Gelatin/Montmorillonite Hybrid Nanocomposite. II. Swelling Behavior

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ABSTRACT: Gelatin/montmorillonite (MMT) hybrid nanocomposites with improved thermal and mechanical properties were prepared in a previous work. The swelling behavior (swelling rate, swelling kinetics, maximum solvent uptake, etc.) of the obtained composites was investigated. The results showed that the swelling process of the composites followed second-order kinetics identical to those of the original gelatin. The swelling rate and maximum solvent uptake were greatly suppressed by the presence of MMT and were dependent on the MMT content and pH of the gelatin matrix. Moreover, the swelling mechanism of the polyelectrolyte-intercalated nanocomposites was examined. © 2003 Wiley Periodicals, Inc. J Appl Polym Sci 88: 322–326, 2003

Key words: nanocomposites; swelling behavior; gelatin; montmorillonite

INTRODUCTION

Gelatin is an amphoteric polyelectrolyte with plenty of —NH_2 and —COOH in its molecular chains. The crosslinked gelatin network shows high water absorption and quick degradation that are suitable for releasing systems[1,2] and wound dressings[3] 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. There are few reports about suppressing the swelling of gelatin, and the results have not been satisfactory.[4] Wan et al.[5] studied the suppression effect of continuous carbon fibers on gelatin swelling and received good results. Nevertheless, the structure of continuous carbon fibers can exert only a one-dimensional barrier effect for the diffusion of solvent molecules. In addition, there exist various extents of capillary action. Accordingly, the swelling degree of continuous-carbon-fiber-reinforced gelatin composites still seems to be high. Because of the two-dimension layered structure of montmorillonite (MMT) and its excellent barrier effect for the permeation of small molecules,[6] in this article we deal with the swelling behavior of gelatin/MMT hybrid nanocomposites. Furthermore, no study on the swelling kinetics of MMT intercalated materials has been reported yet. We reported the preparation and thermal and mechanical properties of gelatin/MMT nanocomposites in the first article of this series.[7] Intercalated or partially exfoliated nanocomposite were prepared, and the thermal and mechanical properties were obviously improved. In this article, the swelling behavior of the composites is presented. In addition, the unique swelling mechanism of this system is discussed.

EXPERIMENTAL

Materials

The materials used in this study were described in the first part of this series. The gelatin, MMT, glycerol (GLY; used as a plasticizer), and dextran dialdehydes (used as crosslinking agents) were identical to those used in the former experiments. The composition of the phosphate buffer solution (PBS) was as follows: NaCl, 140 m*M*; KCl, 3 m*M*; Na_2HPO_4, 8.1 m*M*; and KH_2PO_4, 1.5 m*M* (pH 7.2). All the reagents constituting the PBS were analytical-grade.

Preparation of the gelatin/MMT nanocomposite

Gelatin powder (1 g) was soaked in 50 mL of deionized water and heated at 70°C, and a homogeneous solution was obtained (with the pH of the gelatin adjusted by a solution of HCl or NaOH). Then, the gelatin solution was added dropwise into a 2 wt % ultrasonically pretreated MMT suspension under vigorous stirring at 70°C. Gelatin powders were added to

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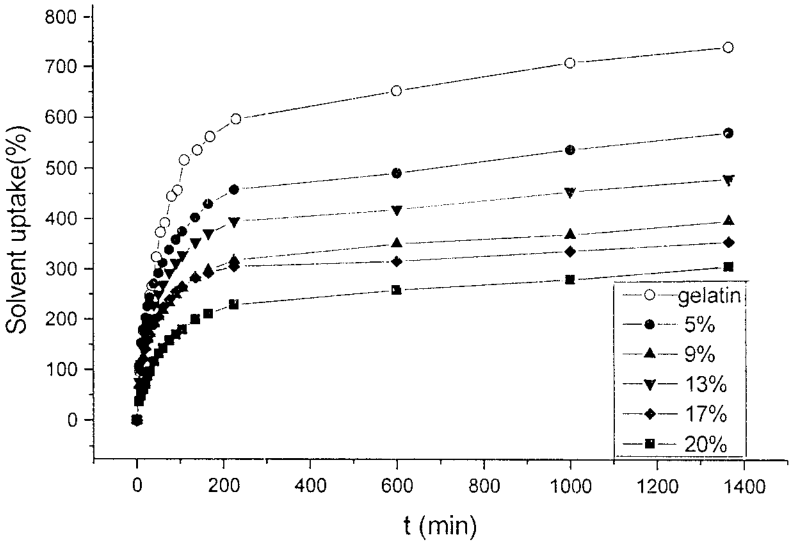

Figure 1 Swelling curves of the gelatin and composites.

the homogeneous mixture under agitation at 70°C until the gelatin concentration reached 10 wt %. Then, 0.25 g of GLY was added, the mixture was stirred for 20 min at 70°C, 10 mL of a 10% dextran dialdehyde solution was slowly added under the same conditions, 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.

