Influence of Polycaprolactone/Polyglycolide Blended Electrospun Fibers on the Morphology and Mechanical Properties of Polycaprolactone

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ABSTRACT: Polycaprolactone (PCL) and polyglycolide (PGA) are two biopolymers that have been used as *in situ* biomedical devices for various applications. The obstacle of creating a composite that captures the benefit of PCL's long degradation time, while acquiring the strength from PGA is overcoming the lack of surface adhesion between the two biopolymers for stress transfer to occur. This study investigates the use of miscible PCL-PGA blended fibers, created by electrospinning, to increase the interfacial bonding of fibers to the PCL matrix of the polymer–polymer composite. The use of the blended fibers will thereby create the ability of load transfer from the long-term PCL matrix to the stronger PCL-PGA fiber reinforcement. The incorporation of the PCL-PGA fibers was able to increase the tensile yield strength and Young's modulus over that of the bulk PCL, while decreasing the percent elongation at break. © 2013 Wiley Periodicals, Inc. J. Appl. Polym. Sci. **2014**, *131*, 40224.

INTRODUCTION

The manufacturing of composites has long been used to obtain specific properties of each component of the composite and tailor them for an application. With composites, specifically polymer–polymer composites, the interface between the matrix and reinforcement is critical in order for load transfer to occur between the two phases.[1,2] However, most polymers are immiscible to one another[2] and specifically hydrophobic and hydrophilic polymers are predisposed to microscopic phase separation during blending procedures.[3–5]

Polycaprolactone (PCL), a hydrophobic biopolymer,[6] and polyglycolide (PGA), a hydrophilic biopolymer, are Food and Drug Administration (FDA) approved. They have been used as biomedical devices in such applications as drug delivery and tissue repair.[7,8] One quality that makes these synthetic biopolymers desired for human applications is their ability to degrade and be replaced by natural tissues.[9] The molecular structure of each of the biopolymers affects properties such as mechanical strength and degradation rate. PCL is known to have properties such as a low melting point (60°C), slow degradation rate (2 years), and moderate strength.[7,10,11] On the contrary, PGA has a high melting point (230°C), fast degradation rate, and the highest strength of the synthetic biopolymers.[12–14]

For long-term biomedical applications, such as bone repair, the strength of PGA is desired as well as the slow degradation rate of PCL. To alleviate the problem associated with polymer–polymer immiscibility, researchers have done complex chemical modifications of polymers by changing their molecular structure or adding foreign substances such as compatibilizers to create true blends.[1,2] Aghdam and Najarian[15] used coelectrospinning to create a miscible PCL-PGA blend. The process of coelectrospinning ensures the purity of the composite is unaltered by eliminating the use of external agents or changing the molecular structure of the biopolymers.

This work will examine the viability of a load bearing PCL composite with PCL-PGA fiber blend reinforcement. It is expected that the miscible PCL-PGA blend will aid the interfacial adhesion between the electrospun fibers and the PCL matrix, therefore improving the ability of load transfer from matrix to reinforcement. This composite design will increase strength over the bulk PCL while maintaining PCL's long degradation rate by encapsulating the PGA from biological fluids that would start degradation.

EXPERIMENTAL

Materials
PGA was purchased from Purac Biomaterials, US (Purasorb PG 20) and used for the fiber blend. The PCL that was used as the next
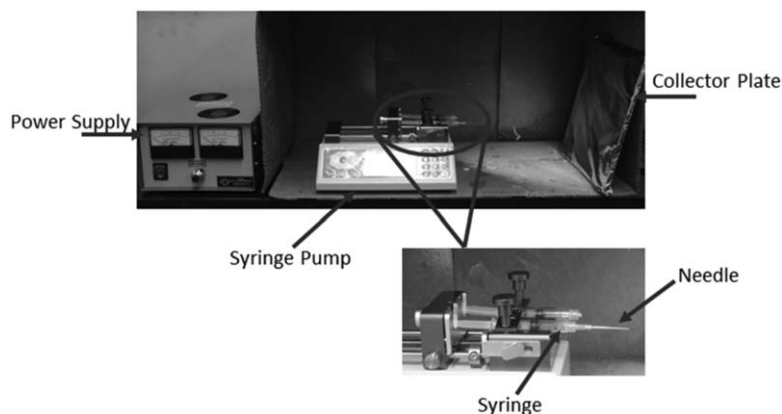
Figure 1. Image of the electrospinning set-up.

