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Mechanical and viscoelastic properties of chitin fiber reinforced poly(ε-caprolactone)

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Abstract

Poly(ε-caprolactone)/chitin fiber (PCL-CF) composites as potential bone substitutes were prepared using a simple melt-processing method. The results from differential scanning calorimetry and dynamic mechanical thermal analysis (DMTA) showed that there was interaction between PCL and CF. Static mechanical testing showed that tensile strength, Young's modulus and flexural strength were increased by the addition of CF. The measurements from DMTA and an advanced rheometric expansion system showed that both the storage modulus and loss modulus were enhanced by CF. The PCL-CF composite with CF of 45% by mass had the best properties among all the tested composites.

Keywords: Poly(ε-caprolactone); Chitin fiber; Interaction; Mechanical properties; Viscoelastic properties

1. Introduction

Poly(ε-caprolactone) (PCL) is a type of biodegradable polymer which demonstrates biocompatibility and the capacity for drug transport. PCL is relatively hydrophobic and has a slow degradation rate, ideal for use as bone substitutes and sustained release drug carriers [1–7]. However PCL cannot be prepared for bone substitute on its own because of its low modulus, typically $350 \sim 450\,\text{MPa}$ [8,9].

Chitin is a natural bio-absorbable polysaccharide with excellent biocompatibility, non-toxicity and enhanced wound healing properties [10–14], so it has been widely imported into medical and healthcare fields such as drug carriers, artificial kidney membranes, anti-coagulants, immunity accelerants and so on [10–17]. Chitin fiber has been used as surgery sutures, wound dressings and artificial skins [18–20]. On this basis, our laboratory has previously synthesized PCL-CF composites with chitin *n*-butyrate as the compatibilizer [21–23]. Since chitin *n*-butyrate is one of chitin's derivatives, its introduction largely increases the cost. Also the improvement on the interfacial compatibility was very limited [21,22]. Thus this work aims to carry out systematic studies on the properties of PCL reinforced by CF without the presence of compatibilizers.

2. Experimental details

2.1. Materials

PCL with number average molecular weight of 80,000 was purchased from Sigma-Aldrich Group (Missouri,

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USA). Chitin fiber with an average diameter of 7 μm was kindly supplied by Dong Hua University (Shanghai, China) and was cut to short fibers with an approximate length of 1 cm.

2.2. Experimental methods

Composites with fiber contents (m_c) of 0%, 15%, 35%, 45%, 55% and 65% (by mass) were prepared by melt blending at 120 °C for 10 min in a blender attached to a Haake Rheometer (Karlsruhe, Germany) until torque reached equilibrium, followed by pressing in a mould at 120 °C and cutting into suitable specimens for the test requirements.

Differential scanning calorimetery (DSC) was performed on a DSC-SP (Rheometric Scientific Inc., New Jersey, USA). The specimens were heated from 20 °C to 120 °C with a ramp of 3 °C/min under flowing nitrogen gas. After a 3-min dwell, the specimens were cooled to 20 °C with the same ramp.

The tensile and bending testing were carried out on a Shimadzu AG100kNA mechanical testing machine (Kyoto, Japan). Both tensile and bending loading rates were 1 mm/min. All the tests were conducted according to ASTM D3039 and D790. At least five specimens were tested for each sample.

Dynamic mechanical thermal analysis (DMTA) was conducted on a DMTA IV (Rheometric Scientific Inc.) with tensile mode. The linear zone of strain was checked at both 20 °C and −110 °C. The controlled temperature was from −100 °C to 50 °C with a heating ramp of 3 °C/min.

The dynamic rheological properties were measured on an advanced rheometric expansion system (ARES, Rheometric Scientific Inc.) at 10% strain with 20 mm parallel plates. Before each rheological test, a linear dependence of viscoelasticity on frequency at the test temperature was checked.

3. Results and discussion

Table 1 shows the melting temperature (T_m) and crystallization point (T_c) of the composites deduced from DSC measurements. Chitin cannot melt [24], thus the endothermic peaks present the melting transition for PCL. In the presence of 45% CF, the melting point of PCL was increased up to 9 °C. However for all the other composites, both the T_m and T_c only shifted slightly compared to those for the unfilled PCL, implying a modest interaction.

Table 1
Melting and crystallization points of PCL-CF composites deduced from DSC measurements[a]

m_c	0	15%	35%	45%	55%	65%
T_m/°C	58	59	59	67	60	60
T_c/°C	37	39	38	39	39	40

[a] Measured with a heating or cooling rate of 3 °C/min under nitrogen gas flowing.

