

Preparation of pH sensitive poly(vinylidene fluoride) porous membranes by grafting of acrylic acid assisted by supercritical carbon dioxide

Alessandro Galia*, Loredana Ferro, Vanessa Firetto, Giuseppe Filardo, Onofrio Scialdone

Dipartimento di Ingegneria Chimica dei Processi e dei Materiali, Università di Palermo,
Viale delle Scienze Ed 6 Palermo (Italy)

email: galia@dicpm.unipa.it fax: 0039-091-7025020

Aim of this work is to study the preparation of pH sensitive membranes for biomedical applications via thermal induced graft polymerization of acrylic acid (AA) on poly(vinylidene fluoride) (PVDF) assisted by supercritical carbon dioxide (scCO₂). Using scCO₂ as a solvent and swelling agent, the monomer and initiator (benzoyl peroxide) could diffuse faster and distribute more uniformly into the polymer matrix. A better control of the final molecular architecture should be achieved because bimolecular grafting reactions are accelerated with respect to chain degradation processes. Commercial hydrophobic PVDF porous matrixes were selected as model membranes. Grafted polymers were characterized by FT-IR spectroscopy, field emission scanning electron microscopy (FE-SEM), thermogravimetric analysis (TGA) and water permeability test at different pH values. Preliminary results indicate that the grafting degree can be tuned by controlling the monomer concentration and the carbon dioxide density. Moreover, the water permeation of grafted membranes decreases considerably as pH increases from 1 to 7, contrary to virgin membranes whose water permeability was substantially pH independent.

Research activity is going on to study the microstructure of the membrane and to optimize the level and distribution of poly(AA) grafts.

INTRODUCTION

PVDF is known for its excellent mechanical and physicochemical properties. Moreover, because of its chemical inertness and good processability, PVDF has been extensively investigated for its application in the preparation of membranes.¹⁻³ However, the application of PVDF membranes is limited to some extent by the hydrophobic nature of the polymer. Moreover, in some applications, such as bio-filtration and controlled drug release, it could be useful that membranes are sensitive to changes of environmental parameters, such as pH.⁴ Several approaches have been developed to endow the conventional hydrophobic membranes with hydrophilic properties and pH-sensitivity. An interesting method to reach this goal was based on the preactivation of the fluoropolymer, dissolved in N-methylpyrrolidone (NMP) or N,N-dimethylformamide, by ozone treatment. After precipitation and drying, the peroxide containing PVDF is redissolved in NMP and reacted in homogeneous phase with acrylic acid (AA) or 4-vinylpyridine.^{5,6} A similar approach in the presence of 1-phenylethyl dithiobenzoate as chain transfer agent was also used to graft living poly(acrylic acid) on

PVDF.⁷ This method is anyway based on the utilization of low-volatile toxic solvents that must be thoroughly removed from the polymer before its utilization in biomedical applications. A different tested approach was the activation of PVDF by ionizing radiation and subsequent modification of the matrix by heterogeneous grafting of AA from aqueous solutions.⁸ By this route, nonuniform grafting levels can be obtained. In this work we have studied the preparation of hydrophilic and pH-sensitive PVDF membranes by grafting of the AA monomer using supercritical carbon dioxide as solvent and swelling agent to take benefit of scCO₂ properties i.e. biocompatibility, easy recovery from the processed polymer by depressurization and good swelling capability towards amorphous fluoropolymers.

MATERIALS AND METHODS

Durapore PVDF hydrophobic membranes were used as model substrates. They have an average pore size of 0.22 μm, a diameter of 47 mm, a thickness of about 100 μm and 75% vol/vol porosity. Acrylic acid 99% anhydrous (with 200 ppm of monomethyl ether hydroquinone as inhibitor) and ethanol (ACS, 99.8%) were purchased from Aldrich; CO₂ was Air Liquide 99.998 pure. All these chemicals were used without further purification. Benzoyl peroxide, purchased from Aldrich (75% remainder water, USP grade), was recrystallized from methanol.

