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Swelling behavior of gelatin-g-methyl methacrylate copolymers

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Gelatin-methyl methacrylate graft copolymers were prepared with gelatin and methyl methacrylate (MMA). The effect of various reaction parameters on the swelling behavior was investigated systematically, such as the concentration of the monomer, the content of the initiator, reaction time and temperature. In addition, the effect of intercalation of graft copolymers with montmorillonite (MMT) on swelling behavior was studied. The results indicated that the graft copolymerization and intercalation with MMT could greatly reduce the swelling degree of gelatin. The swelling process of the copolymers followed second-order kinetics identical to that of the original gelatin.

1. Introduction

Gelatin is a denatured derivative of the structural protein collagen [1]. The crosslinked gelatin network shows high water absorption and quick degradation that are suitable for delivery systems [2, 3] and wound dressings [4] but limit its applications for structural biomaterials such as osteosynthetic devices. For structural biomaterials, especially for implants *in vivo*, swelling should be suppressed because changes in the dimensions of the structural parts are not permitted in some circumstances, such as bone fixation devices. Moreover, swelling is often accompanied by a reduction in the mechanical properties.

Interest in the modification of gelatin through graft copolymerization has grown significantly. The combination of natural and synthetic polymers via grafting yields hybrid materials which may produce desirable properties. The effects of grafting monomers, initiators and reaction conditions on the percentage of grafting and the grafting efficiency have been studied systematically [5–8]. However, there are few reports about the swelling behavior of the graft copolymers [9] and no study on the swelling kinetics of gelatin graft copolymers has been reported yet. We had reported the swelling behavior of gelatin/MMT hybrid nanocomposites, and intercalation with MMT could significantly suppress the swelling of gelatin matrix [10]. As an extension, this article discusses the swelling behavior of the gelatin-g-MMA copolymers and gelatin-g-MMA/MMT nanocomposites. In addition, the swelling kinetics of gelatin graft copolymers is investigated.

2. Experimental

2.1. Materials

Gelatin (Type B, extracted from bovine skin) was purchased from Sigma Chemical Co. (St. Louis, MO, USA). MMA (Analytical grade, provided by Tianjin Chemical Reagent Institute, Tianjin, China) was purified in a manner reported earlier [6]. Potassium persulfate ($K_2S_2O_8$, analytical grade, supplied by Kemi'o Co. Ltd. of Tianjin, China) was used as received. Sodium MMT (Na^+ MMT, the particle size is 40 μm) was supplied by Huate Chemical Co. (Zhejiang, China). Glutaraldehydes (GLA, used as crosslinking agent) was provided by Tiantai Fine Chemical Co. (Tianjin, China). The composition of the phosphate buffer solution (PBS) was as follows: NaCl, 1.4×10^5 mmol/m^3; KCl, 3×10^3 mmol/m^3; Na_2HPO_4, 8.1×10^3 mmol/m^3; KH_2PO_4, 1.5×10^3 mmol/m^3 (pH 7.2). All the reagents constituting the PBS were analytical grade.

2.2. Preparation

2.2.1. Preparation of gelatin-g-MMA copolymers

Gelatin powder (1 g) was soaked in 5×10^{-5} m^3 of deionized water and heated to 40°C to obtain a homogeneous solution. It was then poured into a four-necked round-bottom of 1×10^{-4} m^3 capacity flask placed in a constant-temperature water bath, stirred and bubbled with N_2 gas for 1 h. The required amount of $K_2S_2O_8$ was added. After 30 min, the desired amount of refined MMA was added dropwise. After the desired period of

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time, the reaction flask was immersed in a freezing mixture to stop the reaction. Then, 1×10^{-5} m^3 of 0.25% GLA was slowly added into the reaction products, and the mixture was stirred for another 10 min. The product was poured into a specially self-made mold and dried at the ambient temperature for several days.

