

Carbon Fiber-Reinforced Gelatin Composites.

I. Preparation and Mechanical Properties

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ABSTRACT: Composites were made from carbon fibers and gelatin using a solvent-casting or solution-impregnation technique. Relationships between the fiber volume fraction (V_f), glycerol (plasticizer) content, gelatin content, fiber form, and mechanical properties (tensile strength and modulus, elongation at break, and shear strength) of the composites were investigated. In long carbon fiber gelatin composite (C_L /Gel), tensile strength, modulus, and shear strength increased steadily with the V_f . In the case of a short carbon fiber gelatin composite (C_S /Gel), an initial improvement in tensile strength and modulus was followed by a reduction, whereas the shear strength improved with the V_f and then reached a constant value. The elongation decreased with the V_f for both composites. It is shown that C_L /Gel had higher values of strength, modulus, and elongation than did C_S /Gel at any V_f level. The effects of glycerol and gelatin contents on the mechanical properties of the composites were found to be much less significant as compared to the V_f . According to scanning electron microscopic observation of the fracture surfaces, the fibers were uniformly distributed in the gelatin matrix, but the interfacial adhesion between the gelatin matrix and the carbon fibers was not very good for both composites. Fiber surface modification would be necessary to further improve the mechanical properties of the two composites. © 2000 John Wiley & Sons, Inc. *J Appl Polym Sci* 75: 987–993, 2000

Key words: gelatin; carbon fiber; composites; mechanical properties

INTRODUCTION

In recent years, an increasing interest in biodegradable polymers has been observed in biomedical or environmental engineering applications. Polylactide (PLA) and poly(glycolic acid) (PGA) are typical biodegradable materials that are used in controlled-release systems or internal-fixation devices for bone fracture in developed countries. Nevertheless, the complex synthesizing processes and, therefore, their high cost delayed their development in developing countries, such as in

China. Thus, biomaterials of low cost are currently being searched for in order to replace highly expansive PLA or PGA.

Gelatin, a natural-derived biopolymer, is the degradation product of structural protein collagen¹ and is readily available at low cost. Gelatin has been widely used in the food, pharmaceutical, and photographic industries.² The use of gelatin in trauma and bone surgery such as in internal-fixation screws, plates, and rods is attractive because the biopolymer is nontoxic, biodegradable, and inexpensive. Bone-fixing screws prepared from gelatin were obtained by Parkany and Horvath as early as the 1970s.³ Animal experiments proved that gelatin bone screws cannot bear the weight of the body and, therefore, cannot replace metallic screws due to their poor mechanical

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properties.⁴ Considerations of cost and environmental problems urged us to try to develop high-performance gelatin or gelatin-based materials.

A number of attempts have been made to improve their mechanical properties. Maeda and Motoyoshi prepared gelatin with a tensile strength above 100 MPa by vapor crosslinking.⁵ In other reports, unusually good mechanical properties have been obtained by an orientation technique.^{6–8} Recently, composites of ceramic powder with natural degradable polymers have attracted much interest as bone implants.^{9–11} For example, Yao et al.¹⁰ showed composite implants of formaldehyde-crosslinked gelatin and tricalcium phosphate to be osteoconductive and bioabsorbable for filling small irregular defects.

On the other hand, carbon fiber as an implant material for ligament replacement showed excellent biocompatibility and has been used successfully in a number of clinical applications.^{12–15} Combining these materials could well result in a composite with improved mechanical properties, desirable biocompatibility, and potential promising prospects for applications, for example, in orthopedic surgery as an osteosynthetic device or as a repair material for bone defects. Surprisingly, strengthening of gelatin with carbon fibers has not been reported until now.

In view of this situation, we report here a novel biomaterial—carbon fiber-reinforced gelatin composite. The presentation is split into several parts: In the first part, we present the preparation and mechanical properties of the gelatin-based composites reinforced, respectively, with continuous (long) and chopped (short) carbon fibers. The following parts will describe the swelling behavior of the composites and their influencing factors and the biodegradation rate and, eventually, evaluate whether the gelatin-based composites can be used as osteosynthetic devices (structural biomaterials).

