Poly(vinylidene fluoride-trifluoroethylene) (72/28)(%mol) Interconnected Porous Membranes Obtained by Crystallization from Solution.

Poly(vinylidene fluoride-trifluoroethylene) (72/28) interconnected porous membranes obtained by crystallization from solution

Armando Ferreira[1], Jaime Silva[1,2], Vitor Sencadas[1], José Luís Gómez-Ribelles[3,4,5] and Senentxu Lanceros-Méndez[1,*]

[1]Centro/Departamento de Física, Universidade do Minho, 4710-057 Braga, Portugal.

[2] IPC-Institute for Polymers and Composites, University of Minho, 4800-058, Guimarães, Portugal.

[3]Centro de Biomateriales y Ingineria Tisular, Universidad Politécnica de Valencia, 46022, Valencia, Spain.

[4]Regenerative Medicine Unit, Centro de Investigación Príncipe Felipe, Autopista del Saler 16, 46013 Valencia, Spain.

[5]CIBER en Bioingeniería, Biomateriales y Nanomedicina, Valencia, Spain.

ABSTRACT

Electroactive macroporous poly[(vinylidene fluoride)-co-trifluoroethylene] membranes have been processed by solvent evaporation at room temperature with different polymer/solvent concentrations. The pore architecture consists on interconnected spherical pores and this morphology is independent of the membrane thickness. The porosity of the produced membranes increases from 57% for the higher polymer concentration in the polymer/solvent solution (15/85), up to 83% for the lowest polymer amount in the polymer/solvent solution.

Far infrared and differential scanning calorimetry measurements reveal that the polymer crystallizes in the ferroelectric phase and the polymer/solvent ratio does not changes the Curie transition and the melting temperature of the polymer.

INTRODUCTION

Poly(vinylidene fluoride) (PVDF) and its copolymers with trifluoroethylene (P(VDF-TrFE)) have attracted technological and scientific interest due to their outstanding electroactive properties [1-2] among polymer materials and as they can be implemented from industrial [3] to biomedical applications [4]. Concerning applications as a biomaterial, PVDF and VDF (vinylidene fluoride) copolymers can be unique materials due to their piezoelectric properties that can be used in cell culture "ex-vivo" under mechanical and electrical excitation in tissue engineering techniques [5].

Laroche *et al.* reported that PVDF can be applied in form of non absorbable syntetic sutures for vascular surgery [6]. It was observed some surface oxidation and water imbibitions of

the polymer with no significantly modification of the tensile strength of the PVDF suture, which retained 92.5% of its original value.

PVDF porous structures can also be taylored for applications as smart scaffolds with controled fiber distribution and electroactive β-phase content [7-8]. A number of experimental procedures are available to produce porous PVDF with controlled pore morphology. One of the most important requirements for cell culture is an interconnected pore structure that allows cell seeding and, diffusion of nutrients and waste products of the cell metabolism.

One of the successful procedures to prepare porous PVDF is thermally induced phase separation, TIPS [9]. In this procedure, PVDF is dissolved at high temperature in a mixture of a high boiling point good solvent and a certain amount of a bad solvent. The decrease of temperature in controlled conditions produces phase separation when entering into a two phase coexisting zone of the phase diagram [5]. Depending of the solvents and the initial composition of the solution, liquid-liquid spinodal phase separation can take place or liquid-solid phase separation can occur when PVDF crystallizes from the solution. Nucleation and growth of the coexisting phases will determine later the pore morphology when, after cooling to low temperatures, the solvents are extracted in order to leave the porous PVDF membrane [9].

Following a previous work [5], this paper reports on the pore size and architecture, polymer phase and thermal behavior of electroactive macroporous poly(vinylidene fluoride-trifuoroethylene), P(VDF-TrFE) (72/28), membranes with a well organized porous structure and thickness from 30 to 250 µm produced by solvent evaporation at room temperature starting with a diluted solution of the co-polymer in dimethylformamide (DMF).

