Perfluoropolymer Membranes of Tetrafluoroethylene and 2,2,4Trifluoro-5Trifluorometoxy-1,3Dioxole.

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Abstract

Perfluoropolymers represent the ultimate resistance to hostile chemical environments and high service temperature, attributed to the presence of fluorine in the polymer backbone, i.e. to the high bond energy of C-F and C-C bonds of fluorocarbons.

Copolymers of Tetrafluoroethylene (TFE) and 2,2,4Trifluoro-5Trifluorometoxy-1,3Dioxole (TTD), commercially known as HYFLON® AD, are amorphous perfluoropolymers with glass transition temperatures (Tg) higher than room temperature, showing a thermal decomposition temperature exceeding 400°C.

These polymer systems are highly soluble in fluorinated solvents, with low solution viscosities. This property allows the preparation of self-supported and composite membranes with desired membrane thickness.

Symmetric and asymmetric perfluoropolymer membranes, made with HYFLON® AD, have been prepared and evaluated. Porous and not porous symmetric membranes have been obtained by solvent evaporation with various processing conditions. Asymmetric membranes have been prepared by the wet phase inversion method.

Measures of contact angle to distilled water have been carried out. Figure 1 compares experimental results with those of other commercial membranes. Contact angles of about 120° for our amorphous perfluoropolymer membranes demonstrate that they posses a high hydrophobic character.

Measures of contact angles to hexadecane have been also carried out to evaluate the organophobic character. Results are reported in Figure 2. The observed strong organophobicity leads to excellent fouling resistance and inertness.

Porous membranes with pore size between 30 and 80 nanometers have shown no permeation to water at pressures as high as 10 bars. However high permeation to gases, such as O_2, N_2 and CO_2, and no selectivity were observed. Considering the porous structure of the membrane, this behavior was expected.

In consideration of the above properties, possible useful uses in the field of gas-liquid separations are envisaged for these membranes.

A particularly promising application is in the field of membrane contactors, equipments in which membranes are used to improve mass transfer coefficients in respect to traditional extraction and absorption processes.

Gas permeation properties have been evaluated for asymmetric membranes and composite symmetric ones. Experimental permselectivity values, obtained at different pressure differences, to various single gases are reported in Tab. 1, 2 and 3.

Experimental data have been compared with literature data obtained with membranes made with different amorphous perfluoropolymer systems, such as copolymers of Perfluoro-2,2dimethyl dioxole (PDD) and Tetrafluoroethylene, commercialized by the Du Pont Company with the trade name of Teflon® AF. An interesting linear relationship between permeability and the glass transition temperature of the polymer constituting the membrane has been observed.

Results are discussed in terms of polymer chain structure, which affects the presence of voids at molecular scale and their size distribution. Molecular Dynamics studies are in progress in order to support the understanding of these results. A modified Theodoru-Suter method provided by the Amorphous Cell module of InsightII/Discover was used to determine the chain packing. A completely amorphous polymer box of about 3.5 nm was considered.

Last but not least the use of amorphous perfluoropolymer membranes appears to be ideal when separation processes have to be performed in hostile environments, i.e. high temperatures and aggressive non-aqueous media, such as chemicals and solvents. In these cases Hyflon® AD membranes can exploit the outstanding resistance of perfluoropolymers.

References

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Table 1: *Gas permeance of asymmetric membranes (polymer HYFLON AD 60X).*

HYFLON AD 60X	Mean Permeability, GPU		
Δp, bar	**N_2**	**CO_2**	**O_2**
1		15,3	6
5	1,7	14	5,3
7,5	1,7	14,7	5,3
10	1,8	15,3	

$$(1\ \text{GPU}) = 10^{-6} \cdot \frac{cm^3(STP)}{cm^2\ cmHg \cdot s}$$

Table 2: *Selectivities for membranes at different coagulation bath temperatures.*

T of coagulation bath (裂)	Selectivity	Δp, bar 5	Δp, bar 7,5	Δp, bar 10
12	O_2/N_2	3,1	3,1	
20	O_2/N_2	3,2	3,2	
12	CO_2/N_2	8,2	8,5	8,5
20	CO_2/N_2	7,9	7,9	7,9

Table 3: *Gas permeability of composite membranes (with kind permission of Raychem Corporation).*

Polymer type		P (Barrer)				
		O_2	N_2	CH_4	H_2	CO_2
HYFLON AD	60 X	51,4	16,5	8,01	202	124
HYFLON AD	80 X	190	76,8	48,9	563	473

Figure 1: Contact angles to distilled water.

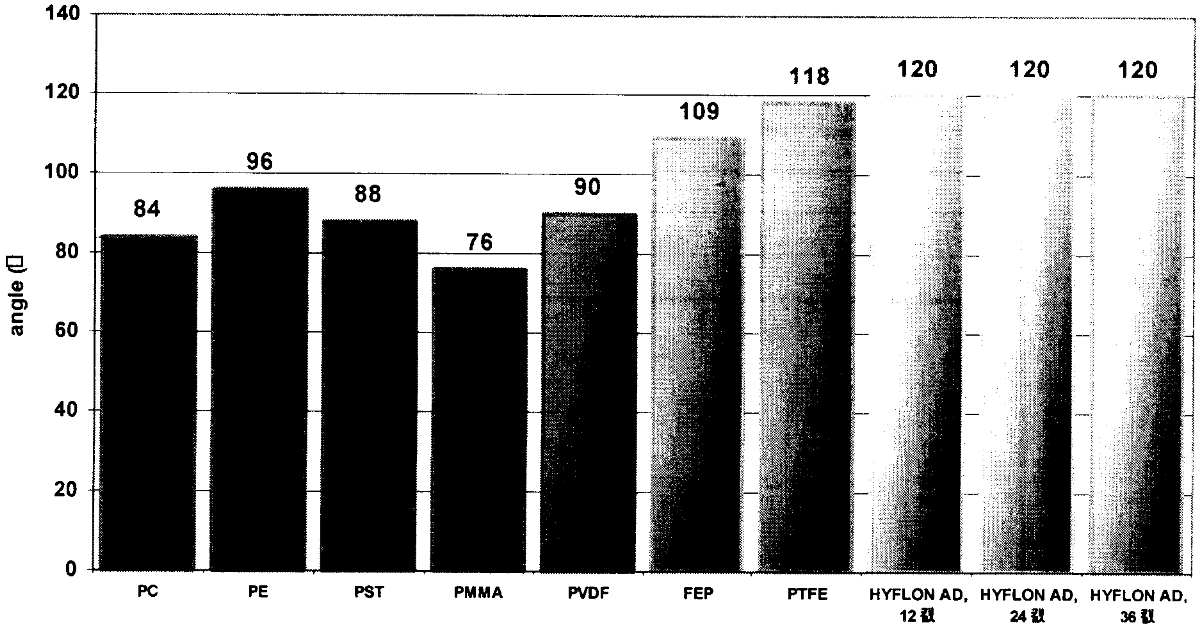

Figure 2: Contact angles to hexadecane.