The experiments were carried out in an AISI 316 fixed volume (27 mL in the completely assembled setup) batch reactor, stirred by a magnetic bar and heated by an electronically controlled electric tape. The proper amounts of AA and initiator were charged in the reactor together with the PVDF pristine membrane, the vessel was then purged by a controlled flow rate of CO₂ maintained for at least 20 min to remove air. After sealing the reactor, CO₂ was added at room temperature by using an ISCO syringe pump. The total amount introduced was measured weighing the vessel with an electronic scale (Sartorius LP 8200S, precision 0.01 g). The vessel was then inserted in the control system and heated at the reaction temperature (65°C for BPO and 100°C for DCP). The time interval to reach the set-up temperature was roughly 20 min in each run. At the end of the reaction the reactor was cooled in an ice bath to room temperature and then the vessel was slowly depressurized. The reactor was then opened and the membrane was recovered, washed at room temperature with ethanol for 1 h to remove monomer and initiator and at 90°C with the same solvent for 2 h to remove poly(AA) homopolymer. Then the grafted membrane was dried under vacuum at 40°C overnight. Such procedure was repeated until constant weight of the sample was obtained. At this point it was assumed that the unreacted monomer and homopolymer had been removed completely.

RESULTS

Grafting experiments

The phase behaviour of the CO₂/AA/initiator mixture was investigated under conditions adopted to perform grafting reactions, by a constant volume stainless steel high pressure view cell, and it was found that the mixture was single phase in agreement with data reported in the literature⁹.

The graft copolymerization of AA on the PVDF porous membrane was conducted under different conditions in order to investigate the effects of monomer and initiator

concentrations, reaction time and fluid phase density on the grafting level DG calculated with the following equation:

$$DG (\%) = 100 (W_1 - W_0)/W_0 \quad (1)$$

where W_0 stands for the weight of virgin PVDF membrane and W_1 is the weight of modified membrane after aforementioned washing procedure. Figure 1 shows the effect of reaction time on the DG. It is evident that the DG increased significantly when reaction time was higher than 18 h.

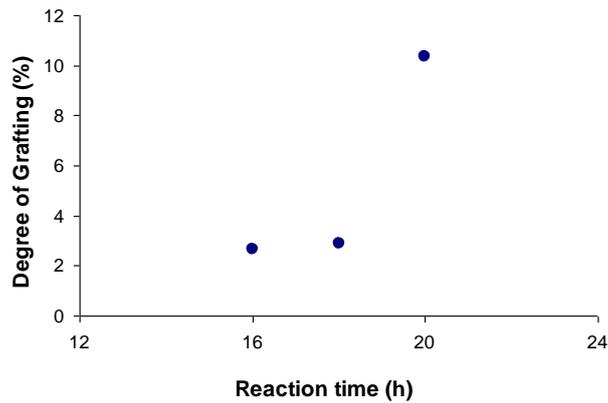


Figure 1 – Effect of reaction time on degree of grafting ([BPO]=0.15mM, [AA]=0.2M, ρ_{CO_2} =0.5g/mL, 65°C)

We performed several experiments changing the initial concentration of AA ([AA]) and of BPO initiator ([BPO]) and the density of the fluid phase. The effects of these parameters are shown in figure 2-3. The degree of grafting increased considerably at the highest investigated values of [AA] and [BPO] and decreased at the highest density probably because monomer partitioning is biased towards the continuous phase.

