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Fluoropolymers in Membrane Applications

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Abstract: Performances of fluoropolymers related to membranes manufacturing for different purposes are reviewed in the present article. In particular the main physical, mechanical and chemical properties of PVDF, ECTFE and PFSA ionomers are described in their specific applications. The excellent chemical resistance and suitable electrochemical properties make fluoropolymers an especially good choice in membranes manufacturing.

Keywords: *fluoropolymers, PVDF, ECTFE, Hyflon® Ion, membranes, fuel cells*

1. Introduction

Membrane technology is a wide field of research that covers many different materials, processing techniques and applications. Fluoropolymers have a relevant position in this respect thanks to their excellent properties for special purposes: poly-vinilydene fluoride (PVDF), ethylene-chlorotrifluoro ethylene (ECTFE), poly-tetrafluoroethylene (PTFE) and perfluorosulfonic acid (PFSA) ionomers are examples of the importance of these materials in different applications such as low pressure water treatment, gas separation, energy storage.

A wide selection of physical, chemical or electrochemical properties of membrane materials allow the application of membrane technology in a variety of different processes. The final device is used for special purposes such as water treatment, hemodialysis, food & beverage processing, gas separation, tools for energy storage and conversion. The importance of membrane technology is linked to the increase in human welfare by supplying drinking water for millions of people in the world and by warranting survival of people suffering from kidney disease. Well known is also its relevance in the food industry, as in the juice concentration and in the manufacture of dairy products. The chemical and pharmaceutical industries take advantage of membrane special design with exceptional stability and high purity [1,2]. The demand of new energy sources and conversion systems such as portable power tools and alternative power supply for the automotive industry is strongly increasing. Also in this field fluoropolymers are widely used for different specific purposes: for instance PVDF is used as separator in gel-polymer type batteries and PFSA ionomer is employed as proton conductive polymer in fuel cell technology.

Fluoropolymers are an excellent choice for various applications because of their outstanding properties, such as exceptional chemical resistance, excellent mechanical strength and stiffness, good stability in a wide range of pH, high thermal properties and low surface energy. Among the fluoropolymers employed in membrane applications, the most widely used are the homopolymer and copolymer polyvinylidene fluoride (PVDF). Recently copolymers of ethylene-chlorotrifluoroethylene (ECTFE) [3,4] are receiving increasing attention.

PFSA ionomer membranes recently developed and based on the "short-side-chain" chemistry show improved mechanical properties and better proton conductivity compared to standard materials, with increased final fuel cell performances.

In the present review we are comparing these fluoropolymers in terms of their specific properties as re-

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Table 1. Chemical Structures of Fluoropolymers for Membranes

	Shorthand notation	Chemical structure
PVDF homopolymer	VF_2	$(CH_2\text{-}CF_2)_n$
PVDF copolymers	VF_2-HFP and VF_2-CTFE	$(CH_2\text{-}CF_2)_n\text{-}(CF_2\text{-}CFCF_3)_m$ and $(CH_2\text{-}CF_2)_n\text{-}(CClF\text{-}CF_2)_m$
ECTFE	E-CTFE	$(CH_2\text{-}CH_2)_n\text{-}(CFCl\text{-}CF_2)_m$
PSFA ionomer	TFE-SFVE	$(CF_2\text{-}CF_2)_n\text{-}(CF_2\text{-}CF\text{-}OCF_2CF_2SO_3H)_m$

lated to membrane technology.

2. Properties of PVDF, ECTFE and PSFA Fluoropolymers

For a better understanding of why these materials are suitable for membranes applications, in this paragraph the main properties of PVDF and ECTFE polymers and PFSA membranes are reviewed. In particular Solvay Solexis products are considered, as a supplier of a wide range of high-purity fluoropolymers such as Solef® and Hylar® PVDF, Halar® ECTFE and Hyflon® Ion PFSA membranes.

PVDF can be polymerized via emulsion and via suspension polymerization. The two final products show slightly different properties: in such a variety of possibilities it is possible to find the right material for a specific purpose. Solef® series are produced by suspension polymerization and Hylar® series by emulsion polymerization. In the first case, the powder particle size is around 10 μm; in the second one, the powder particle size is in the range between 20 and 150 μm, with a narrower molecular weight distribution and fewer head-to-tail inversions in the chain.

Homopolymers such as Solef® 1000 and Solef® 6000 series have limited chain branching and have a high crystallinity degree. The difference between the two series is the narrower molecular weight distribution of Solef® 6000.

Homopolymers Hylar® 460 and Hylar® 461 have a broad molecular weight distribution and a 40~60% insoluble gel fraction with a high concentration of chain branching.

PVDF can also be copolymerized with hexafluoropropylene, HFP (CH_2-$CFCF_3$), and chlorotrifluoroethylene, CTFE ($CFCl$-CF_2).