EXPERIMENTAL

Samples with thickness between 10 and 250 µm were prepared by spreading a solution of poly(vinylidene fluoride-trifluorethylene) P(VDF-TrFE) (72/28) (*Solvay*, Brussels, Belgium) in N,N dimethylformamide (DMF, *Merck*) on a glass slide. The initial concentration of the solution and the viscosity (measurement performed in a *Fungilab* ViscoStar apparatus) is shown in Table 1. Solvent evaporation took place by room temperature solvent evaporation and crystallization of P(VDF-TrFE). The P(VDF-TrFE) (72/28) co-polymer obtained by this procedure is in the ferroelectric phase, being therefore also piezoelectric [1-2].

Scanning electron microscopy (SEM) measurements were performed in a *FEI Nova NanoSEM 200* with an accelerating voltage of 20 kV, in previously gold coated samples (*Polaron, model SC502 sputter coater*). The samples analysed in cross-section, were previously immersed in liquid nitrogen for 180 s, in order to ensure that the sample temperature decreases below glass transition (Tg), and then were mechanically broken.

Infrared measurements were performed at room temperature in a *Perkin-Elmer Spectrum 100* apparatus in ATR mode from 4000 to 650 cm^{-1}. FTIR spectra were collected with 64 scans and a resolution of 4 cm^{-1}. The thermal behavior of the samples was analyzed by differential scanning calorimetry measurements (DSC) with a *Perkin Elmer Diamond* DSC apparatus. The samples were cut into small pieces, placed into 40 µl aluminum pans and heated between 30 and 200 ℃ at a heating rate of 10 ℃.min^{-1}. All experiments were performed under a nitrogen purge.

Table 1. Viscosity and porosity of the films of P(VDF-TrFE) for the different concentrations.

Fraction P(VDF-TrFE) / DMF	Concentration ⎯⎯⎯⎯ w/v (g/cm^3)	Viscosity ⎯⎯⎯⎯ cP	Porosity %
15 / 85	0,2	629,3	57
10 / 90	0,15	267,6	72
5 / 95	0,1	81,2	83

Due to the porous nature of the membrane a suitable method to estimate the porosity of the samples is the measurement with a pycnometer. In this work, the porosity of the samples was measured by an improved weight-method. The weight of the pycnometer filled with ethanol, was weighted and labeled as W1; the sample, whose weight was Ws, was immersed in ethanol. After the sample was saturated by ethanol, additional ethanol was added to complete the volume of the pycnometer. Then, the pycnometer was weighted and labeled as W2; the sample filled with ethanol was taken out of the pycnometer. The residual weight of the ethanol and the pycnometer was labeled W3. The porosity of the scaffold was calculated according to [10]:

$$\varepsilon = \frac{W_2 - W_3 - W_s}{W_1 - W_3} \qquad \text{Eq. 1}$$

The mean porosity of each membrane was obtained as the average of the values determined in three samples.

