Biodegradable Copolyester Fibers by Solution Electrospinning

Alvaro Iregui[1], Lourdes Irusta[*,1], Loli Martin[2] and Alba González[1]

[1] *POLYMAT, Department of Polymer Science and Technology, University of the Basque Country (UPV-EHU), P.O. Box 1072. 20080 Donostia-San Sebastián, Spain*

[2] *Macrobehavior-Mesostructure-Nanotechnology (SGIker), Polytechnic School, University of the Basque Country (UPV-EHU), Plaza Europa 1, 20018 Donostia-San Sebastián, Spain*

Received September 15, 2014; Accepted November 18, 2014

ABSTRACT: In this work, solution electrospinning technique was used to produce biodegradable fibers using a commercially available polyester (Ecoflex F Blend C1200). These materials (mats) could be of potential interest in tissue engineering. The effect of polymer concentration and the solvent nature on the obtained morphology was related to the wettability of the mat, characterized by water contact angle measurements. According to the results, the electrospun mats presented water contact angles characteristic of hydrophobic surfaces.

KEYWORDS: Electrospinning, ecoflex, hydrophobic, biodegradable

1 INTRODUCTION

Biodegradable materials are a group of products whose worldwide consumption has increased 15 times in the last ten years. The dynamic production growth of these materials results from concerns about the natural environment, the economy, the exploitation of energetic raw materials which are nearing an end and, last but not least, legislature. Synthetic polymers and biologically derived (or natural) polymers have been extensively investigated as biodegradable biomaterials. This work deals with the synthetic polymer Ecoflex F Blend C1200, an aliphatic-aromatic copolyester which is compostable and fully biodegradable [1,2]. Ecoflex can be used alone or in combination with renewable raw materials like starch for producing high quality biodegradable and biobased plastic films.

There are many applications that require the use of biodegradable materials. For example, tissue engineering uses a biodegradable scaffold as the basic element. This scaffold must present a highly porous microstructure with interconnected pores and a large surface area. These types of structures can be obtained using the process called electrospinning [3,4]. This process creates ultrafine fibers through an electrically charged jet of polymer solution [5,6]. Depending on the solution concentration, the obtained mats may exhibit fiber or fiber-bead morphologies [7].

In this work, the electrospinning technique was used to produce biodegradable fibers with hydrophobic properties from a Ecoflex solution. The effect of the polymer concentration on the obtained morphology was related to the wettability of the mat.

2 EXPERIMENTAL

2.1 Materials

Ecoflex F Blend C1200 is an aliphatic-aromatic copolyester based on the monomers 1,4-butanediol, adipic and terephthalic acids supplied by BASF.

Tetrahydrofurane, chloroform (HPLC grade) and deuterated chloroform were purchased from the Aldrich Chemical Company. All materials were used as received. Water was doubly distilled and deionized (Millipore, Milli-Q).

2.2 Electrospinning

For the electrospinning process, polymer solutions in chloroform and tetrahydrofurane (THF) (concentration 5–20 wt%) were placed into a syringe mounted in a pump (Cole-Parmer). The THF solutions were

*Corresponding author: lourdes.irusta@ehu.es

DOI: 10.7569/JRM.2014.634128

prepared by heating them at 60ºC. Randomly oriented nanofibers were electrospun by applying a voltage of 4–7 kV to the needle using a Spellman CZE1000R high voltage supply (0–30 kV CZE1000R; Spellman High Voltage Electronics Corp.), with a low current output (limited to a few A). The ground plate (stainless steel sheet on a screen) was placed at 15 cm from the needle tip. The syringe pump delivered the polymer solutions at a controlled flow rate, which ranged from 0.7 to 1 mL/h. All the experiments were performed at least twice. The resulting fibers were collected on the screen in order to produce a sheet of nonwoven fabric.

2.3 Characterization Techniques

Ecoflex was chemically characterized by ^{1}H-NMR (Bruker 300 MHz spectrometer, model Advance 300 DPX). Deuterated chloroform was used as solvent.

The molecular weight of Ecoflex was calculated by gel permeation chromatography (Thermo Scientific, Ultimate 300) and referred to polystyrene standards. Tetrahydrofurane was used as solvent at a flow rate of 1 mL min^{-1} (injected volume: 20 mL; sample concentration: 2 % wt/v).

Static and dynamic water contact angle (CA) measurements were carried out using the sessile drop method on an OCA20 contact angle goniometer at 25°C and 55% relative humidity. The angles reported were the average of 30 measurements.