component of the blend had a molecular weight of 50,000 and came in granular form. Hexafluoroisopropanol (HFP) used as a solvent for the blend, as well as the acetone used for composite production, was purchased from Sigma Aldrich, US.

Preparation of Fibers

A 50/50 ratio of the PCL-PGA blend was chosen for the polymer composite design. It was shown that this ratio can lead to the highest mechanical properties while maintaining a miscible blend.[15] The starting solution for electrospinning was made by dissolving 0.32 g of PGA and 0.32 g of PCL into 5 mL of HFP to make an 8% (wt/wt) solution. To ensure that the solution was homogenous, it was heated and stirred with a magnetic stirrer for 5 h at 50°C. Solutions of pure PCL and pure PGA were also produced as controls to determine the effect of processing on the thermal and molecular properties of the fibers. PCL and PGA were dissolved separately into HFP to produce 8% (wt/wt) solutions each.

Electrospinning to produce the fibers was executed with a syringe pump under a fume hood (Figure 1). The fibers were generated by spinning with the following parameters: voltage 18 kV, feed rate 1 mL/h, distance 35 cm, needle 1.27 mm diameter, and samples collected on an aluminum plate covered with foil. The fibers were allowed to sit over night to allow any residual solvent to evaporate before use.

Composite Preparation

Compression molding was used to encapsulate the PCL-PGA blended fibers into the PCL matrix for all of the samples. The electrospun fiber mats were cut down to dimensions of 3 mm × 3 mm then mixed with granulated PCL. Acetone was then added to the mixture and heated to assist with the distribution of the fibers into the PCL matrix. The PCL-PGA blended fibers, granular PCL used for matrix, and acetone were heated to 100°C and stirred for 1 h. Once the acetone had evaporated prepregs containing 40 wt % of fibers were manufactured for each characterization test. The mixture was then transferred into the mold and heated again to 100°C to continue degassing. The mold was then transferred to a preheated (100°C) press where 1.0 metric ton of pressure was applied. After 10 min the heat was removed, however the pressure remained for 45 min. The mold was allowed to cool overnight. An illustration of the composites design is shown in Figure 2.

Characterization

Scanning Electron Microscopy. Scanning electron microscopy (SEM) was used to analyze the fibers. The images were taken on a Hitachi S-4300 SE/N. The samples used for analyses were cut from the electrospun fiber mats and attached to an aluminum stud with double sided carbon tape. The morphology was studied with a voltage of 3.0 kV and a working distance of 5 mm.

Fourier Transform Infrared Spectroscopy Analysis. The FTIR spectra were recorded under environmentally controlled conditions (65% relative humidity and 21°C) using an FTIR instrument (Spotlight 400) equipped with an UATR accessory (PerkinElmer, USA). The UATR-FTIR was also equipped with a ZnSe-Diamond crystal composite (1 bounce) that allows collection of FTIR spectra directly on a sample without any special preparation. The "pressure arm" of the instrument was used to apply a constant pressure (monitored by software) to the samples positioned on top of the ZnSe-Diamond crystal to ensure a good contact between the sample and the incident IR beam, thereby minimizing loss of the IR beam. All FTIR spectra were collected at a spectrum resolution of 4 cm^{-1}, with 32 co-added scans over the range from 4000 cm^{-1} to 650 cm^{-1}. A background scan of the clean ZnSe-Diamond crystal was acquired before scanning the samples.

