Investigating the Effect of PGA on Physical and Mechanical Properties of Electrospun PCL/PGA Blend Nanofibers

Rouhollah Mehdinavaz Aghdam,[1,2] Siamak Najarian,[1] Saeed Shakhesi,[2] Samaneh Khanlari,[3] Keyvan Shaabani,[2] Shahriar Sharifi[4]*

[1]Biomedical Engineering Department, Amirkabir University of Technology, Tehran, Iran
[2]Engineering Research Institute, Tehran, Iran
[3]Department of Chemical and Biological Engineering, University of Ottawa, Ottawa, Canada
[4]Novel Drug Delivery System Department, Iran Polymer and Petrochemical Institute, Tehran, Iran

ABSTRACT: In the field of tissue engineering there is always a need for new engineered polymeric biomaterials which have ideal properties and functional customization. Unfortunately the demands for many biomedical applications need a set of properties that no polymers can fulfill. One method to satisfy these demands and providing desirable new biomaterials is by mixing two or more polymers. In this work, random nanofibrous blends of poly (ε-caprolactone) (PCL) and polyglycolic acid (PGA) with various PCL/PGA compositions (100/0, 80/20, 65/35, 50/50, and 0/100) were fabricated by electrospinning method and characterized for soft-tissue engineering applications. Physical, chemical, thermal, and mechanical properties of PCL/PGA blend nanofibers were measured by scanning electron microscopy (SEM), porosimetry, contact angle measurement, water uptake, attenuated total reflectance Fourier transform-infrared spectroscopy (ATR-FT-IR), X-ray diffraction (XRD), differential scanning calorimetric (DSC), dynamic mechanical thermal analysis (DMTA), and tensile measurements. Morphological characterization showed that the addition of PGA to PCL results in an increase in the average diameter of the nanofibers. According to these results, when the amount of PGA in the blend solution increased, the hydrophilicity and water uptake of the nanofibrous scaffolds increased concurrently, approaching those of PGA nanofibers. Differential scanning calorimetric studies showed that the PCL and PGA were miscible in the nanofibrous structure and the mechanical characterization under dry conditions showed that increasing PGA content results in a tremendous increase in the mechanical properties. In conclusion, the random nanofibrous PCL/PGA scaffold used in this study constitutes a promising material for soft-tissue engineering. © 2011 Wiley Periodicals, Inc. J Appl Polym Sci 124: 123–131, 2012

Key words: nanofiber; electrospinning; PCL; PGA; blending

INTRODUCTION

Electrospinning is a relatively simple and efficient technique in which polymer fibers with diameters ranging from several microns down to 100 nm or less can be produced.[1,2] The typical electrospinning setup consists of: a syringe pump, which pumps the polymer solution out through a spinning nozzle at a constant speed; a high-voltage supplier, which induces a high static electron to the polymer solution and gives the solution a positive charge; and a collector, which is a grounded or negatively charged electrode.[3,4]

Recently, electrospun nonwoven nanofibrous structures have been widely used in multiple biomedical applications, such as tissue engineering, wound dressing, drug delivery, and medical implants.[5] The attraction of electrospun biomaterials in the context of tissue engineering is manifested in several ways. First, very high surface to volume ratio and high porosity can be achieved for better cell incorporation and perfusion. Second, the process allows for control of structure at the nano, micro, and macroscales for flexible tissue design and it has been suggested that nanofibrous extracellular matrices (ECM)-mimicking features may improve cellular response and biocompatibility because of the morphological similarities to the three-dimensional ECM protein fiber network. Third, the electrospinning process is versatile, since it offers the ability to incorporate multiple polymers and bioactive ingredients; it can also be used to enhance mechanical properties of the obtained nanofibrous materials compared with solid-wall equivalents.[6]

*Present address: Biomedical Engineering Department, University Medical Center Groningen, A. Deusinglaan AQ4 1, Building 3215, FB40, 9713 AV Groningen, The Netherlands.
Correspondence to: R. Mehdinavaz Aghdam (mehdinavaz@aut.ac.ir) or S. Sharifi (sh.sharif@gmail.com).

A wide variety of biodegradable and biocompatible synthetic and natural polymers have been investigated to fabricate nanofibrous scaffolds. Electrospun scaffolds can be fabricated using both synthetic and natural polymers, such as poly(lactic acid) (PLA), polyglycolic acid (PGA), poly(lactic-co-glycolic acid) (PLGA), poly(ε-caprolactone) (PCL), poly(L-lactide-co-ε-caprolactone) (PLCL), poly urethane (PU), chitosan, and collagen.[7–12] These biodegradable polymers have been used to electrospin the engineered scaffolds for bone tissue, musculoskeletal tissue, myocardial tissue grafts, and blood vessel substitutes.[6,13]

Natural and synthetic polymers cannot meet all the requirements of a perfect scaffold individually: natural polymers lose their mechanical properties very early during degradation while synthetic polymer, such as synthetic polyesters are usually less hydrophilic, lack binding sites for cell adhesion and release acidic degradation products. To overcome the aforementioned problems, hybrid materials which are blends of two or more types of polymers have been devised by researchers that assimilate the desirable characteristics of component materials.[14]

