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Phase morphology and crystallinity of poly(vinylidene fluoride)/poly(ethylene oxide) piezoelectric blend membranes

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ABSTRACT

Polymer blends based on poly(vinylidene fluoride), PVDF, and poly(ethylene oxide), PEO, with varying compositions, have been prepared by solvent casting, the polymer blend films being obtained from solutions in dimethyl formamide at 70 °C. Under these conditions PVDF crystallizes from solution while PEO remains in the molten state. Then, PEO crystallizes from the melt confined by PVDF crystals during cooling to room temperature. PVDF crystallized from DMF solutions adopts predominantly the electroactive β-phase (85%). Nevertheless when PEO is introduced in the polymer blend the β-phase content decreases slightly to 70%. The piezoelectric coefficient (d_{33}) in pristine PVDF is −5 pC/N and decreases by increasing PEO content in the PVDF/PEO blends. Blend morphology, observed by electron and atomic force microscopy, shows the confinement of PEO between the already formed PVDF crystals. On the other hand, the sample contraction when PEO is extracted from the blend with water (which is not a solvent for PVDF) allows proving the co-continuity of both phases in the blend. PEO crystallization kinetics have been characterized by DSC both in isothermal and cooling scans experiments showing important differences in crystalline fraction and crystallization rate with sample composition.

1. Introduction

In recent years, there has been a growing interest in the field of membrane technology, more specifically, in polymer porous membranes with the objective to promote or improve its performance in applications such as water purification [1], reverse osmosis [2], biomedical [3] and energy applications [4–6], etc. Polymer porous membranes show many advantages in comparison with other membrane types, such as metal and liquid membranes. In particular, they can show a high variety of pore sizes and a high degree of porosity, various membrane shapes (flat sheet, tubular, etc.) and can be chemically resistant, among others [7–9].

Different methods have been developed to generate a well-controlled pore structure and pore interconnectivity. Solvent casting with phase inversions is one of the most used methods [9–12], but many other have been proposed [13,14].

The most used polymer materials for porous membrane development for different applications are polycarbonate (PC) [15], poly(vinylidene fluoride) (PVDF) [16], polytetrafluoroethylene (PTFE) [17], polypropylene (PP) [18], polyamide [19] and cellulose-ester [20]. Taking into account the excellent properties (high mechanical strength and chemical stability) of fluoropolymers, PVDF has been used in porous membranes fabrication. PVDF is known for its electroactive properties (piezo, pyro and ferroelectric properties) [21,22]. On the other hand, PVDF is a hydrophobic biocompatible and non-biodegradable material, suitable for cell culture applications.

We propose in this work the combination of PVDF with PEO in a non-porous membrane in which a hydrophobic phase and a hydrophilic phase are co-continuous. This structure will allow water sorption and diffusion when the membrane is used as a cell culture support allowing cell attachment to PVDF domains but, at the same time, allowing the diffusion of water soluble proteins or growth factors through the substrate for cell signalling [23–25]. The ability of absorbing polar solvents is crucial in the use of these mem-

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branes as lithium-ion battery separator [26,27], or in microfiltration [28,29].

PVDF is a semi-crystalline polymer that can crystallize in four crystalline phases known as: α, β, γ and δ and depending on the temperature and processing conditions [22,30–32]. The most important phase of PVDF for technological applications is the β-phase, as it exhibits piezoelectric, pyroelectric and ferroelectric, properties. The α-phase is the most stable one from a thermodynamic point of view when the material is directly obtained from the melt [28–30]. Porous β-PVDF samples can be obtained directly from solution crystallization at temperatures below 70 °C [33]. Mechanical stretching applied to an α-phase PVDF film at temperatures below 100 °C and with a stretch ratio higher than or equal to 3 transforms it to a non-porous β-phase film. Different morphologies and microstructures were obtained for PVDF microporous membranes by crystallizing at different temperatures (thermal induced phase separation, TIPS) [33,34]. TIPS allows controlling both porosity and pore size [34,35]. The crystalline phase, dielectric and thermal properties of PVDF membranes depend of the solvent evaporation temperature that influences the solvent evaporation rate below the melting temperature [36,37]. For biomedical applications, the influence of the polarization state of non-porous electroactive poly(vinylidene fluoride), PVDF, on the biological response of cells cultured under static and dynamic conditions has been addressed [38,39]. It was observed that positively charged β-PVDF films promote higher osteoblast adhesion and proliferation, which is higher under dynamic conditions on poled samples, showing that the surface charge under mechanical stimulation improves the osteoblast growth.

