

Swelling Behavior of Gelatin-g-Poly(Butyl Acrylate) Copolymers

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ABSTRACT: Gelatin-g-poly (butyl acrylate) copolymers were prepared with gelatin and butyl acrylate. The effects of various reaction parameters, including the concentration of the monomer, the concentration of the initiator, the concentration of gelatin, the reaction time, and the temperature, on the swelling behavior were studied systematically. In addition, the effect of the intercalation of graft copolymers with montmorillonite on the swelling behavior was investigated.

The results indicated that the graft copolymerization and intercalation with montmorillonite could greatly reduce the swelling degree of gelatin. The swelling process of the copolymers followed second-order kinetics identical to those of the original gelatin. © 2005 Wiley Periodicals, Inc. *J Appl Polym Sci* 97: 1033–1037, 2005

Key words: graft copolymers; nanocomposites; swelling

INTRODUCTION

Gelatin is an abundant and relatively inexpensive protein derived from collagen with the capacity to form network structures and gels.¹ It is used in a variety of gel applications, including photography, drug delivery, holography, microencapsulation, and food preparation.^{2–4} However, the crosslinked gelatin network shows high water absorption and quick degradation, which limit its applications for structural biomaterials. Moreover, swelling is often accompanied by a reduction in the mechanical properties.

The graft copolymerization of gelatin with various vinyl monomers is an effective method for improving the properties of gelatin. For example, poly(butyl acrylate) has a low glass-transition temperature and quite good elasticity. Grafting it onto gelatin can greatly improve its physicomaterial properties and, in particular, increase the strength of gelatin film, which is very important for light-sensitive materials.⁵

In previous studies, the effects of grafting monomers, initiators, and reaction conditions on the percentage of grafting (G%) and the grafting efficiency have been studied systematically.^{5–8} However, there are few reports about the swelling behavior of graft copolymers,⁹ and no study on the swelling kinetics of gelatin graft copolymers has been reported yet. We reported the swelling behavior of gelatin/montmoril-

lonite (MMT) hybrid nanocomposites, and intercalation with MMT significantly suppressed the swelling of the gelatin matrix.¹⁰ As an extension, this article discusses the swelling behavior of gelatin-g-poly(butylacrylate) (gelatin-g-PBA) copolymers and gelatin-g-PBA/MMT nanocomposites. In addition, the swelling kinetics of gelatin graft copolymers are investigated.

EXPERIMENTAL

Materials

Gelatin (type B, extracted from bovine skin) was purchased from Sigma Chemical Co. (St. Louis, MO). Butyl acrylate (BA; analytical-grade; Tianjin Chemical Reagent Institute, Tianjin, China) was purified in a manner reported earlier.⁵ Potassium persulfate ($K_2S_2O_8$; analytical-grade; Kemi'o Co., Ltd., Tianjin, China) was used as received. Sodium MMT (particle size = 40 μm) was supplied by Huate Chemical Co. (Zhejiang, China). Glutaraldehyde (GLA; used as a crosslinking agent) was provided by Tiantai Fine Chemical Co. (Tianjin, China). The composition of the phosphate-buffered solution (PBS) was as follows: NaCl, 140 mM; KCl, 3 mM; Na_2HPO_4 , 8.1 mM; and KH_2PO_4 , 1.5 mM (pH 7.2). All the reagents constituting the PBS were analytical-grade.

Preparation of gelatin-g-PBA copolymers

Gelatin powder (1 g) was soaked in 50 mL of deionized water and heated to 40°C to obtain a homogeneous solution. Then, the solution was poured into a four-necked, round-bottom, 100-mL flask placed in a constant-temperature water bath, stirred, and bubbled