Swelling studies

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 immersed in a separate 250-mL glass bottle containing 150 mL of a PBS solution at 25°C for 1000 min at most. The degradation of gelatin was assumed to be very small in this period and was neglected. The capped bottles were placed in a constant-temperature bath for the duration of the swelling experiments. At regular intervals, samples were taken out from the PBS solution, surface-blotted up 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 is usually expressed as the grams of the solvent absorbed by each gram of dry gelatin and is 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.

RESULTS AND DISCUSSION

Effect of the MMT content

The swelling kinetic curves of the composites as a function of the MMT content are shown in Figure 1. For comparison, the swelling curve of the original gelatin with identical dextran dialdehyde and GLY contents is also included in the figure. All swelling curves are characterized by two phases: fast swelling and sequential slow swelling. Furthermore, as revealed by the graphs, swelling basically decreases with increasing MMT content. According to previous research,[8] the swelling kinetics of gelatin can be described by a second-order rate equation:

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

where K is the rate constant; W_∞ represents the maximum or equilibrium solvent uptakes; and W is the solvent absorbed per gram of gelatin at time t; ($W_\infty - W$) is defined as the swelling capacity. By integration and rearrangement, eq. (1) can be rewritten as follows:[9]

$$\frac{t}{W} = A + Bt \tag{2}$$

where A and B is 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 1 were calculated according to eq. (2), and the results are shown in Figure 2. Figure 2 reveals that straight lines are obtained by linear regression, and this means that the swelling processes of the gelatin and the composites

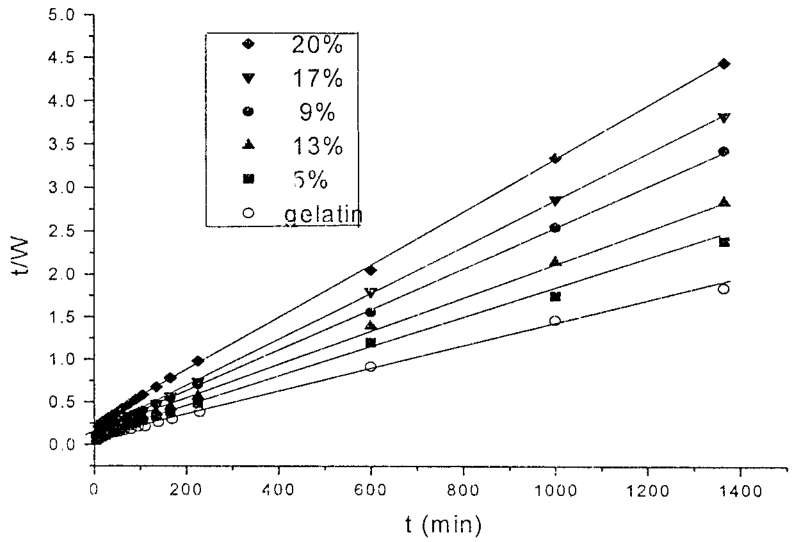

Figure 2 Linear regression of the swelling curves of Figure 1 according to eq. (2).

follow second-order kinetics. This suggests that the incorporation of MMT 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. W_∞ and K_∞ of the composites greatly decrease in the presence of MMT in comparison with those of the original gelatin, and the basic trend is that W_∞ and K_∞ decrease as the MMT content increases. This indicates that intercalation with MMT can not only improve the thermal and mechanical properties but also effectively hinder the swelling of gelatin.

