Effects of Bioactive Glass Particles on the Mechanical and Thermal Behavior of Poly(ε-caprolactone)

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Summary: Poly(ε-caprolactone)/Bioactive glass (BG) composites were prepared to study the effects of bioactive glass on mechanical and thermal behavior of poly(ε-caprolactone) (PCL). Composites were fabricated using a solvent casting/sonication technique. Composite characterization was conducted by differential scanning calorimetry (DSC), thermogravimetric analysis (TGA) and tensile tests. Interphase adhesion between filler and matrix, a prerequisite for good mechanical properties, was evaluated by dynamic mechanical analysis (DMA). The obtained results showed that BG leaded to an acceleration of the composite thermal degradation accompanied by a general enhancement of the mechanical properties.

Keywords: adhesion; biopolymers; bioactive glass; mechanical properties; poly(ε-caprolactone)

Introduction

Reinforcing polymeric biomaterials with bioactive inorganic fillers can be a quite successful strategy to extend the use of composites for medical applications. The use of bioactive fillers such as ceramic phosphates including hydroxyapatite and/or BG particles may improve both mechanical properties and bone regeneration.[1,2] Based upon this idea, hydroxyl apatite (HA) and BG reinforced biodegradable polymer composites have been developed.[3–5]

Although mechanical properties of composites can be improved to a certain extent by the addition of bioactive fillers there is still a need to improve adhesion between filler and matrix.[2] The objective of this study is also to develop a suitable method to improve the interphase adhesion properties of PCL/BG composites.

There have been previous studies in the literature focusing on the composites made by combination of biodegradable polymers and bioglasses.[6,7] In this study we have manufactured PCL/BG composites, as promising materials for tissue engineering applications and further as interesting biomaterials suitable for implants to the human body. PCL/BG films have been prepared via solvent casting configuration and the effects of BG on thermal and mechanical properties of PCL were analyzed.

Experimental Part

Materials

Poly(ε-caprolactone) was kindly supplied by Purac Biochem (The Netherlands). Bioglass® 45S5 was provided by Novabone® (US) with composition on a weight base 45% SiO_2, 24.5% Na_2O, 24.5% CaO, and 6% P_2O_5. $CHCl_3$ was purchased from Panreac (Spain) for use as solvent.

Preparation of PCL-BG Films

The preparation of PCL/BG composites with different filler concentrations was carried out by solvent casting. PCL pellets were dispersed in chloroform under stirring, then a certain amount of BG powder was added into the solution; 0.278 g for

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Table 1.
PCL and its composites showing volume and weight percentage of BG in PCL and its acronyms.

Materials	Vol% BG	wt% BG	Acronym
PCL	0	0	PCL0BG
PCL/BG	5	11	PCL5BG
PCL/BG	10	21	PCL10BG
PCL/BG	15	30	PCL15BG

Table 2.
Data came out by TGA/DTG analysis.

Material	Reaction Region	Peak Temperature	Weight Loss
	°C	°C	%
PCL0BG	273–443	378	99.9
PCL5BG	189–340	303	84.9
PCL10BG	174–330	291	79.9
PCL15BG	171–299	274	71.9

5 vol% of BG into PCL, 0.587 g for 10 vol% and 0.932 g for 15 vol% (Table 1). Then the mixture was sonicated (30 min). The ratio of the PCL and BG mixture to chloroform was fixed at 10% w/v.

Characterization

DSC analysis was carried out in a TA Instruments Q200-1395. DSC scans were run from −90 °C to 100 °C at 10 °C/min. TGA analysis was performed in a TA Instruments Q50-0545. Experiments were conducted within the temperature range 5–500 °C. Tensile tests were conducted at 5 mm min^{-1} with an INSTRON 5565 equipped with a load cell of 500 N. Samples of 10 mm × 1 mm × 0.2 mm were used. DMA analysis was performed by Mettler Toledo DMA/SDTA 861 in tensile mode at a frequency of 1 Hz. The temperature range was from −100 °C to 40 °C. Samples of 4 mm × 30 mm × 0.2 mm were used.

Results and Discussion

Thermogravimetric Analysis (TGA)

Within the scope of this study, TGA thermograms of samples were analyzed in order to determine the reaction interval, peak temperatures and weight losses of the samples when they are exposed to different heating rates. In Figure 1 PCL/BG combustion TGA curves are represented. Results have been analyzed and tabulated in Table 2.