Concerning HFP copolymers, Solef® 11000 series is manufactured using suspension polymerization with a heterogeneous distribution of HFP among the chains, while Solef® 20000 series is manufactured using suspension polymerization with a more homogeneous distribution of HFP among the chains.

Solef® 30000 is a heterogeneous CTFE copolymer; it is commercially available with levels of the comonomer between 10% and 20%.

ECTFE is a semi-crystalline, thermoplastic copolymer with brittleness temperature of less than -76°C. Its outstanding stability to pH values from 2 to 13 and its limited solubility in organic solvents make this fluoropolymer perfectly suitable for membrane applications. Halar® XPM 1 is a traditional copolymer; an n-butyl-acrylate (nBuA) terpolymer, Halar® XPM 2, is also available (5).

In Table 2a, 2b and 2c the values for the main physical properties of these grades are listed. Values of melting point have been measured according to ASTM D3418 and Glass transition temperature to DMTA/DMTS.

PVDF is well resistant to most inorganic and organic acids, therefore it can be utilized in a wide range of pH. It has a good resistance also to solvents like aromatic and aliphatic hydrocarbons, alcohols, tetrahydrofurane, chlorinated hydrocarbons and to aggressive chemicals such as ozone and chlorine. PVDF can be sterilized by Gamma Radiation and by steam without relevant changes in its properties. These characteristics are essential for the membrane application: the cleaning step of a membrane during its operation in a plant

Table 2a. Physical Properties of Homopolymer PVDF

		SOLEF® PVDF homopolymer			HYLAR® PVDF homopolymer	
		1015	6010	6020	301F	460
Melting point	°C	171	172	170	160	160
Glass transition temperature	°C	-30	-30	-32		-40

Table 2b. Physical Properties of Copolymer PVDF

		SOLEF® PVDF copolymer (HFP)			SOLEF® PVDF copolymer (CTFE)
		11008	21216	21508	31508
Melting point	°C	160	135	135	169
Glass transition temperature	°C	-29	-30	-29	-28

Table 2c. Physical Properties of ECTFE

		ECTFE copolymer HALAR® XPM 1	ECTFE nBuA terpolymer HALAR® XPM 2
Melting point	°C	240~245	180~200
Glass transition temperature	°C	80~130	60

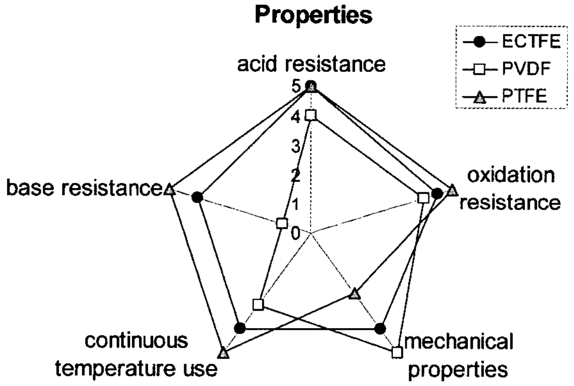

Fig. 1. Comparison of properties of PVDF, ECTFE and PTFE (rank from 0 to 5 are qualitative levels from poor to good performances).

requires a chemical treatment that must not damage the membrane structure itself.

Concerning chemical resistance, ECTFE shows excellent chemical resistance over a wide temperature range to strong acids, such as sulfuric, nitric, hydrochloric and hydrofluoric acids. This fluoropolymer easily handles powder bleaching agents, such as sodium hypochlorite; it has a better performance than PVDF in strong bases, such as sodium hydroxide and potassium hydroxide, and a very good ozone resistance; besides, it is chemically resistant to strong polar solvents, such as N-methyl pyrrolidone and dimethyl formamide.

As a summary of the performance of fluoropolymers, Fig. 1 shows a global view of properties of these fluoropolymers in comparison also with Algoflon® PTFE (polytetrafluoroethylene) which is used for membranes in particular applications. In fact it is particularly inert and extremely hydrophobic and its membranes are especially devoted to the distillation process of aggressive streams. Due to the impossibility to dissolve PTFE in any substance, the processing can be done only by stretching of an extruded dense film.