DISCUSSION

Membranes of P(VDF-TrFE) with thickness between 10 to 250 μm were produced by solvent evaporation at room temperature from a homogeneous solution in DMF. The microstructure of the polymeric membrane is shown in figure 1. It can be observed that all samples present a spherical porous structure with diameter around 15 μm. At higher magnifications (Figure 1b) it is possible to observe small porous, with 4 μm diameter, in the walls of the bigger porous structure, which demonstrates the interconnectivity of the porosity, that results from the spaces between the polymer microspheres that form the pores walls, while larger secondary pores may appear due to some defects in the structure. In a previous work, it was found that the thickness of the membrane does not have influence in the porous structure, as this microstructural effect is due to solvent evaporation [5]. In this way, samples prepared by spin-coating or solvent casting present the same porous morphology.
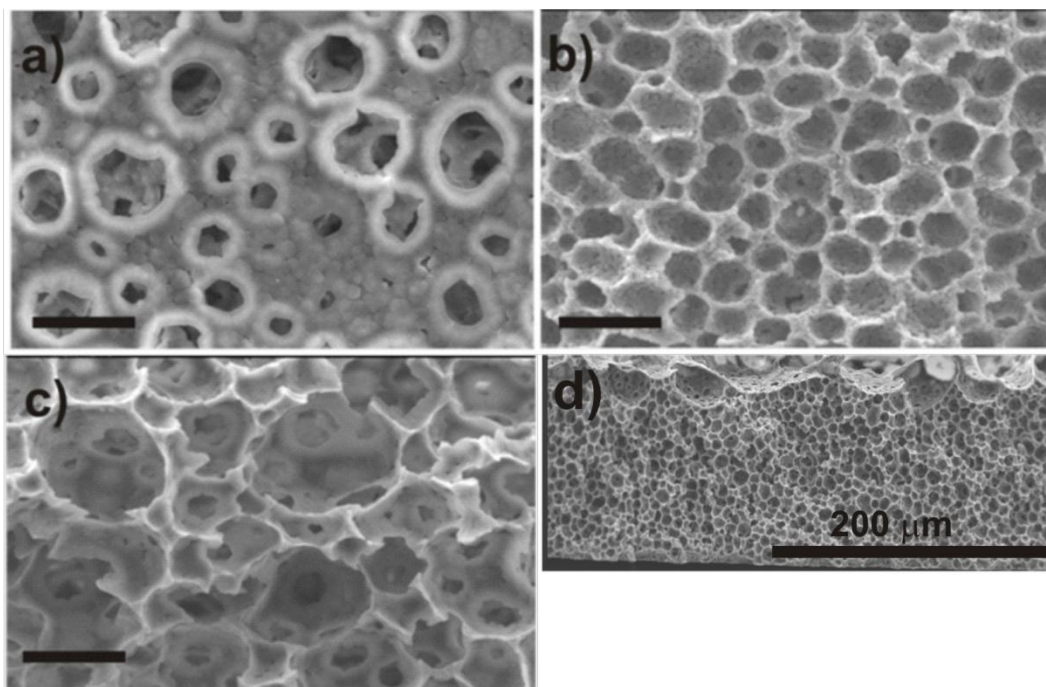
Figure 1 – SEM micrographs of the P(VDF-TrFE) samples crystallized at room temperature: a) topography of the sample with 72% porosity; b) Cross-section for the sample with 57% porosity; c) Cross-section for the sample with 72% and d) Cross-section for the sample with 83%% porosity. The scale bar corresponds to 20 microns.

The nature of the crystalline phase present in the polymer can be identified by differential scanning calorimetry (DSC) and far infrared spectroscopy (FTIR). FTIR spectra for the samples crystallized at room temperature shows that the crystallization of the polymer occurs in the ferroelectric phase (figure 2a) due to the presence of the absorption band at 840 cm^{-1}, characteristic of the ferroelectric phase of the polymer [11].

In the DSC thermograms (figure 2b) two peaks are observed, the one that occurs at the lower temperature corresponds to the ferroelectric-paraelectric transition (FE-PE, Curie transition) with maxima at ca. 117ºC. The higher DSC endotherm corresponds to the melting of the paraelectric phase and it located at ca.145ºC. It can be observed that the crystallization process does not affect the FE-PE transition temperature and the melting temperature of the polymer, what takes to conclude that the solvent evaporation does not play an important role in the final polymer crystalline properties, but in the crystallization dynamics, which affects the porosity and consequently the microstructure of the P(VDF-TrFE) membranes depending on the specific place of the P(VDF-TrFE)/DMF solution phase diagram in which the isothermal crystallization begins [5].

