Carbon Fiber-Reinforced Gelatin Composites. II. Swelling Behavior

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ABSTRACT: Carbon fiber-reinforced gelatin composites have been prepared in our laboratory to obtain a novel biomaterial of improved mechanical properties. The swelling behavior (swelling rate, swelling kinetics, maximum solvent uptake, etc.) for both continuous carbon fiber-reinforced gelatin composite (C_I/Gel) and short carbon fiber-reinforced gelatin composite (C_S/Gel) are investigated. Experimental data show that the swelling process of the original gelatin and gelatin matrixes in both composites follows a second-order kinetics. The swelling of the gelatin matrixes in both composites proceeds slower than that of the pristine gelatin, and depends on fiber form and fiber volume fraction (Vf). Results indicate that the presence of carbon fibers suppresses the swelling of the gelatin matrixes in both composites. It is found that the gelatin matrix in C_S/Gel possesses a smaller swelling rate and maximum solvent uptake than that in C_I/Gel. A mechanism governing these phenomena is discussed in this article. © 2000 John Wiley & Sons, Inc. J Appl Polym Sci 75: 994–998, 2000

Key words: gelatin; carbon fiber; composite; swelling behavior

INTRODUCTION

Gelatin is an abundant and high molecular-weight polypeptide derived from collagen and with relatively low cost. It has been used in a variety of fields including photography, drug delivery, holography, microencapsulation, and food preparation.[1] Gelatin is also a promising structural biomaterial. As a biomaterial, gelatin does not show antigenity and toxicity, and can be completely resorbed *in vivo*. It is found that its physicochemical properties can be suitably modulated.[2] Several studies have elucidated that mechanical properties of gelatin can be improved and adjusted.[3–6] Recently, composites composed by gelatin and inorganic materials, such as tricalcium phosphate and hydroxyapatite, have been reported.[2,7] We have reported the preparation of gelatin-based composites reinforced, respectively, with chopped (short) and continuous (long) carbon fibers in the first part of this series of articles,[8] where the emphasis has been given to the mechanical properties of gelatin-based composite, as a function of fiber volume fraction (*Vf*), gelatin content, and plasticizer content. The long carbon fiber gelatin composite (denoted by C_I/Gel) had the tensile strength of 198 MPa at 0.15 fiber loading, which is the highest strength for gelatin-based material reported until now; the short carbon fiber gelatin composite (denoted by C_S/Gel) had the tensile strength of 70 MPa at 0.094 fiber loading. It is possible to improve their properties further via fiber surface modification. As far as the mechanical properties are concerned, these composites are promising as an alternative to osteosynthetic devices. The swelling of the composites, however, is a remaining problem that needs to be overcome before clinical applications. When gelatin-based composites are used as structural

parts, especially as implants *in vivo*, swelling should be suppressed because changes in dimensions of structural parts are not permitted in some circumstances such as bone fixation devices. Moreover, swelling is often accompanied with reduction in mechanical properties. As a result, this article deals with the swelling behavior of these composites.

The swelling of hydrogel depends on several factors such as crystallinity, crosslinking density, molecular weight, and hydrophilicity, pH, temperature, and ionic strength.[9–14] Even though considerable research has been conducted on gelatin or gelatin-based blends, studies on swelling behavior of carbon fiber gelatin composites have not been reported yet. In this part, the swelling behavior of C_L/Gel and C_S/Gel is presented. Indeed, desirable strength retention or biodegradation rate is another important requirement, which will be investigated later. It is the goal of this series of articles to evaluate their mechanical properties, physicochemical properties and biocompatibility, and finally to determine whether the composites can be used in clinical applications as implantable parts or devices.

EXPERIMENTAL

Materials

The details of materials used in this study, their properties are given in the first part of this series of articles.[8]

The gelatin granules, glycerol (GLY, the plasticizer), and glutaraldehyde (GLA, 50% w/w, the crosslinking agent) were identical to those used in the former experiment. The composition of the phosphate buffer solution(PBS) was the following: NaCl, 140 mM; KCl, 3 mM; Na_2HPO_4, 8.1 mM; KH_2PO_4, 1.5 mM; pH = 7.2.

All reagents comprising the PBS were of analytical grade.

Preparation of the Gelatin Solution

The gelatin was soaked in deionized water at room temperature for 2 h. The mixture was then heated to 60–70°C until a homogenous solution was obtained. GLY was added via a syringe, followed by adding of GLA. After the addition of GLA, the solution was mixed vigorously to obtain a homogenized solution in which the GLA, GLY,

and gelatin concentrations were kept to be 0.0125, 0.5, and 20% by weight, respectively.

