Enhancement of the Mechanical Properties and Interfacial Interaction of a Novel Chitin-Fiber-Reinforced Poly(ϵ-caprolactone) Composite by Irradiation Treatment

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ABSTRACT: The effects of the fiber reinforcement of a novel bioabsorbable chitin-fiber-reinforced poly(ϵ-caprolactone) (PCL) composite were improved by irradiation treatment. The tensile strength and tensile modulus of the treated specimens were enhanced with respect to those of the untreated specimens. An increase in the fiber content (C_f) resulted in an increase in this enhancement tendency until C_f was 45%. A further increase in C_f increased the tensile modulus but decreased the strength. The flexural strength and flexural modulus were increased for the irradiation-treated specimens in the same way as the tensile test. The microstructure of the tensile fracture showed an improvement in interfacial bonding for the irradiated specimens. The glass-transition temperature (T_g) of the composite increased with an increase in C_f for the irradiation-treated specimens, but there was no change in T_g for the untreated specimens with various values of C_f. This indicated that, for the composites with irradiation treatment, the fiber intensively affected the molecular segmental motion of PCL and thereby enhanced the interfacial interaction between the matrices and fibers. The same slope of the storage modulus (G') versus the loss modulus (G'') for the irradiated specimens suggested an increase in the compatibility of the composite in comparison with the decrease in the slope with increasing C_f for the untreated specimens. All this demonstrated that there was some interfacial reaction between the fiber and matrix that resulted in the presence of an interfacial phase and improved the mechanical properties of the materials. © 2002 John Wiley & Sons, Inc. J Appl Polym Sci 84: 486–492, 2002; DOI 10.1002/app.10149

Key words: biomaterials; composites; irradiation; mechanical properties; interface

INTRODUCTION

Polymers based on lactic and glycolic acids (PLA and PGA, respectively) have received a great deal of attention in the field of medical applications because these polyesters can degrade *in vivo* by simple hydrolysis of the ester backbone to nonharmful and nontoxic compounds.[1] Bioabsorbable, internal-fixation devices prepared from these polymers for fractures have two distinct advantages over metallic vehicles: no stress shielding and no need of a second operation for removal. However, the rapid loss of mechanical properties, long-time tissue inflammatory reaction, inconvenient processing, and high cost restrict their further applications.[2]

There have been many studies on chitin as a biocompatible material, and it is used for artificial skin,[3] sutures,[4] wound dressings,[5] drug carriers,[6] and so on. Chitin also degrades *in vivo* by en-

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zymes at a slow degradation rate. Poly(ϵ-caprolactone) (PCL) is another kind of biocompatible and bioabsorbable polyester with a slower degradation rate than the rates of PLA and PGA.[7] Moreover, chitin can be made into a fiber form with high mechanical properties, whereas PCL has good processing behavior due to the low melting viscosity and melting point. Therefore, a composition of chitin fiber and PCL will give a novel composite with good processing properties, good biocompatibility, a slower degradation rate, and lower cost.

A chopped-chitin-fiber-reinforced PCL composite was prepared in this lab, and studies showed that the interfacial bonding between the fiber and matrix was poor because of the lower surface energy of the chitin fiber;[8] therefore, interfacial modification is important for preparing a material with high mechanical properties. It is known that interfacial bonding can be improved by the introduction of an interfacial phase to the composite, which may be fulfilled by a chemical reaction between the fiber and matrix.[9] Therefore, the reaction between the chitin fiber and PCL matrix could result in the introduction of an interfacial phase to the material.

Irradiation by an electron beam is one suitable method used to improve certain properties of polymers by crosslinking or grafting. Polypropylene, irradiated by an electron beam in the presence of multifunctional monomers, results in a material with a high melt strength.[10] PCL, irradiated by an electron beam in a supercooled state, is improved with respect to its strength and heat resistance.[11] Furthermore, styrene has been grafted to chitin in bulk or in solvents by γ irradiation.[12] The crosslinking reaction of PCL and the grafting of styrene to chitin are all based on free-radical mechanisms. Accordingly, it is probable that the irradiation treatment of a chitin-fiber-reinforced PCL composite may cause a radical reaction between the fiber and matrix, which could improve the interfacial bonding of the composite.