2.2.2. Preparation of gelatin-g-MMA copolymer/MMT nanocomposite

After the graft copolymerization, the solution was stirred and the temperature was raised to 70°C. Then, 2×10^{-5} m^3 of a 5 wt% MMT suspension was added dropwise into the vessel. The mixture was stirred for another 1 h. Then the same amount of crosslinking agent was used and the same procedures described for the preparation of gelatin-g-MMA copolymers were followed.

2.3. Methods

The infrared spectra of the samples were taken with BIO-RAD FTS3000 Model FT-IR spectrophotometer using KBr pellets. The grafted products were poured into cold acetone, and the grafted gelatin was precipitated. The products were filtered and dried under vacuum. The dried products were Soxhlet extracted with acetone for 72 h. The purified graft copolymer was dried under vacuum.

To measure the change in the gallery distance of MMT before and after intercalation, X-ray diffraction (XRD) patterns were recorded at 2°/min on a Japan Rigaku DMAX-RC diffractometer by using Cu K_α radiation ($\lambda = 0.15406$ nm) at a generator voltage of 50 kV and a generator current of 180 mA.

Swelling studies were determined according to the following procedure: All the specimens were thoroughly dried before swelling. For the swelling test, rectangular test pieces (15 mm long, 10 mm wide, and 2 mm thick) were used. Each specimen was weighed and immersed in a separate 2.5×10^{-4} m^3 glass bottle containing 1.5×10^{-4} m^3 of a PBS solution at 25°C for 1200 min at most. The degradation of gelatin was assumed to be very small in this period and was neglected. At regular intervals, samples were taken out from the PBS solution, the surface were blotted with filter paper, and weighed with a weighing bottle on an electronic balance. Each point was the average value of three to five samples. The swelling degree is usually expressed as the grams of the solvent absorbed by each gram of dry gelatin and determined by the following weight equation:

$$W = \frac{m - m_0}{m_0} \times 100\%,$$

where m is the weight of swollen pieces measured at time t and m_0 represents the initial weight of the dried sample.

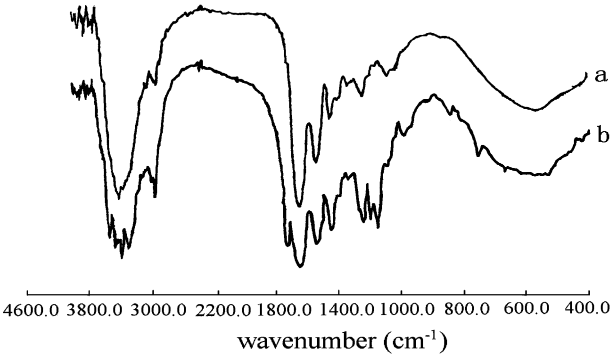

Figure 1 FT-IR spectra of (a) pure gelatin and (b) gelatin-g-MMA copolymer.

3. Results and discussion

3.1. FT-IR spectra characterization

The grafting is generally verified by the FT-IR spectra of the grafted polymers [6]. The FT-IR spectra of pure gelatin and copolymer are shown in Fig. 1. The spectrum of gelatin-g-MMA copolymer displays both the characteristic bands at 1650 and 1535 cm^{-1} of the amide groups of pure gelatin and the carbonyl group absorption at 1730 cm^{-1} of MMA. Therefore, the formation of graft copolymer was confirmed.

3.2. Effect of reaction parameters on swelling behavior

3.2.1. Monomer concentration

The swelling curves of copolymers with various monomer concentration are shown in Fig. 2. It can be seen that with the increase of the monomer concentration, the equilibrium swelling degree decreases slightly and then increases dramatically. It could be explained that, the amount of monomer for grafting increases with increasing monomer concentration, therefore the percentage of grafting (*G%*) increases [6], and the equilibrium swelling degree decreases. When the monomer concentration increased further, too many hydrophobic monomer molecules may bury the growing macroradicals, hindering the graft copolymerization, and leading to the increase of equilibrium swelling degree.

