Thermo-sensitive Hydrogel Incorporating Maleic Anhydride Modified Microcrystalline Cellulose

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Abstract. The thermo-sensitive hydrogel incorporating maleic anhydride modified microcrystalline cellulose was prepared by two steps. At first, the mixture of maleated and fumurated celluloses were produced by a solvent-free procedure, in which the biopolymer was added to molten maleic anhydride. Secondly, the photo-polymerization of n-isopropyl acrylamide (NIPAM) with the modified biopolymer was carried out in water/NaOH/urea/thiourea solution by using 1173 as the photo-initiator. The derivatives were characterized by FTIR and SEM. It was a clear temperature dependence on the volume of the grafted hydrogel in deionized water that generated by the coil-to-globule transition of poly(NIPAM) in aqueous media from the lower critical solution temperature (LCST) of PNIPAM to the upper critical solution temperature (UCST). From the absorbance of the gel to methylene blue, it was shown that the quasi-second-order kinetics could fit the experimental data well.

1. Introduction

Cellulose is a kind of abundant renewable resource on earth produced by plants, microorganisms, and cell-free systems[1]. Microcrystalline cellulose (MCC)[2] is a naturally occurring substance obtained from purified and partially depolymerized cellulose, which are now emerging as a realistic alternative to other polymeric composites. MCC has a number of unique characteristics and properties, including renewability, non-toxicity, biodegradability, high mechanical properties, large surface area, low density, biocompatibility.

Compared to other natural polysaccharide polymers, MCC also suffers some drawbacks that are desired for some applications, such as poor wettability, moisture absorption, incompatibility with most polymeric matrices and limitation in processing temperature[2]. Thus, plenty of treatments have been given out to modified MCC before manufacture[3-5]. One of the important modification is grafting polymerization[6]. In this work, the photo-grafted polymerization to form thermo-sensitive gel has been studied by the implement of solid phase grafting of maleic anhydride(MAH) onto MCC.

2. Materials and methods

2.1 Materials
The microcrystalline cellulose (MCC) purchased from Sigma-Aldrich, ~20 μm, was dried before used, maleic anhydride (MAH), n-isopropyl acrylamide (NIPAM), thiourea, urea, methylene blue (MB) and the other analytical grade reagents were used without prior purification.

2.2 Instruments
The FTIR spectra of samples, such as MCC and the maleic anhydride incorporated into MCC (modified MCC), were obtained in KBr pellets through a Nicolet Avatar 330 Spectrophotometer. The SEM images were shot on JSM-6010LA. The concentration of MB was characterized by UV-vis spectrum on UV-1600PC.

2.3 Methods
2.3.1 Synthesis of MCC modified with maleic anhydride. As described in literature[7], a sample of 10 g MCC, previously dried at 100 °C for 2 h under vacuum, was added to 50 g of molten MAH in a 250mL reaction flask immersed in a oil bath at 120°C, under magnetic stirring. The flask was fitted with a dried CaCl₂ trap to maintain constant pressure and to keep out moisture from the air. After 6 h the mixture was filtered and washed intensively with water to a neutral pH. The white solid that modified as MAH-MCC was then dried in vacuum at 100 °C for 24 h.

2.3.2 Photo-polymerization of n-isopropyl acrylamide (NIPAM) and MAH-MCC. The MAH-MCC and NIPAM with the weight ratio of 1/1.4 were dissolved in 50mL mixed solution of water/NaOH/urea/thiourea at -2~0 °C after 30 minutes for stiring in dark, with N₂ ambient. The monomer solution could polymerize into hydrogel under UV irradiation for 2h, which was initiated by 1173. The hydrogel incorporated MAH-MCC was obtained after immersion in ethanol for 24h to remove monomers and drying in vacuum at 60 °C.

2.3.3 Determination of the substitution degree for MAH-MCC. MAH-MCC was added into a conical flask with 0.1 M prefabricated NaOH-ethanol solution. Then the mixture was sealed up and kept in a bath at 50°C for 3h under magnetic stirring. When the flask was cool at ambient temperature, the titration of 0.1 M HCl standard solution was conducted. The degree of substitution (DS) for MAH-MCC could be estimated by the amount of HCl solution consumed according to equation (1) and (2).

$$n = c_{NaOH} \cdot V_{NaOH} - c_{HCl} \cdot V_{HCl}$$

Equation (1)

$$DS = \frac{162n}{m_{MAH-MCC} - 114n}$$

Equation (2)

Where the numbers 162 and 114 denoted the molecular weight of an anhydroglucopyranose unit of cellulose and -OOCCH=CHCOOH, respectively. \(n\) was the amount (mol) of -COOH that esterified with MCC in the sample MAH-MCC.

2.3.4 Determination of thermo-sensitivity of the hydrogel incorporating MAH-MCC. The hydrogel was immersed into deionized water to reach swelling balance for 24h before heated to 60°C. Then the calibration of the volume to the gel in a graduated cylinder was conducted during the cooling process.

2.3.5 Adsorption to MB. The dried hydrogel was prepared to have a size of about 1mm in diameter. Then it was added into the MB solution with the concentration of 10.0 mg/L. The concentration of MB was characterized by the UV-vis spectrum at each 10 min during the adsorption process. When the hydrogel adsorbed to a state of equilibrium, it was put into the deionized water to release MB as the desorption.
3. Results and Discussion

3.1 Characterization

MAH had such high activity in esterification that it could react with MCC without solvent. Meanwhile, it also possessed an unsaturated C=C bond so that it would potentially be incorporated into vinyl polymerization. The proposed scheme of reaction with the structures of reagent and product was shown in Figure 1, whereas the MAH-MCC reacted as a crosslinker.