The Hyflon® Ion product range is a family of products based on the unique Short Side Chain (SSC) perfluorosulfonic acid (PFSA) polymer. It is specifically designed for today's fuel cells industry. These materials are copolymers of tetrafluoroethylene and a Sulfonyl Fluoride Vinyl Ether (SFVE) and feature lower equivalent weight and higher crystallinity than competitive perfluorosulfonic acid (PFSA) polymers. Hyflon® Ion polymers are available in the form of extruded membranes for a wide range of fuel cell applications, operating on pure hydrogen, reformate and direct methanol

Table 3a. Physical-Chemical Properties of Standard Hyflon® Ion Membrane

Density	g/cm^3	2.06
Equivalent weight	g/eq	850~890
Total acid capacity	meq/g	> 1.12

Table 3b. Mechanical Properties of Standard Hyflon® Ion Membrane, according to ASTM D0638. MD: Machine Direction, TD: Transverse Direction

Stress at break (MD/TD)	MPa	> 25/20
Elongation at break (MD/TD)	%	> 140/180
Yield stress (MD/TD)	MPa	> 11/11
Yield strain (MD/TD)	%	> 8/8

Table 3c. Fuel Cell Performance and Water Uptake Properties of Hyflon® Ion Membrane

Power output @ 0.8 A/cm^2 (*)	W/cm^2	> 0.45
Uptake by weight (water soaking @ 100°C)	%	< 45
Dimensional elongation (MD/TD) (water soaking @ 100°C)	%	< 15/25

(*) T (cell) = 75°C, T (*gas humidification*) = 80°C, P (Air, H_2) = 2.5 bar abs, LT250EW E-Tek electrodes with 0.5 mg Pt/cm^2 and 0.7 mg ionomer/cm^2

("DMFC"). Dispersions are also obtainable in various solvent systems. Typically, water-alcohol based dispersions are made available in concentrations (6% by weight) suitable for ink formulation with catalysts and subsequent electrode manufacturing in the electrolysis and fuel cell industry (Hyflon® Ion D83-06(A)).

In Tables 3a, 3b, 3c are shown the main properties of Hyflon® Ion extruded membranes.

3. Applications

Among different applications PVDF is devoted to produce flat sheet membranes, hollow fibers and spiral wounded modules for low pressure water treatment such as microfiltration (MF) and ultrafiltration (UF) processes. The purpose of these products is mostly for hemodialysis, low pressure water, food and beverage treatment, and sometimes gas separation. This material can be easily processed by thermally induced phase separation (TIPS) process. Diffusion inversion phase separation (DIPS) is also feasible due to its high solubility also at room temperature in organic solvents like n-methylpyrrolidone (NMP), dimethylformamide (DMF), dimethylacetamide (DMAc). In Table 5 solution viscosity data of NMP solutions at 10% weight concentration measured at 23°C are reported.

Table 5. Solution Viscosity of PVDF

		Solef® PVDF homopolymer			Hylar® PVDF homopolymer	
		1015	6010	6020	301F	460
Viscosity	cps	1400	330	2700	540	1000

PVDF membranes show a very good control of pore dimension and distribution. It is quite easy to form MF membranes that show excellent UV resistance and have a continuous use temperature up to 150°C [3].

Copolymers of PVDF and HFP or CTFE are employed also in lithium batteries manufacturing: a fluoropolymer-based membrane is suitable as separator between electrodes of the battery. The use of PVDF is appropriate in this application thanks to its mechanical resistance and flexibility, to the easy processing and to the electrochemical stability. The ability of PVDF to swell into the electrolyte is an important characteristic: this property allows to avoid the presence in the battery of the pure liquid electrolyte, that is not safe during the operation of the battery. In fact the PVDF separator absorbs the electrolyte avoiding the presence of a liquid phase in the battery and increasing safety performances. All these properties lead to a high flexibility in the final design of the battery, useful for thinner portable power tools.

ECTFE is a new promising material for different applications like membrane distillation, contactors, carrier for liquid membranes and chemicals treatment because of its high basis and solvent resistance and hydrophobic behavior. The insolubility at room temperature does not allow the processing of this polymer starting from a solution, below 150°C, therefore the main process to make membranes is the standard TIPS [4]. A modified compression molding process can be employed in order to obtain a semi-permeable porous membrane via a plasticization step and subsequently extraction of the plasticizer with a specific solvent [6].

The material allows the possibility to consistently obtain a huge variety of symmetric and asymmetric structures for MF and UF processes [4].

All the properties so far described make fluoropolymers as optimal material for membranes manufacturing due to the easy processability and performance of the final product. Furthermore their properties are generally better in comparison with other materials employed in the membrane field. Only polysulfones can compete with their performances: they lead to membranes formation with a wide range of pore size. Final membranes show excellent mechanical and thermal properties and good chemical resistance; they can be handled in a full pH range.

PFSA ionomer membranes can be produced through a variety of processes conferring to the final membrane different characteristics. Typically, commercial dense membranes are produced by extrusion and casting methods. In the field of filtration, porous membranes can be obtained by the hydrophilization of microporous inert substrates with a thin layer of ionomer.