In this way, the final polymer porous microstructure taking place in the P(VDF-TrFE)/DMF system undergoing solvent evaporation is explained by a liquid/liquid spinodal decomposition followed by polymer crystallization [5].
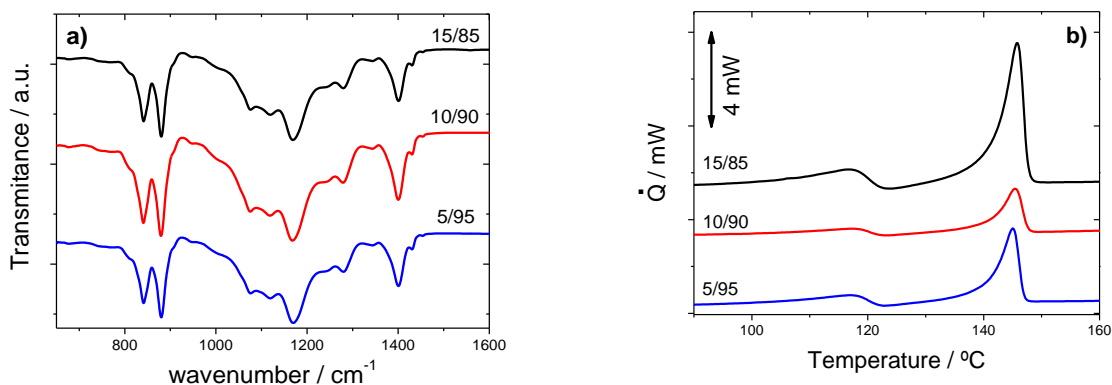
Figure 2 – *a)* Infrared measurements for the PVDF-TrFE samples obtained by room temperature crystallization from P(VDF-TrFE)/DMF solutions with different amounts of DMF solvent (15/85, 10/90 and 5/95, corresponding to 57, 72 and 83% of porosity, respectively); *b)* Differential Scanning Calorimetry results for the same samples.

CONCLUSIONS

Isothermal solvent evaporation from an homogeneous P(VDF-TrFE)/DMF solution allows to obtain a well organized tridimensional porous structure, in membranes from 30 up to 150 μm thick. The pore architecture consists of spherical pores of around 15 μm with small porous of 4 μm in the walls of the first ones.

The polymer/solvent ratio determines the final porosity of the membrane, the mechanism being a liquid/liquid spinodal decomposition followed by polymer crystallization. The porosity ranges from 57% to 83%, being the highest degree of porosity obtained for the P(VDF-TrFE)/DMF solution with the highest amount of initial DMF. The degree of crystallinity and ferroelectric phase of the obtained samples are not affected by the initial P(VDF-TrFE)/DMF ratio.

ACKNOWLEDGMENTS

REFERENCES

1. A. J. Lovinger, "Developments in Crystalline Polymers", London: Elsevier Applied Science, 1982.
2. H. S. Nalwa, "Ferroelectric Polymers: Chemistry, Physics, and Applications" New York: Marcel Decker, Inc., 1995.

3. Q. Zhang, C. Huang, F. Xia, and J. Su, "Electroactive polymer (EAP) actuators as artificial muscles: reality, potencial and Challenges", New York, 2004.

4. U. Klinge, B. Klosterhalfen, A. P. Öttinger, K. Junge, and V. Schumpelick, Biomaterials 23 (16): 3487-3493 (2002)

5. A. Ferreira, J. Silva, V. Sencadas, J. L. Goméz-Ribelles, and S. Lanceros-Méndez, Macromolecular Materials and Engineering 295 (6): 523-528 (2010)

6. G. Laroche, Y. Marois, E. Schwarz, R. Guidoin, M. W. King, E. Pâris, and Y. Douville. Artificial Organs 19 (11): 1190-1199 (1995)

7. V. Sencadas, J. C. R. Hernández, C. Ribeiro, J. L. Goméz-Ribelles, and S. Lanceros-Mendez, 1140. Materials Research Society Symposium Procceedings, vol. 1140. Boston (2009)

8. C. Ribeiro, V. Sencadas, J. L. Goméz-Ribelle, and S. Lanceros-Méndez, S. Soft Materials 8 (3): 274 – 287 (2010).

9. G-L Ji, B-K Zhu, Z-Y Cui, C-F Zhang, and Y-Y Xu. Polymer 48 (21): 6415-6425 (2007).

10. C. Ribeiro, V. Sencadas, C. Caparrós, J. L. Gómez-Ribelles, and S. Lanceros-Méndez. Journal of Nanoscience and Nanotechnology *To be published* (2010).

11. R. D. Simões, M. A. Rodriguez-Perez, J. A. De Saja, and C. J. L. Constantino. Polymer Engineering & Science 49 (11): 2150-2157 (2009).