

Novel PVDF-HFP membranes tailored by supercritical drying process

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Abstract

The work is based on the drying of PVDF-HFP gels with a procedure assisted by supercritical CO₂ to obtain nano-sized porous membranes at high quality/low cost ratio. Poly(vinylidene fluoride) (PVDF) as homopolymer or copolymer with hexafluoropropylene (PVDF-HFP) is a very interesting material largely used in catalytic membrane reactors, chemical and biomedical applications and various filtration processes. For this reason, many studies have been performed concerning the formation of porous PVDF-HFP structures by means of traditional phase inversion or gels drying methods. The classic gels drying presents some problems. These problems can be avoided using supercritical CO₂, which preserves the polymeric network of gels during the drying and aerogels formation. Moreover, this new approach appears advantageous with respect to conventional phase inversion methods, due to the reduced-solvent manufacturing process.

PVDF-HFP gels have been prepared from polymer/acetone solutions adding ethanol; then, the solutions have been cooled at -20°C for 30 min. Series of supercritical drying experiments have been performed at 35°C, 200 bar and at various polymer concentrations (from 5 to 12% w/w). Effects of the tailoring conditions on the membrane structural parameters have been evaluated by SEM analysis. In all cases, the membranes exhibit interconnected structures with nano-sized pores and highly porous surfaces.

Keywords: PVDF-HFP, Membranes, Supercritical, Nanostructure

INTRODUCTION

Poly(vinylidene fluoride) (PVDF) as homopolymer or copolymer with hexafluoropropylene (PVDF-HFP) is acid-resistant and inert, it has a good degree of compatibility with human tissues and has good mechanical and chemical characteristics. As a consequence, it is largely used in catalytic membrane reactors [1-3], in biomedical applications [4-5] and in various filtration processes [6-7]. Until now, many works have been developed with the aim of producing porous PVDF-HFP structures. In particular, the formation of aerogels by gel drying processes has been studied [8-10].

Aerogels are porous structures characterized by highly interconnected polymeric network with submicronic pores and porous surface. Cho et al. [8] processed PVDF gels obtained starting from PVDF/ γ -butyrolactone solutions using a drying process assisted by hot air. They obtained non-porous structures characterized by polymeric spheres. Dasgupta et al. [9-10] studied two different drying processes to obtain aerogels. In the first work [9], they processed gels obtained starting from PVDF-organic diesters solutions. First, the gel was immersed in cyclohexane bath for 12 h where cyclohexane replaced diesters in the gels. Such process was repeated for 6-7 days. Then, the cyclohexane was decanted and the gel was dipped into methanol for 1 day. It was then dried in vacuum at 60°C for 3 days. At the end of the process, a partially porous structure was obtained. Indeed, the surface tension of the liquid solvent caused the collapse of the structure during the drying process. In a subsequent work, Dasgupta et al. [10] tried to avoid the collapse of the structure starting from PVDF-camphor solution. In this way, they removed the solvent using its tendency of easily sublimating under near “freeze-drying” conditions but the drying time was longer. A method to avoid the collapse of the structure and to obtain aerogels in shorter time was presented by Daniel et al. [11]. In this work, a supercritical drying process assisted by CO₂ was tested on syndiotactic polystyrene gels. This process allows to obtain aerogels in a single-step and to keep intact the structure of the gel avoiding the collapse of the structure.

In the present work, we proposed, for the first time, the supercritical CO₂ drying process to obtain PVDF-HFP aerogels and analyzed the effect of process parameters (polymer concentration, pressure and temperature) on aerogels morphology and pore size. In particular, considering the difficulty in generating PVDF-HFP membranes by the traditional formation techniques (i.e., NIPS, TIPS, etc) [12-15], we studied the possibility of using the aerogels produced as membranes and we analyzed the effects of the tailoring conditions on the structural parameters by SEM analysis.

MATERIALS AND METHOD

Materials

PVDF-HFP (Number Average $199 \cdot 10^3$, Weight Average $353 \cdot 10^3$, Polydispersity 1.8, Density 1.78 g cm^{-3}) was kindly supplied by Solvay S.A. (Ixelles, Belgium); acetone and ethanol (purity 99.8%) was bought from Sigma-Aldrich; CO₂ (purity 99%) was purchased from S.O.N. (Società Ossigeno Napoli, Italy). All materials were processed as received.