Abnormal phenomena around MMT concentrations of 9 and 13 wt % may be ascribed to the unique swelling mechanism of this system. Even though extensive research has been conducted on the swelling of pure gelatin material,[10–12] a study on the swelling behavior of gelatin/MMT intercalated composites has not been reported yet. It can be expected that the swelling mechanism of composites will be different from that of pure gelatin because of the presence of MMT. It is well known that the swelling process depends considerably on the structure of the polymer network and is governed by the collective diffusion of polymer and solvent molecules.[10] According to this theory, the structure of the original gelatin network changes because of the incorporation of MMT. Consequently, there are two opposite effects of MMT on the swelling of the gelatin matrix. On the one hand, the interaction between gelatin and MMT consumes some of —NH_2 of gelatin molecular chains, and this reduces the reactive sites for crosslinking; the dispersed MMT sheets hinder the formation of the gelatin crosslinking network. As a result, the degree of chemical crosslinking decreases with the increase in the MMT content. On the other hand, the presence of MMT also serves as physical crosslinking sites, which enhance the stability of the network. Meanwhile, the strong interaction between gelatin molecular chains and MMT sheets consumes some hydrophilic groups and depresses the solvent uptake through capillary action at the interface. The most important reason is that the nanodispersion of MMT sheets in the composite impede the diffusion of the solvent molecules. The motion model of solvent molecules in a matrix containing layered barrier fillers is consistent with that of gas permeability. According to a model of gas permeability,[6] if a plate of length *L* and thickness *W* is dispersed parallel in a polymer matrix, the tortuosity factor τ is given by eq. (3):

$$\tau = 1 + (L/2W)V_f \tag{3}$$

where V_f represents a volume fraction of a plate. The relative permeability coefficient (P_c/P_p, where P_c and P_p are permeability coefficients of the composite and polymer matrix, respectively) is given by eq. (4):

$$P_c/P_p = 1/[1 + (L/2W)V_f] \tag{4}$$

TABLE I
W_∞ and K_∞ of Gelatin and Composites with Various MMT Contents

MMT content (wt %)	*A*	*B*	W_∞	K_∞
0	0.0512	0.00128	778	4.419
5	0.0723	0.00166	599	3.719
9	0.0839	0.00245	407	3.452
13	0.0784	0.00188	529	3.571
17	0.0929	0.00265	376	3.281
20	0.116	0.00304	328	2.936

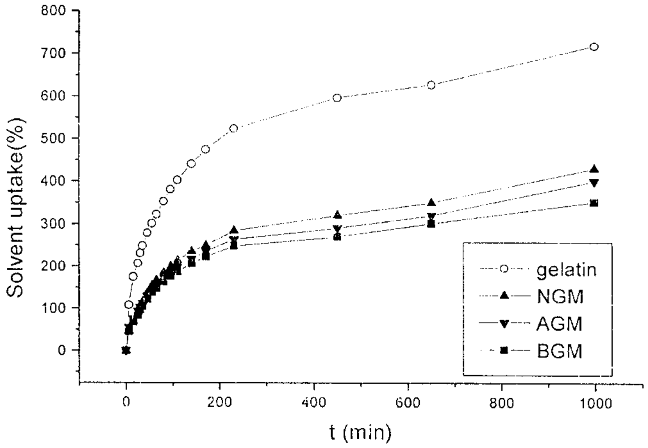

Figure 3 Swelling curves of the gelatin and composites with various pHs of the gelatin matrix.

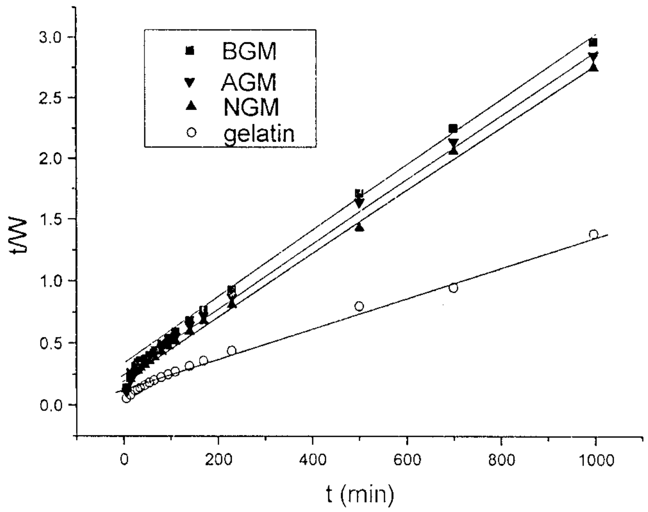

Figure 4 Linear regression of the swelling curves of Figure 3 according to eq. (2).

According to eq. (4), P_c/P_p should become smaller as the length of the plate becomes longer. MMT is a clay mineral about 200 nm long and 1 nm thick. Therefore, L/W is very large and leads to a small value of P_c/P_p. It is reasonable to think that the sheets of MMT suppress the dispersion of solvent molecules.

Therefore, the suppression of the swelling is mainly ascribed to the barrier effect of MMT. Meanwhile, the results also reflect that the swelling process of the gelatin/MMT composite is complicated.