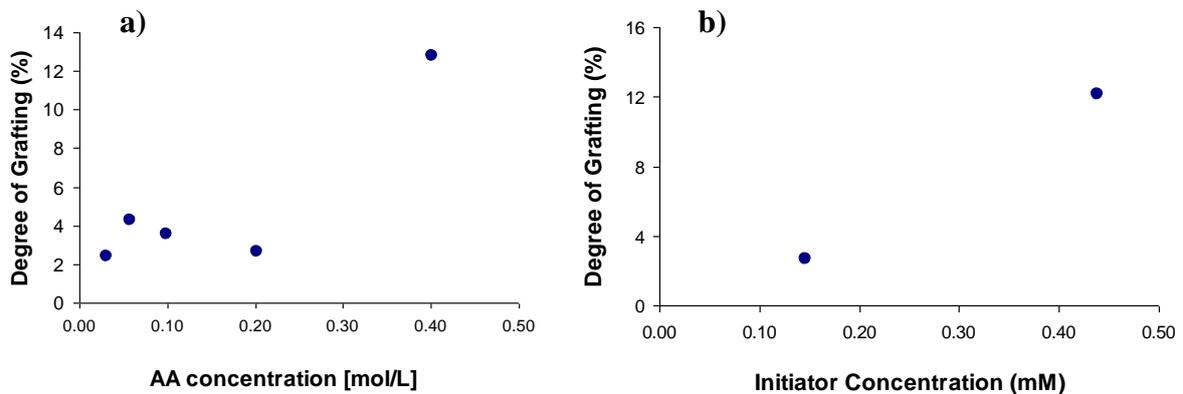


Figure 2 – a) Effect of AA concentration on DG ([BPO]=0.15mM, ρ_{CO_2} =0.5g/mL, 65°C, 16 h);
 b) Effect of BPO concentration on DG ([AA]=0.2M, ρ_{CO_2} =0.5g/mL, 65°C, 16 h)

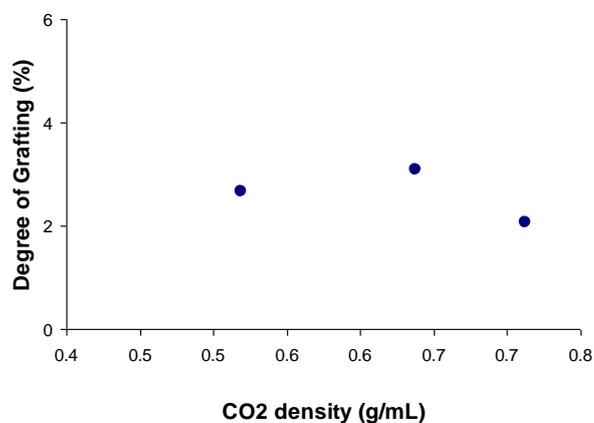


Figura 3 – Effect of CO2 density on DG ([BPO]=0.15mM, [AA]=0.2M, 65°C, 16h)

Characterization

FT-IR/ATR measurements were used to investigate the structure of pristine and modified PVDF membranes. In figure 4 are reported the FT-IR/ATR spectra of the virgin and the grafted matrices. In the latter (spectra (b) and (c)) it can be seen an absorption peak at around 1714 cm^{-1} which is absent in the virgin PVDF (spectrum (a)). This peak is assigned to the stretching of the carbonyl group (C=O) and its presence confirms that AA was grafted onto PVDF membrane.

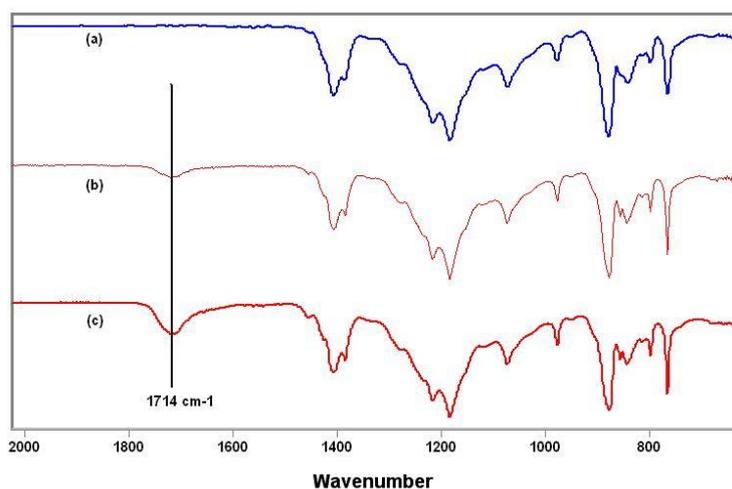


Figura 4 – FT-IR/ATR Spectra of (a) pristine PVDF, (b) 4.4% DG, (c) 10.3% DG.