To design an optimum scaffold for tissue regeneration aims, various factors such as pore size and morphology, mechanical and surface properties, and appropriate biodegradability should be considered. Of these, the importance of mechanical properties on cell growth is particularly obvious in tissues such as cartilage, muscles, blood vessels, tendons, and bone. To improve the deficiency of mechanical properties of electrospun fibers, several studies have researched various blending systems, controlling processing parameters, and postprocessing treatments.[15]

The blend electrospun method not only overcomes the limitations associated with a single polymer, but also creates a new component without the need for synthesizing a new copolymer, which is difficult and complex to achieve using coelectrospinning of two single biopolymers.[16] In the blend electrospinning method, one can blend the two polymers using an electrospinning 2-eject system, which contains a mix of the polymers and then electrospin the mixture.[17]

Poly(ε-caprolactone) (PCL), a semicrystalline biodegradable polymer, belongs to the family of polyhydroxy polyesters.[18] Compared with other polyester family members such as poly(glycolic acid) (PGA), poly(lactide) (PLA), and poly(lactide-co-glycolide) (PLGA), PCL has been less frequently used as a material for fabricating biomaterial scaffolds, mainly because of concern over its slower degradation kinetics and lack of bioactivity,[19] although it may be suitable for applications such as long-term drug delivery systems. The use of PCL alone as a scaffold material is limited due to its poor mechanical properties, hydrophobic properties, and poor cell attachment as

well. Blending a bioabsorbable polymer with PCL is expected to modulate its degradation rate, mechanical, and hydrophilicity,[20,21] while should improve the bioactivity of the synthetic polymers. Blending PCL with PGA has furnished a better biocompatibility and hydrophilicity as well as mechanical properties suited for soft-tissue engineering.

PGA is semicrystalline polyester that degrades in the body over a period of several weeks. It is approved for biomedical use and has been used extensively as a suture material in surgical applications. PGA is suitable for such applications not only because of its convenient timescale of degradation, but also because it is nontoxic and biocompatible and degrades to products that are metabolized in the body.[22] This has been shown experimentally in several studies involving blends in which one or both components were polyesters. In particular, Dickers et al. investigated blends of PGA with PCL, poly(d, l-lactide), and poly(3-hydroxybutyrateco-3-hydroxyvalerate) (PHBHV).[23,24]

In this research, we employed the electrospinning method to prepare PCL, PGA, and PCL/PGA blend nanofibers with different PGA contents, with the aims to investigate the effect of PGA content on physical, chemical, and mechanical properties of nanofibrous structures. One limitation of electrospun scaffolds fabricated with synthetic polymers such as PCL is low cell affinity toward them due to low hydrophilicity and mechanical properties. PGA which is a flexible and hydrophilic biopolymer has been used to overcome the brittle and low elongate properties of PCL. We prepared a new nanofiber component that it holds promise for use as a biomaterial for soft-tissue engineering and biomedical scaffolds.

EXPERIMENTAL

Materials

Poly(ε-caprolactone) (PCL; Mw = 80,000 g/mol) and polyglycolic acid (PGA, with inherent viscosity of 1.4–1.8 dL/g and MFI = 0.4–0.7 g/10 min at 190°C) were obtained from ς-Aldrich (St. Louis, MO); 1,1,1,3,3,3-hexafluoro-2-propanol (HFIP) which was purchased from Fluka Co. was used as the solvent to prepare polymer blends as the solution for electrospinning process.

Solution blend preparation

PCL and PGA with a weight ratio of 80/20, 65/35, and 50/50 was dissolved in HFIP and a series of PCL/PGA blend solutions with the concentration of 6 wt % were prepared. This was followed by magnetic stirring for 48 h until the polymers dissolved completely at 45°C. Neat PCL (100%) and neat PGA

(100%) at a total polymer concentration of 6 wt % were prepared for comparison.

Electrospinning processing

The electrospinning apparatus used in this work consisted of a high voltage source, a programmable syringe pump, and a stainless steel spindle as a nanofiber collector (Custom Design and Fabrication, Engineering Research Institute, Tehran, Iran).

PCL/PGA blend solutions were fed into a 5-mL plastic syringe with a needle diameter of 0.45 mm (22 gauge). The syringe was then placed in a syringe pump and a high voltage (17 kV) was applied to the tip of the needle attached to the syringe when a fluid jet was ejected. The mixed solution was electrospun onto a custom-made spindle (outer diameter 12 cm, length 8 cm), located at a 10-cm distance from the needle tip, and covered with an aluminum foil. The flow rate was set at 2 mL/h. The electrospun nanofibers on the foil were dried overnight at room temperature.

