Preparation and characterization superporous hydroxypropyl methylcellulose gel beads

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ABSTRACT

Stearic acid monoglyceride as suspension agent, divinylsulfone (DVS) as the crosslinker, cyclohexane as the continuous organic phase and nano-calcium carbonate as the porogen were used to produce hydroxypropyl methylcellulose (HPMC) porous gels in bead form by inversing phase suspension cross-linking. Effects of porogen dosage on the gel surface and inner morphology, density, porosity, swelling kinetics have been studied. Results show that the interpenetrate pores can be formed in gel beads when the porogen dosage reached 70 wt% of the dry HPMC. The equilibrium swelling ratios of the gel beads increased from 30.1 (g/g) to 37.4 (g/g) when the fraction of $CaCO_3$ dosage increased from 0 to 100 wt% of the dry HPMC and the equilibrium swelling time of the gels decreased from about 400 to 20 min. The results also show that the gel re-swelling capability is related to the porous structure.

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1. Introduction

Hydrogels are cross-linked hydrophilic materials which can absorb large quantities of water without dissolving. Because of their water-absorbing ability, gels have been found widespread applications in various areas (Can, Abdurrahmanoglu, & Okay, 2007; Guo & Gao, 2007; Kim, Serpe, & Lyon, 2004; Oosthuysen, Zilla, Human, Schmidt, & Bezuidenhout, 2006; Wu, Su, & Ma, 2006). The most popular application is being in drug delivery control (Park, Shalaby, & Park, 1993; Peppas, 1986). For most of these applications, response rate has been considered as a critical performance indicator factor from both technical and economic standpoints. However, it has been shown that the kinetic behavior of gels is controlled by the cooperative diffusion of the polymer chains in the solvent (Stevin & Gehrke, 1993). Since this diffusion coefficient is of the order of 10^{-7} cm^2/s, the rate of swelling macroscopic gel sample is generally quite slow. The response time of the gels can be reduced by reducing the characteristic diffusion path length. Unfortunately in many cases, reducing the dimension of the gels neither solves the problem nor is desirable for many potential applications; therefore, porous gels are desirable.

In porous hydrogels, pores have to be introduced into hydrogels and connected to provide capillary channels so that water can get into the dry hydrogels by capillary wetting. When the dried gel with the opened pore structure is placed in an aqueous solution, water flows through the open channels by the capillary effect, reaching swelling equilibrium in relatively short period of time (Askari, Nafisi, Omidian, & Hashemi, 1993; Chen, Park, & Park, 1999). Currently available techniques for porous gel preparation are porogenation (Badiger, McNeil1, & Graham, 1993), freeze-drying (Petel & Amiji, 1996), microemulsion formation (Bennett, Burford, & Tilley, 1995) and phase separation (Sannino, Maffezzoli, & Nicolais, 2003). Among all these techniques, porogenation has the advantage of controlling the pore size and porosity through the control of porogen size and amount.

When the hydrogels are used in controlled release or chromatography, gels are needed in the form of particulates. Desired sizes are usually achieved by grinding. However, the irregular shaped pieces generated from grinding process are usually considered undesirable. Grinding also creates a large amount of fines, which can hinder mass transfer on the gel bed. For example, "gel blocking" can occur where, upon contact with fluid, the outer particles of the gel bed stick together, effectively blocking transport of fluid to the inner particles (Stephen, O'Connor, & Gehrke, 1997). Producing uniform spherical gel can eliminate these problems.

In this paper, we use calcium carbonate as a porogen to prepare superporous HPMC gel beads by inversing phase suspension cross-linking. We investigated the effect of porogens on swelling, porosity and gels morphologies. Effect of the porogen on the porous gel re-swelling ratio is also investigated.

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2. Experimental

2.1. Materials

HPMC [degree of substitution (DS) is 28% and molar substitution (MS) is 6%; number-average molecular weight: 4×10^5; Taian Ruitai Cellulose, Shandong China] was dried in a vacuum desiccator over calcium chloride. Divinylsulfone (Aldrich) with purity of 97%. Nano-calcium carbonate, used as received. All the other reagents were laboratory-grade chemical and were used without further purification.

2.2. Preparation of the superporous gels

Various amount of calcium carbonate as porogens were mixed with the HPMC solution (10 wt%) using ultrasonication. Sodium hydroxide as a catalyst was also added to adjust the pH value to 12. The detailed procedure was as follows. The gels beads were produced in a 250 ml four-necked flask equipped with a stirrer. Stearic acid monoglyceride (2.4 g) was dissolved in 120 ml cyclohexane for the preparation of the continuous phase. Then the 30 g mixture was poured in continuous phase while it was being stirred. As the mixture dispersed into droplets then added DVS 0.1 g/g dry HPMC. Eighteen hours later, the reaction stops and the cyclohexane decanted, the gels beads obtained. Then the gel beads were immersed in the 1 M hydrochloric acid solution for 20 h to remove the calcium carbonate. The beads were then repeatedly swollen and shrunk in distilled water to remove the sol fraction from the gels. The sample was simple water elimination by evaporation in air atmosphere at ambient condition to obtain the dry gels beads.