To study the modification of the surface morphology of the matrices it was employed FE-SEM. The SEM images are shown in figure 5. The typical morphology of the original membrane, characterized by high porosity, was obtained for all samples with DG lower than about 10%. Differently, when higher grafting values were obtained the number and the size of the pores decreased.

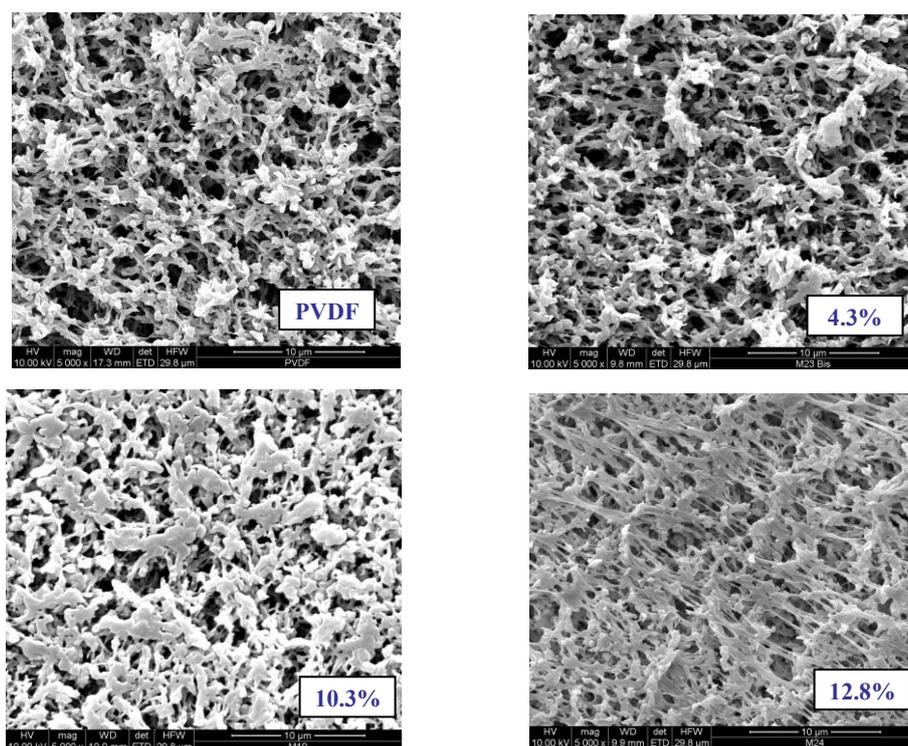


Figure 5 – SEM micrographs of virgin and grafted PVDF membrane

The thermal stability of the grafted membranes was studied by thermogravimetric analysis (TGA). Thermograms of the pristine and the grafted PVDF membranes and of PAA homopolymer are shown in figure 6. PVDF resulted thermally stable up to about 430°C. PAA starts to decompose at about 200°C. The grafted membranes showed an intermediate behaviour. The extent of the weight loss at 280°C is proportional to degree of grafting of the samples. The membranes obtained at the highest investigated reaction time and initiator concentration exhibited an higher thermal stability at $T > 360^{\circ}\text{C}$. This is probably connected with the chemical structure of the polymer as Jantas² et al. showed that higher thermal stability was reached in reticulated polymers when the crosslink density was increased. It seems reasonable that more crosslinked membranes were obtained at high reaction time and initiator concentration.