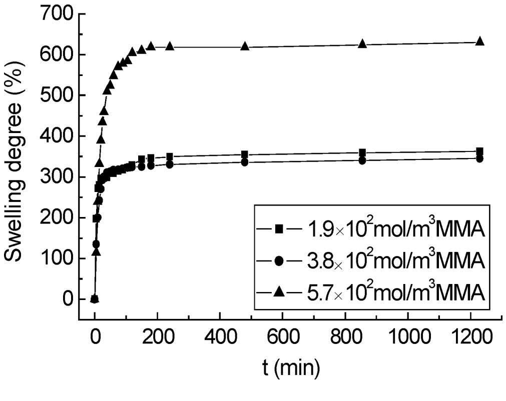

Figure 2 Swelling curves of copolymers with various monomer concentration.

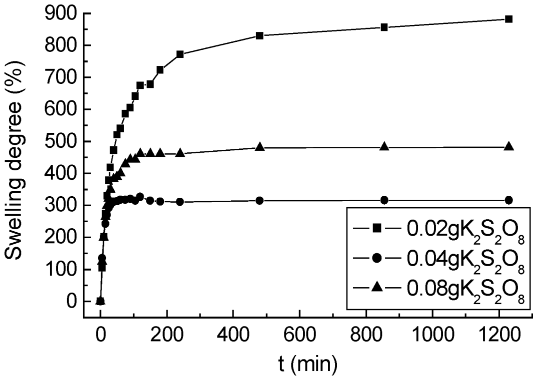

Figure 3 Swelling curves of copolymers with various $K_2S_2O_8$ content.

3.2.2. Initiator content

The effect of the initiator content is plotted in Fig. 3, where the equilibrium swelling degree first decreases and then increases with a further increase in $K_2S_2O_8$ content. The decreasing trends of equilibrium swelling degree may be attributed to the fact that, since both gelatin and $K_2S_2O_8$ are water-soluble, when at lower initiator contents, the initiator prefers to approach gelatin macromolecular chains rather than hydrophobic monomer in aqueous media. So the $K_2S_2O_8$ was mainly used to initiate the gelatin macromolecules, forming a great number of grafting sites on the gelatin chains. On the other hand, when at lower initiate contents, the reaction is mostly terminated by the recombination of double radicals, so that *G%* increases with increasing $K_2S_2O_8$ content [8].

But when at higher $K_2S_2O_8$ content, the number of primary radicals, gelatin macromolecular radicals, and grafting side chains radicals increases, the growing grafted polymeric chains may be easily terminated by these radicals. Therefore, side chain termination took place even before the full growth of the side chains. As a consequence, G% was lowered [8] and the equilibrium swelling degree was increased.

3.2.3. Reaction time

Fig. 4 shows the swelling curves of copolymers with various reaction times. The decrease in equilibrium swelling degree with time is accounted for the increase in the number of grafting sites on the gelatin chains in the initial stages of the polymerization. Misra has reported that *G%* had a maximum versus reaction time [11]. So, the equilibrium swelling degree decreased. With the prolongation of reaction time, more chain-transfer and chain termination processes occurred, leading to the increase of the equilibrium swelling degree.

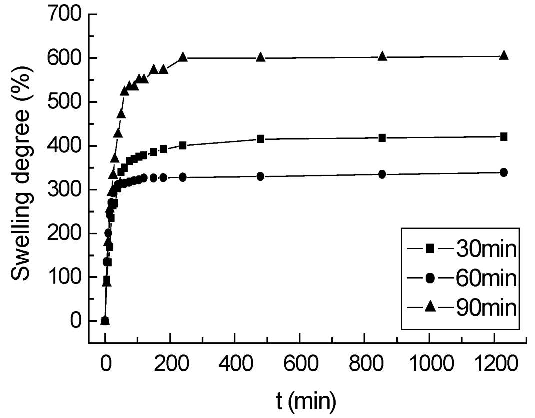

Figure 4 Swelling curves of copolymers with various reaction time.