The thermogravimetric behavior of PCL varies compared with that of composites containing different volume compositions of BG (5, 10, 15 vol%). Likewise it was observed that the onset of thermal degradation of the polymer was shifted to lower temperatures by increasing BG content. In a similar study, the incorporation of particles of BG into poly (ε-caprolactone-

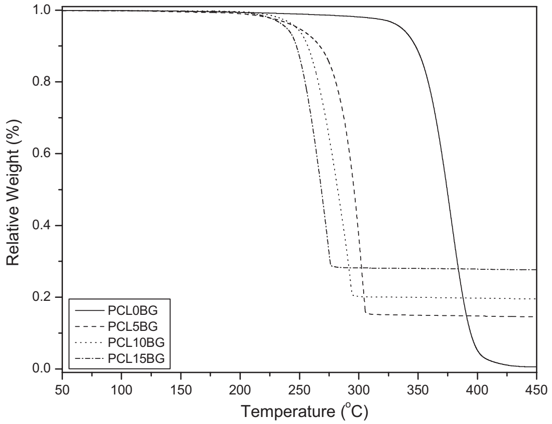

Figure 1.
PCL/BG thermal degradation (TGA) curves at 5 °C/min.

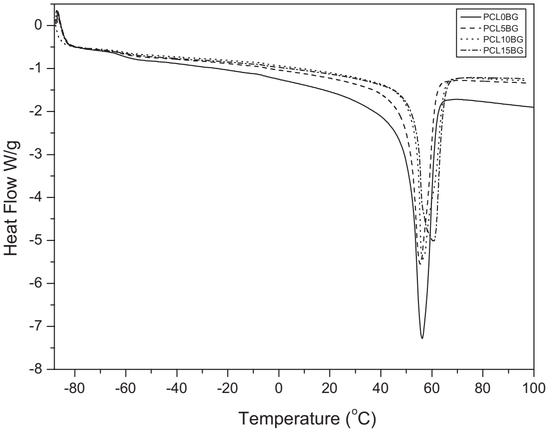

Figure 2.
PCL/BG composites: DSC curve analysis at temperature range from −100 °C to 100 °C.

co-DL-lactide) also accelerated the thermal degradation process; the presence of glass particles during processing is responsible for the degradation. In the same study the composites showed a reduction in M_w of the matrix with the inclusion of BG particles; it was reported that during hydrolytic degradation M_w decreased faster in the presence of BG than in neat polymer matrix.[8]

Differential Scanning Calorimetry (DSC)

DSC curves are represented in Figure 2. The glass transition temperature (T_g), melting temperature (T_m) and enthalpy of fusion (ΔH_m) of PCL/BG composites remain almost the same. It is well known that thermal stability of organic/inorganic hybrids depends on the interaction between the polymer chain and the inorganic phase, and the degree of uniform distribution of the latter in the former. The glass transition temperature of the hybrid composites is associated with a cooperative motion of polymer chain segments, which may be elongated by the presence of a BG network. The fact that the T_g values of the fabricated composite system are almost the same in PCL and composites suggests that the nature of interaction at the interphase is weak. The increase in BG content neither affected the onset in the melting point or the degree of crystallinity of the composite. In addition there is no nucleating effect on the crystallization of PCL.[9]

Tensile Tests

The mechanical properties of PCL-based composite films were determined by tensile tests. Typical stress-strain curves obtained from tensile tests for PCL and its composites are shown in Figure 3. The calculated mechanical properties are shown in Table 3. Figure 3 clearly shows the influence of BG fillers on the mechanical behavior of PCL-based composite films. The films reinforced with 10 and 15 vol% of BG filler display higher Young's modulus (E) as well as lower tensile strain at break (ε_b), than the one with 5 vol% which seems to accompany the pure polymer's mechanical behavior. A 64% and 70% of enhancement of the modulus for 10 vol% and 15 vol% amount of BG respectively are obtained.

A logical reduction of ductility (ε_b) was also accompanied by a drop in ultimate tensile stress (σ_b) as filler content increased, suggesting bad adhesion at the filler/PCL interphase.