In this investigation, composites of chitin-fiber-reinforced PCL with various fiber contents (C_f) were irradiation-treated with an electron beam. The mechanical properties of the composites were studied with tensile and flexural tests, the microstructure of the tensile fracture was investigated with scanning electron microscopy (SEM), and the interfacial interaction was studied with a differential mechanical thermal analyzer (DMTA) and an advanced rheometric extended system (ARES).

MATERIALS AND MEASUREMENTS

Chopped chitin fiber (50 mm long) was obtained from China Textile University (Shanghai, China); the number-average molecular weight of the PCL used was 80,000; chitin *n*-butyrate (CB) was prepared in our laboratory and used as a compatible agent, which was clarified in the chitin/PCL blend.[8] The composite was prepared from chitin fiber, CB, and PCL by mixing at 140°C in a Haake mixer (Karlsruhe, Germany) until the torque reached a constant level. The CB content was kept at 5%, and C_f (in mass) was 0 (pure PCL without CB; the others all contained 5% CB), 15, 35, 45, 55, and 65%; the composite specimens were mold-pressed at 100°C for the measurements.

The electron-beam irradiation treatment was performed in an electron accelerator with a dose of 200 kGy for the molded specimens before the measurements.

The tensile and flexural tests were conducted with a Shimadzu AG100 kNA machine (Kyoto, Japan), and the loading rate was 1 mm/min. The size of the specimens for the flexural test was 50 mm × 10 mm × 2 mm, and the size of the dumbbell-shaped specimens for the tensile test was 50 mm × 6 mm × 2 mm in the middle part. SEM was performed with a Philips SEM 515 instrument (Eindhoven, The Netherlands) after a gold film was sprayed on the tensile fracture of the sample. The DMTA study was conducted with a DMTA IV machine (Rheometric Co., Piscataway, NJ), and the temperature ramping sweep was −100 to 60°C at a rate of 3°C /min. The viscoelastic behaviors of the composites were also studied with dynamic rheological characterizations of the composite melts at 100°C (plate tests) by ARES, and the frequency sweep was 100–0.01 rad/s.

RESULTS AND DISCUSSION

Effects of the Irradiation Treatment on the Tensile Strength and Modulus of the Composites with Various Values of C_f

Figure 1 shows a comparison of the tensile strength and tensile modulus of composites with and without irradiation treatment with various

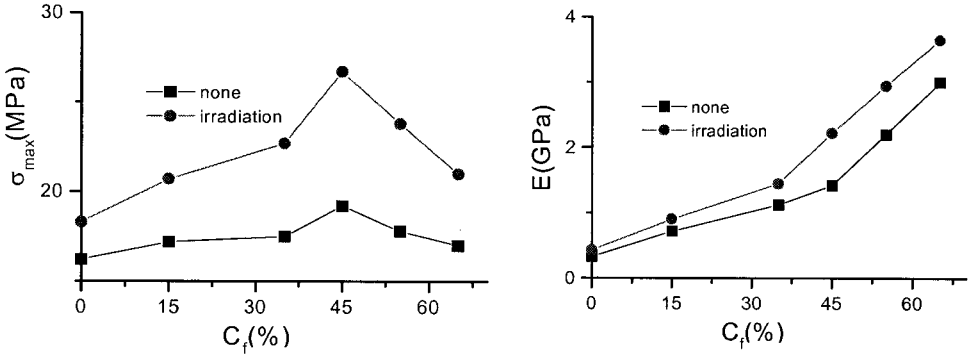

Figure 1 Effect of the irradiation treatment on the tensile strength and tensile modulus of composites with various values of C_f.

amounts of chitin fiber. For the composites without irradiation treatment, the addition of chitin fiber into the PCL matrix did not improve the tensile strength until C_f was 35%. Although the tensile strength was improved when C_f was 45%, this improvement was not significant. The further increase in C_f resulted in a decrease in strength because a greater content of chitin fiber caused poor wetting of the fiber by PCL. For the composites with irradiation treatment, the tensile strength was clearly enhanced, and an increase in C_f resulted in an increase in this enhancement. When C_f was 45%, the strength reached its maximum value, and the reinforcement of chitin fiber for the material was more obvious than that of the untreated one. For the two kinds of specimens, the tensile modulus showed a two-stage increase with an increase in the amount of chitin. When C_f was less than 45%, the elastic modulus was improved linearly in a lower slope, whereas it increased linearly more steeply with C_f over 45%.

