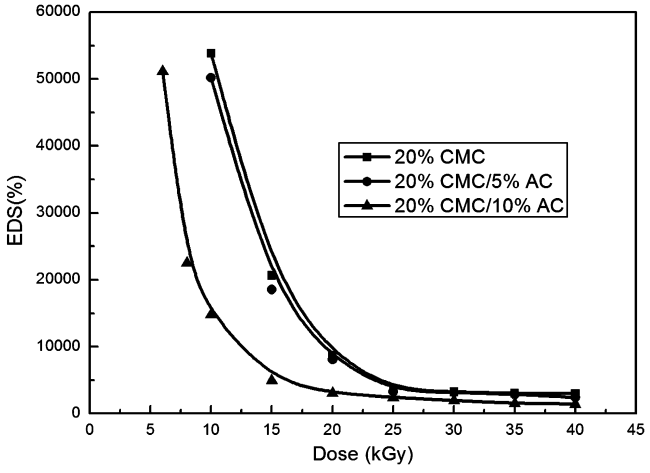

Fig. 4. EDS of CMC/AC hybrid hydrogels.

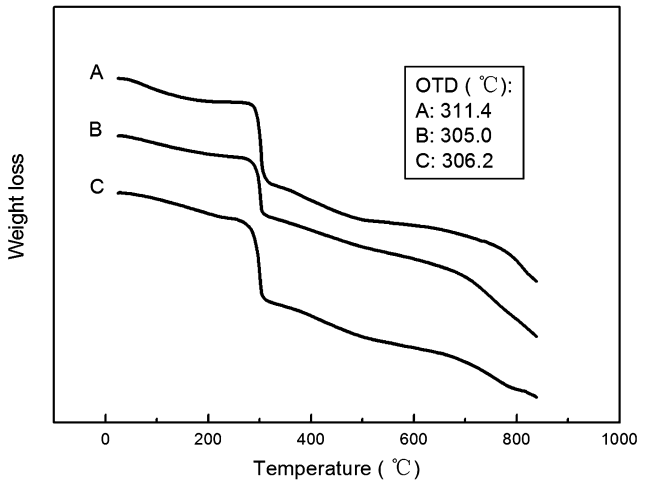

Fig. 5. TG thermograms of: 20%CMC/10%AC hybrid gel (A); 20%CMC gel (B); physical mixture of CMC gel and AC (2:1) (C). Gels used here were irradiated at 25 kGy.

3.3. Thermal analyses of gel portion

Incorporation of inorganic composition into polymers usually can improve the thermo-stability of the polymers. The effect of AC on the TG thermograms of CMC/AC hybrid gels after extracting the sol part are shown in Fig. 5. The onset temperatures of decomposition (OTD) of CMC/AC hybrid hydrogel (A), CMC hydrogel (B) and mixture of CMC hydrogel/AC (C) were 311.4, 305.0 and 306.2 °C, respectively. Compared with sample C, sample A increased the OTD of CMC hydrogel more significantly than physical mixture of AC in CMC gel. Because hydrogen bonding is not effective in such a high temperature, this result indicated that besides the hydrogen bonding, AC was also binding to CMC by other interaction, probably the hydrophobic interaction between carbon basal planes and $–CH_2$, and took part in the crosslinking reaction of CMC under irradiation, enhancing thermal stability of CMC gel.

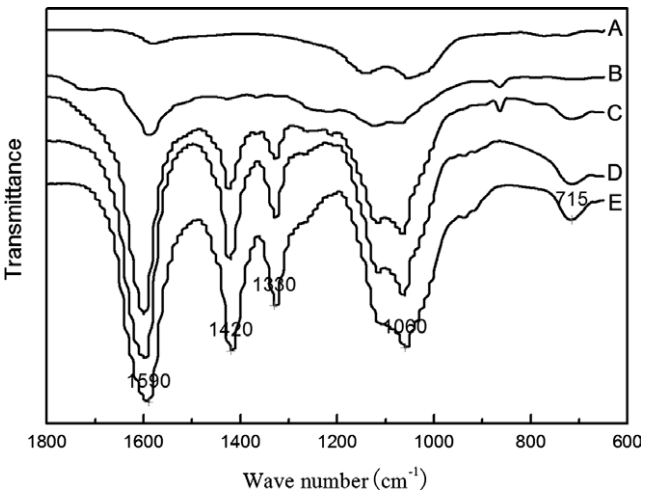

Fig. 6. FTIR spectra of different samples: AC (A); 20%CMC/10%AC gel (B); 20%CMC/5%AC gel (C); 20%CMC gel (D); CMC (E). (B, C and D were irradiated at 25 kGy).

3.4. FTIR and morphology of CMC/AC hybrid hydrogels

FTIR spectra of CMC gel and CMC/AC hybrid gel are shown in Fig. 6 and spectra of CMC and AC materials were also exhibited for comparison. As reported in literatures, the strong absorption band at 1590 cm^{-1} confirms the presence of COO^- group; absorption bands at 1420 and 1330 cm^{-1} are assigned to $–CH_2$ scissoring and –OH bending vibration, respectively; absorption band at 1060 cm^{-1} is due to the stretching vibration of the 1,4-β-D-glucoside group (>CH–O–CH<) of cellulose (Said, Abd Alla, & El-Naggar, 2004; Biswal & Singh, 2004). Under irradiation, macromolecular radicals are produced and lead to reactions like chain scission and side chain reactions, which lead to degradation and crosslink of the macromolecular chains, respectively. It has been reported that cellulose and its derivatives degrade by the rupture of glycosidic bond under irradiation (Wach et al., 2002). It has been reported that the radical formed in the side chain ($R–O–\dot{C}H–COO^-$) takes an important role in formation of the CMC gel, which will lead to decrease in intensity of absorption band at 1420 cm^{-1} (Wach et al., 2003). So, it can be proposed that evidence of crosslink and degradation of CMC can be obtained by FTIR analysis. However, the change of FTIR spectra after crosslinking was seldom reported.