EXPERIMENTAL

Materials

Polyacrylonitrile (PAN)-based carbon fibers were purchased from the Shanghai Xinxing Carbon Co., Ltd. (Shanghai, China). They have the following characteristics: tensile strength, 2000 MPa; tensile modulus, 196 GPa; diameter, 6–8 μm ; and density, 1.75 g/cm^3 . All fibers were used as sup-

plied in this preliminary experiment without surface modification.

Samples of gelatin granules (biochemical reagent) were supplied by Tianjin Chemicals Co. (Tianjin, China) and used as received. Glycerol (GLY, analytical grade) and glutaraldehyde (GLA, 50% w/w) were used as the plasticizer and crosslinking agent, respectively.

Preparation of the Gelatin Solution

The gelatin was soaked in deionized distilled water at room temperature for 2 h. The mixture was then heated to 60–70°C until the solution became homogeneous. Solutions with concentrations of 15, 20, 25, and 30% were obtained. GLY was added via a syringe, followed by the addition of GLA. The concentration of GLA in the final gelatin solution was 0.0125 wt %, while the concentration of GLY in the final gelatin solution varied between 0.1 and 0.5 wt %.

Composite Fabrication

C_L/Gel

The long carbon fiber gelatin composite (denoted C_L/Gel) was produced by a solution impregnation technique. The gelatin solution produced was poured into a special self-made mold where the carbon fibers were aligned parallel to each other. They were air-dried for several days and finally demolded, thus producing the C_L/Gel plates (about 2 mm in thickness). The fiber volume fraction (V_f) in the composite (with respect to the volume of the dried gelatin) can be altered by adjusting the fiber spacing. The V_f of the C_L/Gel composite was limited to 0.30 in this preliminary study since wetting of the fibers was found to be difficult at a higher fiber loading.

C_S/Gel

The short carbon fiber gelatin composite (denoted C_S/Gel) was produced by a solvent-casting method: The chopped short carbon fibers, 5 mm in length, were added to the homogeneous gelatin solution and mixed for another 60 min, followed by the addition of GLY and, finally, GLA. The resulting solution containing the short fibers was transferred into a polymer mold. The C_S/Gel plates were prepared using the same procedures as those utilized for the C_L/Gel plates. The highest V_f of C_S/Gel was not above 0.25 since a higher fiber volume fraction led to fiber entanglements

and the solution containing short fibers almost cannot flow, resulting from its higher viscosity.

Measurements

The tensile strength (σ) of the dumbbell specimens, 6.5 mm width at the straight edge, was measured at room temperature using a Shimadzu tensile testing machine (Model DSS-25T) at a crosshead speed of 5 mm/min and a gauge length of 65 mm. The tensile modulus (E) and elongation at break (ϵ) of the two composites were calculated from the load-displacement curves. The shear strength (τ) was tested on a DL-1000B materials tester using a measurement tool similar to the procedure of Majola et al.¹⁶ The dimensions of the shear specimens were $30 \times 10 \times 2$ mm. At least five specimens were tested for each set of samples and the mean values are reported. For the C_L /Gel samples, the properties were tested longitudinally.

Scanning Electron Microscope

Examination of the fracture surfaces was carried out using a Hitachi X-650 scanning electron microscope (SEM). The objective was to obtain some idea of the condition of the matrix and fiber surfaces. The fracture ends of the tensile specimens were molded on aluminum stubs and sputter-coated with a thinner layer of gold to avoid electron charging during examination.

RESULTS AND DISCUSSION

Stress–Strain Behavior

Typical tensile stress–strain curves calculated from the load-displacement curves for pure gelatin, C_L /Gel, and C_S /Gel, are shown in Figure 1. One can see that the stress–strain curve of pure gelatin exhibited a yield point, followed by a slight drop in stress and a steady plateau and, finally, by a second increase in stress, which may be due to the hardening effect, before final breaking occurred. Slight nonlinearity observed after the yield point is attributed to slight plastic deformation. It is evident from that figure that the C_L /Gel and C_S /Gel samples behaved rather similarly. For the two composites, the yield point disappeared, indicating that the presence of long or short fibers reduced the extent of plastic deformation. As expected, at any particular strain level, incorporation of either short or long carbon fibers