Effects of the Irradiation Treatment on the Flexural Strength and Modulus of the Composite with Various Values of C_f

Figure 2 shows a comparison of the flexural strength and flexural modulus of the composite with and without irradiation treatment. For the untreated specimens, the increase in C_f gradually enhanced the strength, and the maximum strength was obtained when the fiber amount was 45%, and this was followed by a gradual decrease in the strength. The addition of chitin fiber enhanced the flexural strength more obviously than the tensile strength, which was the feature of the chopped-fiber-reinforced polymeric matrix composite, indicating that the flexural test was less sensitive to the defects of the material than the tensile tests.

The flexural strength was more evidently enhanced for the irradiated composite than for the untreated composite. Furthermore, the larger C_f value resulted in this enhancement being more

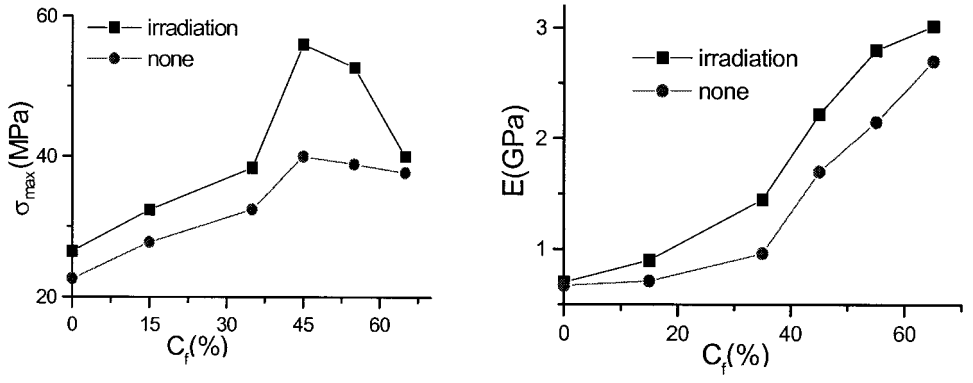

Figure 2 Effect of the irradiation treatment on the flexural strength and flexural modulus with various values of C_f.

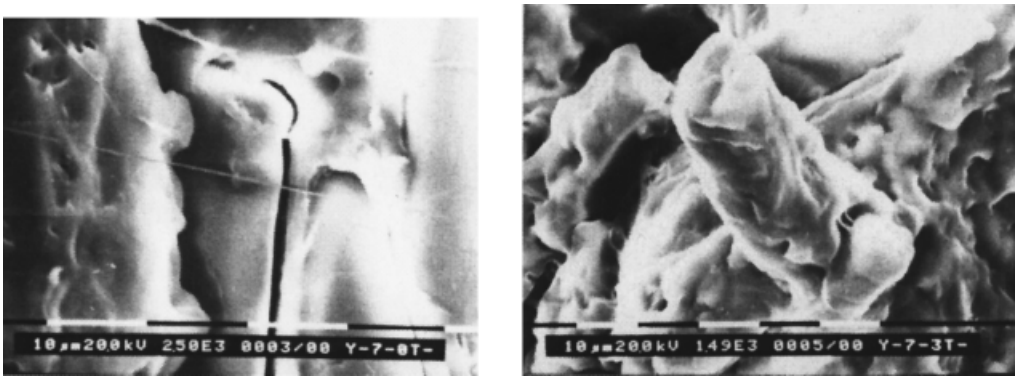

Figure 3 SEM photographs of the tensile fractures of irradiation-treated (right) and untreated (left) composites.

evident. Meanwhile, the flexural modulus was enhanced for the composite after the irradiation treatment in the same way as the tensile modulus.

