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Self-assembly of polypyrrole/chitosan composite hydrogels

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ABSTRACT

Hydrogels based on the polypyrrole (PPy)/chitosan (CS) composite are self-assembled and characterized for their electrical and swelling properties. The static polymerization of pyrrole monomer in aqueous solution containing CS is accompanied with the formation of PPy/CS composite hydrogel. The feed order in the reaction process plays a key role in the formation of the hydrogels. The participation of one-dimensional PPy blocks in the formation of the hydrogel network avoids a possible migration of PPy from the hydrogel. The effect of pH and ionic strength on the physical properties of PPy/CS composite hydrogels are investigated in detail. The results indicate that the pH-sensitive PPy/CS composite hydrogels show good water absorbencies in distilled water and saline solution. This method may open a new opportunity for the fabrication of composite hydrogels associating the biomacromolecules and conducting polymers, and the improvement of the comprehensive performance of the resulting products.

1. Introduction

Chitosan, a polysaccharide composed mainly of β-(1,4)-linked 2-deoxy-2-amino-D-glucopyranose units, is the deacetylated derivative of chitin, one of the most plentiful natural polymers. Due to its specific structure and properties, chitosan (CS) has been extensively investigated for several decades in a broad range of applications in food packaging (Arvanitoyannis, Nakayama, & Aiba, 1998; Tual, Espuche, Escoubes, & Domard, 2000), water treatment (Baroni, Vieira, Meneghetti, da Silva, & Beppu, 2008; Crini, 2006), separation membrane (Beppu, Vieira, Aimoli, & Santana, 2007; Won, Feng, & Lawless, 2002), and biomedical fields (Coche-Guerente et al., 2005; Gupta & Ravikumar, 2000; Shivaishi, Imai, & Otagiri, 1993; Tsai, Chen, & Liaw, 2007). Generally, CS gel can be easily obtained through a reaction with glutaraldehyde as a cross-linking agent. The biocompatible and non-toxic CS gel is a suitable candidate as drug carriers, artificial muscles or tissue scaffolds (Ismail, Martinez, Al Harrasi, Kim, & Otero, 2011; Kim, Shin, Spinks, Kim, & Kim, 2005; Zhu, Dong, Wejinya, Jin, & Ye, 2011). However, their developments are limited to some extent in this domain of applications by the poor electrical conductivity resulting in a poor stimulus response.

Recently conducting polymers, such as polyaniline and polypyrrole have received great interest owing to their easy synthesis, controlled conductivity, and good stability (Huang, Virji, Weiller, & Kaner, 2003; Jiao, Tu, Fan, Hou, & Fray, 2011; Kwon, Park, Yoon, & Jang, 2012). Therefore, as a novel class of materials that possess both the swelling properties and the electrical properties, conducting polymer hydrogels have been extensively investigated (Guo, Finne-Wistrand, & Albertsson, 2011; Pepin-Donat, Viallat, Blachot, & Lombart, 2006; Siddhanta & Gangopadhyay, 2005; Xiao, He, & Che, 2012). Composite hydrogels of polyaniline/polyacrylamide, polypyrrole/poly(2-hydroxyethyl metharylate) have been elaborated from adsorption of monomer inside a polymer network followed by the polymerization of the aniline according to a radical or electrochemical process (Brahim, Narinesingh, & Guiseppi-Elie, 2002; Lira & Cordoba, 2005; Xu et al., 2006). Interfacial polymerization has also been carried out to prepare conducting polymer hydrogels. In this case, polyaniline could grow from the solution–gel interface to the gel interior, perhaps leading to a gradient concentration material and the non-homogeneous hydrogel in bulk (Blinova, Trchova, & Stejskal, 2009; Dai, Qing, Wang, Shen, & Lu, 2010). Moreover, in the above methods, the conducting polymer is entrapped in the cross-linked hydrophilic polymer matrix

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Table 1
Experimental conditions of the synthesis of PPy/CS composites hydrogels.