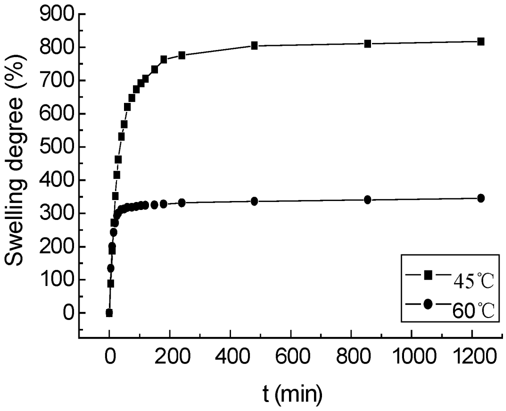

Figure 5 Swelling curves of copolymers with various reaction temperature.

3.2.4. Reaction temperature

Fig. 5 shows the swelling curves of copolymers prepared at 45 and 60°C respectively. Among a specific range, high temperature benefits the formation of primary radicals and the initiation reaction of gelatin. Rising temperature increased the rate of graft copolymerization and the *G%* [8]. Moreover, the lower equilibrium swelling degree may also be attributed to the increasing solubility of the monomer in the aqueous phase at higher temperature, thus increasing the possibility of the monomer to contact gelatin macromolecules.

3.3. Effect of the intercalation of graft copolymers with MMT on swelling behavior

Gelatin/MMT hybrid nanocomposites can be successfully prepared [12], and intercalation with MMT can significantly decrease the equilibrium swelling degree from 778% of pure gelatin to 315% [10]. In order to investigate the intercalation of graft copolymers with MMT, the XRD patterns of pristine MMT and gelatin-g-MMA/MMT composite are shown in Fig. 6. Pristine MMT exhibits a sharp peak at $2\theta = 6.0°$, and using Bragg's equation:$\lambda = 2d\sin\theta$, d_{001} is 1.47 nm. The XRD pattern of the composite changes dramatically in comparison with pristine MMT. The d_{001} diffraction peak shifts towards lower angle value at $2\theta = 4.55°$, and becomes broad, $d_{001} = 1.94$ nm. The result indicated that the grafted gelatin chains could still intercalate into the galleries of MMT, and gelatin-g-MMA/MMT intercalated nanocomposite was formed.

Fig. 7 displays the swelling curves of gelatin-g-MMA copolymer and gelatin-g-MMA/MMT nanocomposite. Intercalation with MMT further reduces the equilibrium swelling degree of the graft

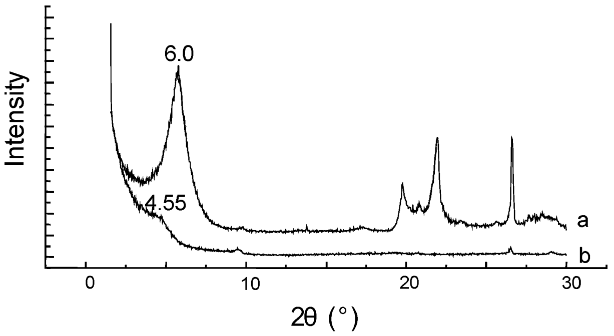

Figure 6 XRD patterns of pristine MMT and graft copolymer/MMT nanocomposite (a) MMT (b) gelatin-g-MMA/MMT nanocomposite.

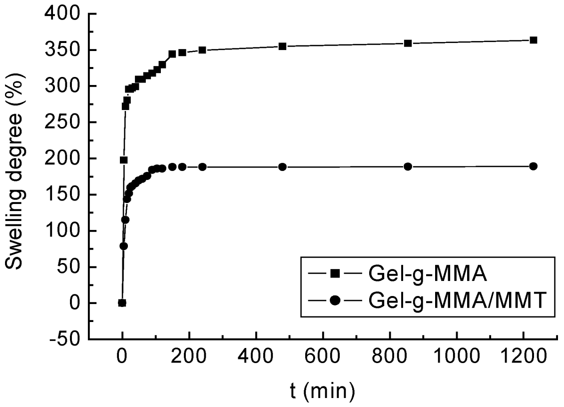

Figure 7 Swelling curves of gelatin-g-MMA copolymer and gelatin-g-MMA/MMT nanocomposite.

copolymer from 350 to 188%. Nano-dispersion of MMT in gelatin matrix and barrier effect of MMT sheets to solvent molecules suppress the swelling of the gelatin network. Meanwhile, MMT sheets interact with hydrophilic groups of gelatin such as $-NH_3^+$, $-COO^-$, weaken their hydrations.