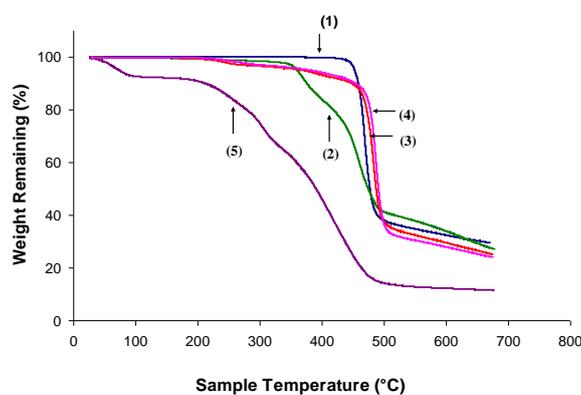


Figure 6 – Thermograms of (1) pristine PVDF, membrane with DG of (2) 2.7%, (3) 10.3%, (4) 12.2%, (5) PAA homopolymer

The water permeability of grafted membranes was investigated at different values of pH in aqueous solutions. Figure 7 shows the trend of the fluxes across the membranes with different grafting levels as a function of the pH of the solution.

The results indicated that the water permeation of grafted membranes decreased considerably as pH increased, contrary to virgin membranes characterized by a pH-independent water permeation.

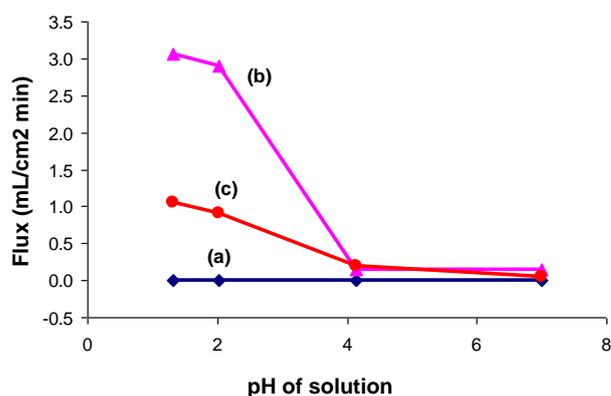


Figure 7 – Flux measurements of aqueous solutions through (a) pristine PVDF, (b) 10.3% DG, (c) 12.2% DG

CONCLUSION

Grafting of AA monomer was successfully performed on PVDF membranes as confirmed by FT-IR/ATR spectroscopy and TG analyses. Results collected until now indicated that the grafting degree can be tuned by controlling the monomer and initiator concentrations, the reaction time and the carbon dioxide density. Flux measurements across the pristine and the grafted membranes at different pH-values demonstrated that a pH-sensitive behaviour was obtained after AA grafting in scCO₂.

REFERENCES :

- [1] Khayet, M., Matsuura, T., *Ind. Eng. Chem. Res.*, Vol. 3, **2001**, p. 379
- [2] Hietala, S., Maunu, S. L., Sundholm, F., *Macromolecules*, Vol. 32, **1999**, p. 788
- [3] Fan, L., Harris, J. L., Roddick, F. A., Booker, N. A., *Water Res.*, Vol. 35, **2001**, p. 4455
- [4] Brophy, P. D., Mottes, T. A., Kudelka, T. L., McBryde, K. D., Gradner, J. J., Maxwold, N.J., Bunchman, T. E., *Am. J. Kidney Dis.*, Vol. 38, **2001**, p. 173
- [5] Ying, L., Wang, P., Kang, E. T., Neoh, K. G., *Macromolecules*, Vol. 35, **2002**, p. 673
- [6] Zhai, G., Ying, L., Kang, E. T., Neoh, K. G., *Macromolecules*, Vol. 35, **2002**, p. 9653
- [7] Ying, L., Yu, W. H., Kang, E. T., Neoh, K. G., *Langmuir*, Vol. 20, **2004**, p.6032
- [8] Betz, N., Begue, J., Goncalves, M., Gionnet, K., De le'ris, G., Le Moe'l, A., *Nucl Instrum Methods B*, Vol. 208, **2003**, p. 434
- [9] Jantas, R., Szocik, H., Stawski, D., *Polymer Bulletin*, Vol. 53, **2005**, p. 277