INTRODUCTION

Superabsorbent hydrogels, a kind of functional crosslinked polymer materials with significantly hydrophilic properties, can absorb several hundred to thousand times of water to their own mass despite the insolubility in water [1]. These water-absorbent hydrogels have so excellent water retention features that they have been widely used as baby diapers [2], farm water-retention agents [3, 4], concrete additives [5–7], soil amendments [8], drug delivery carriers [9, 10], metal removal media [11, 12], conducting materials [13, 14], fertilizers [15, 16], and so on.

Acrylamide (AM)—based absorbents have been extensively studied [17–23], due to their significantly absorbent properties as well as low price and easy preparation. Marcos R. Guilherme prepared a novel superabsorbent hydrogel using chemically modified cashew gum (CGMA) and AM as reactants by solution polymerization [24], and the obtained P(CGMA-co-AM) hydrogels swelled about 1500 times to their own dried weight. As reported by Erdener Karadağ, the swelling percentage of the AM/maleic acid (MA) hydrogels prepared by solution polymerization was in the range of 1660–6050% in water [25]. The solution polymerization used in the reported researches is a classical way to obtain highly absorbed hydorgels. However, inverse suspension polymerization is considered to be a better choice to prepare hydrogels, due to its easy heat dissipation and low viscosity compared to the solution polymerization [26–29]. Moreover, micrometer-sized particles with high molecular weight can be prepared through inverse suspension polymerization.

Generally, the swellabilities and absorbencies of the hydrogels are measured by changes in the sample weights before and after water absorption, which is called gravimetric determination. The absorbencies calculated by this method have large deviations, due to the whole sample containing many particles as one research system. To reduce the deviations of the swelling percentage, it is necessary to develop a more accurate method. Since the size and volume of each particle changed after swelling, each particle can be as one research subject. Thus, volumetric method can be employed to obtain more accurate sweallability and absorbency of the particles.

Itaconic acid (IA), having two carboxyl groups, was good hydrophilic property. However, there are few reports to prepare hydrogel microspheres using IA as comonomer. Herein, a series of poly(acrylamide-co-itaconic acid) (P(AM-co-IA)) hydrogel microspheres were prepared by inverse suspension polymerization method, using potassium persulfate (KPS) as initiator, \( N,N' \)-methylenebisacrylamide (Bis-A) as cross-linker, and sorbitan monooleate (Span–80) and polyoxyethylene-60-sorbitan monooleate (Tween–60) as co-stabilizers. The sizes of the obtained microspheres were easily controlled by changing the polymerized parameters. Absorption behaviors of the P(AM-co-IA) microspheres in water and saline were investigated in detail and the absorbed amounts were calculated by changing in the sizes before and after absorption.

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EXPERIMENTAL

Materials

Itaconic acid (IA) was purchased from Alfa and used without purification. Acrylamide (AM), sorbitan monooleate (Span-80), polyoxyethylene-60-sorbitan monooleate (TWEEN-60), potassium persulfate (KPS), N,N'-methylenebisacrylamide (BiS-A), cyclohexane, and ethanol were all purchased from Sinopharm Chemical Reagent Co., Ltd (China). Deionized water was used throughout the research.

Preparation of P(AM-co-IA) Hydrogel Microspheres

P(AM-co-IA) hydrogel microspheres were synthesized via inverse suspension polymerization (W/O) method using KPS as the initiator. Typical polymerized parameters were as following: 3.60 g AM, 0.40 g IA, 52.5 mg KPS (1.3 wt % of the total monomers), and 0.08 g BiS-A (2 wt % of the total monomers) were dissolved in water. This aqueous solution was charged into a three-neck round-bottom flask, in which included the co-stabilizers of 0.976 g Span-80 and 0.524 g Tween-60 (37.5 wt % of the total monomers) and cyclohexane. Then, the mixture was heated at 50°C for 40 min under stirring, and subsequently kept at 68°C for 4 h. The mixture was then cooled to room temperature and kept stirring to avoid aggregation. The prepared materials were purified by removal of the organic phase and co-stabilizers by precipitating the aqueous phase in ethanol, washing with ethanol, and centrifugation. The sedimented particles were finally dried in a vacuum oven at 40°C for 24 h. Various P(AM-co-IA) microspheres were prepared by changing the mass ratio of AM and IA and the concentration of the initiator, co-stabilizer concentration, and cross-linker, according to the same procedure.

The structures of the P(AM-co-IA) microspheres were analyzed by Fourier transform infrared spectroscopy (FTIR) using a KBr method (FTIR 2000-104, ABB, USA). The sizes of the P(AM-co-IA) hydrogel microspheres were measured by dynamic light scattering (DLS) at 25°C using a DB-525 Zeta PALS instrument (Brookhaven, USA) by dispersing the microspheres in ethanol. The morphologies of the hydrogel microspheres were determined by scanning electron microscope (SEM; OM, BA-400 digital optical microscope purchased from MOTIC corporation). The swellabilities of the hydrogel microspheres were calculated depending on Eqs. (1) and (2):

\[
\text{Swellability}_1 (%) = \frac{D_D}{D_0} \times 100, \quad (1)
\]

\[
\text{Swellability}_2 (%) = \frac{D_D}{D_0} \times 100. \quad (2)
\]

The absorbencies of each particle in water and saline were calculated by the following Eqs. (3) and (4):

\[
\text{Water absorbency} = \frac{4}{3} \pi \left(\frac{D_1}{2}\right)^3 \rho_{\text{water}}, \quad (3)
\]

\[
\text{Saline absorbency} = \frac{4}{3} \pi \left(\frac{D_2}{2}\right)^3 \rho_{\text{saline}}, \quad (4)
\]

where \(D_0\) represents the number-average diameter of the original particles before swelling from DLS results. \(D_1\) and \(D_2\) refer to the number-average diameters at the maximum swelling point after immersed in water and saline for 24 h, respectively. Here, density of the hydrogel microspheres was assumed to be close to the densities of water (\(\rho_{\text{water}} = 1.00 \text{ g/cm}^3\)) and saline (\(\rho_{\text{saline}} = 1.01 \text{ g/cm}^3\)), and then, \(\rho_{\text{water}}\) and \(\rho_{\text{saline}}\) were used directly to calculate the absorbencies.

RESULTS AND DISCUSSION

Preparation of the P(AM-co-IA) Hydrogel Microspheres

The structures of the P(AM-co-IA) hydrogel microspheres and the AM and IA monomers were analyzed by FTIR. As shown in Fig. 1 carbonyl stretching resonances for AM and IA were observed at 1708 and 1673 cm\(^{-1}\), respectively. A distinctly different absorption band at 1603 cm\(^{-1}\) was observed for the P(AM-co-IA) microspheres in Fig. 1 (curve 3), which could be attributed to the hydrogen-bond interaction from the \(-\text{C}=\text{O}\) present in the PAM segments. Another distinct absorption band at 1657 cm\(^{-1}\) was assigned to the carbonyl groups of IA in the microspheres. These results suggested the successful preparation of the P(AM-co-IA) hydrogel microspheres.

Figure 2 shows SEM image of the typical P(AM-co-IA) hydrogel microspheres, which was prepared when the mass ratio of AM/IA was at 6/1 and the concentrations of KPS, co-stabilizer and BiS-A were fixed at 1.3, 37.5 and 2 wt % of the total monomers, respectively. The P(AM-co-IA) hydrogel microspheres were highly monodispersed with an average diameter of about 1.2 μm (SD = 0.06). DLS measurement in ethanol showed that the particle size was 1.19 μm, which was well corresponding with the results from SEM.