Physical, chemical, thermal, and mechanical characterization

Scanning electron microscopy (SEM)

The morphology and diameters of nanofibers was studied with the use of SEM (XL30-philips, Japan) at an accelerating voltage of 20 kV. Before SEM observation, all of the samples cut from the electrospun fiber mats (1 cm × 1 cm) were coated with gold using sputter-coater (Bal-Tec, SCD050, Germany) operated at 15 kV for 80 s. The average diameter of the nanofibers was measured from the SEM micrographs using image analysis software (JMicroVision Image analysis, Switzerland).

Porosity

The apparent density and porosity characteristics of the electrospun blend nanofiber were determined using eqs. (1) and (2), respectively.[25] The thickness of the nanofiber mats was measured by a micrometer and bulk density of PCL/PGA blend nanofibrous mats was estimated according to eq. (3).

Apparent density of scaffold (g/cm^3)

$$= \frac{\text{mass of scaffold (g)}}{\text{Area of scaffold (cm}^2) \times \text{Thickness of scaffold (cm)}} \tag{1}$$

Porosity of scaffold $= 1$

$$- \frac{\text{Appranet density of scaffold (g/cm}^3)}{\textit{Bulk density of the material (g/cm}^3)} \tag{2}$$

$$\frac{1}{\rho_{total}} = \frac{\text{wt\%}_{PCL}}{\rho_{PCL}} + \frac{wt\%_{PGA}}{\rho_{PGA}} \tag{3}$$

Viscosity

The viscosity of the solutions was measured by Physica MCR 301 rheometer (Anton-Paar; GmbH, Graz, Austria) using a double-gap concentric cylinder geometry with a radius ratio of 1.035 for dilute solutions.

Contact angle and water uptake measurement

For determination of the hydrophilic/hydrophobic properties of the PCL/PGA blend nanofiber, the contact angle of electrospun materials was measured by the sessile drop method using a video contact angle instrument (KRÜSS G10, Germany) at room temperature. For this aim, the electrospun mats were cut into a rectangular shape (20 mm × 10 mm) first and then about 5 μL of distilled water was pipetted onto the mats and temporal images of the droplet were taken and the contact angles were calculated by computer analysis of the acquired images.

To determine the water uptake of PCL/PGA blend nanofibers, samples were weighed and subsequently immersed in distilled water for 1 h at room temperature. After 1 h of immersion, the samples were taken and weighed after removing the surface water with filter paper. The water uptake (%) was calculated as follows:

$$\text{Water uptake}(\%) = [(W - W_0)/W_0] \times 100 \tag{4}$$

where W_0 and W represent the weight of the sample before and after immersion in water, respectively.

ATR-FT-IR

Attenuated Total Reflectance Fourier transform-infrared spectroscopy (ATR-FT-IR) spectra were recorded for the nanofiber blends using an IR spectrophotometer (Tensor 27 Bruker, Germany). The spectra were obtained with 32 scans per sample at a resolution of 4 cm^{-1} between 4000 and 500 cm^{-1}.

X-ray diffraction

X-ray diffraction (XRD) analysis was characterized by X-ray diffractometer (Philips Analyzer, Germany) equipped with Ni filter and Cu-Kα source and operating at 40 kV and 40 mA. The diffraction patterns were obtained at a scan rate of 5°/min.

Differential scanning calorimetry

The thermal properties and compatibility of two components of the blends in electrospinning mats were investigated by the differential scanning calorimetry (DSC) measurements (DSC1-Mettler Toledo)

in a temperature range from −80 to 100°C at a heating rate of 10°C/min under a nitrogen atmosphere. Samples with a weight of approximately 5 mg were loaded in an aluminum crucible under dry condition.

Dynamic mechanical thermal properties

The dynamic mechanical thermal (DMTA) properties of the blend nanofibrous sample were performed employing 10 mm × 5 mm × 0.1 mm flat sheets cut from electrospun nanofibrous mats using a dynamic mechanical analyzer (TRITON—TRITEC 2000 DMA) in tension mode with a heating rate of 10°C/min over the temperature range from −100 to 100°C and 5% strain amplitude for neat PCL, PGA, and all PCL/PGA blend nanofibrous samples. The frequency for all of the experiments was 1 Hz.

Mechanical properties

Mechanical characterizations of the blend nanofibrous mats was carried out with uniaxial tensile testing machine (STM-20, SANTAM Design and Manufacturing Co.) applying a 10 N load cell under a cross-head speed of 10 mm/min at ambient conditions. All samples were prepared in the form of rectangular shape with dimensions of 50 × 10 mm^2 from the nanofibrous scaffolds and vertically mounted on two mechanical gripping units of the tester, leaving a 40-mm gauge length for mechanical loading. The sample thicknesses were measured with a micrometer having a precision of 100 μm. The average values for the tensile property were obtained from the results of three tests.

RESULTS AND DISCUSSION

Morphological characterization

Figure 1 shows the SEM micrographs of electrospun blend nanofibers of PCL, PGA, and PCL/PGA prepared by electrospinning from 6 wt % solutions in HFIP. The PCL/PGA ratio in blends are 80/20, 65/35, and 50/50, respectively.