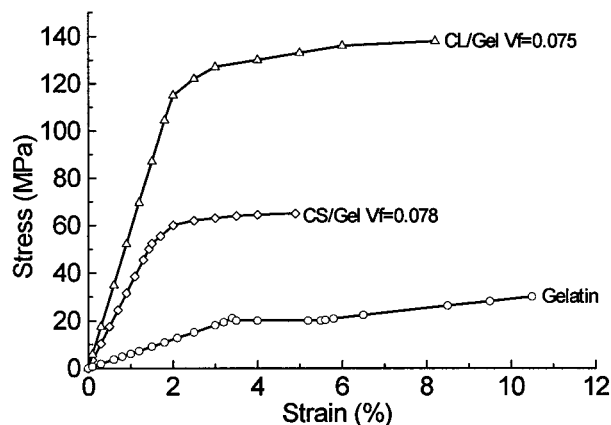


Figure 1 Typical stress–strain curves for two composites and pure gelatin.

into the gelatin matrix led to higher stresses. Nevertheless, differences existed in the stress at break and deformation at break between C_L /Gel and C_S /Gel. The C_L /Gel samples showed a significant improvement—the stress increased more than fourfold. On the other hand, only a twofold increase of stress was observed for C_S /Gel. Further discussion of the mechanical behavior (tensile strength, modulus, and elongation at break) for those materials will be given later.

Mechanical Properties and Governing Factors

The results of the experiments are discussed according to the various variables investigated. In our experiments, one variable was varied at a time while the others were constant. The GLY, GLA, and gelatin contents were identical for two composites for comparison purposes.

Fiber Volume Fraction (V_f)

The effect of the fiber volume fraction V_f on the mechanical properties of the two composites is illustrated in Figures 2 and 3. It is seen that both C_L /Gel and C_S /Gel possess higher σ , E , and τ values, but lower ϵ values as compared to neat gelatin, indicating that the addition of long or short carbon fibers can greatly improve σ , E , and τ but decrease the ϵ of neat gelatin. But big differences between C_L /Gel and C_S /Gel were noticeable. In the case of C_L /Gel, σ , E , and τ were all steadily and sharply increased in accordance with the rule of mixture. For the C_S /Gel, with increasing V_f , τ was enhanced in the V_f range of 0–0.094 and then leveled off above this value, whereas σ and E showed a decrease after showing a gradual

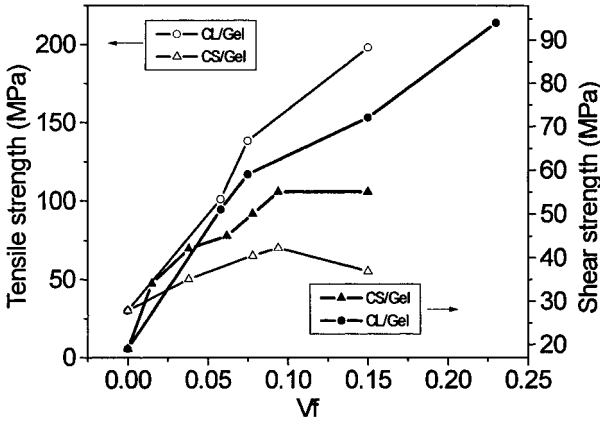


Figure 2 Tensile and shear strength versus V_f for two composites.

increase. Clearly, improvement in the strength and modulus of C_L /Gel was greater than that of the C_S /Gel. For example, the σ of C_L /Gel increased to 138 MPa at a V_f of 0.075 compared to 30 MPa of the pure gelatin and to 65 MPa of the C_S /Gel at a V_f of 0.078.

For both composites, ϵ decreased with incorporation of the carbon fibers. In the range between 0 and 0.075, there was a serious decrease in the ϵ of C_L /Gel; thereafter, only a slight decrease was observed. Compared with C_L /Gel, the decline in ϵ of the C_S /Gel was more significant. It is noted that the ϵ of C_L /Gel was greater than that of the C_S /Gel at any V_f level.