Composite Fabrication

The C_L/Gel was produced by a solution impregnation technique, while the C_S/Gel was obtained with solvent casting method. The composite plates are fabricated according to the method reported elsewhere.[8]

Swelling Studies

All 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 PBS solution at 27°C for 180 min at most. Degradation of gelatin was assumed to be very small in this period, and was neglected. The capped bottles were placed at a constant temperature bath for the duration of the swelling experiments. At regular intervals, samples were taken out from the PBS solution with a self-made strainer, wiped dry using a 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 solvent absorbed by per gram of dry gelatin and determined by the weight equation:

$$W = \frac{m - m_0}{m_0} \times 100\% \qquad (1)$$

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

For simplifying, swelling for the composites was normalized with respect to the gelatin matrix which was expressed as:

$$W = \frac{m_c - m_{c,0}}{m_{m,0}} \times 100\% \qquad (2)$$

where the subscripts m and c stand for gelatin matrix and composites, respectively.

RESULTS AND DISCUSSION

Swelling Kinetics

Typical swelling kinetic curves as a function of Vf for C_L/Gel and C_S/Gel are shown in Figures 1 and
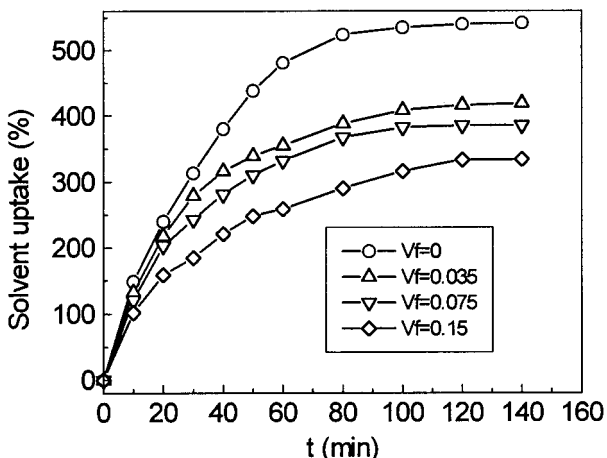
Figure 1   Swelling curves of gelatin matrix in C_L/Gel of different *Vf*.

2, respectively. For comparison, the swelling curve of the original gelatin with identical GLA and GLY contents is also included in the two figures. All swelling curves are characterized by two phases: fast swelling and sequential slow swelling. Furthermore, as revealed by the two graphs, swelling is appreciably controlled by *Vf* for both C_L/Gel and C_S/Gel. The details will be discussed below.

Linear Regression of Swelling Data

Swelling can be described in terms of rate and of maximum uptake at equilibrium, W_∞. An earlier investigation indicated that the rate of swelling of gelatin could be described by a second-order rate
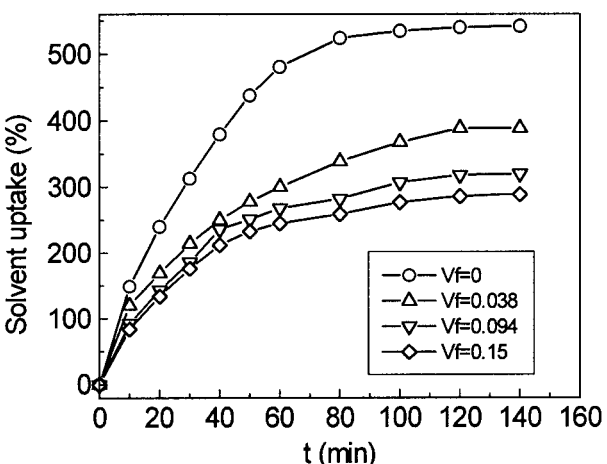

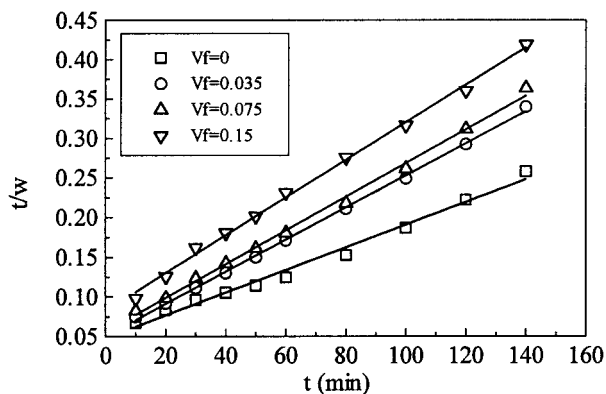**Figure 2**   Swelling curves of gelatin matrix in C_S/Gel of different *Vf*.

