

Direct fluorination of polymer vessels and membranes

Enhancement of barrier and gas separation properties

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Résumé **Augmentation par fluoration directe de l'étanchéité des récipients en polymères et de la sélectivité des membranes séparatrices de gaz**

La fluoration directe des polymères présente de nombreux avantages au niveau industriel. En effet, en raison de la forte exothermicité des principales étapes élémentaires, la fluorination se produit spontanément dès la température ambiante dans la plupart des cas. De plus, c'est une technologie sèche qui permet de traiter des objets en polymère de formes très variées. Ces caractéristiques de la fluoration directe font que cette méthode est largement utilisée dans l'industrie pour améliorer l'étanchéité des réservoirs à essence en polymère ainsi que celle des récipients de stockage de produits toxiques, et également pour renforcer les propriétés d'adhésion. Elles permettent aussi d'améliorer fortement la sélectivité des membranes polymères pour la séparation des gaz.

Mots-clés **Fluoration directe, polymères, étanchéité, technologie sèche, réservoirs à essence, membranes polymères.**

Abstract Direct fluorination of polymers has many advantages when applied to industry problems. Due to the high exothermicity of the main elementary stages, fluorination proceeds spontaneously at room temperature which is convenient for industrial applications purposes. Direct fluorination is a dry technology and polymer articles of any shape can be treated. These features of direct fluorination have initiated a wide industrial utilization for the enhancement of the barrier properties of automotive polymer fuel tanks and vessels for storage of toxic and volatile liquids and also for the enhancement of adhesion properties. Gas separation properties of polymer membranes can be also highly improved.

Keywords **Direct fluorination, polymers, barrier properties, dry technology, polymer fuel tanks, polymer membranes.**

Fluorinated polymers have a set of unique properties such as enhanced chemical stability, thermostability, good barrier properties, etc. [1-6]. However practical use of fluoropolymer articles is restricted due to their high cost and complexity of synthesis. Very often application properties of polymer goods are defined mainly by their surface properties. Hence it is not necessary to fabricate articles from fluoropolymers but it is simpler, cheaper and more convenient to apply a surface treatment of articles made from commonly used polymers. Direct fluorination of polymers is a heterogeneous reaction of gaseous F_2 and its mixtures with a polymer surface. Direct fluorination has many advantages when applied to industry problems. Due to the high exothermicity of the main elementary stages, fluorination proceeds spontaneously at room temperature which is very convenient for industrial applications purposes. It is a dry technology and polymer articles of any shape can be treated. There are safe and reliable methods to neutralize (by converting into the solid phase) unused F_2 and the end-product HF. Direct fluorination of polymers is a surface modification process: only ~ 0.01 - $1 \mu\text{m}$ thickness of the material is modified. Bulk properties of fluorine treated polymer articles remain unchanged.

These features of direct fluorination have initiated a wide industrial utilization for enhancement of the barrier properties of automotive polymer fuel tanks, vessels for storage of toxic and volatile liquids and also for enhancement of adhesion properties. Gas separation properties of polymer membranes can be also highly enhanced by direct fluorination.

Surface treatment of polymers

The following polymers were investigated: high density and low density polyethylene (HDPE, six varieties, and LDPE, two varieties), polyvinylfluoride (PVF), polyvinylidene fluoride (PVDF), polystyrene (PS), poly(ethylene terephthalate) (PET), polymethylmethacrylate (PMMA), poly(phenylene oxide) (PPO, two varieties), polyimide Matrimid® 5218 (PI), poly(4-methyl-pentene-1) (PMP), polypropylene (PP), sulfonated polyetheretherketone (SPEEK), block-copolymer of sulfone and butadiene (Seragel® S3760/3), polyvinyltrimethylsilane (PVTMS), polycarbonatesiloxane Carbosil® (PCS), polysulfone Udel 3500 (PSul), polyvinylalcohol (PVA), epoxy resin (ER).