2.3. Morphology of HPMC gels

The optical microscope was used to observe the size of the gel beads. The bead size was determined by measuring a sample of beads as described by Stephen (Stephen et al., 1997). Morphology of the dried gel structure was studied by scanning electron microscope. Dried superporous gel beads was coated with a thin layer of palladium gold alloy and imaged under SEM instrument (PHILIP XL30).

2.4. Calculation of the porosity and density of the gels

The porosity of the dry gel is measured in a 50 ml volumetric flask, with the inert solvent cyclohexane, and the produce is as following:

The empty flask weight (W_1) was measured. One gram gel beads was added in flask and the solvent was slowly added to removed the air, and then the weight (W_2) was measured. The porosity of the porous gel (P) is calculated using the follow equations

$$V_g = 50 - (W_2 - W_1 - 1)/\rho_h \tag{1}$$

$$\rho_g = 1/V_g \tag{2}$$

Take out the porous gel beads and measure the weight (W_3). The gel beads pores were fully filled with cyclohexane, the volume of the cyclohexane in gels beads pore is the pore volume of the gel beads.

$$V_p = (W_2 - W_3 - 1)/\rho_h \tag{3}$$

$$P = V_p/(V_p + V_g) \tag{4}$$

where ρ_g – density of the hydrogels (g/cm^3); ρ_h – density of the cyclohexane (g/cm^3); V_g – volume of the hydrogels (cm^3); V_p – volume of the cyclohexane in pore (cm^3).

2.5. Measurement of swelling ratio

A 0.5 g sample was immersed in excess distilled water (500 ml) at room temperature. Swollen samples were then separated from the unabsorbed water by filtering through a 100-mesh, the swelling ratio (SR) of the gel beads was defined as following equation.

$$SR = (m_t - m_d)/m_d \tag{5}$$

where m_d and m_t are the masses of the dry and swollen gel beads, respectively, at time t.

2.6. Measurement of the re-swelling capability

The re-swelling capability of the gels was measured according Wang (Li, Wang, & Chen, 2004), the specimen was immersed into excess distilled water to ensure the swelling equilibrium achieved, the gels was placed in an oven at 100 °C untilled the dried. A similar procedure was repeated and then the saturated water absorbency of the sample was obtained after several times of re-swelling to evaluate the re-swelling capability of the gels.

3. Results and discussion

3.1. The morphologies of the gel beads

It has been shown that the gel beads diameter were influenced by the stirred speed, phase ratio and suspension agent (Stephen et al., 1997), in this condition the gel beads diameter about 260 μm. SEM is a good method to measure surface morphology and characterize the gel structure at micrometer scale (Antonietti, Caruso, Göltner, & Weissenberger, 1999). The SEM micrograph of the gel beads prepared with 30 wt% porogen is presented in Fig. 1a. The sample is coarse and dense and has no porous structures. The porous structures of samples with 70 wt% and 100 wt% porogens are shown in Fig. 1b and c. The pore sizes increases with increasing the porogen dosage and the surface of the gel beads becomes much rougher. From the Fig. 1d, we can see interpenetrating pores were formed in the inner of the gel beads, so the water can be absorbed by capillarity, and the gel swelling rate is quicker.

3.2. Effect of porogens on gel density and porosity

As Fig. 2 shown, the density of the hyrogels is less than the nonporous hydrogel when the porogen dosage is no more than 70 wt% of the dry HPMC. Pores can be formed in gel beads by porogenation. When the porogens level is low, closed pores will be present. So the density of the gels will be lower. Fig. 2 also indicates that most of the pores will be closed pores when porogen dosage is less than 30 wt%. From Fig. 2, we conclude that 70 wt% or more porogen dosage will be sufficient to prepare the interpenetrating pores.

As is shown in Fig. 3 the porosity of the hydrogel increased with increasing porogen, the porosity increased dramatically, when increasing the porogen dosage from 50 to 70 wt%. This is an indication of transferring from closed pores to interpenetrating pores.