Fiber morphology was characterized by Scanning Electron Microscopy (SEM). The measurements were performed on a Hitachi S-2700 microscope; the samples were put on a SEM disk and sputter-coated with an 8 nm Pt/Au layer.

3 RESULTS AND DISCUSSION

3.1 Polymer Characterization

Ecoflex is an aliphatic-aromatic copolyester based on the monomers 1,4-butanediol, adipic and terephthalic acids. The composition and sequence distribution analysis [8] was performed by proton NMR (Figure 1).

The area of signals of protons 1 and 2 was used to determine the mol fractions of the two acids. According to this, the adipate (AD) and terephthalate (TF) fractions were 0.52 and 0.48 respectively.

Protons of the butadiene named as 4 in Figure 1 were sensitive to the diad effect and gave rise to 4 signals assigned to the TF-TF (4.45 ppm), TF-AD (4.40 ppm), AD-TF (4.17 ppm) and AD-AD (4.11 ppm) diads. From the area of these signals a degree of randomness of 1.03 was obtained, which means that Ecoflex is a random copolymer.

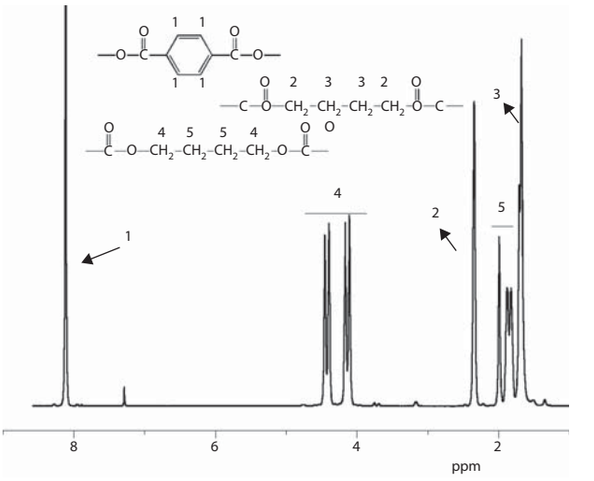

Figure 1 ^{1}H-NMR spectrum of Ecoflex.

The molecular weight of Ecoflex was calculated by GPC and values of 37000 and 2 were obtained for the number-average molecular weight (Mn) and polydispersity index respectively.

3.2 Electrospinning

A series of polymer solutions with different concentrations of Ecoflex dissolved in Chloroform and Tetrahydrofurane were electrospun. At each concentration a stable jet was obtained using the parameters shown in Table 1.

As observed, for the same solvent, the electrical field needed to obtain a stable jet increased with the concentration, even using lower flow rates. The high viscosity of the more concentrated samples prevents the flow of the solution and therefore higher voltages had to be applied.

The electrical field applied to obtain a stable jet in THF was lower than that applied in chloroform solutions. This fact can be due to other variables such as surface tension or conductivity of the solution that were not measured in this work.

The SEM images of the samples obtained in chloroform are shown in Figure 2. As can be observed, the resulting mats presented different morphologies. As is well-known, for obtaining fibers by electrospinning a critical concentration of the polymer solution is required as extensive chain entanglements are necessary [5,6]. In our case, this critical concentration was 15%, since images of the mats obtained from the lower concentration solutions (A and B) showed a bead-like morphology. As expected, the bead diameter increased with the polymer concentration. However, the diameter of the fibers obtained from the 20% solution was

Table 1 Electrospinning parameters for the studied solutions.

Solvent	Concentration wt/v	Flow rate (mL/h)	Voltage (kV)	Collection time (hours)
Chloroform	5	0.85	5.0	2
Chloroform	10	1.0	5.0	2
Chloroform	15	1.0	5.3	2
Chloroform	20	0.7	7.0	2
THF	5	0.9	3.9	2
THF	10	1.0	4.0	2
THF	15	1.0	4.3	2
THF	20	0.9	5.0	0.5

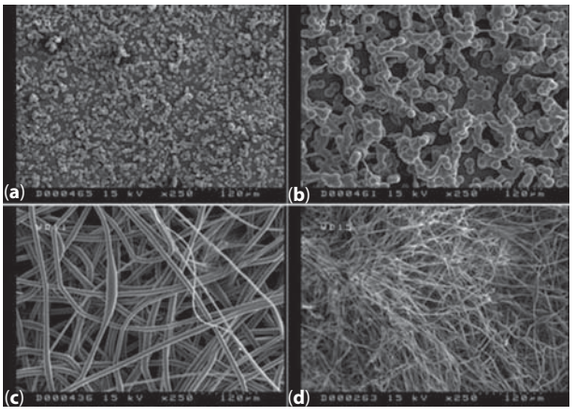

Figure 2 SEM images of the mats obtained from chloroform using a concentration of 5 wt% (A), 10 wt% (B), 15 wt% (C) and 20 wt% (D).