Figs. 1 and 2 show the mechanical properties of PCL-CF composites. The data points presented the mean strength or modulus for each sample. As the pristine PCL and the PCL composite containing 15% (denoted as 15%PCL-CF) underwent yielding behaviour, the tensile strength referred to the yield strength. When m_c was greater than 15%, the composites became brittle rather than ductile, thus there was no yielding and necking stage in the stress–strain curve. The tensile strength and Young's modulus of PCL were improved significantly by the addition of CF. The greatest values for these two parameters occurred at $m_c = 45\%$, indicating that too much fiber (>5%) deteriorates the interaction of PCL matrix and chitin fiber. This corresponds to the result from DSC. When $m_c > 45\%$, the external loading cannot be transferred from PCL to the fiber so that chitin fiber did not play a strengthening role effectively.

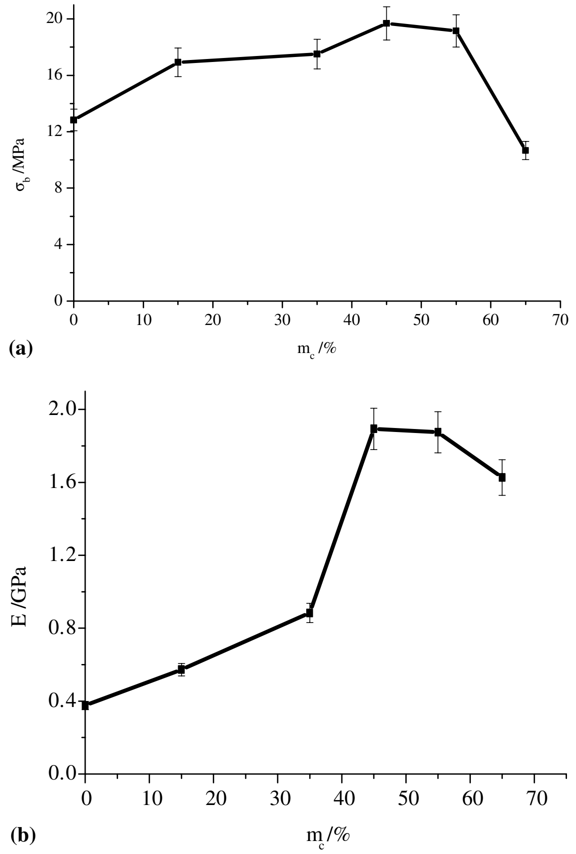

Fig. 1. (a) Tensile strength σ_b and (b) Young's modulus E vs. m_c for PCL-CF composites.

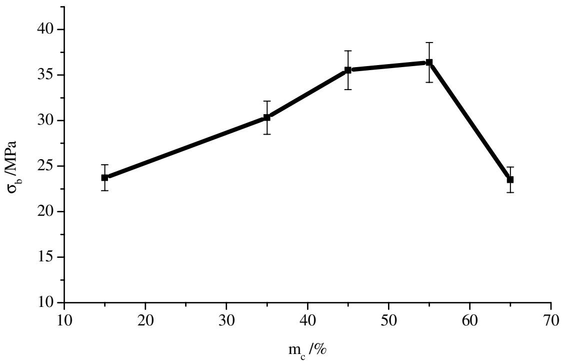

Fig. 2. Flexural strength σ_b vs. m_c for PCL-CF composites.

The change of flexural strength with m_c was somewhat different from tensile strength in that the greatest flexural strength occurred at 55% CF. However there was little difference in the strengths between 45%PCL-CF and 55%PCL-CF. Similarly, when m_c was lower than 45%, the flexural strength increased considerably with m_c, supporting the deduction that too much CF cannot effectively share the external load with PCL.

The storage modulus E', loss modulus E'' and loss factor $\tan\delta$ for the composites measured at a frequency of 1 Hz using DMTA are shown in Fig. 3. For each composite, E' decreased with the increasing temperature, especially in the glass transition zone. The critical m_c below which E' increased with increasing m_c and above which E' decreased with greater m_c, was 45%. This result indicates that 45% PCL-CF can 'store' energy during deformation and release it on unloading to the most extent among the composites. At ambient temperature (20 °C), E' was coincident with the results from the static mechanical testing as shown in Fig. 1b.