3.3. Effect of the porous structure on gels swelling ratio and swelling rate

It has been reported previously that the surface morphology of the gels could affect their swelling behavior (Marsano, Bianchi, & Sciutto, 2003). Fig. 4 illustrates that the equilibrium water absorbency for the porous is higher than for the non-porous gel beads. It can be seen that the swelling degree was increased from 30.1 (g/g) to 37.4 (g/g) with increasing the fraction of CaCO$_3$ dosage from 0 to 100 wt% of the dry HPMC. This can be attributed to the
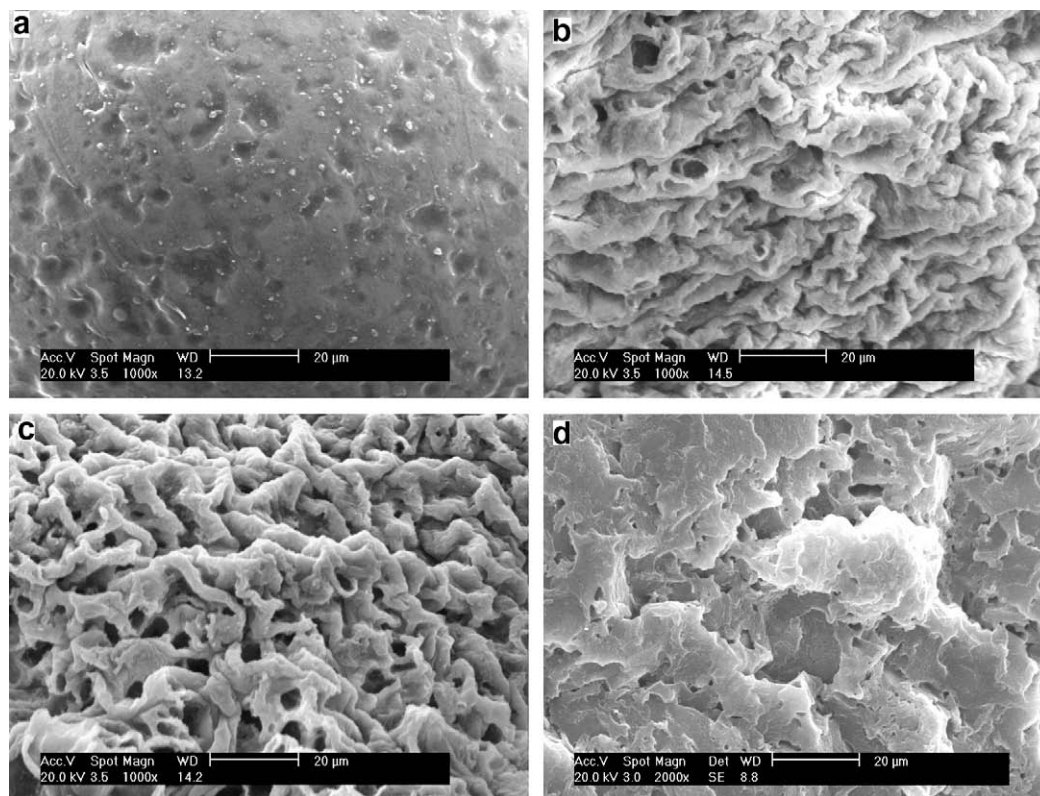
Fig. 1. SEM micrographs of the gel beads prepared with different fraction porogens of dry HPMC ((a) 30; (b) 70; (c) 100; and (d) 100 wt%, inner morphology).
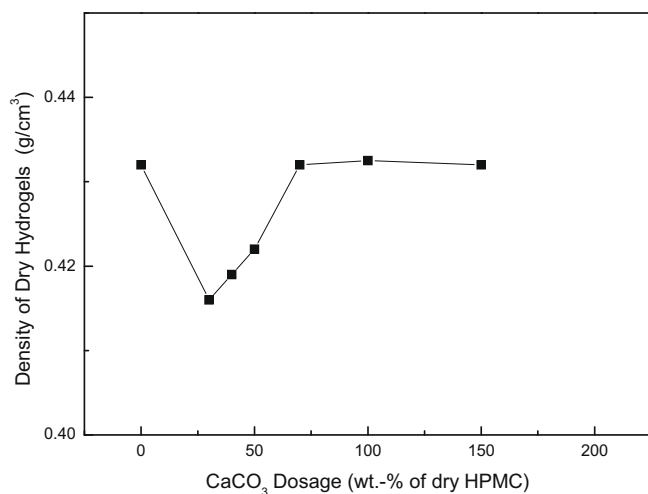

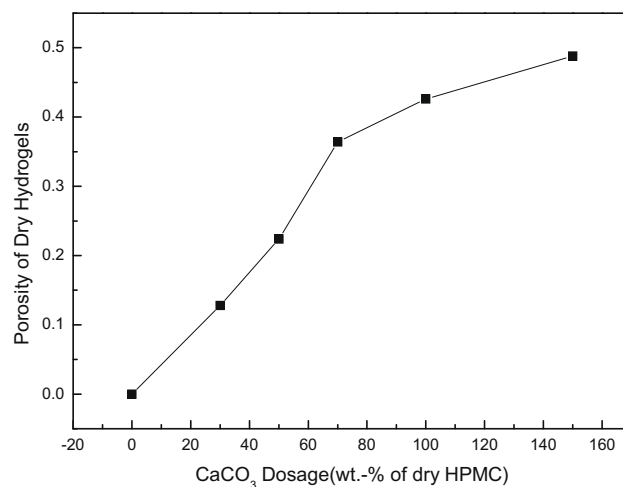**Fig. 2.** Effect of porogen dosage on gel beads density.