Sample name	Feed sequence		
	1st	2nd	3rd
MCA-PPy	20 mL MO	3 mL CS	1 mmol APS
MAC-PPy	20 mL MO	1 mmol APS	3 mL CS
CAM-PPy	3 mL CS	1 mmol APS	20 mL MO

as the main network in the hydrogel, resulting in a possible migration of the conducting polymer from the hydrogel matrix during the process of swelling-shrinking or upon exposure to pH change.

The design and controllable fabrication of composite hydrogels with particular morphology and properties are still a big challenge. Herein, the strategy we develop within this study leads to a new kind of composite hydrogel. The polymerization of pyrrole monomer and the formation of PPy/CS composite hydrogel occur simultaneously. The one-dimensional polypyrrole blocks are piled up to construct the main network of the hydrogels. The physical properties of PPy/CS composite hydrogels are investigated in terms of reaction conditions and the external environment.

2. Experiment

2.1. Materials

Pyrrole monomer was purchased from Aldrich and distilled under reduced pressure. Chitosan with a deacetylation degree of 86% and viscosity-average molecular weight of 186,000 g/mol was prepared from shrimp shells, kindly supplied by Zhejiang Golden-Shell Co., Ltd., China. Methyl orange (MO), ammonium peroxysulfate (APS) and other reagents were purchased from Shanghai Chem. Co., in China and used as received.

2.2. Preparation of PPy/CS composite hydrogels

CS solution of 2 wt% was prepared by dissolving CS in a 2% (v/v) aqueous acetic acid solution. 20 mL of 5 mmol/L MO deionized water solution, 3 mL of CS solution and APS were added in the beaker in different sequence. The feed sequence was given in Table 1. Then 1 mmol of pyrrole monomer was added to the above solution. After stirring the resulting system for 1 min, the reaction was allowed to proceed without stirring for 24 h at room temperature. Finally, the product was repeatedly rinsed in a large amount of deionized water.

2.3. Characterization

The morphologies of the resulting materials were observed by scanning electron microscopy (SEM, JSM-5510LV). FTIR spectra of pellets of the freeze-dried product with KBr were recorded on a Nicolet Impact-420 spectrometer at 64 scans with a resolution of 4 cm^{-1} with the frequency range of 4000–400 cm^{-1}. The water absorbencies of PPy/CS composite hydrogels were measured in distilled water in different pH or NaCl solutions at room temperature. The dried hydrogels were immersed in different solutions until reaching the swelling equilibrium. The hydrogels were then removed from the solution and the surfaces of the samples were gently wiped with filter paper. The value of water absorbency was calculated with the following equation:

$$\text{water absobency} = \frac{m_s - m_d}{m_d}$$

in which m_d and m_s were the weights of the dried samples and the swollen samples, respectively. For each sample, the test was performed 4 times. The averaged result was reported.

3. Results and discussion

During the syntheses for all of the samples, a black whole appeared in the beaker after 10 min from the addition of pyrrole monomer regardless of the feed sequence of MO, CS, and APS. However, it was worth noticing that the experimental phenomena during the purification in distilled water were different for the samples of MCA-PPy, MAC-PPy and CAM-PPy. For MCA-PPy, it behaved like a sludgy whole. Its shape was destroyed and the volume was reduced by more than half during the purification. While the sample of MAC-PPy was more stable than MCA-PPy, its volume was also reduced by 20% during the purification. But in the case of CAM-PPy, it could be totally self-standing and behaved like a real hydrogel. Apparently the feed sequence had an important influence on the macroscopic appearance of the as-prepared PPy/CS composite hydrogel. For comparison, PPy/CS composites were also prepared in the absence of MO or with stirring. It was observed that only some flocculent deposition was formed during the preparation of PPy/CS composite in the absence of MO under the static condition. On the other hand, even in the presence of MO, only the powder of the products could be obtained during the preparation of PPy/CS composite with stirring. Thus, the results demonstrated that both MO and static condition were indispensable for the fabrication of PPy/CS composite hydrogel.