The following standard methods were used: Fourier IR spectroscopy, spectroscopy in the visible and near UV

Why surface properties of polymers should be modified?

Advantages of polymers	Disadvantages of common polymers
Low cost (very often)	Poor adhesion and printability (often)
Processable:	Bad barrier properties (often)
Films, bottles, fuel tanks, membranes, pipes etc. can be fabricated	Low permeability/selectivity correlation for polymer membranes
	Often low antibacterial properties
	Large coefficient of friction
	Low chemical resistance
Two routes to enhance commercial properties which are defined by the surface layer properties:	
High cost	Low cost
Synthesis of new polymers (e.g. fluorinated polymers)	Surface modification

region of spectra, refractometry, electron microscopy, gas-chromatographic and volumetric measurement of transport properties of polymer membranes, measurement of the surface energy and permeation of petrol through polymer films. Two original interference methods were developed to study the kinetics of the growth of thickness of fluorinated layer *in situ* and density of fluorinated thin polymer layers (over 0.5-10 μm).

In all studied polymers, fluorination resulted in (a) disruption of C-H bonds followed by fluorine atoms addition and (b) saturation of double (conjugated) C=C bonds with fluorine. C-N and C-Si bonds are mainly disrupted and F atom is attached to C atom. When the thickness of fluorinated layer exceeds $\sim 1 \mu\text{m}$, the degree of fluorination is close to unity for the case of studied polymers, excluding HDPE, LDPE, PVF and PVDF. Oxygen admixture results in a formation of controlled amount of C=O-containing groups, e.g. -COF, which are transformed into -COOH under moisture action. Concentration of C=O-containing groups inside fluorinated layer (i.e. amount of C=O-containing groups per one monomeric unit) does not depend on the thickness of fluorinated layer and is increased with concentration of oxygen in fluorinating mixture. For some polymers (PS, PPO, LDPE), almost any monomeric unit may include (when polymers are treated with $\text{F}_2:\text{O}_2 \sim 1$ mixture) C=O-containing groups.

Visible region transmittance spectra of fluorine treated films exhibit interference features and consist of a set of equidistance (in wavenumber scale) maxima and minima, due to the following reason: fluorine treated polymers consist of substantially (in many cases- practically totally fluorinated) fluorinated layer and virgin (unmodified) layer, which are separated by a very narrow ($\ll 0.1 \mu\text{m}$ in thickness) transient reaction zone. The main chemical conversion processes proceed inside that reaction zone. The formation of fluorinated layer is limited by penetration of molecular fluorine through fluorinated layer to untreated one. For all the studied polymers, the following dependence of the thickness δ_F of fluorinated layer on treatment duration t was observed:

$$\delta_F = A \cdot t^{0.5} = B \cdot (p_F)^k \cdot t^{0.5} + \text{const} \quad (1)$$

where A depends on F_2 , O_2 , He, Ar, N_2 and HF partial pressures and temperature. "const" value can be neglected for all the polymers excluding HDPE, LDPE and PVF. B and

k values for different polymers are shown in table I. O_2 and HF inhibit the rate of formation of fluorinated layer, but N_2 , Ar and He presence in fluorinating mixture weakly influence kinetics of fluorination.

The rate of formation of fluorinated layer increases with temperature. Would the A value be represented as $A \sim A_0 \cdot \exp(-E_{act}/RT)$, the activation energy E_{act} be equal to 13.4 kJ/mole, 28.1 kJ/mole and 34.2 kJ/mole for LDPE (density 0.918 $\text{g}\cdot\text{cm}^{-3}$), HDPE (density 0.945 $\text{g}\cdot\text{cm}^{-3}$) and HDPE (density 0.949 $\text{g}\cdot\text{cm}^{-3}$) respectively. An average density of fluorinated PVTMS, PS, PET and PPO does not depend on the thickness δ_F of fluorinated layer over $\delta_F = 0.5\text{-}10 \mu\text{m}$ and markedly exceeds density of virgin polymers (table II). Density of fluorinated PI increases from 1.24 $\text{g}\cdot\text{cm}^{-3}$ (virgin polymer) to $\sim 1.9 \text{g}\cdot\text{cm}^{-3}$ when δ_F rises from 0 to 5-8 μm . Refraction indexes of fluorinated polymers (for the case when oxygen is not added to fluorinating mixture) are close to 1.37-1.41.