Dynamic Mechanical Analysis (DMA)

Further studies were conducted by DMA. Figure 4 shows the temperature dependence of the storage modulus (E′) and the

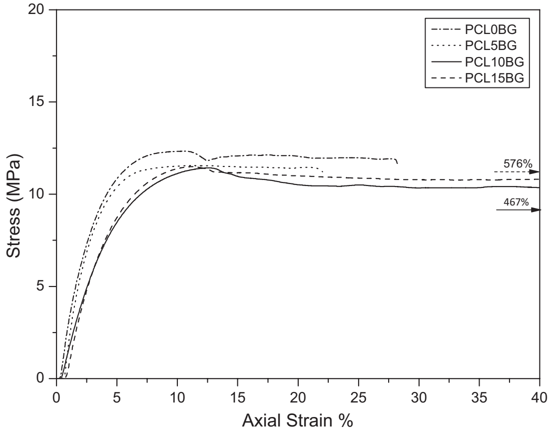

Figure 3.
Tensile stress-strain behavior of PCL/BG composites.

Table 3.
Tensile properties of PCL and its bioglass composites.

Materials	E	σ_b	ε_b
	MPa	MPa	%
PCL0BG	146 ± 17	14.9 ± 2.5	457 ± 20
PCL5BG	151 ± 14	17.6 ± 1.6	600 ± 31
PCL10BG	414 ± 40	11.6 ± 0.7	27 ± 12
PCL15BG	485 ± 33	10.7 ± 0.5	15 ± 4

evaluation of tanδ of PCL/BG composites. It is noticed that E′ increases monotonously as the BG content increases. On the other hand, the polymer becomes more and more constrained leading to a decrease in the magnitude of the tanδ peak (Figure 4).

The adhesion effect of the filler into PCL was evaluated by the equation: $(\tan\delta)c/(\tan\delta)m = 1\text{-}bV_F$, where the m and c indexes refer to matrix and composite respectively, V_F to BG volume content, and b is a parameter that can be interpreted in terms of adhesion at the BG-matrix interphase.[10] The value of b parameter calculated from the slope of the linear regression fit was $b = 2.98$. Further investigations are being conducted to improve interphase adhesion by preparation of composites

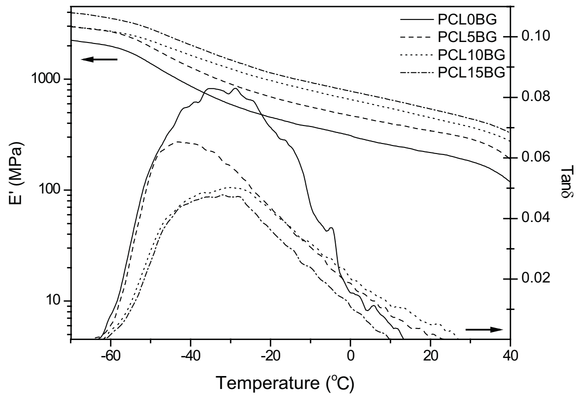

Figure 4.
Temperature dependence of storage modulus (E′) and dissipation peak (tanδ) for PCL/BG composite system at 1 Hz.

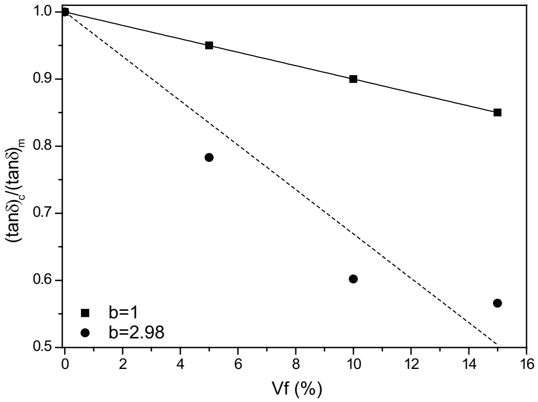

Figure 5.
The tanδ (composite)/tanδ (matrix) versus the filler volume content (V_f) in PCL/BG composites.

using BG particles plasma polymerized with ε-caprolactone.

Conclusion

This study has demonstrated that in presence of BG the thermal degradation of PCL is initiated at lower temperatures. Mechanical tests showed that the incorporation of BG into the PCL matrix mechanically reinforces the polymer; particularly composites' elastic moduli are significantly larger than that of pure polymer. PCL is a ductile material; higher concentrations of BG increase the elastic modulus, the material loses its ductility and becomes more fragile. The dynamic mechanical analysis (DMA) revealed that composite showed also larger storage modulus in regard to the neat polymer. The loss modulus also increased and there was a significant drop in the magnitude of the tanδ peak.

Further investigations on the adhesion between filler and matrix include the preparation of PCL/BG composites using plasma polymerized BG particles with ε-caprolactone as monomer. By this route the creation of a good bonding at the filler/matrix interphase is expected and eventually a much better dispersion and reinforcement effect of BG on PCL.

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