Not only the macroscopic appearances of all of the samples were not same, but also their microscopic morphologies were different. SEM images of MCA-PPy, MAC-PPy and CAM-PPy were shown in Fig. 1. The one-dimensional structures of PPy could be fabricated by the soft templates of MO molecules in the previous report (Dai & Lu, 2007). In our work, the addition of CS and also the feed sequence affected the MO templates, resulting in the change of the PPy mophology. As shown in Fig. 1a, although there were small amount of one-dimensional blocks in MCA-PPy, the irregular integrative structure was major in its SEM image. However, the morphologies of MAC-PPy and CAM-PPy were totally different with that of MCA-PPy. As shown in Fig. 1b and c, there were lots of intertwisted one-dimensional blocks with the length of several micrometers and the diameter of 40–140 nm. Moreover, several nanoparticles were distributed between the one-dimensional blocks. The microscopic network of the hydrogel was composed of the one-dimensional bloks and the nanoparticles. The intersected one-dimensional blocks in the network was more favorable to the stability of the hydrogel. Therefore, as shown in Fig. 2, the self-standing CAM-PPy hydrogel exhibited a highly swollen macroscopic appearance, which contained a substantial amount of water.

The effect of the amount of APS on the physical properties of CAM-PPy hydrogels was further studied. FTIR of CAM-PPy hydrogels prepared with different APS amount were shown in Fig. 3. There was a characteristic absorbance band centered at 1635 cm^{-1}, which corresponded to the C=O stretching vibration of —NHCO— in CS. The peaks at 1550 and 1481 cm^{-1} could be attributed to C=C and C—N asymmetric and symmetric stretching vibration of the pyrrole ring, respectively. The peak at 779 cm^{-1} belonged to C—H ring-wagging vibration of the pyrrole ring (Li, Wan, Wei, Shen, & Chen, 2006; Romero, Cascales, & Otero, 2005). Moreover, with the increase of the amount of APS during the preparation process, a decrease in the intensity of C=O stretching vibration in CS and an increase of the intensity of C=C stretching vibration in PPy could be easily observed in the FTIR spectra. It indicated that more APS resulted in the more polymerization of pyrrole monomer.

Conductivities and water absorbencies of the CAM-PPy hydrogels prepared with different APS amount were shown in Table 2. The conductivity of CAM-PPy hydrogel prepared with 3 mmol of APS was measured above 10^{-2} S/cm, but in the case of 0.6 mmol of APS, the sample had no conductivity due to the lowest amount