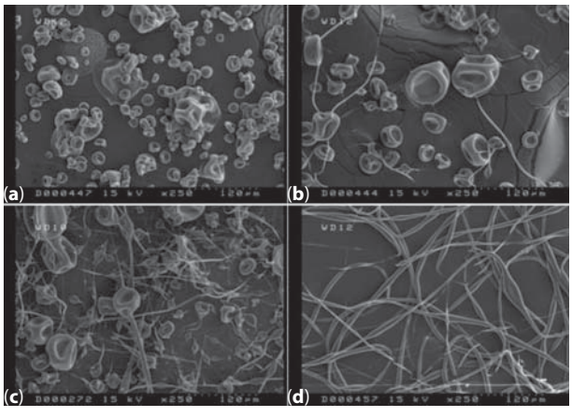

Figure 3 SEM images of the mats obtained from THF using a concentration of 5 wt% (A), 10 wt% (B), 15 wt% (C) and 20 wt% (D).

lower than the diameter obtained using a concentration of 15%. The higher electrical field that had to be applied in the most concentrated solution (Table 1) was responsible for the lower diameter of these fibers.

Figure 3 shows the morphology of the mats obtained from THF. Using this solvent, the minimum concentration to obtain only fibers was 20% higher than the one necessary using chloroform. This fact is probably due to the bad solvent character of THF that prevents the chain entanglements necessary to obtain fibers. In addition, the mats obtained using THF showed nanometer scale pores. Figure 4 shows an enlarged image of the mats obtained using a concentration of 10% in Chloroform and in THF.

Porous structures previously described in literature [7,9,10] have been related to the high volatility of the solvent and to the relative humidity of the air during the electrospinning process. As the volatility of the solvents used in our work was similar, it can be argued that the formation of the porous structure in THF was due to its hygroscopic character.

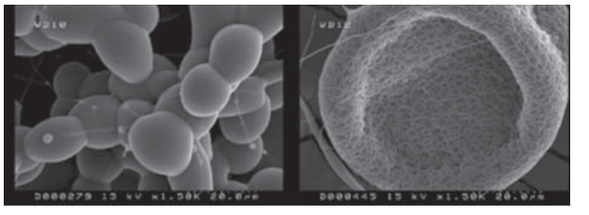

Figure 4 SEM images of the mats obtained from 10% of Chloroform (left) and THF (right).

3.3 Wettability of the Mats

It is well known that the wettability of a surface is governed by the surface energy and roughness. Even when using high surface energy materials, the mats obtained using electrospinning show hydrophobic properties because the fibrous structure provides surface roughness [10,7].

Table 2 Water contact angle and hysteresis of the mats.

Solvent	Properties	5 wt. %	10 wt. %	15 wt. %	20 wt. %
Chloroform	Contact angle (°)	94	100	118	139
	Hysteresis (°)	6	3	3	2
THF	Contact angle (°)	64	82	134	/
	Hysteresis (°)	5	3	3	/

The wettability of the mats was characterized by water contact angle measurements (Table 2).

As can be observed in Table 2, in the majority of the samples the contact angle values were higher than 90º, which means that the samples were hydrophobic. In addition, in all the samples, the obtained hysteresis values (difference between the advancing and receding angles) were lower than 10º. Low hysteresis values are governed by the Cassie state in which water droplets are in contact with peaks of the rugged surface as well as the "air pockets" trapped between surface grooves. In the Cassie state, the liquid water droplets slide off easily (and take contaminants with them) even if the film is only slightly tilted. This behavior is very interesting, as the surfaces are kept clean.

Hysteresis values were low and very similar for all the samples. Moreover, for both systems, the water contact angle increased with the polymer concentration. This result revealed that a bead-predominant morphology generated lower contact angles than those generated in a morphology mainly consisting of fibers. Some literature studies conclude that, contrary to our results, the beaded morphologies give rise to higher contact angles [7]. However, references about systems with a similar behavior to that exhibited by our samples can also be found [11]. This discrepancy in the results can be due to the complex morphology of the electrospun mats that makes the comparison between different systems difficult.