Aerogels preparation and characterization

Aerogels were prepared in a laboratory apparatus equipped with a 316 stainless steel high-pressure vessel with an internal volume of 80 mL, in which SC-CO₂ contacted the polymer gel in a single pass. Gels of PVDF were prepared by stirring the solution of polymer and acetone, then adding ethanol. The solution was placed in a formation cell (steel caps with a diameter of 2 cm

and height of 200 μm or steel caps with a diameter of 2 cm and height of 3 mm). The formation cell was placed in a freezer at $-20\text{ }^{\circ}\text{C}$ until gel was formed. Then, it was placed in the vessel that was closed and filled from the bottom with SC- CO_2 , up to the desired pressure using a high-pressure pump (Milton Roy–Milroyal B). We operated in continuous mode for 1h; i.e., with a constant CO_2 flow rate of 1.5 kg/h. Then, the vessel was slowly depressurized for 10 min.

Phase diagram

Phase diagrams of the PVDF-HFP/Acetone/Ethanol system was obtained by drop-wise addition of nonsolvent (i.e., ethanol) under continuous stirring at 20°C . The gelation point was visually observed by occurrence of consistence modification (upon non-solvent addition). The maximum concentration of the polymer in the starting solution was 20% w/w in acetone and was limited either by the excessive viscosity creating difficulties in efficient stirring, or by a too strong inherent turbidity of the polymer solution

Scanning electron microscopy (SEM)

PVDF-HFP aerogels were cryofractured with a microtome (Bio-optica S.p.A, Italy, Mod. Microm HM 550 OMVP); then, the sample was sputter coated with gold and was viewed by scanning electron microscope (SEM) (mod. LEO 420, Assing, Italy) to study aerogels structure.

Aerogels porosity

The porosity (ϵ) represents the “void space” inside the aerogel and was calculated from the density of the aerogel (ρ_m) and the density of untreated PVDF-HFP ($\rho_p=1.78\text{ g cm}^{-3}$):

$$e = 1 - \frac{r_m}{r_p} \quad (1)$$

The aerogel density was determined by measuring the volume and the weight of the aerogel.

RESULTS AND DISCUSSION

Phase diagram

In the first part of the work we focused our attention on the study of the phase diagram of PVDF-HFP/Acetone/Ethanol system with the aim of obtaining the gelation line. Experimental determination of the phase diagrams was limited to a maximum polymer concentration of 20% w/w, in order to avoid inefficient stirring as a consequence of the high viscosity of the solutions. In figure 1, the phase diagram generated is reported.

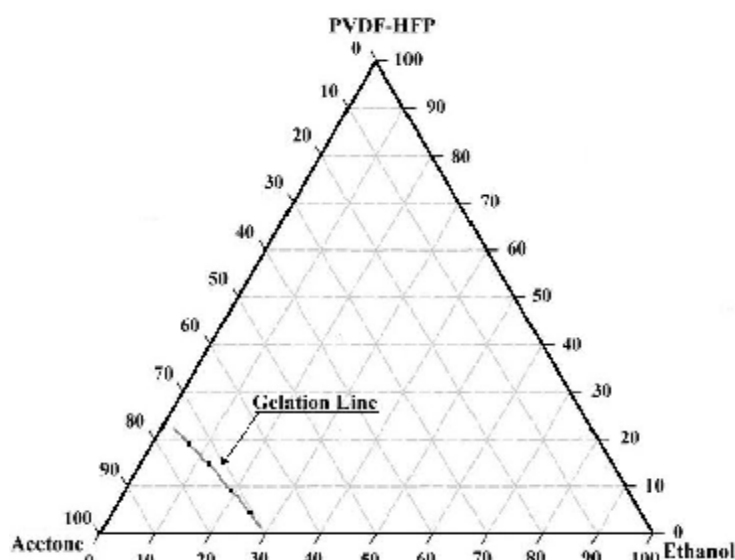


Figure 1: Phase diagram of PVDF-HFP/Acetone/Ethanol system

As it is possible to observe, the gelation line of the solution is very close to the solvent (i.e., acetone) apex. This result confirms the general behavior of crystallizable polymers such as PVDF-HFP [12-16]; indeed, for these kind of polymers, the precipitation by solid-liquid demixing (i.e., gelation) usually takes place during the immersion process controlling the process too. This is also the reason for which it is difficult to prepare membranes of crystallizable polymers by the traditional formation techniques.