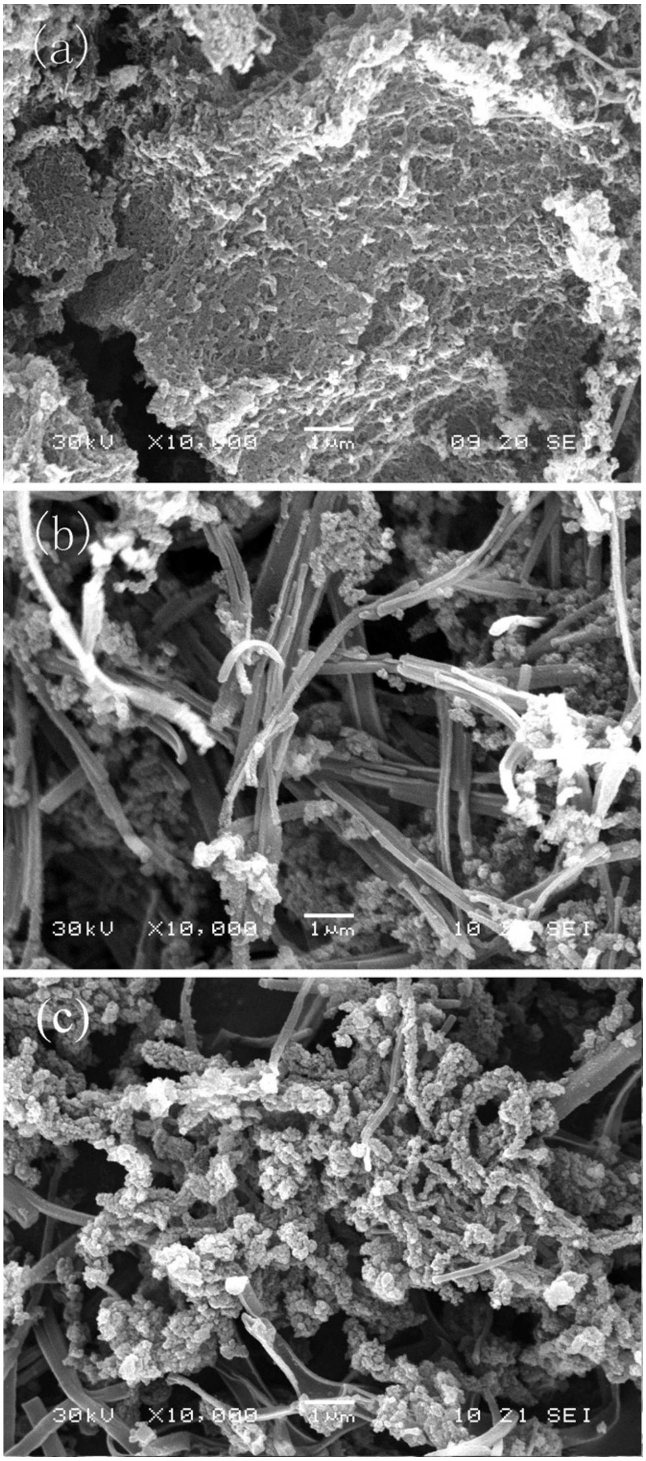

Fig. 1. SEM images of (a) MCA-PPy, (b) MAC-PPy and (c) CAM-PPy samples. The samples were freeze-dried before SEM measurements.

Table 2
Conductivities and water absorbencies of the CAM-PPy hydrogels.

APS amount	Conductivity (S/cm)	Water absorbency (g/g)
3 mmol	$3.12 \times 10^{-2} \pm 0.84 \times 10^{-2}$	19.5 ± 1.2
2 mmol	$7.46 \times 10^{-4} \pm 1.52 \times 10^{-4}$	11.8 ± 1.0
1 mmol	$6.67 \times 10^{-4} \pm 1.37 \times 10^{-4}$	9.3 ± 0.8
0.6 mmol	–	5.2 ± 0.6

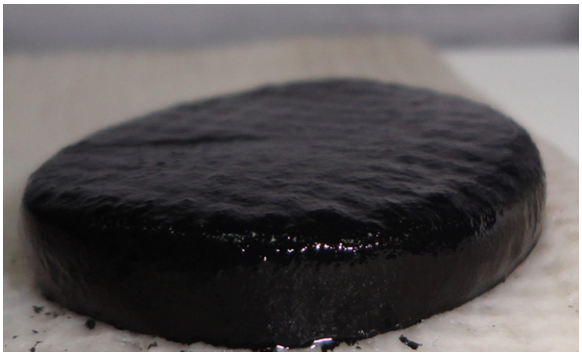

Fig. 2. Photo of CAM-PPy hydrogel.