Microstructure of the Tensile Fracture for Samples with or without Irradiation Treatment

Figure 3 shows SEM photographs for the tensile fractures of composites with and without irradiation treatment. For the irradiated specimen, the fiber was obvious covered by a layer of PCL matrix, and the surface of the pulled-out fiber was irregular and matrix-rich, whereas for the untreated sample, the surface was much smoother with no matrix remnant on it. Because the irradiation-treated specimen was molded first with the same process as the untreated one, the two kinds of specimens should have the same physical structure. Moreover, the irradiation process could not make the PCL molecule migrate to the interfacial region. Therefore, it revealed that the improvement of the interfacial bonding of the composite was due to the production of the interfacial phase, which might result from the irradiation reaction of the fiber surface and the matrix. Because good interfacial bonding makes fibers accept loads transferred from the matrix, the effects of fiber reinforcement depend very much on the level of interfacial bonding between the fiber and matrix. Consequently, the mechanical properties of the composite were greatly improved.

Effects of the Irradiation Treatment on the DMTA Curves of Composites with Various Values of C_f

A DMTA is useful for investigating the interactions between components of a composite, and it was used in this investigation to intensify the study of the interfacial interaction between the fiber and matrix. The corresponding comparison curves of the storage modulus (E'), loss modulus (E''), and loss factor (tan δ) versus temperature (T) for the composites are shown in Figures 4–6 with and without irradiation treatment at different C_f values.

In the E' curve, there is a plateau from -80°C followed by a gradual decrease in the modulus due to the glass transition of the PCL component. A comparison of the E' curves showed an increase in E' with the irradiation treatment, and a decrease in the modulus in the transition region was somewhat reduced for the irradiated specimens.

In the tan δ curves (Fig. 5), the temperature of the corresponding peak of the loss factor increased slightly with an increase in C_f for the irradiated specimens, whereas there was no obvious change in the peak temperature for the untreated ones.

For the irradiated specimens, the increase in C_f increased the temperature of the loss peak in the E''–T curve, whereas the peaks for the untreated specimens remained almost at the same temperature (Fig. 6).

The temperature at the E'' peak or tan δ peak within the glass-transition region was used to characterize the glass-transition temperature (T_g) of the polymer. The aforementioned peaks in both curves represented the T_g of the PCL component in the composite, which also characterized the relaxation process of the chain-segment motion. Therefore, the irradiation treatment of the composites heightened T_g with an increase in C_f.

The improvement of T_g of the composite with various values of C_f after irradiation treatment might be explained as follows:

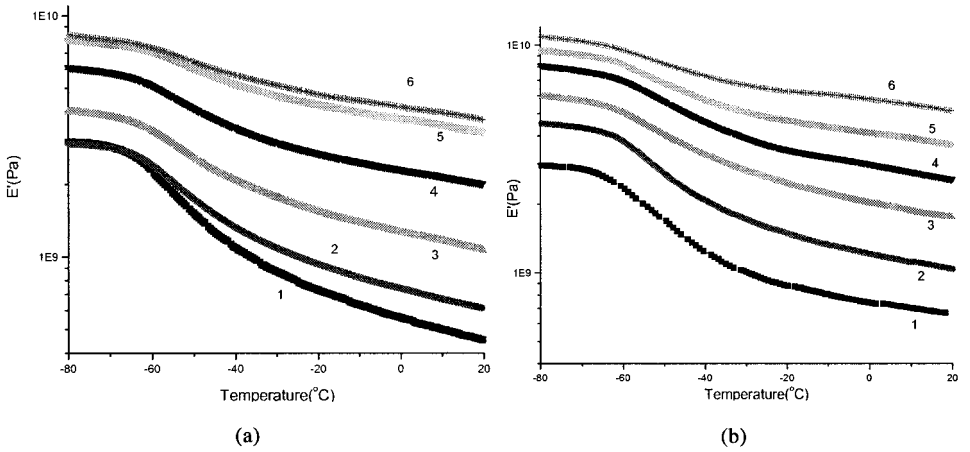

Figure 4 Comparison of E'–temperature plots of composites with various values of C_f [(1) 0, (2) 15, (3) 35, (4) 45, (5) 55, and (6) 65%]: (a) untreated specimens and (b) irradiated specimens.