Differential Scanning Calorimetry. To determine whether the electrospinning process produced a truly miscible PCL-PGA blend differential scanning calorimetry (DSC) was used to study the thermal properties of the fibers. Thermal evaluation was performed on Perkin–Elmer Diamond DSC. All samples were
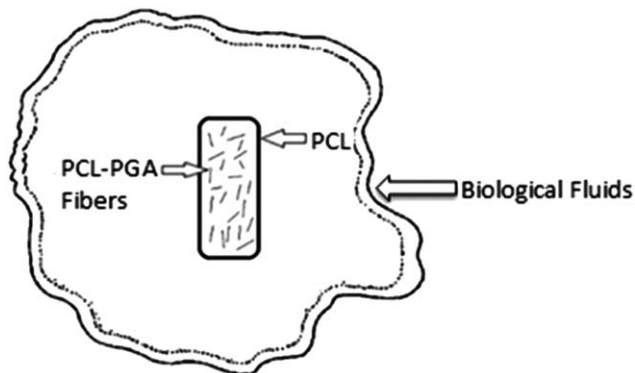

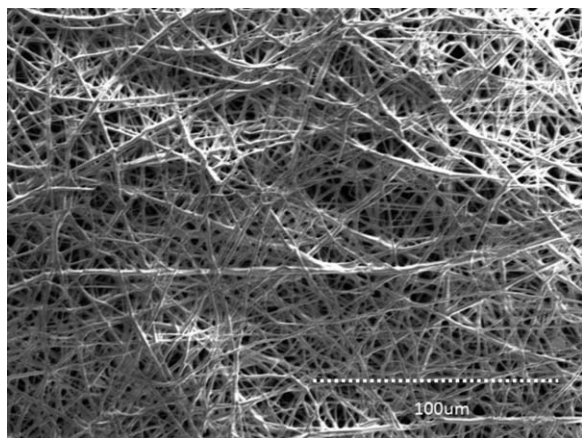Figure 2. Illustration of biopolymer composite design.

Figure 3. An SEM image of electrospun 50/50 PCL-PGA blended fibers.

tested from −100°C to 250°C, quench cooling first. Testing was done at temperature rates of 10, 20, 30, and 40 °C/min in a liquid nitrogen atmosphere.

Tensile Testing. ASTM International standard D638-08 was used for tensile testing of the biopolymer samples. Tensile test samples were molded to the following dimensions, 63.5 × 3.25 × 4.23 mm^3. Mechanical testing was done on an AGS-J Shimadzu Autograph. Tensile testing of the composite samples was done with a 1 kN load cell. The samples had a 20 mm gauge length and were tested at a rate of 5.0 mm/min.

RESULTS AND DISCUSSION

Fiber Characterization

SEM image of the PCL-PGA blended fibers electrospun with HFP is shown in Figure 3. The electrospinning parameters were the same for all biopolymer solutions. The electrospinning of the PCL-PGA blend produced interconnected fibers without any bubbles attached that would cause mechanical failure. These images also show no phase separation between the two biopolymers, indicating that the two polymers were compatible in the blend.

Molecular Structure

To examine the molecular structure of the electrospun fibers, FTIR was performed. Analysis was performed on PCL fibers, PGA fibers, and PCL-PGA fiber blend. The FTIR spectra are shown in Figure 4. The FTIR spectrum of the pure PCL fibers shows a C=O carbonyl stretching at 1723 cm^{-1}, C—O stretching at 1173 cm^{-1}, C—O—C ether group at 1049 cm^{-1}, and two C—H peaks at 2950 and 2873 cm^{-1}.

The spectra of the PGA fibers show the C=O carbonyl stretch at 1747 cm^{-1}, C—O stretching at 1156 cm^{-1}, C—O—C ether group at 1091 cm^{-1}, and a C—H stretch at 2976 cm^{-1}. The spectra of the PCL-PGA blends show two C=O carbonyl peaks at 1747 cm^{-1} and 1723 cm^{-1} for the PGA and PCL, respectively. The dual C—H peaks from the PCL are also seen in the blend. While the C—O and C—O—C peaks are at 1156 cm^{-1} and 1091 cm^{-1}, respectively.