The micrograph images depict randomly interconnected structures forming a nonwoven structure. From the SEM images, the diameters of the nanofibers were calculated by image analysis software. As shown in Figure 1(a), the electrospun pure PCL nanofibers had the lower average diameter (86 ± 32m nm) than PCL/PGA nanofibers. Fiber diameter was found to increase with raising the concentration of PGA in PCL/PGA blend polymeric system. The average fiber diameter for the 80/20 blend system was 303 ± 76 nm, and further addition of PGA to 35%, led to an increase in average diameter of 368 ±

114 nm. However, at 50% PGA composition, the average diameter increased to 445 ± 126 nm, but it was still lower than that of neat PGA (597 ± 162 nm). The same solution concentration and spinning conditions were used have to PCL, PGA, and PCL/PGA nanofibers. Therefore, we believe that this difference in the fiber diameters may be associated with viscoelastic properties of PGA that has an effect on the solutions.

For electrospinning, solution viscosity is an important factor that influences the fiber diameter and fiber diameter distribution.[26] Under the electrostatic field, the droplet of polymer solution at the nozzle connected to electrical pole would deform into a Taylor conical shape and charge or dipole orientation would be formed at the interface between air and droplet to form tensile force. Once the tensile force overcame the surface tension of droplet, a jet of solution would eject from droplet and underwent a process of stretching, splitting, and whipping in the air and finally changed into fiber when the solvent evaporated from the jet. Therefore, polymer solution with higher viscosity would need more tensile force, if the solution flow was enough, thicker jet would eject by greater tensile force which led to thicker fiber diameter.[27]The lower molecular weight of neat PCL solution (6 wt % having a viscosity of 0.005 Pa.s vs. 6 wt % for the PCL/PGA(50/50), viscosity of 0.06 Pa.s) leads to significantly lower viscosity and viscoelastic behavior resulting in the smaller fiber diameter.

Porosity and pore size

The porosity of electrospun nanofibrous mats indicates the space between the fibers which is necessary for tissue growth. To study the effect of PGA presence in porosity of scaffolds, the porosity and pore size of PCL/PGA blend nanofibers and neat PCL and PGA nanofibrous scaffolds were tested and summarized in Table I.

The porosity of PCL nanofibers was about 81.3% while that of PGA fibers was about 90%. As PGA content was increased, the porosity was notably increased. The different porosity may be a result of the presence of PGA which has a higher molecular weight and viscosity that causes the fiber diameter to increase compared with PCL which has a lower molecular weight and consequently, a lower fiber diameter.

Also, Table I indicates that with increasing PGA content, the pore diameter increased. This can be attributed to the rising in fiber diameter by incorporation of PGA into the electrospinning solution. More layers of fibers might overlap with each other, especially when the fiber diameter is smaller, resulting in smaller pore diameter.
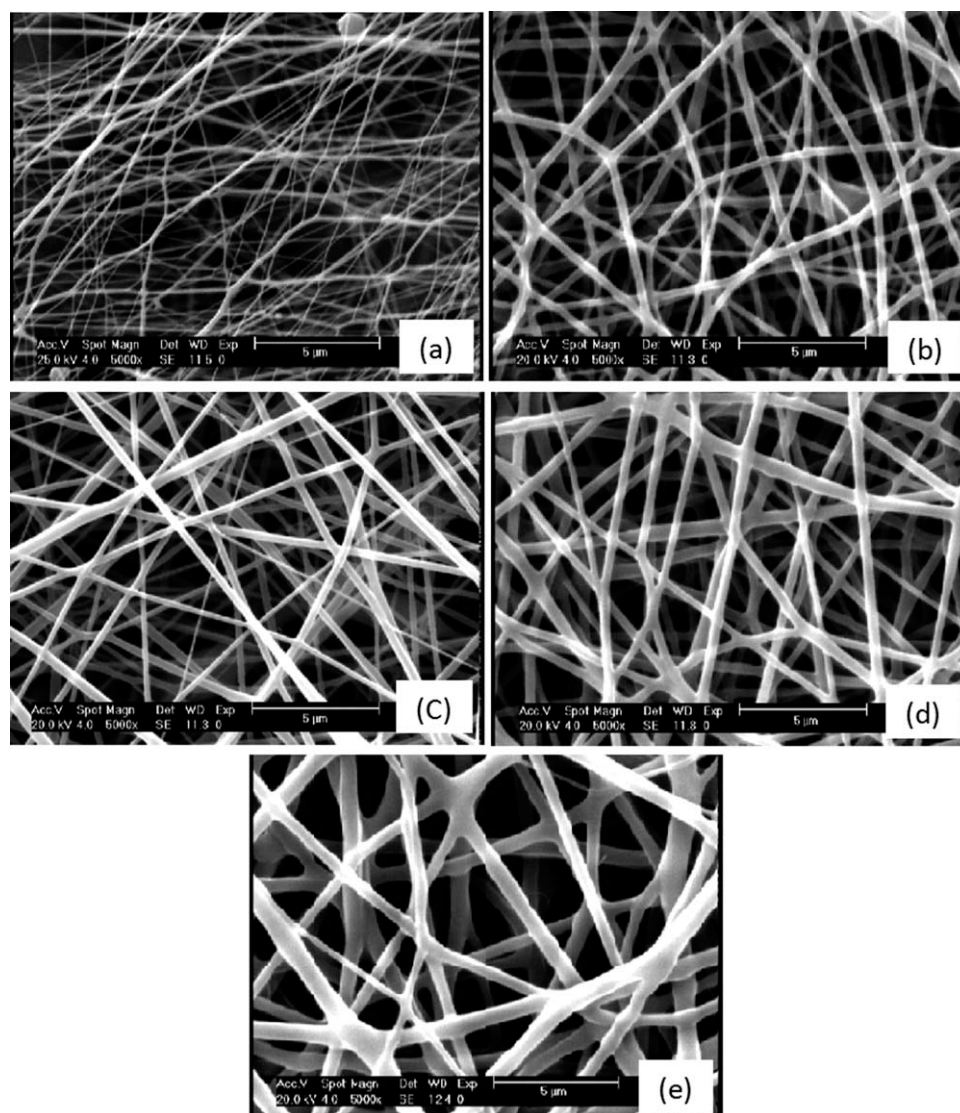
Figure 1 SEM image of electrospun. (a) PCL, (b) PCL/PGA (80/20), (c) PCL/PGA (65/35), (d) PCL/PGA (50/50), and (e) PGA nanofibers.