Poly(ethylene oxide), PEO, is a hydrophilic, biocompatible polymer that has been intensively used in biomedical application [40]. Polymer blends of PVDF and PEO have been developed to improve the pore configuration, such as pore size, porosity and pore connectivity of PVDF-based microporous membranes [41,42]. This polymer blend has been proven to be suitable for polymer electrolyte applications [42].

Taking into account the properties of both PVDF and PEO, the main goal of this work is the preparation of new polymer blends based on these polymers in order to properly tune morphological features, with suitable piezoelectric and thermal properties for biomedical and energy applications. The correlation between the phase morphology and electroactive phase of PVDF is extremely important for these applications. A new membrane preparation method has been developed in which PVDF crystallizes from the solution in DMF while PEO polymer crystallizes from the melt, confined between PVDF crystals.

2. Experimental details

2.1. Blend preparation

PVDF (M_w 700,000 g/mol) and PEO (M_w 100,000 g/mol) were acquired from Solvay and Polysciences, respectively. PVDF/PEO blends were prepared with compositions of 100/0, 70/30, 50/50 weight ratios. Blends were prepared by dissolving the adequate amounts of both polymers in *N*,*N*-dimethylformamide (DMF) at a 15/85 w/v polymer/solvent ratio. The polymers were dissolved at 80 °C for 48 h with the help of a magnetic stirrer in a glass vessel with outer jacket for the circulation of water until a homogeneous and transparent solution could be observed. The solutions were deposited in Petri's capsules and the solvent was allowed to evaporate at 70 °C for two hours. Finally, complete removal of the solvent was achieved in vacuum for another 3 h at 70 °C.

2.2. Removal of PEO

As PEO is a hydrophilic polymer, it can be removed by water immersion. The membranes were cut into cylinders of 5 mm in diameter. The cylinders were immersed in water and stirred for up to 7 days, while the water was changed every day. After 7 days, the samples were dried in open air and subsequently dried in vacuum at 40 °C for one day. The mass, thickness and diameter of the samples were measured before and after being washed in water.

The percentage of removal of PEO was measured at various times and calculated through the following Eq. (1):

$$\%\mathrm{PEO}_{\mathrm{removal}} = \left(\frac{W_0 - W_i}{W_0}\right) \times 100 \qquad (1)$$

where W_0 and W_i denote the weight of blend membrane and the weight of membrane after PEO extraction by soaking in water, respectively.

2.3. Sample characterization

The microstructure of the blend films were examined in a field emission scanning electron microscope (FESEM), ZEISS Ultra-55, after the deposition of a conductive layer of sputtered platinum. AFM experiments were performed in tapping mode in air, immediately after sample preparation, using a Multimode AFM equipped with NanoScope IIIa controller from Veeco (Manchester, UK), at ambient conditions. Si-cantilevers with a constant force of 2.8 N/m and a resonance frequency of 75 kHz were used. All the samples were characterized using a set-point amplitude ratio of around 0.7 The NanoScope 5.30r2 software version was used for the simultaneous recording of the height, phase, and amplitude magnitudes of the images.

The PVDF crystalline phase was identified by Fourier Transformed Infrared spectroscopy (FTIR) at room temperature with a Jasco FTIR-4100 set-up. FTIR spectra were collected in attenuated total reflectance mode (ATR) from 4000 to 600 cm^{-1} after 32 scans with a resolution of 4 cm^{-1}.

For the determination of the piezoelectric coefficient, the PVDF/PEO blends were first poled by corona discharge at a controlled temperature inside a home-made corona chamber with the following parameters, obtained after an optimization process: applied voltage of 10 kV at a constant current of 20 μA; constant distance of 1.5 cm between the sample and the tip; poling time 60 min, poling temperature of 60 °C and then cooled to room temperature under the applied electric field.

Differential scanning calorimetry (DSC) analysis was carried out with a PerkinElmer DSC 8000 instrument under a flowing nitrogen atmosphere between 25 and 200 °C at a heating rate of 20 °C min^{-1} for cooling and heating. All samples were measured in 30 μL aluminum pans with perforated lids to allow the release and removal of volatiles.

3. Results and discussion

3.1. Phase morphology

PVDF/PEO blend films were cast from the solution in a good solvent for both components. Solvent casting was performed at 70 °C to ensure that during the whole process PEO is amorphous. PVDF crystallizes from the solution during solvent evaporation and, it is expected that PEO chains are pushed by the growing PVDF crystals, being finally confined in spaces between PVDF spherulites or in interlamelar spaces mixed with amorphous PVDF chains. Then when the already dry film is cooled to room temperature, PEO crystallizes from the melt since there are no solvent rests in the sample. As we will see below, PEO crystallization rate is highly affected