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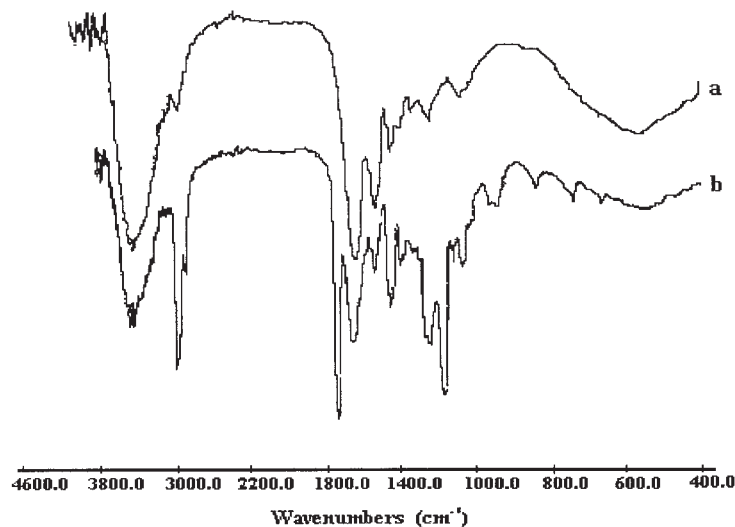


Figure 1 FTIR spectra of (a) pure gelatin and (b) gelatin-g-PBA copolymer.

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 BA was added dropwise. After 45 and 60 min, the reaction flask was immersed in a freezing mixture to stop the reaction. Then, 10 mL of 0.25% GLA was slowly added to 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.

Preparation of gelatin-g-PBA copolymer/MMT nanocomposites

After the graft copolymerization, the solution was stirred, and the temperature was raised to 70°C . Then, 20 mL of a 5 wt % MMT suspension was added dropwise to the vessel. The mixture was stirred for another 1 h. Then, the same amount of the crosslinking agent was used, and the same procedures described for the preparation of gelatin-g-PBA copolymers were followed.

Measurements

IR spectra

The IR spectra of the samples were taken with a Bio-Rad FTS3000 Fourier transform infrared (FTIR) spectrophotometer with KBr pellets. The grafted products were poured into cold acetone, and the grafted gelatin was precipitated. The products were filtered and dried *in vacuo*. The dried products were Soxhlet-extracted with acetone for 72 h. The purified graft copolymer was dried *in vacuo*.

X-ray diffraction (XRD)

To measure the change in the gallery distance of MMT before and after intercalation, XRD patterns were re-

corded at $2^\circ/\text{min}$ on a Japan Rigaku DMAX-RC diffractometer with Cu $K\alpha$ radiation ($\lambda = 0.154 \text{ nm}$) at a generator voltage of 50 kV and a generator current of 180 mA.

Swelling studies

Swelling studies were determined according to a procedure reported earlier.¹⁰

RESULTS AND DISCUSSION

Characterization of the grafted copolymers

Grafting is generally verified by the FTIR spectra of grafted polymers.^{6,7} The FTIR spectra of the pure gelatin and copolymer are shown in Figure 1. The spectrum of the gelatin-g-PBA 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 BA. Therefore, the formation of the graft copolymer has been confirmed.

Effect of the reaction parameters on the swelling behavior

Monomer concentration

The swelling curves of the copolymers with various monomer concentrations are shown in Figure 2. With an increase in the monomer concentration, the equilibrium swelling degree decreases dramatically and then increases slightly. As the amount of the monomer for grafting increases with increasing monomer concentration, G% increases,⁷ and the equilibrium swelling degree decreases. When the monomer concentration increases further, too many hydrophobic monomer molecules may bury the growing macroradicals;

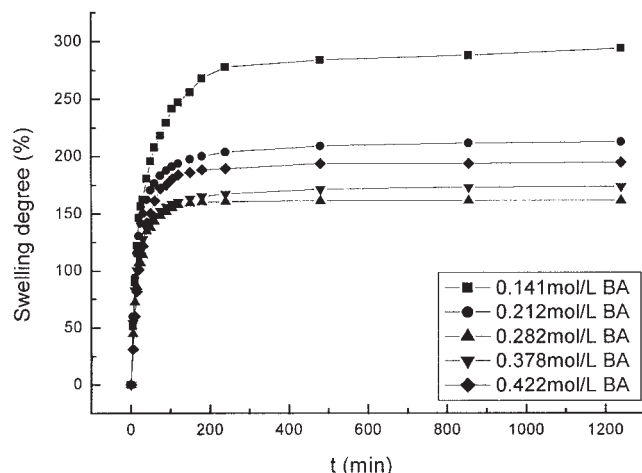


Figure 2 Swelling curves of copolymers with various monomer concentrations.

this hinders the graft copolymerization and leads to an increase in the equilibrium swelling degree.