Figure 3   Linear regression of the swelling curves of Figure 1 according to eq. (4).

equation.[15] In light of this, the rate of swelling at any time is directly proportional to the quadratic of the swelling capacity before reaching the maximum or equilibrium uptake, W_∞. The swelling capacity is defined as $W_\infty - W$, where W is the solvent absorbed by per gram gelatin at time t. The equation can be expressed as:

$$\frac{dW}{dt} = K(W_\infty - W)^2 \tag{3}$$

where K is the rate constant. By integration and rearranging, eq. (3) can be written as:[16]

$$\frac{t}{W} = A + Bt \tag{4}$$

where A and B is the intercept and slop of plots of t/W vs. t. $A = 1/K_\infty^2$ and $B = 1/W_\infty$.

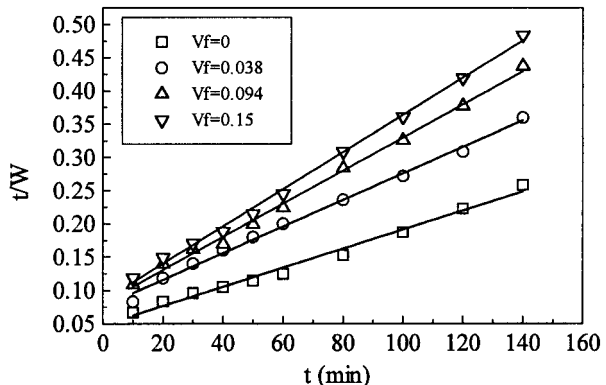Figures 3 and 4 reproduce the swelling data of

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

Figures 1 and 2, calculated according to eq. (4). The straight lines are obtained by linear regression. The agreement between the experimental points and the regression lines is satisfactory, confirming the validity of eq. (4).

The constants A, B, and the corresponding K_∞ and W_∞ can be calculated by means of eq. (4). The effects of Vf and fiber form on K_∞ and W_∞ are discussed below.

Effect of Vf

Figure 5 shows K_∞ as a function of Vf for the gelatin matrixes in C_L/Gel and C_S/Gel. As can be seen, the original gelatin exhibits a much higher K_∞ than the gelatin matrixes do, indicating incorporation of carbon fibers into the gelatin can greatly decrease its swelling rate. Moreover, K_∞ decreases as Vf increases. That is, the swelling process is slower (lower K_∞) at higher Vf values for the two composites. This suggests that carbon fibers, either short fibers or continuous fibers, incorporated into the gelatin can hinder its swelling.

It is well known that the swelling process depends considerably on the structure of polymer network and is governed by the collective diffusion of polymer and solvent molecules.[17] It is easy to understand that the presence of carbon fibers acts as the barriers for molecular diffusion of gelatin and solvent.

It should be stated here that the capillary action may not be excluded in swelling process of the composites because the kinetics of swelling can also be treated from the sorption point of view. In this case, the sorption process is not only a diffusion of the solvent molecules into void spaces of the gelatin network, but includes a dif-
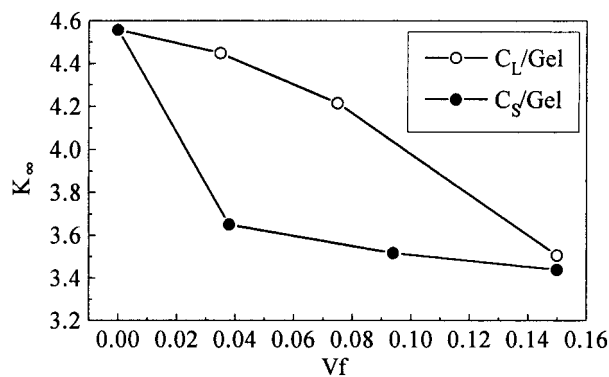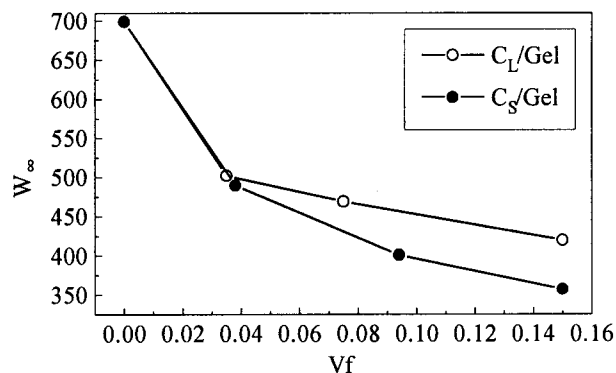
Figure 6 W_∞ as a function of Vf for gelatin matrixes in C_L/Gel and C_S/Gel.