There was a loss peak between −50 °C and −40 °C in the curves of E'' and $\tan\delta$ against temperature. The transition temperature at the peak in the $\tan\delta$ curve (T_g) was higher than the temperature in E'' curve, which is a characteristic of semi-crystalline polymers. Moreover, T_g of

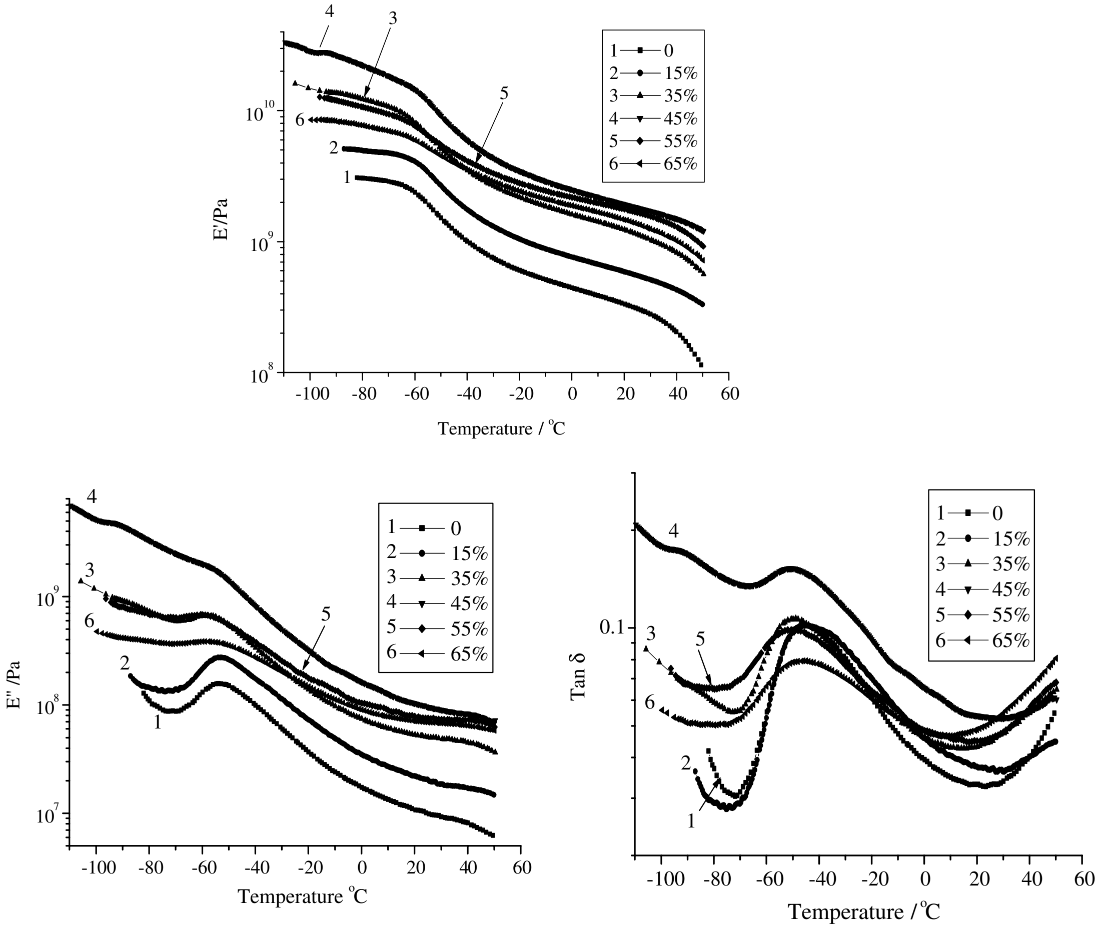

Fig. 3. Storage modulus E', loss modulus E'' and loss factor $\tan\delta$ vs. temperature for PCL-CF composites measured using DMTA.

PCL slightly shifted downward after the addition of CF, which indicates that CF affects the relaxation process of PCL chain segments but the interaction between PCL and CF is not strong. The composites containing 35%, 45% and 55% CF had relatively large decrease in the T_g in contrast to the other two composites, again suggesting that too much fiber can decrease the interaction. Like in E', 45% was also the critical m_c in E'' and $\tan\delta$; these two parameters increased to the greatest value at m_c of 45% and then decreased with increasing m_c. The highest loss peak suggests the largest loss on energy accompanying the motion of PCL molecular segments in the viscoelastic zone.