Long-lived peroxy RO_2^* and fluororadicals were observed in all the fluorinated polymers (up to $2.4 \cdot 10^{20}$ radicals per cm^3 of fluorinated layer); radicals are placed inside fluorinated layer only. The amount of those radicals was decreased by a factor of 2 in several hours (in 1 to 15 hours, depending on the polymer nature). Peroxy radicals are formed due to oxygen admixture in fluorine, absorbed oxygen and water in polymer bulk and on the reaction vessel walls.

Additional modification of a polymer surface can be arranged *via* grafting of monomers with double bonds to long-lived radicals. The maximum thickness of a grafted layer of acrylonitrile reached 7.5% and 80% with respect to the thickness of fluorinated layer of PI and PVTMS respectively.

It was shown that endothermic dissociation of molecular fluorine $\text{F}_2 \rightarrow \text{F}^* + \text{F}^*$ cannot be regarded as the main path of initiation of the chain fluorination process. Initiation proceeds *via* exothermic reactions of molecular fluorine with $-\text{CH}_2-$ monomeric units or with double (conjugated) bonds. Possible chain continuation and termination were proposed.

Change of chemical composition and density of the surface polymer layer under fluorination results in surface energy change. Total surface energy γ , its polar and dispersion components depend on treatment conditions. Direct fluorination of PP and PI results in increase of γ . For the case of PVTMS, input of polar component into the total energy depends on treatment conditions and can be varied over wide range.

Enhancement of barrier properties

At the present time, the most commercially significant application (on industrial scale) of direct fluorination of polymeric goods is the enhancement of their barrier properties of automotive HDPE (high density polyethylene) fuel tanks and pipes. The loss of petrol (due to a diffusion of liquids through tank walls) can be reduced upon direct fluorination by a factor of 50-100. At present time alcohol is added to petrol to enhance ignition, and permeability of petrol-alcohol mixtures through walls of fluorinated tank is increased as compared with permeability of undiluted petrol. Indispensable presence of oxygen in fluorinating mixture and in the reaction vessel results in formation of polar groups

Table I - k and B value (see formula 1), composition of fluorinating mixture and treatment temperatures T .

Polymer	Fluorinating mixture	T (K)	B ($\mu\text{m}\cdot\text{s}^{-0.5}$)	k
PS	F_2	293 ± 1	0.14	0.67
PCS	F_2	296 ± 2	0.09	0.81
PPO (molecular weight 224,000)	F_2	293 ± 1	0.14	0.76
PPO (molecular weight 34,000)	F_2	296 ± 2	0.073	0.53
PVTMS	F_2	294 ± 1	0.095	0.65
PVTMS	20% F_2 + 80%He	294 ± 2	0.079	0.60
PVTMS	5% F_2 + 95%He	294 ± 2	0.082	0.64
PVTMS	2% F_2 + 98%He	294 ± 2	0.054	0.50
PI	F_2	295 ± 2	0.073	0.41
PI	10% F_2 + 90% N_2	295 ± 2	0.19	
PET	F_2	295 ± 2	0.080	0.45
PVA	F_2	295 ± 2	0.025	0.48
ER	F_2	295 ± 2	0.070	0.52
S3760/3	F_2	295 ± 2	0.037	0.60
PMP (RT181)	F_2	295 ± 2	0.049	
PMP (RT181)	94% F_2 + 5%HF + 1% O_2	295 ± 2	0.025	
PP (20PCT)	F_2	295 ± 2	0.34	0.66
PP (40HST)	F_2	295 ± 2	0.22	0.65
LDPE (density 0.926 $\text{g}\cdot\text{cm}^{-3}$)	F_2	295 ± 2	0.017	0.56
LDPE (density 0.926 $\text{g}\cdot\text{cm}^{-3}$)	9.7% F_2 + 90.3%He	295 ± 2	0.018	0.57
LDPE (density 0.918 $\text{g}\cdot\text{cm}^{-3}$)	F_2	295 ± 2	0.020	0.52
PSul (Udel 3500)	F_2	295 ± 1	0.046	0.43
SPEEK	F_2	297 ± 1	0.057	0.70
70% SPEEK + 30% PSul	F_2	297 ± 1	0.069	0.73
PVDF	F_2 ; F_2 & UV-irradiation	295-430	0	-