The peaks from both biopolymers can be seen, indicating that the biopolymers were not covalently bonded just blended. As ascertained by Aghdam and Najarian,[15] HFIP had no effect on the molecular structure of the PCL, PGA, or the PCL-PGA blend.

Thermal Properties

Imaging using SEM showed that the PCL-PGA biopolymer blend was compatible with one another, however to determine whether the biopolymer was miscible, DSC was employed. The DSC results (Figures 5 and 6) show only one glass transition temperature (T_g) for the biopolymer blend found just before the PCL starts to melt. Blends that are immiscible will produce a T_g for each component present in the blend. Whereas a true miscible blend will have only one T_g present.[15–18] The T_g of the 50/50 blend (41.62°C) was calculated by determining the midpoint of the inflectional tangent between the onset and endpoint temperatures. The T_g of the blend in this research is similar to the T_g found in the research by Agham and Najarian (39.5°C).[15] No distinguishable T_g peaks were observed for the PCL and PGA fiber controls. Therefore, it can be concluded that the electrospinning process was successful in creating a miscible PCL-PGA biopolymer blend.
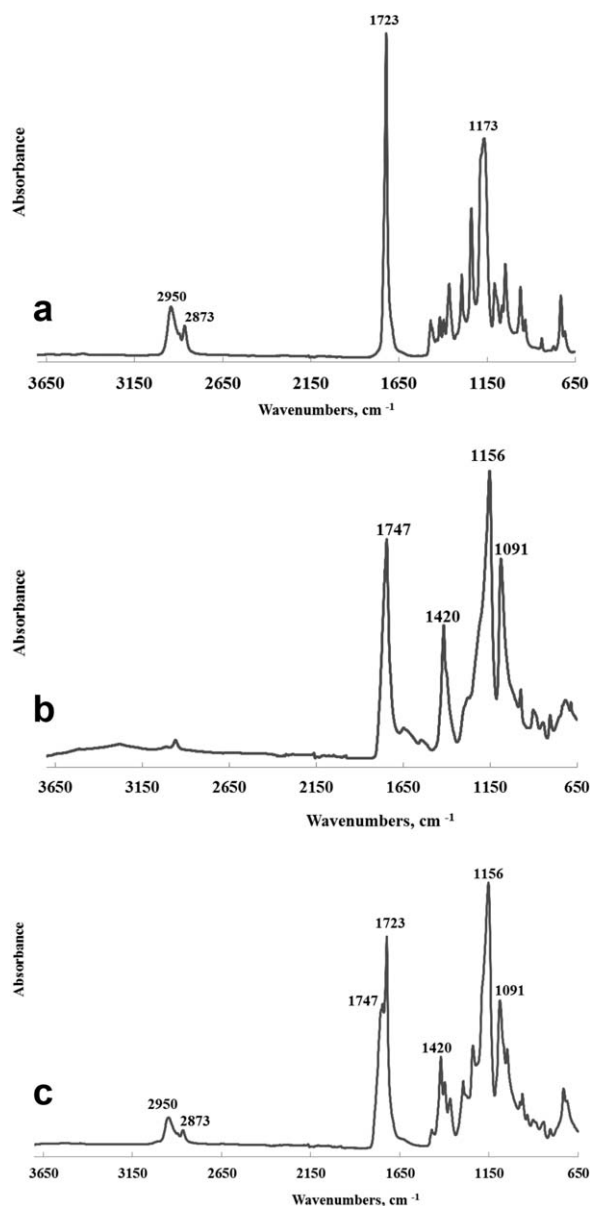