fusion of the solvent molecules through the fiber/gelatin interfaces. Contrary to the hindrance effect of the carbon fibers, which slows down the swelling process, the capillary action is expected to result in an increase in swelling rate, and therefore, lead to an enhancement in K_∞. Consequently, the overall raising trend in K_∞ with Vf suggests that the hindrance effect dominates the swelling process of the composites. As capillary action is directly related to interfacial adhesion, it is reasonable to predict that interfacial bonding will affect the swelling process of the composites. The details are currently under investigation.

The maximum solvent uptake, W_∞, as a function of Vf for the two composites is shown in Figure 6. Included for the purpose of comparison is a curve of the original gelatin. Similar to K_∞, W_∞ is also found to be inversely proportional to the Vf of the composites. Obviously, the pristine gelatin is observed to have a much higher (ca. 700%) maximum solvent uptake. The decrease in W_∞ with Vf cannot be ascribed to the fact that carbon fibers can not swell because the swelling of the composites is normalized to the gelatin matrixes. This dependence of W_∞ on Vf may be due mainly to the hindrance effect of the carbon fibers.

Effect of Fiber Form

There are considerable differences in the values of K_∞ and W_∞ for identical gelatin matrixes in two different composites; although, their K_∞ against Vf and W_∞ vs. Vf curves exhibit a similar trend (see Figs. 5 and 6). It is interesting to note that the gelatin matrix in C_S/Gel samples shows lower K_∞ and W_∞ compared to its counterpart in C_L/Gel. This reflects that the fiber form exerts a great effect on swelling behavior of carbon fiber gelatin

Figure 5 K_∞ as a function of Vf for gelatin matrixes in C_L/Gel and C_S/Gel.

composites, and indicates short carbon fibers can more effectively restrict the swelling of the gelatin matrix when compared to continuous carbon fibers on the basis of the mechanism proposed above. The differences can be attributed to the difference of their structures. The short carbon fibers embedded in the gelatin have three-dimensional structures that hinder the swelling of the gelatin matrix in all directions, while the long fibers in C_L/Gel can restrict the swelling in only the radial direction. In other words, the complex orientation distribution and/or a wide fiber length distribution in C_S/Gel can give rise to discontinuity of the diffusion path in the gelatin matrix. Another reason why the gelatin matrix in C_S/Gel has lower K_∞ and W_∞ is because capillary action in the short carbon fiber composite is less significant compared with the continuous carbon fiber composite due to the discontinuity of a fiber/gelatin interface in the short fiber composite.[18] In C_L/Gel, the continuous fibers serve to wick solvent into the specimen through the fiber/gelatin interface, which increases the swelling rate. In the case of C_S/Gel, the discontinuous arrangement of the fibers make it less vulnerable to wicking. Thus, the short fibers embedded in the gelatin matrix lead to less increase in K_∞ in comparison to continuous fibers.

Our experimental results suggest that C_S/Gel demonstrates swelling characteristics superior to C_L/Gel because quicker swelling and higher W_∞ often means quicker deterioration of the composites. This is in contrast to the mechanical properties presented in the first part,[8] where C_L/Gel exhibited better mechanical behavior than C_S/Gel did.

We should stress here that the swelling of fiber composites is complicated, and there are no reports in the literature regarding the swelling mechanisms of fiber composites. Therefore, this mechanism may be considered only as a possible or partial mechanism. A deeper investigation is needed to conclude a more exact mechanism.

CONCLUSIONS

1. Like the pristine gelatin, the swelling kinetics of gelatin matrixes in carbon fiber composites follows a second-order equation.
2. Incorporation of carbon fibers into gelatin makes a contribution to slow down its swelling rate and reduce its maximum solvent uptake, W_∞. The contribution is found to increase with enhancing Vf for both C_S/Gel and C_L/Gel. This characteristic makes it possible to control the swelling of the gelatin composites, and will be useful in the development of implantable devices.
3. The gelatin matrix in C_S/Gel exhibits smaller swelling rate (smaller K_∞) and W_∞ than that in C_L/Gel. This indicates that the fiber form can influence the swelling process of the composites, and short carbon fibers can more effectively restrict the swelling of the gelatin matrix compared to continuous ones.

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