such as -COF and -COOH and peroxy radicals on the polymer surface. Those radicals may take part in reactions resulting in scission of polymer chains and formation of polar groups. All the mentioned factors result in worsening of polymer barrier properties when petrol-alcohol mixtures are used. In industry, temperature of fuel tanks at the end of fluorination is around 55-65°C; time interval available for termination of radicals cannot exceed 15-20 minutes; treatment technology should be a "dry" one. We have proposed that treatment of freshly fluorinated HDPE with gases, reacting very quickly with radicals, may result in enhancement of barrier properties of fluorinated HDPE. The kinetics of self-terminations of long-lived radicals and kinetics of the reactions of long-lived radicals with several gases has been studied at room temperature and at 55-65°C. Kinetic curves for radical termination at 20-22°C are similar each to other: radical concentration is decreased by a factor of 2 in 4-10 hours after removing of fluorine from the reaction vessel. Termination kinetics of radicals for the case of fluorinated HDPE (Finanthen®, density 0.949 $\text{g}\cdot\text{cm}^{-3}$) and temperatures 22 and 64°C is shown in the figure 1.

Increase of temperature results in a significant increase of the termination rate. Additional treatment of fluorinated HDPE with triethylamine results in remarkable increase of termination rate both at 22°C and around 60°C. In the latter case, the amount of radicals is decreased by an order of magnitude in 15-20 minutes, but in the case of absence of triethylamine, only by a factor of ~ 2.

To study the influence of treatment of freshly fluorinated HDPE films (density 0.949 and 0.945 $\text{g}\cdot\text{cm}^{-3}$) with various gases on HDPE barrier properties, a set of comparative experiments has been carried out. To minimize amount of formed polar groups, fluorine was purified from oxygen admixture. HDPE films were treated with undiluted fluorine at 0.036 bar pressure and $21 \pm 1^\circ\text{C}$ during 125 minutes. Control fluorinated samples were not treated with gaseous radical quenchers, other films were treated just after fluorination. Mixtures of petrol grade "CEC-RF-02-99 Oxy 08-1.2" ("Haltermann", Germany) and 5% of methanol or 10% of ethanol were used. Petrol and alcohol were dried. Permeability of petrol-alcohol mixtures through HDPE films was studied at room temperature and at 40 ± 0.5 . Triethylamine was found to be the best radical quencher. Optimum treatment conditions (gas pressure, treatment duration and temperature) to provide best barrier properties of freshly fluorinated HDPE films were determined. Treatment at those conditions results in enhancement of the barrier properties (i.e. decrease of permeability) of HDPE (density 0.949 $\text{g}\cdot\text{cm}^{-3}$) by a factor of 3.3 with respect to mixtures of 5% of methanol and 95% of petrol as compared to the case, when the film were fluorinated only but not treated additionally with triethylamine. When

mixtures of 10% of ethanol and 90% of petrol were used, above mentioned treatment resulted in a decrease of the HDPE permeability to the same value as for the case of 5% methanol + 95% petrol mixture. Treatment of HDPE (Lupolen®, density 0.945 $\text{g}\cdot\text{cm}^{-3}$) with triethylamine provided the same effect as for the case of HDPE (Finanthen®, density 0.949 $\text{g}\cdot\text{cm}^{-3}$). The developed method can be successfully used to decrease permeabilities of petrol-alcohol mixtures through fluorinated HDPE. The described above method was patented [7].