Figure 4. FTIR spectra of electrospun (a) PCL, (b) PGA, and (c) 50/50 PCL-PGA blended fibers.
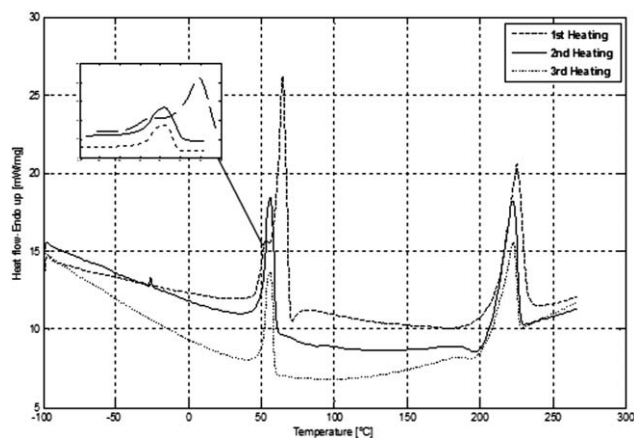
Figure 5. DSC thermographs of the electrospun 50/50 PCL-PGA blended fibers with three heating scans.

The PCL-PGA fiber blend was quenched cooled then heated to ensure that the effect of processing was realized in the thermal analysis. Upon testing a second and third time, PCL's melting temperature had a 15% decline and the melting enthalpy decreased by 48.5 and 43.7% respectively (Table I). In these runs, the T_g is overshadowed by the melting temperature of the PCL. The melting temperature of PGA was not significantly affected by the multiple test runs; however heating the second and third time did increased the melting enthalpy by 14.1 and 14.9%, respectively (Table I). The second and third runs had no significant effect on PCL and PGA's crystallization temperature (Table II). Analysis of the control PCL and PGA fibers generated melting temperatures of 63°C and 218°C with crystallization temperatures of 6.25°C and 156°C, respectively.

The effect of processing was seen in the percent crystallization (X_c) of the fibers. The reference heats of melting (ΔH_m^o) used for calculating X_c were 135.44 J/g for PCL and 183.2 J/g for PGA.[19,20] The initial complete heating and cooling runs were calculated as having X_c of 31.3% for PCL and 19.2% for PGA. After heating and cooling again the X_c of PCL decreased to 16.2% while the X_c of PGA increased to 21.9%. These findings correlate with the changes found for the T_g and melting enthalpies of the polymers which indicate that the electrospinning blending process clearly had an effect on the thermal
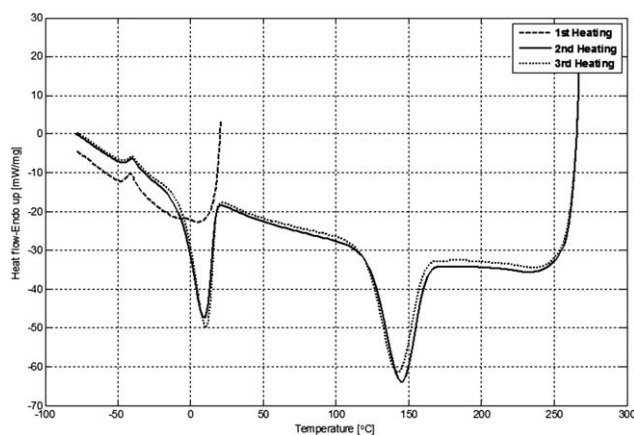

Figure 6. DSC thermographs of the electrospun 50/50 PCL-PGA blended fibers with three cooling scans.

Table I. Thermal Analysis of PCL-PGA Blend During Cooling

	PCL		PGA	
Cooling scan	ΔH_c (J/g)	T_c (°C)	ΔH_c (J/g)	T_c (°C)
Initial cooling	–	–	–	–
1st cooling	−23.7	11.7	−36.8	147.8
2nd cooling	−23.1	11.7	−36.2	144.4

stability of the fibers. The addition of PGA to PCL decreased space for movement of molecules as was found in the research by Su et al.,[21] where the acrylic acid grafted PCL was used to blend with poly(glutamic acid). Also, the higher melting enthalpy shows that processing produced better adhesion between PCL and PGA.