Comparing the contact angle values obtained in both solvents, at low concentrations lower values were obtained using THF, while higher values were obtained when the concentration was increased. It might seem that the lower contact angle values could be related to the porosity of the mats (water is introduced into the pores). However, the hysteresis values are also low, suggesting that water droplets are in contact with the peaks of the rugged surface. Unfortunately, it was not possible to obtain fibers without pores and, therefore, the effect of the pores in the hydrophobicity could not be stated.

Finally it should be noted that although the complex morphology of the electrospun mats makes it difficult to reach general conclusions, the higher contact angles were obtained using mats that presented fiber-like morphology, regardless of the employed solvent.

4 CONCLUSIONS

The results of this work showed that biodegradable polyester mats can be obtained by solution electrospinning. In relation to the employed solvent, Chloroform is more adequate than Tetrahydrofurane since lower polymer concentrations could be used in the electrospinning process. Hydrophobic surfaces characterized by high contact angles and low hysteresis values were obtained when the electrospun mats presented fiber-like morphologies. These mats present potential applications in tissue engineering.

ACKNOWLEDGEMENTS

The authors thank Professor J.J. Iruin for the scientific advice received to develop this work and Jordi Simón i Roca, from BASF Española, for providing Ecoflex F Blend C1200.

Technical and human support provided by Macrobehaviour-Mesostructure-Nanotechnology and general NMR SGIker services (UPV/EHU, MICINN, GV/EJ, ERDF and ESF) is gratefully acknowledged.

The authors acknowledge the University of the Basque Country UPV/EHU (UFI 11/56), the Basque Government (Ayuda a grupos de investigación del sistema universitario vasco IT618-13) for the funding received to develop this work.

REFERENCES

1. F. Trinh Tan, D.G. Cooper, M. Marec, and J.A. Nicell, Biodegradation of a synthetic co-polyester by aerobic mesophilic microorganisms. *Polym. Degrad. Stab.* **93**, 1479 (2008).
2. K.O. Siegenthaler, A.K Unkel, G. Skupin, and M. Yamamoto, Ecoflex® and Ecovio®: Biodegradable, performance-enabling plastics. *Adv. Polym. Sci.* **245**, 91 (2012).

3. W.J. Li, C.T. Laurencin, E.J. Caterson, R.S. Tuan, and F.K. Ko, Scaffold for tissue engineering. *J. Biomed. Mater. Res.* **60**(4), 613 (2002).
4. T.J. Sill and H.A. von Recum, Electrospinning: Applications in drug delivery and tissue engineering. *Biomaterials* **29**(13), 1989 (2008).
5. D.H. Reneker and A.L. Yarin, Electrospinning jets and polymer nanofibers. *Polymer* **49**, 2387 (2008).
6. D. Reneker, H. Darrell, and C. Iksoo, Nanometer diameter fibers of polymer produced by electrospinning. *Nanotechnology* **7**(3), 216 (1996).
7. L. Buruaga, A. González, L. Irusta, and J.J. Iruin, Production of hydrophobic surfaces in biodegradable and biocompatible polymers using polymer solution electrospinning. *J. Appl. Polym. Sci.* **120**, 1520 (2011).
8. R. Herrera, L. Franco, A. Rodríguez-Galán, and J. Puiggalí, Characterization and degradation behaviour of poly(butylene adipate-co-terephthalate)s. *J. Polym. Sci. Part A: Polym. Chem.* **40**, 4141 (2002).
9. Z. Xie, and G. Buschle-Diller, Electrospun Poly(D,L-lactide) fibers for drug delivery: The influence of cosolvent and the mechanism of drug release. *J. Appl. Polym. Sci.* **115**, 1 (2010).
10. M. Minglin, M. Gupta, Z. Li, K. Zhai, K.K. Gleason, R.E. Cohen, M.F. Rubner, and G.C. Rutledge, Decorated electrospun fibers exhibiting superhydrophybicity. *Adv. Mater.* **19**, 255 (2007).
11. K. Papadopoulou, C. Tsioptsias, A. Pavlou, K. Kaderides, S. Sotiriou, and C. Panayiotou, Superhydrophobic surfaces from hydrophobic or hydrophilic polymers via nanophase separation or electrospinning/electrospraying. *Colloids Surf. A Physicochem. Eng. Aspects* **387**, 71 (2011).