These results demonstrated that the fiber form exerted a great effect on the mechanical properties of the carbon fiber gelatin composites. In the longitudinal direction, C_L /Gel possessed higher

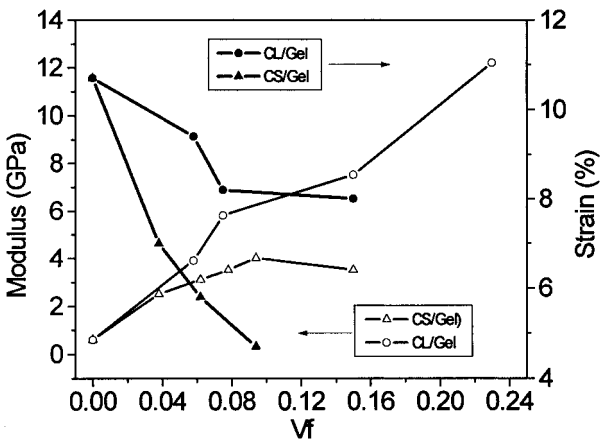


Figure 3 Tensile modulus and strain versus V_f for two composites.

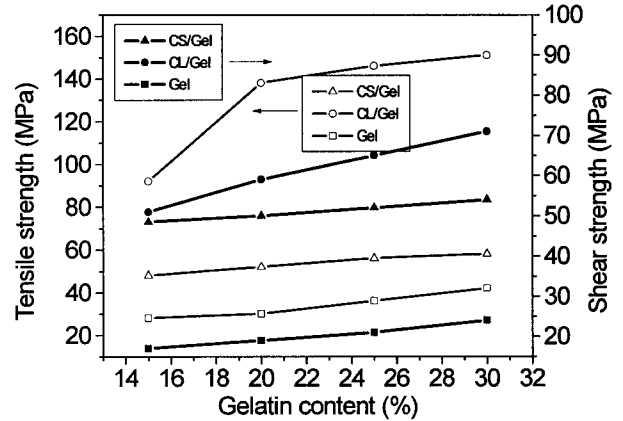


Figure 4 Effect of gelatin content on tensile and shear strength for two composites and pure gelatin.

mechanical properties than those of the C_S /Gel. In other directions, however, the C_S /Gel was shown to have mechanical properties superior to those of C_L /Gel. It is possible to obtain a higher performance C_S /Gel by altering the fiber-length distribution and fiber-orientation distribution.¹⁷ In addition, C_S /Gel can be easily produced by a rapid solvent-casting process and will be low cost. Anyhow, the selection of the fiber form will depend on the service conditions.

Gelatin Content

Figures 4 and 5 show the effect of gelatin content on the mechanical properties of the two composites. For comparison purposes, a pure gelatin was included. For the pure gelatin, an increase in gelatin content led to a trivial increase in σ , E ,

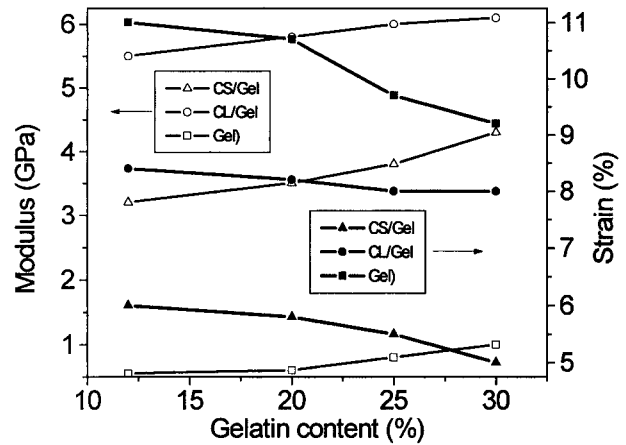


Figure 5 Effect of gelatin content on tensile modulus and strain for two composites and pure gelatin.

and τ and a decrease in ε . This is because a higher gelatin concentration would lead to higher numbers of contact points between protein chains of the gelatin and more helices could form.¹⁸ A higher gelatin concentration than 30% might not be obtained because the gelatin solution would not wet the carbon fibers or could not flow due to its higher viscosity.

Analogous results were obtained for both the C_L /Gel and C_S /Gel samples, that is, σ , τ , and E increased slightly with the gelatin content and ε decreased slightly with the gelatin content for both composites. C_L /Gel was found to possess higher σ , E , and ε in comparison to C_S /Gel. Data from Figures 4 and 5 show that variation in the gelatin content had a relatively smaller effect on the mechanical properties for the two composites as compared to the V_f .