Tensile Properties

Determining the biopolymer composite's behavior under tensile load is a major factor when placed in load bearing *in situ* areas of the human body. Tensile testing of the biopolymer samples showed that the PCL/PCL-PGA blended fiber composites have higher yield strength than pure PCL samples. The pure PCL samples had yield strength of 13.4 MPa, which coincides with values found in literature for tensile testing of compression molded pure PCL samples.[22,23] The PCL/PCL-PGA blended fiber composites had yield strength of 17.51 MPa. Hypothesis testing using a significance level of 90% with $\alpha = 0.10$ showed that there was a significant difference between the yield strength of the samples. The increase in strength coincides with the data found from the thermal analysis of the fibers, where the addition of PGA increased the X_c of the PCL.

The ASTM International standard D638-08 was used for calculating the modulus of elasticity of the biopolymer samples. The modulus followed the same trend as that of the yield strength results, with the PCL/PCL-PGA composites having the higher Young's modulus. During yielding the percent strain of the pure PCL and PCL/PCL-PGA composite samples were analogous. Hypothesis testing using the Young's modulus also showed a significant difference between the biopolymer samples. There was a greater change in the modulus of the samples than the changes observed in their strength. This is due to the strength being primarily affected by the matrix in composites, while the modulus is primarily affected by the fiber reinforcement.[1] Hence, the addition of the blended fibers brought forth an increase in stiffness. This can further be seen by the effect on the strain elongation of the samples.

It was noticed that the overall percent elongation was also affected by the changes made to the biopolymer samples. These changes are shown in Table III. By adding stiff reinforcements to matrices the elongation at break is reduced due to stress concentrations from the reinforcements.[29] Therefore as expected,

Table II. Thermal Analysis of PCL-PGA Blend During Heating

	PCL		PGA	
Heating scan	ΔH_m (J/g)	T_m (°C)	ΔH_m (J/g)	T_m (°C)
1st heating	42.4	64	35.2	225
2nd heating	21.9	54	40.1	220
3rd heating	23.9	54	40.4	220

Table III. Comparative Tensile Testing Data of Bulk PCL and PCL/PCL-PGA Fiber Composites

	Yield strength (MPa)	Young's modulus (MPa)	Percent elongation (%)
PCL	13.37 ± 0.41	220.43 ± 9.72	51.7
PCL/PCL-PGA Fibers	17.51 ± 1.1	313.34 ± 35.4	12.2
PGA[a]	45	6.37 ± 0.72	12.17 ± 7.8

[a] PGA values from literature.[24–28]

the highest percent elongation occurred with the pure PCL samples, which stretched 51.7% of its original 20 mm gauge length. The PCL/PCL-PGA blended fibers stretched 12.2% of its original length. As stated before the percent elongation before the yield point of both samples is analogous, and therefore the difference in elongation between the samples occurred after the yield points. As the yield strength and modulus of the samples increased the elongation decrease. The higher elongation of the pure PCL samples show that they are tougher than the fiber composites, however the higher modulus, yield strength, and low elongation show that the fiber composites are harder and stronger. For this reason, the incorporation of the blended fibers created a more brittle like fracture behavior in the composite.

CONCLUSIONS

This study shows the feasibility of creating a load bearing PCL/PCL-PGA fiber blend composite. The addition of 40 wt % of PCL-PGA blended fibers to the PCL matrix showed an increase in the tensile yield strength and Young's modulus. With the increase in yield strength and modulus there was a decrease in the percent elongation of the composites. Morphological analysis of the PCL-PGA fiber blend showed the consistency of the blend and that the fibers were free of voids. The FTIR spectrum of the blend has the peaks for both PCL and PGA without any molecular effects from electrospinning or HFP. Thermal analysis revealed the miscibility of the 50/50 blend of PCL and PGA when electrospun with HFP. Thermal analysis of the fibers also concurred with the mechanical analysis found with the composites in which the addition of PGA to PCL increased the X_c of the fibers; thus increasing the mechanical properties of the overall composite. A stronger long-term biodegradable composite was achieved with a PCL matrix and PCL-PGA blended fiber reinforcement without the use of compatibilizers.

ACKNOWLEDGMENTS

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