1. The irradiation treatment of PCL caused crosslinking, branching, and perhaps degradation of the polymer, and branching and crosslinking of the polymer formed highly rigid structures and resulted in an increase in T_g. However, the degradation of the polymer caused a decrease in the molecular weight and, therefore, a decrease in T_g.
2. The interfacial reaction between PCL and chitin fiber introduced rigid chains and resulted in an increase in T_g.

Because the first effect of branching and crosslinking of PCL was smaller for the composite than for pure PCL (Figs. 5 and 6), the larger increase in T_g for the composite with a higher value of C_f might be contributing to the second effect. This indicates that the irradiation treatment for the composite initiated an interfacial reaction between the fiber and matrix, which resulted in a increase in T_g, and so the interfacial phase was formed, as also shown in the SEM photographs.

Effects of the Irradiation Treatment on the Viscoelastic Behavior of Composite Melts Characterized by Plots of the Storage Modulus (G') versus the Loss Modulus (G'')

A plot of G' versus G'' of the melts in oscillatory flow is a useful empirical tool in comparing the

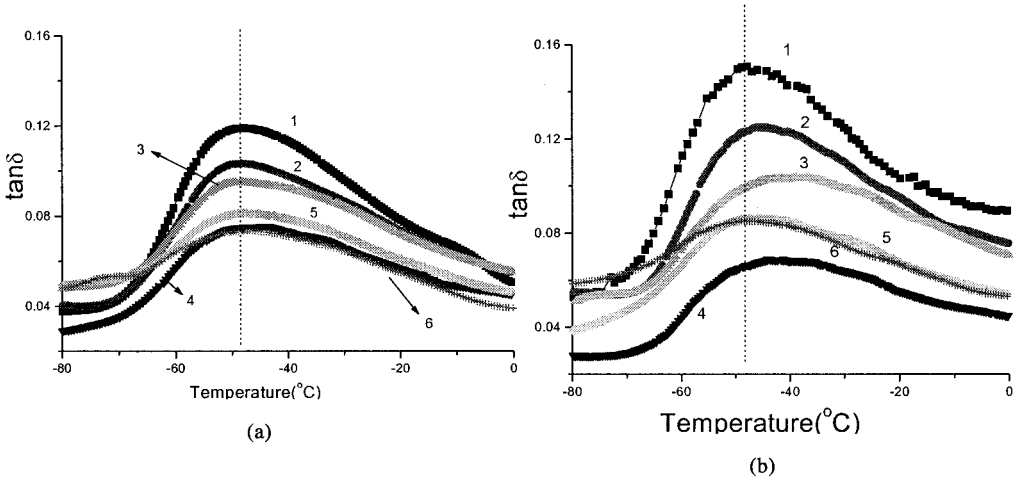

Figure 5 Effect of the irradiation treatment on tan δ–temperature curves of composites with various values of C_f [(1) 0, (2) 15, (3) 35, (4) 45, (5) 55, and (6) 65%]: (a) untreated specimens and (b) irradiated specimens.

