



ELSEVIER

Contents lists available at ScienceDirect

Polymer Testing

journal homepage: www.elsevier.com/locate/polytestPOLYMER
TESTING

ROGER BROWN

Material properties

Microstructural variations of poly(vinylidene fluoride co-hexafluoropropylene) and their influence on the thermal, dielectric and piezoelectric properties



R.E. Sousa^a, J. Nunes-Pereira^a, J.C.C. Ferreira^a, C.M. Costa^a, A.V. Machado^b,
M.M. Silva^c, S. Lanceros-Mendez^{a,*}

^a Departamento/Centro de Física, Universidade do Minho Campus de Gualtar, 4710-057 Braga, Portugal

^b IPC – Institute for Polymers and Composites, Universidade do Minho, Campus de Azurém, 4800-058 Guimarães, Portugal

^c Departamento/Centro de Química, Universidade do Minho Campus de Gualtar, 4710-057 Braga, Portugal

ARTICLE INFO

Article history:

Received 9 August 2014

Accepted 13 September 2014

Available online 28 September 2014

Keywords:

PVDF-HFP

Membranes

Thermally induced phase separation (TIPS)

Phase diagram

ABSTRACT

Polymer films and membranes of poly(vinylidene fluoride co-hexafluoropropylene), PVDF-HFP, have been prepared by thermally induced phase separation (TIPS), allowing the tuning of microstructure and morphology.

The obtained microstructure is explained by the Flory-Huggins theory, depending on polymer concentration and solvent evaporation temperature. The formation of a porous membrane is attributed to a spinodal decomposition of the liquid-liquid phase separation. The effect of the processing conditions on the morphology, degree of porosity, degree of crystallinity and crystalline polymorph, thermal, dielectric and piezoelectric properties of the PVDF-HFP polymer were evaluated.

The crystalline phase and degree of crystallinity depend on the processing conditions and further influence the dielectric and piezoelectric response. The piezoelectric coefficient is correlated with the β -phase content and decreases with decreasing polymer concentration in the initial solution at a given evaporation temperature.

© 2014 Elsevier Ltd. All rights reserved.

1. Introduction

Significant advances are being made in scientific and commercial areas for the development of membrane technologies [1]. Polymeric membranes are being used for a variety of areas, including microfiltration (MF) [2], ultrafiltration (UF) [1,2], reverse osmosis (RO) [1,2], nanofiltration (NF) [3], hyperfiltration [3] and gas separation [2]. The applications of membrane technologies cover almost every industrial sector including fuel cell technologies [4], lithium-ion batteries [1,5] and membrane distillation (MD) [6].

Each application imposes specific requirements for the membrane material and structure in terms, of porosity and pore size [2], anti-fouling properties, mechanical strength and chemical resistance [1], the final properties of the polymer membrane depending strongly on processing parameters [7,8].

The most commonly used technique to produce membranes is phase separation of polymer solutions by phase inversion [2]. This separation can be accomplished by different methods including thermally induced phase separation (TIPS) [9], controlled evaporation of solvent [10], precipitation from the vapour phase [11], immersion precipitation (IP) [12] and air-casting [13]. Currently, most of the commercial membranes for microfiltration and ultrafiltration [14] are produced by phase inversion methods [14], mainly due to its simplicity and flexible production scale.

* Corresponding author. Tel.: +351 253 604 073; fax: +351 253 604 061.

E-mail address: lanceros@fisica.uminho.pt (S. Lanceros-Mendez).

TIPS has become one of the main methods used for polymer membrane preparation [15], as it shows some advantages in comparison to traditional phase separation processes: it can be applied to a wide range of polymers [9]; can be used to generate dense and porous films, the latter with isotropic, anisotropic or asymmetric microstructures with an overall porosity as high as 90%; and it is more flexible than wet or dry-casting, since it depends primarily on heat transfer rather than multi-component mass transfer [9].

Poly(vinylidene fluoride) (PVDF) has received much attention as a membrane material due to its outstanding properties such as high mechanical strength, thermal stability, chemical resistance and high hydrophobicity, when compared to other polymer materials, such as polysulfone (PSU), polyethersulfone (PES) and polyimide (PI) [16].

PVDF membranes have been extensively applied in ultrafiltration and microfiltration [17], and are currently being explored as candidates in membrane contactor [18] and membrane distillation applications [19]. PVDF dissolves in common organic solvents, from which porous PVDF membranes can be produced by phase inversion [20].