Initiator concentration

The effect of the initiator concentration is plotted in Figure 3: the equilibrium swelling degree first decreases and then increases with a further increase in the $K_2S_2O_8$ concentration. The decreasing trends of the equilibrium swelling degree may be attributed to the fact that, because both gelatin and $K_2S_2O_8$ are water-soluble, at lower initiator concentrations, the initiator prefers to approach gelatin macromolecular chains rather than the hydrophobic monomer in aqueous media. Therefore, $K_2S_2O_8$ was mainly used to initiate the gelatin macromolecules, forming a great number of grafting sites on the gelatin chains. On the other hand, at lower initiate concentrations, the reaction is mostly terminated by the recombination of double

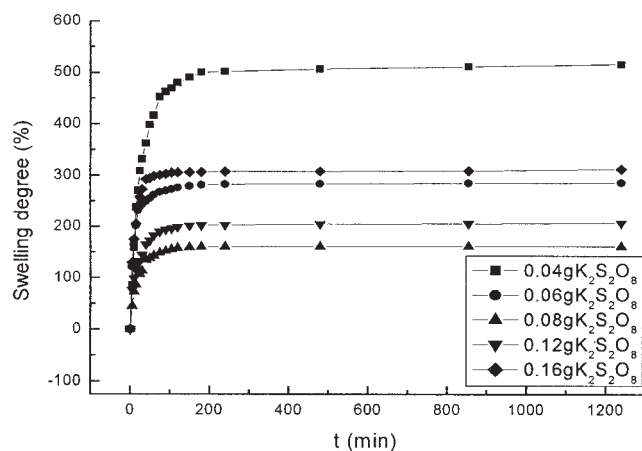


Figure 3 Swelling curves of copolymers with various $K_2S_2O_8$ concentrations.

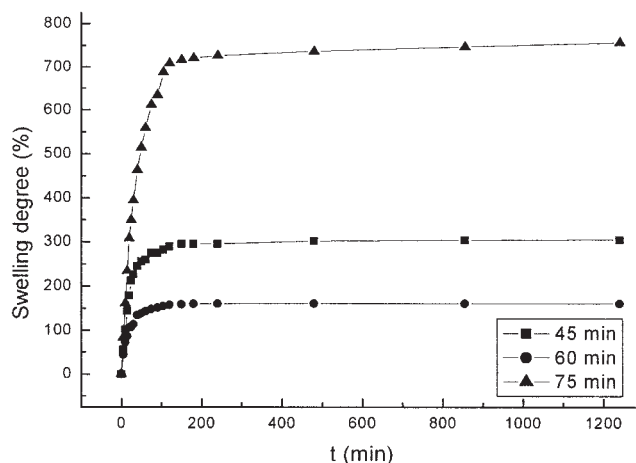


Figure 4 Swelling curves of copolymers with various reaction times.

radicals, so that $G\%$ increases with increasing $K_2S_2O_8$ concentration.⁵

However, at higher $K_2S_2O_8$ concentrations, the number of primary radicals, gelatin macromolecular radicals, and grafting side-chain radicals increases, and 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 result, $G\%$ was lowered,⁵ and the equilibrium swelling degree increased.

Reaction time

Figure 4 shows the swelling curves of the copolymers with various reaction times. The decrease in the equilibrium swelling degree with time can be explained by the increase in the number of grafting sites on the gelatin chains in the initial stages of the polymerization. Misra et al.¹¹ reported that $G\%$ had a maximum versus the reaction time. Therefore, the equilibrium swelling degree decreased. With the prolongation of the reaction time, more chain-transfer and chain termination processes occurred, and this led to an increase in the equilibrium swelling degree.