of PPy while pure chitosan was an insulating material. Water absorbency of the hydrogels increased from 5.2 g/g to 19.5 g/g when the amount of APS increased from 0.6 mmol to 3 mmol. Then the results of conductivities and water absorbencies also indicated that there were more PPy chains in the network with the increase of APS, which was in agreement with FTIR results. CS was vital for water absorbency of the conducting polymer/CS hydrogels in the previous reports (Marcasuzaa, Reynaud, Ehrenfeld, Khoukh, & Desbrieres, 2010). However, in our work, the one-dimensional PPy blocks not only existed in the hydrogel as the conducting component, they were also assembled to the network in the hydrogel as shown in Fig. 1c, which played a key role in the fabrication of PPy/CS composite hydrogels and had an important effect on the conductivities and water absorbencies of the as-prepared hydrogels. Moreover, the participation of PPy in the formation of the hydrogel network avoided a possible migration of conducting component from the conducting polymer hydrogel (Lin, Tang, Wu, & Li, 2010; Tang et al., 2008). Conventional hydrogels contain lots of water via the interactions between polymer chains and water molecules as well as the osmotic pressure of the hydrogel network, while macroscopic networks, such as cotton, contain water via capillarity (Bohidar, Dubin, & Osada, 2002). For PPy/CS composite hydrogels, the above effects may exist together, offering them the unique hydrogel characteristics as well as the conductivity. To highlight the advantages of the route compared with the blends method, the mixture of CS and PPy was prepared in the solvent phase. However, blends were not obtained because both PPy and CS were not well soluble in a common solvent. All of the results demonstrate the interest and

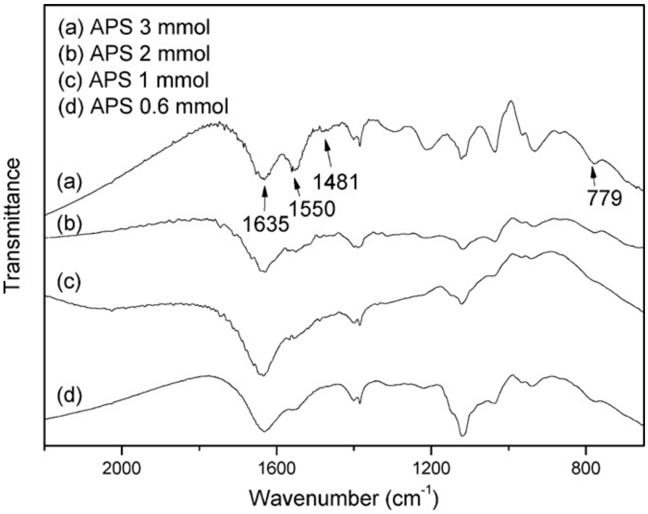

Fig. 3. FTIR of CAM-PPy hydrogels prepared with different APS amount.

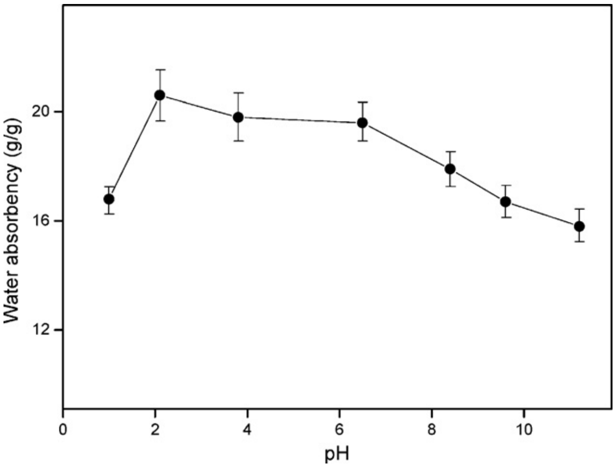

Fig. 4. Water absorbencies of CAM-PPy hydrogel prepared with 3 mmol of APS as a function of pH.

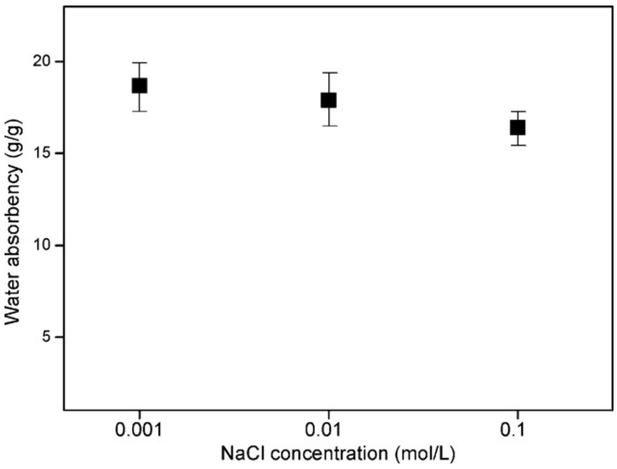

Fig. 5. Water absorbencies of CAM-PPy hydrogel prepared with 3 mmol of APS in NaCl solutions.

advantages of static polymerization of pyrrole in the CS solution with respect to the mechanical mixture.