Hydrophilicity

The hydrophilic/hydrophobic characteristic of scaffold is important in tissue culture and can influence the initial cell adhesion and cell migration to a higher extent. According to various published works, hydrophobic surfaces lead to lower cell adhesion in the initial step of cell culture.[28,29] To assess the effect of PGA on the hydrophilicity/hydrophobicity properties of the PCL/PGA blend nanofibrous scaffolds, the water contact angle and water uptake tests were examined. A high angle of contact indicates that the water droplet does not spread on the substrate due to the hydrophobicity of the substrate and a low one shows spreading of the water droplet on the surface which means wettability by the water droplet, hence contact angle of zero shows complete spreading of water droplet and 100% wettability and hydrophilicity. Moreover, higher water uptake indi-

ces show a better wettability and water absorbance which is important for tissue growth and can act as an efficient parameter in *in vivo* degradation which is necessary in soft-tissue engineering scaffolds. Table II shows the results of contact angle and water uptake measurement for PCL, PGA, and PCL/PGA nanofibrous scaffolds with various PGA content.

TABLE I
The Porosity and Average Pore Size of PCL, PGA, and PCL/PGA Nanofibrous Scaffolds

Sample	Porosity (%)	Pore size (nm)
PCL	81.3 ± 5.6	1.05 ± 0.25
PCL/PGA(80/20)	84.15 ± 2.8	1.26 ± 0.19
PCL/PGA(65/35)	86.2 ± 3	1.7 ± 0.45
PCL/PGA(50/50)	87.8 ± 4.2	1.9 ± 0.38
PGA	90 ± 2.7	2.3 ± 0.5

Sample	Contact angle (°)	Water uptake (%)
PCL	118 ± 5	18 ± 4
PCL/PGA(80/20)	103 ± 4	32 ± 3
PCL/PGA(65/35)	76 ± 4	41 ± 5
PCL/PGA(50/50)	54 ± 6	53 ± 4
PGA	0	62 ± 2.5

As is observed in Table II, the contact angle obtained for PCL scaffold is about 118 ± 5° which implies that the scaffold is highly hydrophobic and nonadsorbent to water. On the other hand, the droplet of water on the PGA nanofibrous scaffold exhibits complete spreading onto the scaffold surface with its water contact angle of zero showing 100% wettability by the water droplet. This fact indicates that PGA has a much higher wettability than that of PCL, owing to the multiple hydrophilic functional groups. Hence, it can be predicted that the increase of PGA in all the PCL/PGA blends would result in a decrease in contact angle that means a more hydrophilicity, as is observed in Table II. As the ratio of PGA increased, the water contact angle significantly decreased, i.e., the hydrophilicity of PCL/PGA (50/50) nanofibers was higher than that of PCL/PGA (65/35), and PCL/PGA (80/20) proving that the hydrophilicity of scaffolds increased with increasing PGA concentration.

Table II also shows that the water uptake of the PCL/PGA blend nanofibers is higher than that of the pure PCL nanofibers as well as that of pure PGA nanofibers which is higher than the water uptake of the all blends. This indicates that the hydrophilicity of the structured mats was improved by increasing in PGA amount of electrospun nanofibers.

ATR-FT-IR spectroscopy

To determine if electrospinning has any adverse effect on chemical structures of neat polymers as well as their blends, the ATR-FT-IR test of PCL, PGA, and PCL/PGA blend nanofibrous scaffolds at different PGA concentrations were performed and the spectra are shown in Figure 2.