Effect of polymer concentration

PVDF-HFP aerogels have been successfully produced using the supercritical CO₂ drying process. Various polymeric gels have been prepared with PVDF-HFP concentration ranging between 5 and 12% w/w. The concentration of acetone in the solution was 60% w/w, whereas the concentration of the non-solvent (i.e., ethanol) varied with the concentration of polymer. The operative conditions, pressure and temperature, have been modified ranging from 100 to 200 bar and from 35 to 45°C.

In figure 2a, an example of PVDF-HFP gel obtained starting from 10% w/w polymer, 60% acetone and 30% ethanol, is showed. In figures 2b-c, the same gel is showed after the supercritical drying process. As it is possible to observe, the dimension and the shape of the

aerogel does not change during the process. On the contrary, in figure 1d an image of gel dried in hot air is reported; it is completely collapsed and a non-porous structure is obtained.

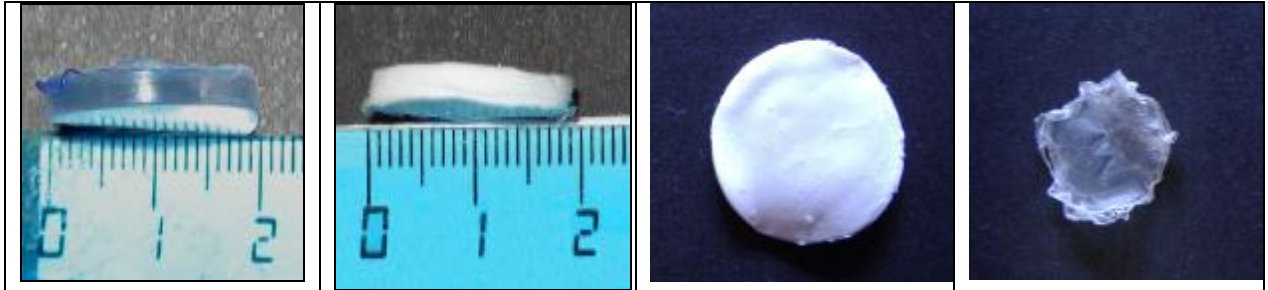


Figure 2: a) PVDF-HFP gel, b-c) PVDF-HFP aerogel dried by SC-CO₂, d) aerogel dried in hot air.

Subsequently, we analyzed the aerogels by SEM. In figure 3, SEM images of the aerogels surfaces are reported. As it is possible to observe the aerogels obtained starting from 5 and 7% w/w polymeric solutions present porous skin whereas the surfaces of aerogels obtained from 10 and 12% w/w solution are more dense.

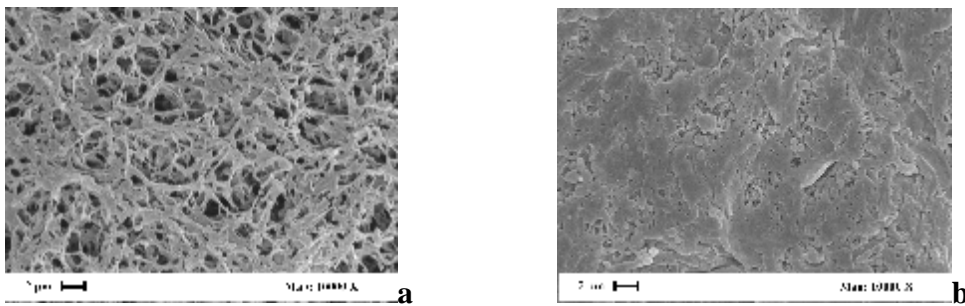


Figure 3: Aerogels surface obtained starting from a) 5% and b) 12% of PVDF-HFP.

We also analyzed aerogels sections and we reported SEM images in figure 4a-c. In this case, SEM images show an increase of porosity with the decrease of the polymer concentration in the starting solution. This result has been confirmed by porosity measurements. Indeed, the porosity of aerogels obtained at 200 bar and 35°C starting from more concentrated solutions is lower than the porosity of the others aerogels; i.e. increasing the polymeric concentration from 5 to 12% w/w, the porosity decreases from 0.95 to 0.87 (figure 4b).