Reaction temperature

Figure 5 shows the swelling curves of copolymers prepared at 45 and 60°C. Within a specific range, a high temperature benefits the formation of primary radicals and the initiation reaction of gelatin. Raising the temperature increased the rate of graft copolymerization and $G\%$.⁵ Moreover, the lower equilibrium swelling degree may also be attributed to the increasing solubility of the monomer in the aqueous phase at higher temperatures, which increased the possibility

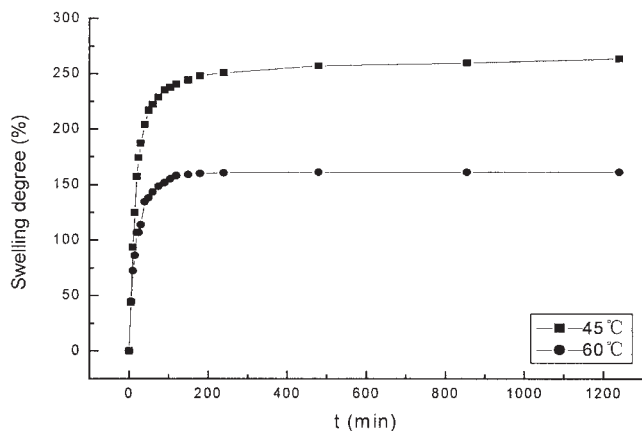


Figure 5 Swelling curves of copolymers with various reaction temperatures.

of the monomer coming into contact with gelatin macromolecules.

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

Gelatin/MMT hybrid nanocomposite can be successfully prepared,¹² and intercalation with MMT can significantly reduce the equilibrium swelling degree from 778% of pure gelatin to 315%.¹⁰ To investigate the intercalation of graft copolymers with MMT, we show the XRD patterns of pristine MMT and gelatin-g-PBA/MMT composite in Figure 6. Pristine MMT exhibits a sharp peak at $2\theta = 6.0^\circ$, and through Bragg's equation, $\lambda = 2d \sin \theta$, d_{001} is 1.47 nm. The XRD pattern of the composite changes dramatically in comparison with that of pristine MMT. The d_{001} diffraction peak shifts toward lower angles at $2\theta = 2.2^\circ$ ($d_{001} = 4.01$ nm). The result indicates that the grafted gelatin chains could still intercalate into the galleries of MMT, and the gelatin-g-PBA/MMT intercalated nanocomposite was formed.

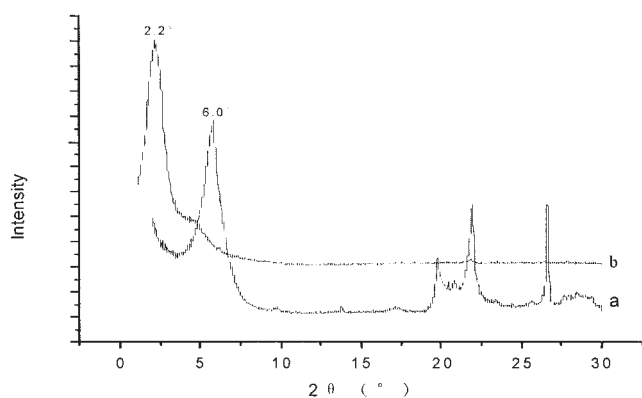


Figure 6 XRD patterns of (a) pristine MMT and (b) gelatin-g-PBA/MMT nanocomposite.