All peaks associated with both PCL and PGA are expected to be seen in all the three blend nanofibers spectra and those of PCL and PGA in the neat specimens of PCL and PGA, respectively. The scans show a carbonyl (C=O) stretch band for the PCL and the PGA at 1717 cm^{-1} and 1747 cm^{-1}, respectively. All three blend specimens show two peaks which are close to each other in the range expected for carbonyl group, one corresponding to that of PCL and the other corresponding to that of PGA. These peaks

are located in (1711 and 1720) cm^{-1} for PCL/PGA (50/50), (1714 and 1729) cm^{-1} for PCL/PGA (65/35), and 1723 cm^{-1} and 1743 cm^{-1} for PCL/PGA (80/20). The intensity of theses peaks increased with increasing the amounts of PGA. The relatively broad peaks centered about 3400 cm^{-1} are the overtones of the carbonyl bands. Dual carbonyl peaks in three blend specimens caused dual overtone peaks in a wave number about two times of the original peaks which is expected for overtone absorbance band. These overtone peaks are located in 3401 cm^{-1} and 3490 cm^{-1} for PCL and PGA, respectively, and in (3355, 3462) cm^{-1}, (3332, 3418) cm^{-1}, and (3347, 3446) cm^{-1} for 80/20, 65/35, and 50/50 PCL/PGA blend nanofibers, respectively.

Other major peaks that all the spectra exhibit are the C-O-C ether group and C-O stretch band in the 1069 to 1087 cm^{-1} and 1137 to 1163 cm^{-1}, respectively.

Figure 2 also demonstrates that in the prepared polymer solutions in HFIP no reaction between PCL and PGA occurred and these materials were just blended together. Altogether the FT-IR spectrums show that the structure of blend electrospun scaffolds contained all the peaks corresponding to PCL and PGA which demonstrate that the blend PCL/PGA electrospun fibrous scaffolds with the desirable concentrations were successfully fabricated.

X-ray diffraction

Figure 3 shows the XRD patterns for electrospun PCL, PCL/PGA, and PGA nanofibrous scaffolds. The PCL/PGA and PCL nanofibrous mats both
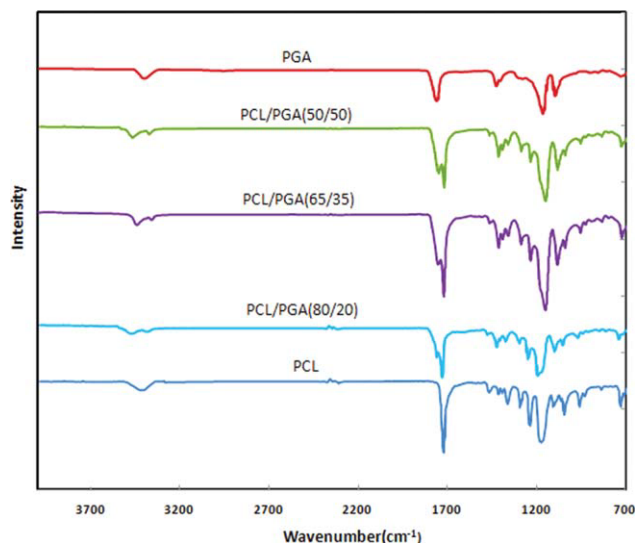

Figure 2 ATR-FT-IR curves of electrospun PCL, PGA, and PCL/PGA nanofibrous scaffolds. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]
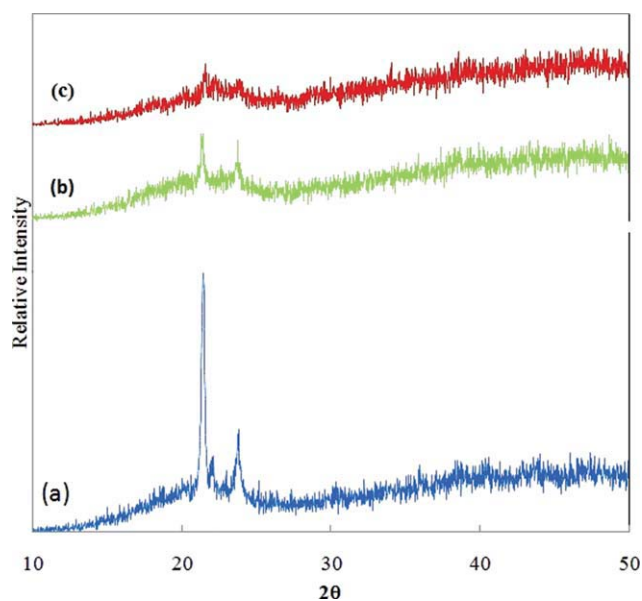
Figure 3 XRD curve of the electrospun nanofibrous scaffolds. (a) Neat PCL, (b) PCL/PGA (50/50), and (c) neat PGA. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

showed a sharp peak at 2θ of 22.3° and a relatively low intensity peak at 24.1°. However, compared with the pure PCL nanofiber, the intensity of two diffraction peaks for PCL/PGA blend nanofiber was significantly decreased, which might be due to a decrease in the concentration of PCL, which causes the peaks in the specimen. However, the pure PGA nanofiber presents no significant peak in the XRD pattern. The results demonstrated that PGA nanofiber was noncrystalline and adding of PGA in PCL did not change PCL nanofibers basic molecular structure. Therefore, the PCL/PGA nanofibers were just the simple blend of PCL and PGA. There was no chemical reaction or intermolecular action or orientation between PGA and PCL molecules.