![Reaction Scheme](image)

Figure 1. Synthesis of MCC with MAH without solvent and the following photo-induced polymerization of NIPAM to form the hydrogel.

Infrared spectra of raw MCC and the modified polysaccharide were shown in Figure 2, with a broad band from 3100 to 3500 cm\(^{-1}\) assigned to OH stretching. Carboxylic acid dimers would produce a band centered at 2530 cm\(^{-1}\) due to the unsaturation. The bands at 1734 cm\(^{-1}\) was assigned to \((C=O)\) from ester; It was known that the two symmetrical bands of the carbonyl groups in carboxylate appear at ~1600 cm\(^{-1}\) and ~1400 cm\(^{-1}\). These were all supported the occurrence that MAH covalently bonded to the backbone structure of MCC. by Equation (1) and (2) the surface carboxyl group content and DS were 0.950 mmol/g and 0.173, respectively.

![Infrared Spectra](image)

Figure 2. Infrared spectra of MCC and its chemically modified form MAH-MCC

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Figure 3 showed typical SEM images of the unmodified MCC, the MAH-MCC and its modified hydrogel. The image in Figure 3(a) displayed the crystalline form of the raw material. The characteristics changed in the MAH-MCC in Figure 3(b), by increasing the rugosity and porosity aspects. The surface of the hydrogel photo-polymerized was porous, with the absence of fibrous morphology in Figure 3(c).
3.2 Adsorption to MB

MB, which was a pollution source in the effluent of the textile and other industries, had a distinct absorbance at wavelength of 664nm by UV-vis spectrum, which could be used to evaluate the capability of adsorbents. The adsorption of MAH-MCC modified hydrogel to MB was analyzed by measuring the concentration of MB remained in solution at each 10 min in Figure 4(a). It presented that the amount of MB remained in solution declined and had a linear relationship with the increasing of time. To understand the adsorption kinetics of MB by the modified hydrogel, the quasi-first-order kinetics and quasi-second-order kinetic equation[8]were used to fit the adsorption process in Equation (3) and (4), respectively.

\[
\ln(q_e - q_t) = \ln q_e - k_1 t \quad \text{Equation (3)}
\]

\[
\frac{t}{q_t} = \frac{1}{k_2 q_e} + \frac{t}{q_e} \quad \text{Equation (4)}
\]

\[
q_t = \frac{(C_0 - C_t) \times V}{W} \quad \text{Equation (5)}
\]

Where \(q_e\) represented the amount of saturated adsorption of the unit adsorbent (mg/g), as well as \(q_t\) indicated the adsorption capacity of the unit adsorbent (mg/g) at t min in Equation (3-5). \(q_t\) could be caculated from Equation (5), as \(C_0\) and \(C_t\) were the concentration of MB (mg/L) remained in solution when exposed time was 0 and t (min) during the process, respectively. \(V\) was the volume of MB solution (L) while \(W\) was the weight of adsorbent (g). \(k_1\) and \(k_2\) stood for the constants in the related equations.

In Figure 4(b), \(\ln(q_e - q_t)\) in quasi-first-order kinetics of Equation (3) was used on the left Y-axis and \(t/q_t\) in quasi-second-order kinetics of Equation (4) was on the right Y-axis, as well as t was used on the X-axis. the \(R^2\) for the two equations was 0.7686 and 0.9572, respectively. It demonstrated that the quasi-second order kinetics was much suitable for the absorbent process of MAH-MCC modified hydrogel to MB.

Figure 4. The relationship of (a) absorbance with time and (b) absorbent kinetics to MB
3.3 Thermo-sensitivity of the hydrogel incorporating MAH-MCC.

The swelling volume was calibrated during the cooling process in Figure 5. It was showed that a platform appears between 44–53°C. The volume rose up steadily from ambient temperature to 38°C, then it hardly increased until the temperature was up to 54°C. It could deduced that the PNIPAM chains were experiencing a coil-to-globule transition, which was a hydrophilic to hydrophobic process. While the hydrogel was immersed in water at 60 °C, the hydrogen bonds intermolecular were weak, as well as the polymerized PNIPAM chains were in a state of curl. Therefore, larger gaps were left in the gel to allow water to enter for there were plenty of hydrophilic moieties. However, the intermolecular force of hydrogen bonding was increasing gradually as the temperature decreased. Thus, some channels to water were shrunk. When the temperature drops to 53–38 °C, the water retained in the gel, owning to the hydrophilic property of PNIPAM to resist to the shrinkage during the stretching. As it was lower than 38 °C, the enhanced force caused an reduce to the gap in the modified bio-polymer hydrogel, which resulted to the further extrusion of water and dwindled in volume. It was obviously that the hydrogel incorporated with MAH-MCC had a compatibility in aqueous media occurred at 54 °C, which was an upper critical solution temperature (UCST)[9]. The low critical solution temperature (LCST) of NIPAM[10] referred to 38 °C.

4. Conclusions

The most abundant biomacromolecule, microcrystalline cellulose (MCC) had attracted considerable attention in recent years due to its biodegradable, biocompatible and renew able characters. The grafting polymerization of n-isopropyl acrylamide (NIPAM) was initiated by UV-light, using MAH-MCC as the crosslinker, which was firstly modified by maleic anhydride (MAH) on MCC. The structures of MCC, MAH-MCC and grafted hydrogel were characterized by FTIR and SEM. The thermo-sensitivity and adsorption to methylene blue (MB) were measured. It was shown that the hydrogel had a lower critical solution temperature of PNIPAM at 38 °C and an upper critical solution temperature (UCST). When exposed to MB solution, the quasi-second-order kinetics could be used to explain the adsorption process.

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