3.4. Swelling kinetics of gelatin graft copolymers

The swelling kinetics of gelatin has been reported extensively [13, 14], and we studied the swelling kinetics of gelatin/MMT intercalated materials recently [10]. However, no study on the swelling kinetics of gelatin grafted copolymer has been reported yet.

According to previous research [15], the swelling kinetics of gelatin can be described by a second-order rate equation:

$$\frac{dW}{dt} = K(W_\infty - W)^2 \qquad (1)$$

where K is the rate constant; W_∞ represents the maximum or equilibrium solvent uptakes, and W is the solvent absorbed per gram gelatin at time t; $(W_\infty - W)$ is defined as the swelling capacity. By integration and rearrangement, Equation 1. can be rewritten as follows [16]:

$$\frac{t}{W} = A + Bt \qquad (2)$$

TABLE I W_∞ and K_∞ of Graft Copolymers with various monomer concentration

MMA × 10^{-2} (mol/m^3)	A	B	W_∞	K_∞
1.9	0.0231	0.00277	361	6.585
3.8	0.0240	0.00296	338	6.454
5.7	0.0149	0.00159	630	8.181

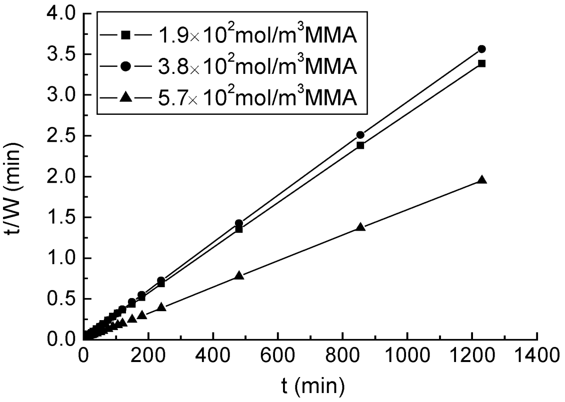

Figure 8 Linear regression of the swelling curves of Fig. 2 according to Equation 2.

where A and B is the intercept and slope of plots of $\frac{t}{W}$ versus t, respectively (i.e., $A = \frac{1}{KW_\infty^2}$ and $B = \frac{1}{W_\infty}$). According to previous research [16], $K_\infty = \sqrt{K}W_\infty$, and K_∞ is defined as kinetic constant. The swelling data of Fig. 2 were calculated according to Equation 2, and the results are shown in Fig. 8. Fig. 8 reveals that straight lines are obtained by linear regression, and this means that the swelling processes of the graft copolymers follow second-order kinetics. This suggests that the graft copolymerization does not change the swelling kinetics of the gelatin matrix.

The constants A and B, as well as the corresponding values of W_∞ and K_∞were obtained with Equation 2. These data are listed in Table I. When the concentration of MMA is 3.8 × 10^2 mol/m^3, both W_∞ and K_∞ of the graft copolymer reach minimum data, which are 338 and 6.454, respectively, suggesting the minimum equilibrium swelling degree and the slowest swelling process.

4. Conclusions

In this study, gelatin-g-MMA copolymers were prepared and the swelling behavior was investigated. Copolymerization with hydrophobic monomer MMA can significantly reduce the swelling degree of the gelatin matrix. Moreover, like that of the pristine gelatin, the swelling kinetics of the graft copolymers follows a second-order equation. The graft copolymerization does not change the swelling kinetics of the gelatin matrix. In addition, the graft copolymer can still intercalate into the galleries of MMT and form nanocomposite. Intercalation with MMT can further suppress the swelling of the graft copolymer due to the barrier effect of MMT.

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