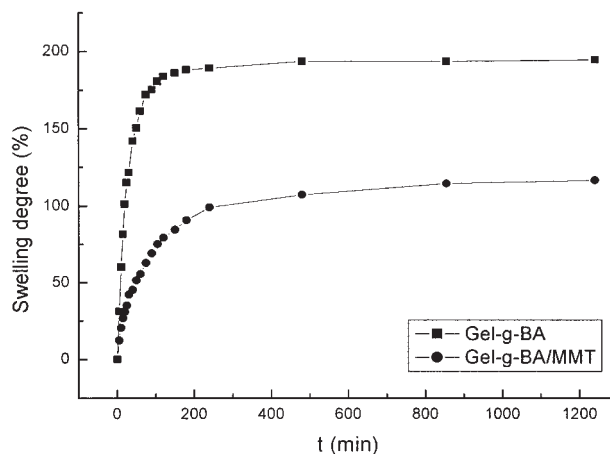


Figure 7 Swelling curves of gelatin-g-PBA copolymer and gelatin-g-PBA/MMT nanocomposite.

Figure 7 displays the swelling curves of the gelatin-g-PBA copolymer and gelatin-g-PBA/MMT nanocomposite. Intercalation with MMT further reduced the equilibrium swelling degree of the graft copolymer from 190 to 120%. The nanodispersion of MMT in the gelatin matrix and the barrier effect of MMT sheets to the solvent molecules suppressed the swelling of the gelatin network. Meanwhile, MMT sheets interacted with hydrophilic groups of gelatin such as $-\text{NH}_3^+$ and $-\text{COO}^-$, weakening their hydration.

Swelling kinetics of the gelatin graft copolymers

The swelling kinetics of gelatin have 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 copolymers has been reported yet.

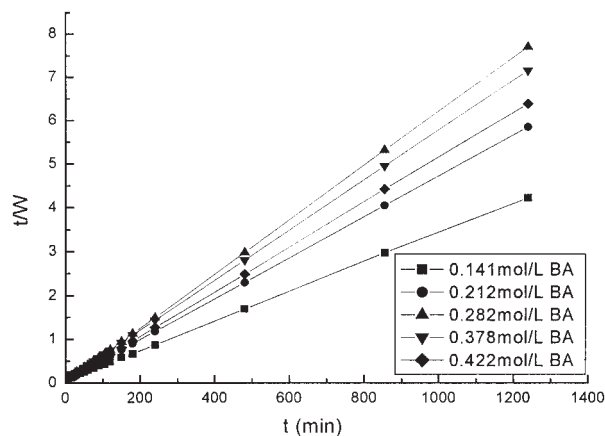


Figure 8 Linear regression of the swelling curves of Figure 2 according to eq. (2).

TABLE I
 W_∞ and K_∞ of Graft Copolymers with Various Monomer Concentrations

[BA] (mol/L)	A	B	W_∞	K_∞
0.141	0.08322	0.00334	299.40	3.466
0.212	0.05996	0.00466	214.39	4.084
0.282	0.05193	0.00614	162.87	4.388
0.378	0.06342	0.00571	175.27	3.971
0.422	0.07726	0.00505	198.02	3.598

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

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

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

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

where A and B are the intercept and slope of plots of t/W versus t , respectively (i.e., $A = 1/K_\infty^2$ and $B = 1/W_\infty$). The swelling data of Figure 2 were calculated according to eq. (2), and the results are shown in Figure 8. Figure 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 eq. (2). These data are listed in Table I. With an increase in the monomer concentration, W_∞ decreased to a minimum and then increased. However, K_∞ reached a maximum at this monomer concentration. This indicates that

grafting with BA can not only suppress the swelling of gelatin but also increase the rate of reaching the equilibrium swelling of gelatin.

CONCLUSIONS

In this study, gelatin-g-PBA copolymers were prepared, and the swelling behavior was investigated. Copolymerization with hydrophobic monomer BA significantly reduced the swelling degree of the gelatin matrix. Moreover, like those of pristine gelatin, the swelling kinetics of the graft copolymers followed a second-order equation. The graft copolymerization did not change the swelling kinetics of the gelatin matrix. In addition, the graft copolymer could still intercalate into the galleries of MMT and form nanocomposites. Intercalation with MMT further suppressed the swelling of the graft copolymer because of the barrier effect of MMT.

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