To investigate the influence of pH of the surrounding on the water absorbencies of the composite hydrogels, the range of pH value was selected from 1 to 11 in this study. As shown in Fig. 4, CAM-PPy hydrogel was pH-sensitive to some extent because the polycationic CS with lots of $-NH_3^+$ was a kind of polyelectrolyte. Under strong acidic conditions such as pH 1, a large number of H^+ and Cl^- in the solution could shield the charge of $-NH_3^+$ ions in CS, which may prevent an efficient repulsion and result in a decrease of water absorbency. At pH 2, the screening effect of the ions was weakened. At the same time, the repulsion in the hydrogel network between the CS chains with positive charges and the polycationic PPy chains in the doped state could be favorable to water absorbency. Therefore, there was a maximum water absorbency for the CAM-PPy hydrogel. Beyond the value of pH 2, the higher pH, the lower the water absorbency of the CAM-PPy hydrogel. Moreover, it decreased markedly when pH exceeded 8. In the base solution, a screening effect of the counter ions could also shield the charge of $-NH_3^+$ ions. Moreover, PPy was dedoped and the polycations in PPy chains decreased gradually upon exposure to base solution. The above two factors were accumulated and prevented the efficient repulsion in the hydrogel network. As a result, a remarkable decrease in water absorbency was observed. However, because of the unique microscopic network in CAM-PPy hydrogel, the change of water absorbencies in different pH was smaller than the conventional polyelectrolyte hydrogel (Li et al., 2012).

The water absorbency of hydrogel materials in saline solutions are critically important for their practical applications in artificial muscles and tissue scaffolds. Therefore, the water absorbencies of CAM-PPy hydrogel in saline solutions with different concentrations were also investigated, as shown in Fig. 5. Compared with that in distilled water, the water absorbencies of CAM-PPy hydrogel decreased to some extent in NaCl solution. It could be ascribed to the decrease of osmotic pressure difference between the hydrogel network and the external salt solution (Flory, 1953). With the increase of ionic strength in the external solution, the external osmotic pressure was increased and led to the decrease of water absorbency. On the other hand, it was worth noticing that the influence of ionic strength on the water absorbency of the as-prepared CAM-PPy was not remarkable compared with that in the conventional polyelectrolyte hydrogel (Castel, Ricard, & Audebert, 1990; Lee & Wu, 1997). In these general cases, the external environment mostly contained salt solutions and thus the pure polyelectrolyte hydrogel often lost their water absorbency due to the collapse of the network. In our work, the one-dimensional PPy blocks participated in the formation of the hydrogel network. The interaction between polymer chains and water molecules as well as the osmotic pressure of the hydrogel network, together with the capillarity interaction in the network, may exist in PPy/CS composite hydrogels and endow them the unique hydrogel characteristics. From this point, participation of PPy blocks into the hydrogel networks should open up an efficient avenue for enhancement of the salt-resistance of the hydrogel materials and may be especially useful in the above biological fields.

4. Conclusions

In summary, an effective and simple approach for the fabrication of PPy/CS composite hydrogels with both electrical properties and hydrogel characteristics has been demonstrated. During the static polymerization process of pyrrole, gelation takes place simultaneously. The formation of the hydrogels relies strongly on the feed order in the reaction process. The one-dimensional PPy blocks not only appear as the conducting component in the hydrogel, they also participate in the assembly of the hydrogel network. Based on their high water absorbency and good salt-resistant performance, it can be expected that the as-prepared PPy/CS composite hydrogels may play a more important role in biochemical and electrochemical applications. Further works are still to be done to study the driving force for the fabrication of the hydrogels and control and optimize the architecture of these hydrogels.

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