GLY Concentration

The effect of GLY content on the mechanical properties of the two composites and the pure gelatin is presented in Figures 6 and 7. As expected, the increase in ε and the decrease in σ , E , and τ were found with an increase in the plasticizer content for the pure gelatin, which were attributed to the fact that the presence of GLY separates the protein chains or lowers the number of entanglements of the chains.¹⁸ Therefore, it is easy to understand that the σ , τ , and E of the two composites were also increased and that ε decreased as the GLY content increased. Obviously, the increase in ε and the decrease in σ , τ , and E were slight, between 0.1 to 0.5% GLY content for the

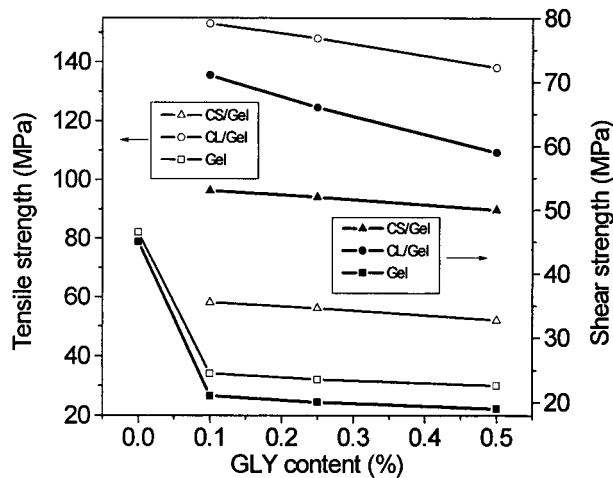


Figure 6 Variation of tensile and shear strength with GLY content for two composites and pure gelatin.

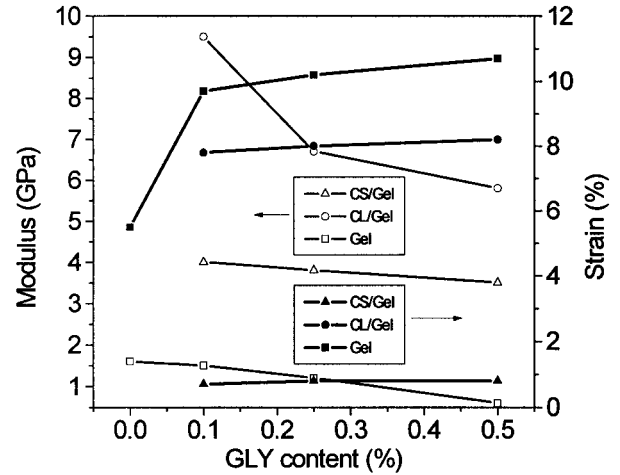


Figure 7 Variation of tensile modulus and strain with GLY content for two composites and pure gelatin.

two composites and the pure gelatin. Similarly, the effect of GLY content on the mechanical properties of the two composites was not significant.

It was found in the present study that C_L /Gel ($V_f = 0.15$) with a tensile strength of 198 MPa and a tensile modulus of 7.5 GPa can be produced by the solution-impregnation technique. It should be stated, however, that the preparation conditions applied in this experiment might not be optimal and the strength of the selected carbon fibers is relatively low. Additionally, surface modification of carbon fibers, another important factor that might significantly affect the mechanical properties of this composite, was not adopted in this preliminary experiment. Therefore, it is reasonable to assume that C_L /Gel (and also C_S /Gel) of higher strength and modulus can be prepared in further studies.

Fractographic Studies

SEM is considered an important tool in the study of composites since it can supply essential information about the degree of fiber–matrix adhesion and fiber dispersion in the matrix.^{19,20} The fracture surfaces of C_L /Gel are shown in Figure 8. It is evident that the fibers were well distributed in the gelatin matrix but almost all fibers were pulled out, indicating that the strength of the gelatin was stronger than was the shear strength between the carbon fibers and the gelatin matrix. There were no pores or cracks at the interfaces, suggesting that the wetting of the fibers by the gelatin is complete.