In our work, compare with spectra D and E, slight red shift and decrease in intensity of absorption bands at 1060, 1330 and 1420 cm^{-1} are observed in CMC hydrogel (shown in Table 2). Because the radical formed in –OH and $–CH_2$ groups of the side chain of CMC molecules is favorable to crosslinking reaction of CMC molecules, the decrease in intensity of absorption bands at 1330 and 1420 cm^{-1} means that –OH and $–CH_2$ groups take part in crosslinking reaction of CMC molecules under irradiation. However, the radical formed in >CH–O–CH< of main chain of CMC molecules lead easily to the scission of CMC molecular chain, so the decrease of intensity of absorption bands at 1060 cm^{-1} imply that besides crosslinking reaction, chain scission reaction of CMC molecules under irradiation occurred at the same time. Furthermore, from Fig. 6 and Table 2 it can be found that the decrease in intensity of absorption bands at 1330 and1420 cm^{-1} is larger than that at 1060 cm^{-1}, which imply that main

Table 2
Changes on FTIR intensity of different hydrogels

Wave length/cm^{-1}	20%CMC/5%AC (C)	20%CMC (D)	CMC (E)
1060	0.631	0.713	0.752
1330	0.289	0.358	0.56
1420	0.426	0.549	0.766
1590	1	1	1

Samples C and D used here were irradiated at 25 kGy.

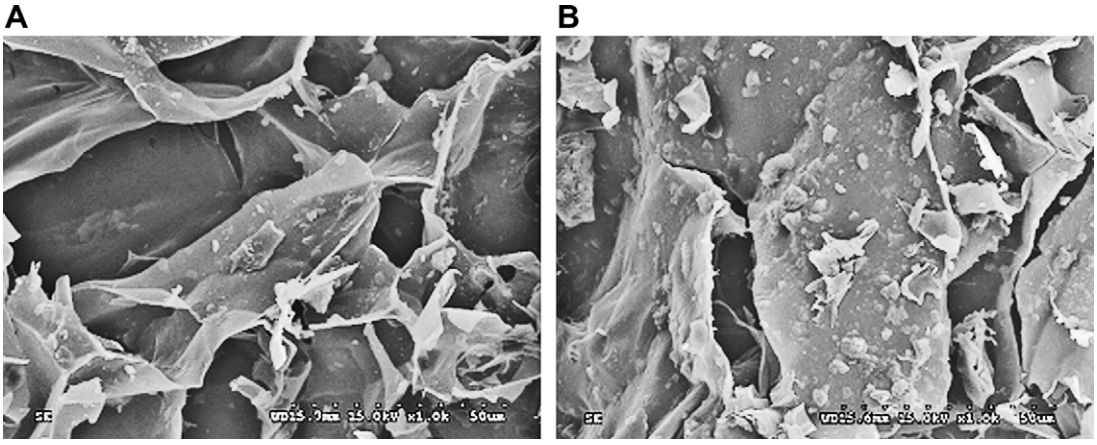

Fig. 7. Cross-sectional SEM photographs of the gels. 20%CMC/5%AC gel (A); 20%CMC/10%AC gel (B).

reaction, i.e. crosslinking reaction occurs in side chain of CMC molecules under irradiation due to the presence of –OH and $–CH_2$ groups. The spectrum of 20%CMC/5%AC gel (C) was similar to that of CMC gel, but the intensity of peaks at 1060, 1330 and 1420 $cm^{-1}$are lower than that of the former gel, which indicated that AC can accelerate the reactivity of CMC molecules due to the formation of hydrogen bond and other interactions between CMC and AC. In the spectrum of 20%CMC/10%AC, the peaks at 1330 and 1420 cm^{-1} were almost diminished and the peaks at 1590 and 1060 cm^{-1} were significantly weaken, which can be explained by the higher portion of AC in the hydrogel and the higher extent of crosslinking.

Morphology of the gels was observed by SEM with magnification of 1000 and showed in Fig. 7. CMC/AC hybrid hydrogel samples had normal porous structure of common hydrogel, and AC was found to be embedded successfully in the hybrid hydrogel. For 20%CMC/10%AC hybrid hydrogel, some AC aggregations can be observed obviously at the surface of CMC gel which means that at this AC content, AC can not dispersed uniformly in CMC so that part of AC was ineffective in the modification of CMC hydrogel (Fig. 7B).

4. Conclusion

Hybrid hydrogels based on carboxymethylcellulose (CMC) and activated carbon (AC) were synthesized using γ radiation technique. The effect of AC's content on the gel formation and gel properties were investigated. The gel fraction, gel strength and thermal stability were improved obviously after incorporating AC into CMC hydrogels. The 20%CMC/5%AC hybrid hydrogel maintained good swelling ability of pure CMC hydrogel, while the swelling capacity of 20%CMC/10%AC ones decreased slightly. FTIR, TGA and SEM of the prepared gels after extracting sol manifested that AC enhanced the crosslinking of CMC. We proposed that AC was binding to CMC through physical adsorption, hydrogen bond as well as other interactions and further accelerated the radiation crosslinking of CMC. In addition with other advantages, the CMC/AC hybrid hydrogels also possess excellent elasticity and flexibility which suggesting their potential application as absorbents, wound covers, mattress in medical and many other fields.

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