Thermal properties of electrospun PCL/PGA nanofibers

DSC is especially used for discrimination between miscible and immiscible polymer blends. An immiscible polymer blend is the blend that does not conform to the thermodynamic conditions of phase stability; a compatible polymer blend is a polymer mixture that is visibly homogeneous. Therefore, a nominal A/B blend can be regarded as immiscible but compatible polymers.[30] In a DSC graph for an immiscible blend of two polymers, each polymer phase represents its T_g while only one T_g is observed for a homogeneous miscible blend without a phase separation.[31] Figure 4 shows T_gs of electrospun PCL/PGA blend nanofibers at different PGA concentrations.

The thermogram shows that PCL and PGA nanofibrous scaffolds have T_gs at −63.31°C and +48.07°C, respectively. All of the DSC curves for PCL/PGA blends at different ratios showed one obvious shift in base-line between −63.31°C and +48.07°C, which are the T_gs for PCL and PGA. A single shift in baseline for the different blend compositions under investigation, which is corresponding to T_g, suggest a miscible blend morphologies. In all specimens other than the neat PCL, T_g was overlapped with or followed by an endothermic peak which is associated with the enthalpic relaxation of PGA.[32]

To examine the miscibility of blends using different test method, T_g of the blends were also measured using dynamic mechanical thermal analysis (DMTA) which has a 1000-fold greater sensitivity compared with DSC.[33]

In this method, T_g is usually identified at the temperature point where a maximum in mechanical loss factor ($\tan \delta = E''/E'$) and a change in slope of E' versus temperature are observed.[34] Mechanical loss factor has two peaks in immiscible blends and a single peak in the completely miscible blends which obeys the Fox equation:

$$\frac{1}{T_g} = \frac{W_1}{T_{g1}} + \frac{1 - W_1}{T_{g2}} \tag{5}$$

where T_g is the glass transition temperature of the blend, T_{g1} and T_{g2} are those of pure components of the blend (all in Kelvin degree), and w_1 is the weight fraction of the component with the glass transition of T_{g1}.[35]

The mechanical loss factor (*tan δ*) versus temperature (*T*) traces for the PCL, PGA and PCL/PGA blends are shown in Figure 5. As shown in this Figure 5, *tan δ* has peaks for the neat PCL and PGA in the temperatures expected from DSC for the T_gs of PCL and PGA while two peaks are seen for other
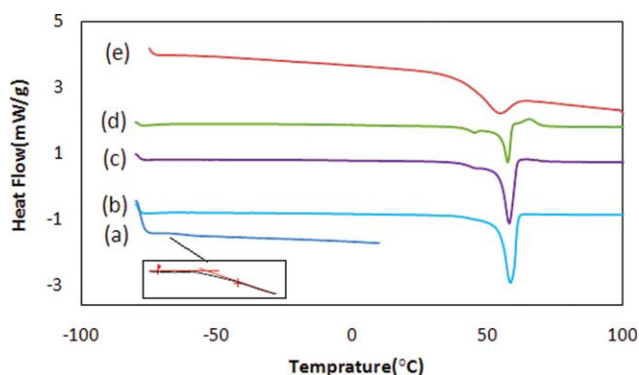

Figure 4 DSC thermograms of the electrospun nanofibrous scaffolds. (a) Neat PCL, (b) PCL/PGA (80/20), (c) PCL/PGA (65/35), (d) PCL/PGA (50/50), and (e) neat PGA. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]
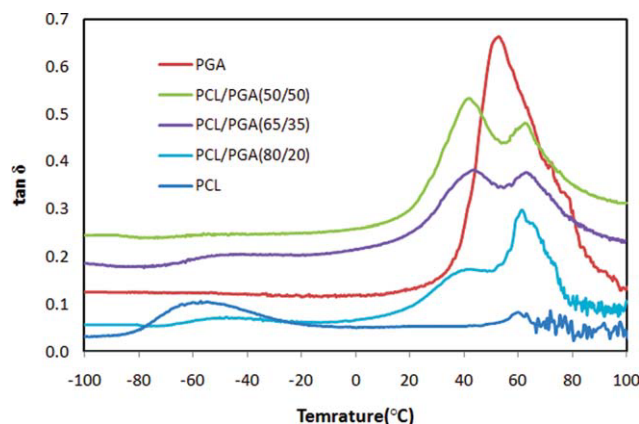
Figure 5 Tan versus temperature for electrospun PCL, PGA, and PCL/PGA nanofibrous scaffolds. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