Another aspect of the SEM photographs of the composites is fiber–matrix adhesion. The pres-

ence of polymeric links to the fibers is an indication of a strong fiber–matrix bonding, and, similarly, the lack of polymeric links represents a weak bonding.¹⁹

As shown in Figure 8, the surfaces of the fibers were smooth and no gelatin adhering on the surfaces of fibers was observed. This result seems to indicate that the fiber–matrix adhesion is weak, maybe resulting from the lack of chemical reaction between the carbon fibers and the gelatin. Therefore, the fiber–matrix bonding is the result of mechanical interlocking between them. In this case, the stress transfer between the fibers and the matrix was due primarily to friction. It is believed that an improved adhesion will be obtained if carbon fibers are surface-treated in further studies, and, hence, composites of higher strength can be prepared.

Figure 9 gives the fracture surfaces of C_S/Gel . One can see that the fibers were uniformly distributed in the gelatin matrix and no fiber aggregation was observed. The bonding between the fibers and the gelatin seemed to be tight since no pores or cracks were found at the fiber/gelatin interface. On the other hand, SEM showed that the fibers were pulled out and no gelatin was adhering to the carbon fibers. This suggests that adhesion between the fibers and the gelatin is not strong enough. Similar to C_L/Gel , the failure mode was primarily interfacial failure for C_S/Gel .

CONCLUSIONS

1. Fully dense composites reinforced with both long and short carbon fibers were suc-

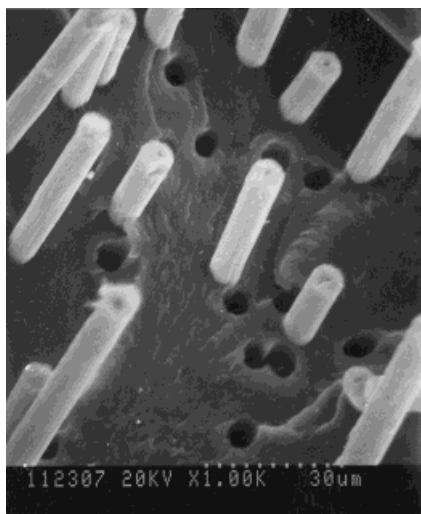


Figure 8 SEM micrographs of fracture surfaces of C_L/Gel .

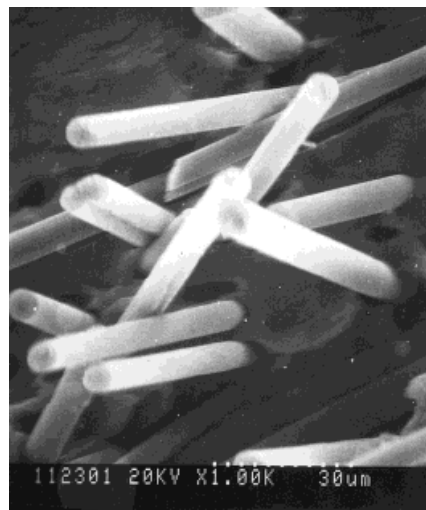


Figure 9 SEM micrographs of fracture surfaces of C_S/Gel .

- cessfully prepared. Both composites had higher tensile strength and modulus, shear strength, and lower elongation at break in comparison to the pure gelatin.
2. For the long-fiber composite (C_L/Gel), the improvement in tensile strength, tensile modulus, and shear strength was more significant, and the reduction in elongation at break was smaller than those for the short-fiber composite (C_S/Gel).
 3. Tensile strength, tensile modulus, and shear strength increased appreciably, while break at elongation decreased with increasing fiber volume fraction V_f for C_L/Gel . In the case of C_S/Gel , shear strength improved gradually and finally leveled off, but tensile strength and modulus increased initially and then declined with the V_f . In addition, elongation at break lowered considerably with the V_f .
 4. The major factor influencing the mechanical properties of the two composites was found to be the V_f . To a much lesser degree, the GLY content and gelatin content had some influence on the mechanical properties of the two composites. The effects of increasing the gelatin content and decreasing the GLY content were found to increase the tensile strength, modulus, and shear strength and to reduce the strain at break of both composites.

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