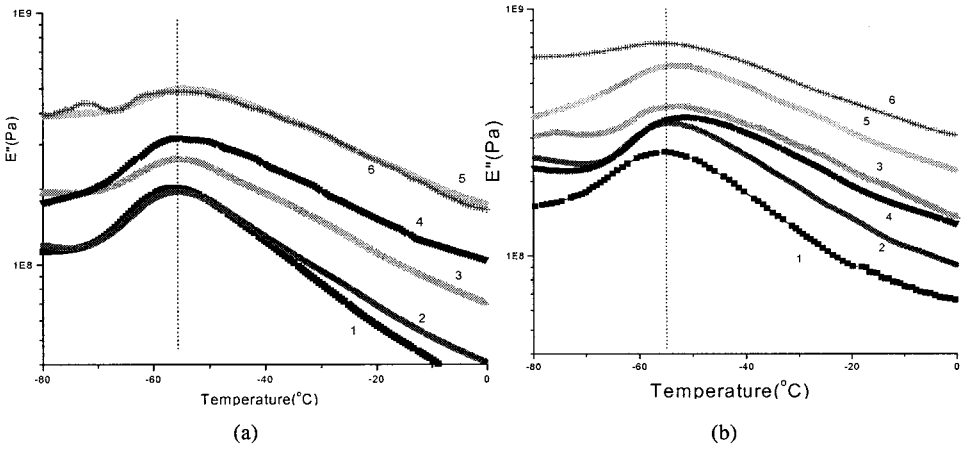

Figure 6 E''–temperature plots of composites with various values of C_f [(1) 0, (2) 15, (3) 35, (4) 45, (5) 55, and (6) 65%]: (a) untreated specimens and (b) irradiated specimens.

elastic behavior of one fluid against another. It has been suggested that the logarithmic plot of G' against G'' is independent of the temperature for melts of miscible blends.[13] Figure 7 shows a comparison of this plot for composites with and without irradiation treatment at different levels of C_f. The low-modulus region corresponded to the low-frequency data. For the untreated specimens, this plot shows different slopes with different levels of reinforcement, whereas for the specimens with irradiation treatment, the change in C_f did not affect the slopes of the plots, which superposed into a single line. This clearly indicates that the interfacial compatibility of the composite increased after irradiation treatment, supporting evidence for an increase in interfacial interaction.

CONCLUSIONS

The interfacial bonding of a novel bioabsorbable chitin-fiber-reinforced PCL composite was easily improved by irradiation treatment, and in this way, mechanical properties such as tensile and flexural strength and modulus were enhanced. For the irradiated composites, the presence of an interfacial phase was evident in SEM photomicrographs, and the increase in T_g for composites with an increase in C_f clearly indicated that there was an interfacial reaction between the fiber and matrix by means of the irradiation treatment. The same slope of G' against G'' for the irradiated specimens suggested an increase in the compatibility of the composite interface in comparison

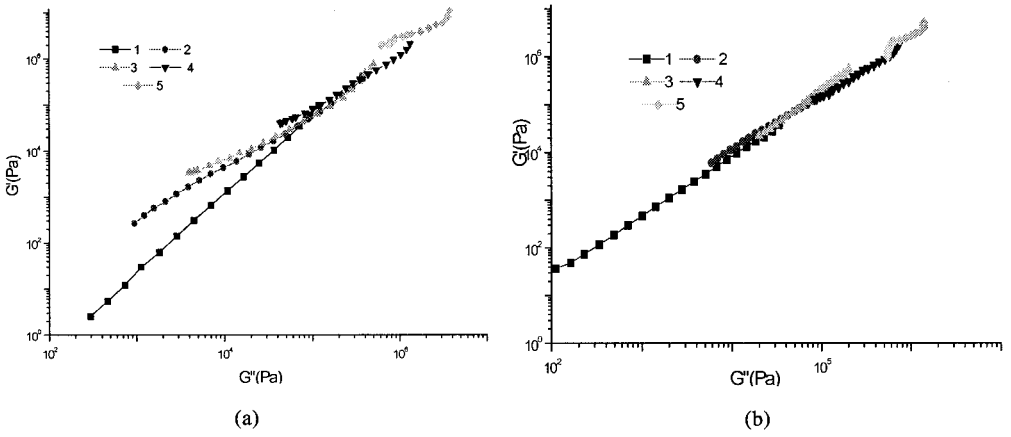

Figure 7 G'–G'' curves of composites in the melting state (>60°C) with various values of C_f [(1) 0, (2) 15, (3) 35, (4) 45, (5) 55, and (6) 65%]: (a) untreated specimens and (b) irradiated specimens.

with the change in the slope for the untreated ones. The mechanism of the reaction might be a free-radical grafting reaction, which will be further clarified in future work.

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