Besides PVDF, there are other fluoropolymers that can be used as membrane materials, such as poly(vinylidene fluoride-co-hexafluoropropylene) (PVDF-HFP) and poly(vinylidene fluoride-trifluoroethylene) (PVDF-TrFE) [20]. PVDF-HFP has drawn much attention [1,21] and seems to be more promising than PVDF for membrane applications. The addition of the amorphous phase related to the hexafluoropropylene (HFP) group to the main VDF blocks increases the fluorine content, leading to a more hydrophobic material [1], soluble in more solvents and with lower degree of crystallinity [22].

Microporous membranes of PVDF-HFP have been prepared by phase inversion from acetone/water/PVDF-HFP solutions with degrees of porosity between 70 and 90% [23].

The effect of PVDF-HFP concentration for the development of hollow fiber membranes has been studied in the system *N,N*-dimethylacetamide (DMAc)/poly(ethylene glycol)/(PEG)/PVDF-HFP, and it was verified that internal and external pore sizes decreased with increasing copolymer content [24].

PVDF-HFP membranes were also produced from PVDF and propylene carbonate (PC) or dimethyl sulfoxide (DMSO) solutions, the gelation occurring at relatively low concentrations and the miscibility area of the ternary diagram being larger for DMSO [25].

Taking into account the reported literature for production of membranes based on PVDF-HFP, a systematic approach to the modification of PVDF-HFP microstructure is still needed. Thus, the present work is devoted to the preparation of membranes from the PVDF-HFP/*N,N* dimethylformamide (DMF) solution by TIPS. Membranes with different microstructures have been obtained and characterized.

2. Experimental

2.1. Materials

Poly(vinylidene fluoride-co-hexafluoropropylene) P(VDF-HFP) (Solef 21216; $M_w = 600,000$ g/mol; 12 wt.% HFP) was

supplied by Solvay. *N,N*-dimethylformamide (DMF, 99.5%) was supplied by Merck.

2.2. Membrane preparation

The polymer was dissolved in DMF at room temperature under constant magnetic stirring until a homogeneous solution was obtained. The PVDF-HFP polymer concentration in solution ranged from 5 wt.% to 20 wt.%. After total polymer dissolution, the solution was placed on a clean glass substrate and spread by blade coating with a thickness of 100 μm , followed by isothermal evaporation in an air oven at temperatures from room to 100 °C.

2.3. Sample characterization

The morphology of the PVDF-HFP membranes was obtained by scanning electron microscopy (SEM) (Cambridge, Leica) with an accelerating voltage of 15 kV. The samples were previously coated with a thin gold layer using a sputter coating (Polaron, model SC502 sputter coater).

The porosity of the membranes was determined from the membrane (ρ_m) and pristine polymer densities ($\rho_{\text{pol}} = 1.77$ g/cm³) [26] using a pycnometer:

$$\rho_m = \frac{\rho_w m_3}{m_1 + m_3 - m_2} \quad (1)$$

where ρ_w is the water density, m_1 is the mass of pycnometer with water, m_2 is the mass of pycnometer with water and the membrane and m_3 is the mass of the dry membrane.

The degree of porosity was then calculated from [26]:

$$\phi = 1 - \frac{\rho_m}{\rho_{\text{pol}}} \quad (2)$$

Contact angle measurements (sessile drop in dynamic mode) were performed at room temperature in a Data Physics OCA20 device using ultrapure water (3 mL droplets) as the test liquid. At least 3 measurements on each sample were performed in different sample locations and the average contact angle was calculated.

The polymer crystalline form was identified by Fourier Transformed Infrared spectroscopy (FTIR) at room temperature with a Jasco FT/IR-4100. 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} .

Melting temperature and degree of crystallinity were determined by differential scanning calorimetry (DSC) with a Mettler Toledo 821e apparatus. The samples were cut from the central region of the membranes, placed in 50 μL crucibles and heated from 50 to 200 °C at a rate of 10 °C/min, under an argon atmosphere. The degree of crystallinity (χ_c) was calculated from the enthalpy of the melting peak (ΔH_f) based on the enthalpy of a 100% crystalline sample, through the following equation:

$$\chi_c = \frac{\Delta H_f}{x\Delta H_{\alpha} + y\Delta H_{\beta}} \quad (3)$$

where x is the weight fraction of the α phase, y is the weight fraction of the β phase determined from the FTIR

Download English Version:

<https://daneshyari.com/en/article/5206171>

Download Persian Version:

<https://daneshyari.com/article/5206171>

[Daneshyari.com](https://daneshyari.com)