Effect of pH of the gelatin matrix

Figure 3 displays the swelling curves of composites with various pHs of the gelatin matrix, that is, just below, equal to, and above the isoelectric point (pI), which are denoted AGM, NGM, and BGM, respectively. Samples composed of 20% MMT (by mass) were used. For comparison, the swelling curve of the original gelatin is also included in the figure. All three composites show much lower swelling rates and maximum solvent uptakes than the original gelatin. Meanwhile, they vary with one another. The swelling rate and maximum solvent uptake are lowered in the following order: BGM, AGM, and NGM. Linear regression results of Figure 3, based on eq. (2), are shown in Figure 4. Similar to that of the original gelatin, the swelling behavior of composites with various pHs of the gelatin matrix also agrees with second-order kinetics, which are not influenced by the pH of the gelatin matrix. The corresponding W_∞ and K_∞ data are listed in Table II. The data for BGM, AGM, and NGM are different. This result may be due to the different interactions between MMT and gelatin with various pHs. Gelatin is an amphoteric polyelectrolyte with a pI equal to 5.05, which abounds with —NH_2 and —COOH in its molecular chains. For pH < pI, there is more —NH_3^+ in the chains that can bind with MMT through static electric interactions and intercalate into MMT interlayers. For pH > pI, there is more —COO^- in the chains that coordinates with MMT sheets. For pH = pI, the ionization degree of gelatin is relatively lower, and there are small amount of active —NH_3^+ and —COO^- interacting with MMT. The weak bond strength between MMT layers and gelatin chains leads to a higher swelling rate and a maximum solvent uptake of NGM. As for AGM, a large amount of —NH_2 for crosslinking with —CHO of the crosslinking agent is protonized, and this results in a decrease in the degree of crosslinking. Therefore, the swelling rate and maximum solvent uptake are higher than those of BGM. In other words, MMT can exert a better effect on suppressing the swelling of an alkaline gelatin matrix.

CONCLUSIONS

In this study, the swelling behavior of gelatin/MMT hybrid nanocomposites was investigated. Like those of the pristine gelatin, the swelling kinetics of the composites follow a second-order equation. The incorporation of MMT does not change the swelling kinetics of the gelatin matrix. Intercalation with MMT can significantly slow down the swelling rate and reduce the maximum solvent uptake of the gelatin matrix. The basic trend is that W_∞ and K_∞ decrease as the MMT content increases, and this is mainly due to the barrier effect of MMT. Meanwhile, the results also

TABLE II
K_∞ and W_∞ of Gelatin and Composites with Various pHs of the Gelatin Matrix

	gelatin	AGM	NGM	BGM
K_∞	4.382	3.279	3.447	2.931
W_∞	763	374	389	322

reflect that the swelling process of the gelatin/MMT composites is complicated. The composites, with various pHs of the gelatin matrix, also agree with second-order kinetics. They exhibit different swelling rates and maximum solvent uptakes under the same conditions, and this is ascribed to the different interactions between MMT and gelatin in various pH states.

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References

1. Akin, H.; Hasirci, N. J Appl Polym Sci 1995, 58, 95.
2. Welz, M. M.; Ofner, C. M. J Pharm Sci 1992, 81, 85.
3. Draye, J. P.; Delaey, B.; Voorde, A. V. D.; Bulcke, A. V. D.; Reu, B. D.; Schacht, E. Biomaterials 1998, 19, 1677.
4. Lin, F. H.; Yao, C. H.; Sun, J. S.; Liu, H. C.; Huang, C. W. Biomaterials 1998, 19, 905.
5. Wan, Y. Z.; Wang, Y. L.; Luo, H. L.; Cheng, G. X.; Yao, K. D. J Appl Polym Sci 2000, 75, 994.
6. Yano, K.; Usuki, A.; Okada, A. J Polym Sci Part A: Polym Chem 1997, 35, 2289.
7. Zheng, J. P.; Li, P.; Ma, Y. L.; Yao, K. D. J Appl Polym Sci 2002, 86, 1189.
8. Robinson, I. D. Photogr Sci Eng 1964, 8, 220.
9. Katime, I.; Velada, J. L.; Novoa, R.; Apodaca, E. D.; Puig, J.; Mendizabal, E. Polym Int 1990, 40, 281.
10. Klepko, V. V.; Yu, B. M. Polymer 1995, 36, 5057.
11. Xie, W. B.; Valleton, J. M. J Membr Sci 1991, 64, 113.
12. Rathna, G. V. N.; Rao, D. V. M.; Chatterji, P. R. Macromolecules 1994, 27, 7920.