Dense membranes for fuel cells are typically produced by melt-extrusion or solvent-casting methods. Production by melt-extrusion requires film formation of the polymer in the thermoprocessable form (-SO_2F or "precursor" form) and subsequent chemical treatment (hydrolysis). Melt-extrusion is usually adequate for obtaining membranes of thicknesses above a minimum value (indicatively 20~25 μm) and preferred vs. other methods for thicker membranes (i.e. in the 100 μm range and above). Applications requiring thicker membranes are e.g. water electrolysis, O_2-fed fuel cells (where thicker membranes are used for safety reasons) and DMFC (in order to minimize methanol cross-over problems from the anode to the cathode of the cell). Solvent-cast membranes are obtained by dispersing the ionomer in the acid form in appropriate solvents, depositing a liquid film on an inert substrate, evaporating the solvent and annealing the obtained film. Proper modes of annealing can guarantee better dimensional stabilities of the final membrane [7]. The solvent-casting process is particularly suitable for fabricating very thin membranes. Furthermore, it is versatile for the introduction of fillers, due to the fact that the membrane undergoes no basic and acidic chemical steps for fabrication. Reinforced membranes can also be obtained by impregnating microporous substrates starting from ionomer dispersions until the porosity is substantially occluded. Most relevant reported substrates are bistretched PTFE [8,9] and high molecular weight polyethylene (HMWPE) webs [10]. Similar strategies of annealing as used in the fabrication of solvent-cast membranes [7] can bring to the production of high dimensional stability reinforced membranes [11]. Reinforced membranes are particularly desired in the fuel cell application when very thin membranes for high power density devices are required (e.g. automotive). Still, reinforcements are not the ultimate solution to membrane failure in durability evaluation and appropriate ionomer grades with ultra-high electrochemical stability need to be developed.

Using impregnation technologies, but applying conditions in which the porosity of the substrate is not fully occluded, perfluoropolymer porous membranes can be obtained [12]. Very recently, the use of amorphous PFSA ionomers to impregnate microporous substrates has led to ultra-high wettability membranes exhibiting high water flux properties [13]. These membranes can be fruitfully applied for the filtration of water-based solutions in a variety of applications, especially where aggressive reactants require a fluoropolymer substrate membrane. The technology described in [13] can allow the incorporation of different amounts of ionomer to obtain membranes of different porosities. Fig. 2b shows the surface structure of a Hyflon® Ion ultra-high wettability membrane obtained by this method starting from a bistretched PTFE substrate shown in Fig. 2a.

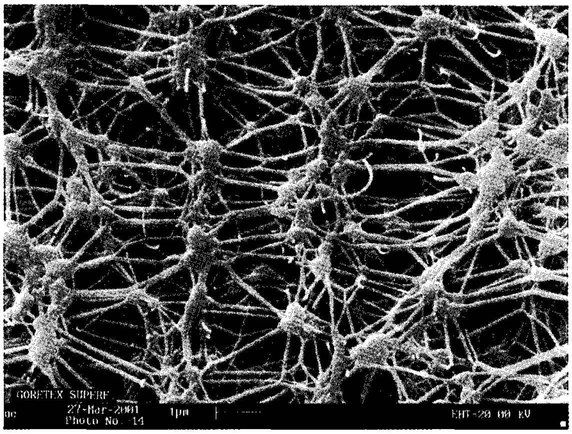

Fig. 2a. Electron microscope image of a bistretched PTFE substrate (Gore-Tex®).

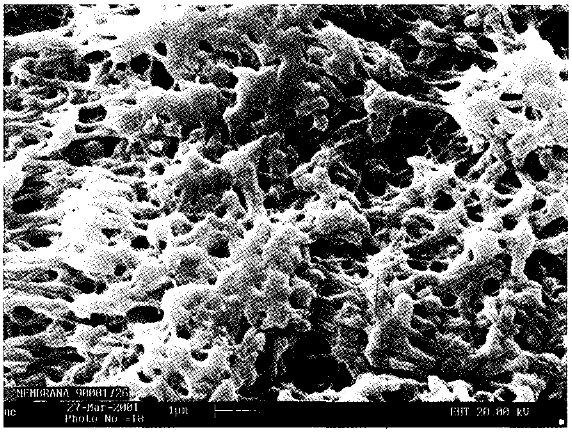

Fig. 2b. Electron microscope image of a Hyflon® Ion-based porous ultra-high wettability membrane incorporating the bistretched PTFE substrate of Fig. 2a.

4. Conclusions

Properties of fluoropolymers related to membrane applications have been shown in the present article. In particular PVDF and ECTFE show excellent performances which are very useful in water treatment operation, such as high resistance to chemicals and water solutions in a wide pH range. A PVDF membrane is employed also in lithium ion batteries as separator and PFSA ionomer membranes are the most attractive basis for current development in fuel cell technology. PFSA ionomer can also be interestingly employed to modify the surface of membranes to obtain highly hydrophilic filtration products.

Further developments are in progress in order to modify these polymers and improve their characteristics for specific purposes of membrane use.

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