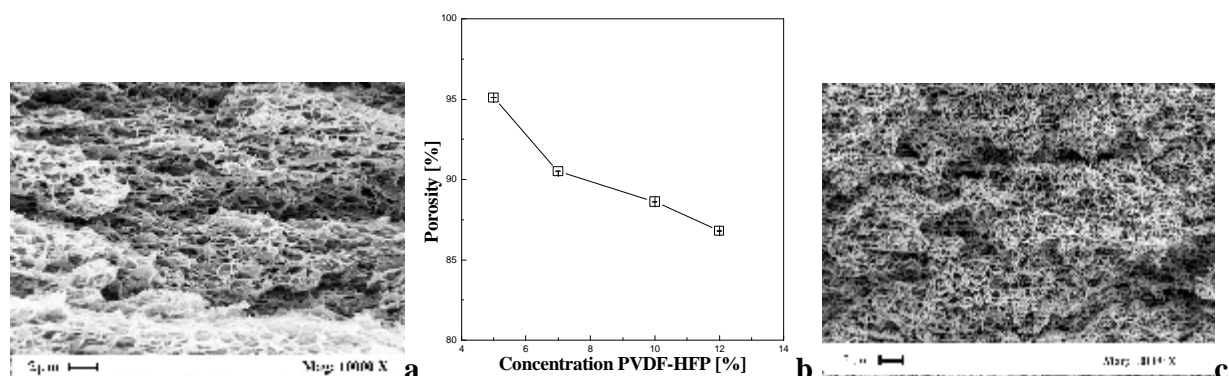


Figure 4: Aerogels section obtained starting from a) 5% and c) 12% of PVDF-HFP. b) Porosity trend with PVDF-HFP concentration.

These results can be easily explained considering that an increase of polymer concentration in the starting solution causes an increase of the amount of polymer for volume unit inside the polymeric matrix of the aerogel obtained. As a consequence, the void space of the aerogel decrease, i.e., the overall porosity decreases.

Effect of pressure and temperature

We also analyzed the effect of operative pressure and temperature on aerogels porosity; in particular, we observed that decreasing pressure from 200 to 100 bar the porosity does not change. This result is also confirmed by SEM analysis; indeed, it is evident that the internal structure does not visibly change with the operative pressure. This result can be explained considering that, a change of pressure influences only the solvent power of supercritical CO₂ (it increases with pressure). In this way, it is possible to dry the gel in shorter time, but the aerogel structure is not influenced.

On the contrary, increasing temperature from 35°C to 45°C, the aerogel porosity changes: it dramatically decreases from 0.89 to 0.40. Also in this case, it is possible to analyze SEM images reported in figure 5; i.e., the increase of temperature causes a partial collapse of the polymeric structure. In particular, in figure 5a it is evident as the starting thickness of gel (i.e., 2 mm) sensibly decreases until ca. 400 μm; moreover, figure 5b shows the porosity decrease of the internal structure.

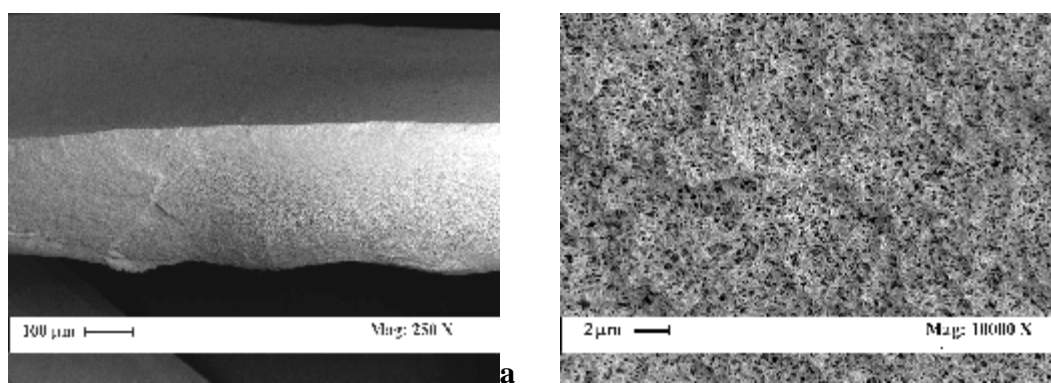


Figure 5: PVDF-HFP aerogel obtained at 45°C; a) whole section, b) internal structure.

This result can be due to the volatility of the liquid solvents used (acetone and ethanol); indeed, probably at 45°C the solvent and the non-solvent that supports the gel structure partially vaporize, leading to structure collapse due to surface tension.

CONCLUSIONS

Supercritical gel drying process assisted by CO₂ has produced aerogels avoiding the collapse of the structure due to absence of surface tension of supercritical CO₂. Polymeric networks are characterized by elevated porosity and small pores size and confirmed to be suitable for membrane applications.

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