Fig. 3. Effect of porogen dosage on the gel beads porosity.

surface and inner morphology. Water absorbed by the gel beads exists in the form of free water, bond water and interfacial water. Enhancing the specific surface area can increase the ability of trapping interfacial water. Another reason is that the porous structure gives the gel beads additional space to hold more water.

It is shown in Fig. 4 the swelling rate rises with the increasing of the porogens, and the equilibrium swelling time of the gels decreased from about 400 to 20 min with the porogens increased from 0 to 100 wt% of the dry HPMC. This can be attributed to the enlarged surface area and pore structure. Since gel swelling is a diffusion-controlled process porous gels have more surface area and more pores offer more diffusion area. And this helps the gel bond more water, and then the bonded water can be absorbed by capil-

larity. The other reason is that the porous gel bead has a looser structure which facilitates the penetration of water molecules.

3.4. Effect of the porous structure on gel beads re-swelling capability

The re-swelling capability is an important factor for superabsorbent gel beads. Fig. 5 shows the equilibrium water absorbency in distilled water for porous and non-porous gel beads. The curves in Fig. 5 show that the equilibrium water absorbency of the porous gel beads decreased, but that about 85 wt% of the initial equilibrium water absorbency was still retained after re-swelling 5 times. The equilibrium water absorbency decreases more with the samples produced with more porogen. The phenomena
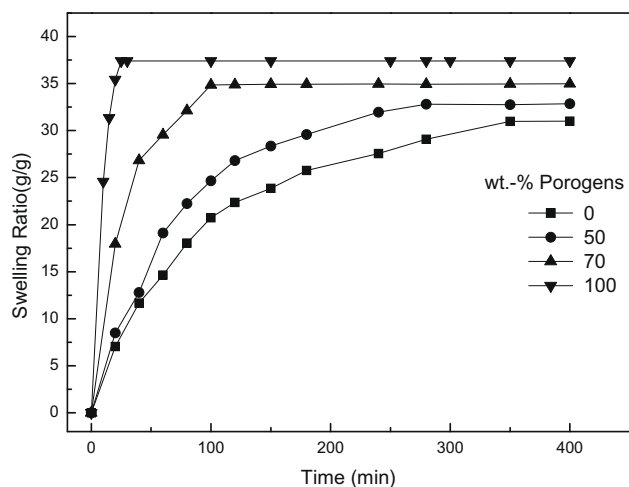
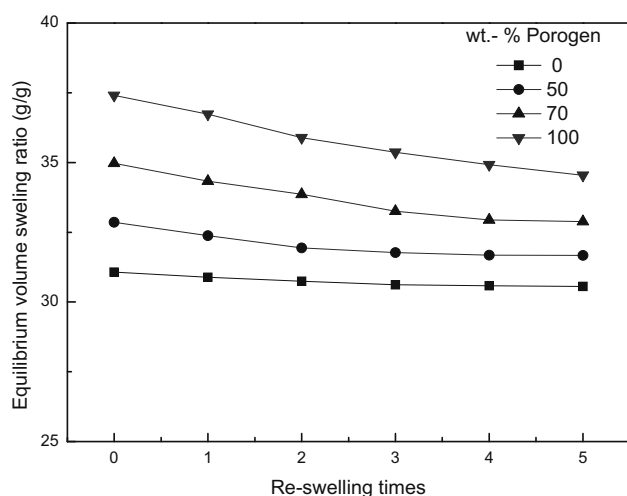**Fig. 4.** Effect of porogen dosage on the swelling kinetics.

Fig. 5. Effect of porogen dosage on gel beads re-swelling ratio.

may be attributed to the irreversible collapse of the samples during the deswelling process, owing to their loose and porous network.

4. Conclusion

Nano-calcium carbonate was used as porogen, a series of porous HPMC gel beads were prepared by inverse-suspending crosslinking. The porogen affect on the morphology of polymeric network structure. When the porogen dosage reached 70 wt%, the porous hydrogels which interpenetrate pores can be formed. The porogen dosage has an influence on swelling behavior, and the gels with bigger pores have higher swelling ratios and swelling rates. The swelling behavior for the porous structure gels is due to larger surface area and looser structure. The re-swelling capability of the porous gel beads decrease with increasing the porogen dosage.

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