specimens in the range between T_gs of PCL and PGA. Each of the other three specimens shows two peaks at 39.5°C and 60.03°C, 40.3°C and 59.8°C, 38.9°C and 60.1°C for PCL/PGA blends of 50/50, 65/35, and 80/20, respectively. For all the blend samples, the second peak is located in about 60°C which is the melting point temperature of PCL. It can be concluded that in these specimens and in the melting point of PCL, well-dispersed molten PCL acts as a plasticizer in the blend and causes a mechanical damping in the dynamic cycles and so results in the mechanical loss factor peaks to be appeared. Note that the other component, PGA, which has a melting point of about 220°C, is still in its solid state and molten phase of PCL just facilitates the movement of PGA chains. The other peaks of three blend specimens which are located in 39.5°C, 40.03°C, 38.9°C for PCL/PGA blends of 50/50, 65/35, and 80/20, respectively, are related to the blends' T_gs and show a good miscibility of these two phases in the three blend samples. These values are different from glass transition point of blends predicted by the Fox equation which are −16.28°C, −31.17°C, and −44.43°C, respectively. This is due to

difference of PCL and PGA in crystallinity and since glass transition is due to change from glassy to rubbery state in amorphous material and crystalline material do not show glass to rubber transition, T_g of blends is more influenced by T_g of the more amorphous phase that is PGA and less depends on T_g of PCL which is more crystalline and less amorphous. This result was very consistent with that of XRD result.

These results corroborate the finding based on DSC and suggest that PCL and PGA are miscible in the all three blends of this study.

Mechanical properties

For tissue-engineering scaffolds, one of the most important properties is the mechanical property. The scaffold should be strong enough to resist the forces from body movement or outer environment.[29]

From stress–strain behavior measurement done on the nanofibrous electrospun scaffolds made up of PCL, PGA, and PCL/PGA blends with different concentrations, Young's modulus, elongation at break, and tensile strength were determined and the results are shown in Figure 6. These presented values are the average of at least three measurements carried out on the same specimens. In these experiments, it was found that the mechanical properties in the electrospun PCL/PGA scaffolds increased as the amount of PGA increased. For example, the elongation at break percentage of PCL/PGA (65/35) nanofibers was notably higher than that of PCL indicating a good deformability and flexibility. Also, the elongation at break of PCL/PGA (50/50) increased significantly due to higher PGA concentration in this blend polymeric system.

The stress–strain data showed that PGA was a flexible polymer and if it was added to PCL materials (nonflexible polymer), the mechanical strength under fine fibrous mats conditions was increased.

Altogether elongation at break, ultimate strength, as well as Young's modulus increases with an increase in the fiber diameter.
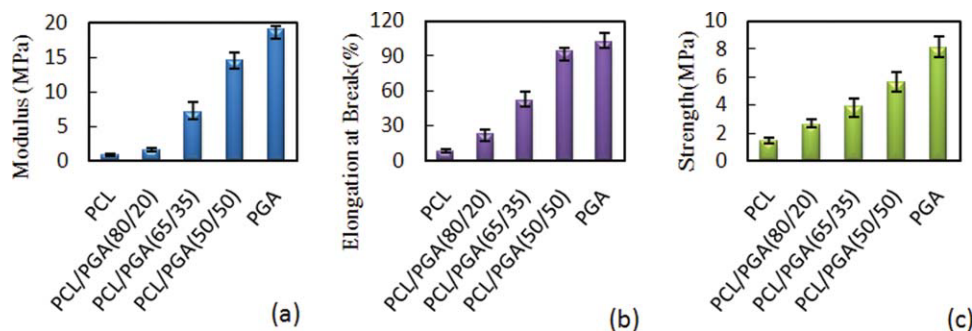

Figure 6 Mechanical properties of the PCL/PGA nanofibrous scaffold at different PGA content. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

The better mechanical properties of blends compared with PCL scaffolds can be correlated to higher fiber diameter of electrospun scaffolds as by raising the concentration of PGA in PCL/PGA blend polymeric system fiber diameter increases.

CONCLUSIONS

In this study, the PCL/PGA nanofibrous scaffold containing different concentrations of PGA (with weight ratios of 100/0, 80/20, 65/35, 50/50, and 0/100) were produced successfully using electrospinning process. The results reported in this work demonstrated that the properties of nanofibrous scaffolds were strongly influenced by the concentration of PGA in the blend. Varying the PGA concentration while keeping constant all other processing parameters resulted in an increase in the average nanofiber diameter from 180 nm for the neat PCL to 540 nm for the PCL/PGA (50/50) with a narrower distribution of the fibers diameter. Electrospinning of PCL/PGA blend solutions produced blend nanofibers without phase-separated structure, because PCL and PGA were miscible in the electrospun nanofibrous structure. The average diameter, porosity, tensile strength, and hydrophilicity of PCL/PGA nanofiber scaffolds increased with increasing amounts of PGA content. Therefore, the electrospun PCL/PGA nanofibrous scaffold has the potential application in biomedical fields such as soft-tissue engineering.

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