The composite with 65% CF could not be tested on ARES due to its high content of filler. For other composite melts, their storage modulus G' and loss modulus G'' against frequency ω are shown in Fig. 4. The addition of CF increased both G' and G'', indicating both elasticity and viscosity were increased. G'' was dominant in the low frequency zone, in which the composites mainly behaved as viscous fluids and the addition of CF did not have much effect on the flowing of PCL melt. However, G' dominated the modulus in the high frequency zone, where elasticity was the major property for the composites. At the same frequency, both G' and G'' of 45%PCL-CF had the greatest value among all the composites. Moreover, the slope of G' vs. ω was decreased as m_c was increased, which is favourable for processing.

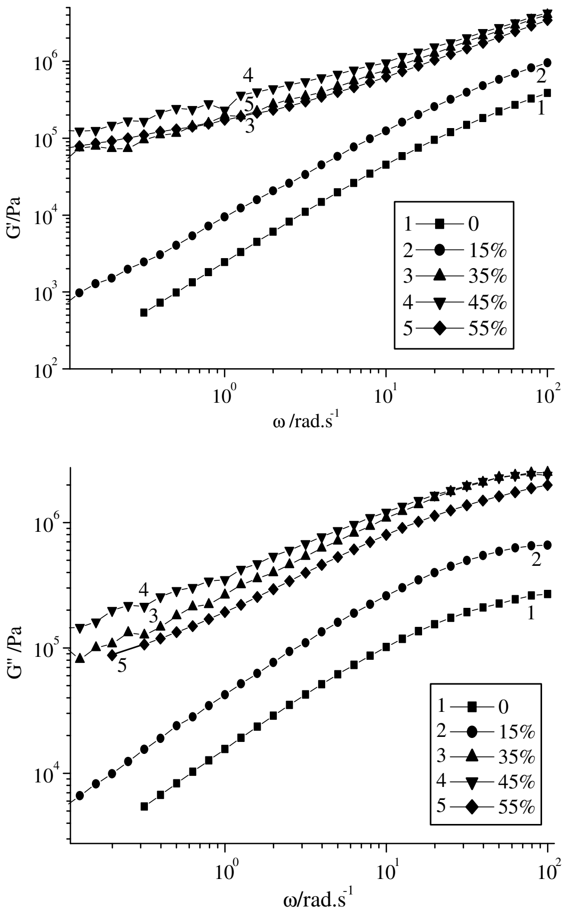

Fig. 4. Storage modulus G' and loss modulus G'' vs. Frequency ω for PCL-CF composite melts measured using ARES.

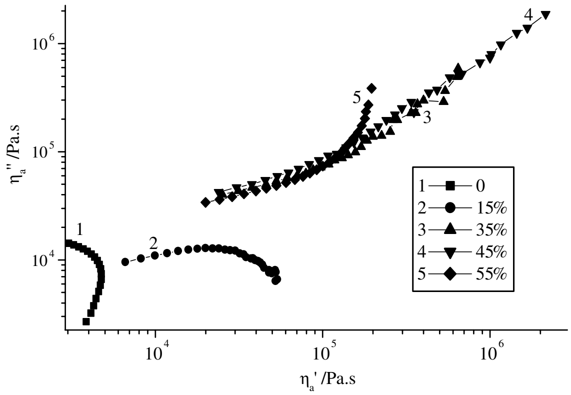

Fig. 5. Imaginary viscosity η''_a vs. dynamic viscosity η'_a for PCL-CF composite melts measured using ARES.

The relaxation process of a complex body can be studied with the curves of imaginary viscosity η''_a vs. dynamic viscosity η'_a [25,26], as shown in Fig. 5. The viscosity curve for PCL was approximately 1/4 arc of a circle. The presence of CF enlarged the diameter of the circle implying longer relaxation time is required to reach the end of the flowing zone. It is again found that the largest change in the diameter of the circle occurred at m_c of 45% at which the viscosity curve is nearly linear, supporting previous conclusions about the largest interaction.

4. Conclusions

Biodegradable PCL-CF composites with different ratios were prepared by melt-blending. DSC and DMTA results show that there is interaction between PCL and CF but this interaction is not very strong because T_g, T_m and T_c of the pristine PCL were not largely affected by the presence of CF. Static mechanical testing shows that tensile strength, Young's modulus and flexural strength were increased by the addition of CF. The results from DMTA and ARES show that both storage modulus and viscous modulus are enhanced by CF. 45%PCL-CF generally had the best properties among all the testing composites. The mechanical properties of PCL-CF composites are comparable to those with chitin n-butyrate as the compatibilizer [21,22].

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