Table II - Density of virgin ρ_V and fluorinated ρ_F polymers.

Polymer	ρ_V ($\text{g}\cdot\text{cm}^{-3}$)	ρ_F ($\text{g}\cdot\text{cm}^{-3}$)
PET	1.46	1.75
PS	1.05	2.05
PVTMS	0.85	1.73
PPO	1.07	1.72

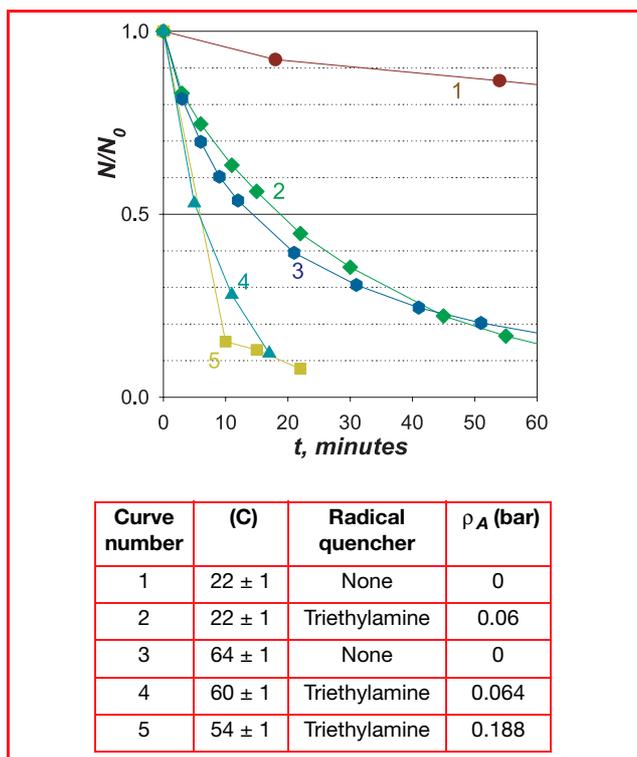


Figure 1 - Dependence of the relative amount of peroxy radicals N/N_0 in fluorinated HDPE (density 0.949 g.cm^{-3}) on storage duration t . Treatment temperature T , radical quencher and its pressure P_A are indicated in the table.

Enhancement of gas separation

Polymeric membranes can be used for the separation of a set of gas mixtures, such as He-CH₄, H₂-CH₄, H₂-CO₂, CO₂-CH₄, CO₂-N₂, CH₄-N₂, H₂-N₂, O₂-N₂, CO₂-H₂S, CH₄-CO₂-H₂-He etc. There is a common problem in gas separation when polymeric membranes are used: membranes with high gas permeability often have a low gas separation factor and on the contrary, membranes with high separation factor have low permeability value (figure 2). The best membrane materials should lie at the upper right corner of the figure 2, but at present time, no materials, placed above the straight line in the figure 2, were synthesized. So the following solution should be provided: fluorinate commercially available membrane which possesses high permeability but low selectivity. Direct fluorination results in a significant decrease of permeability of large size gases (CH₄, C₂H₆, CO₂ etc.) as compared with those of small size (H₂, He etc.). The selectivity of the membrane for (large size-small size) pairs of gases will be enhanced without significant reduction of the permeability value with respect to small size molecules. The selectivity values for He/CH₄ mixture separation are shown in the figure 2 for virgin and fluorinated membranes and modules. It is evident that selectivity values for fluorinated membranes are placed above the straight line. Moreover, decrease of He permeability after fluorination is relatively small.

As it was mentioned above, direct fluorination results in a more significant decrease of permeability of large size gases (CH₄, C₂H₆, CO₂ etc.) as compared with those of small size (H₂, He etc.). Hence fluorination of hollow fiber polyimide membrane modules resulted in a significant – by a factor of 47 and 7 respectively – increase of selectivity of separation

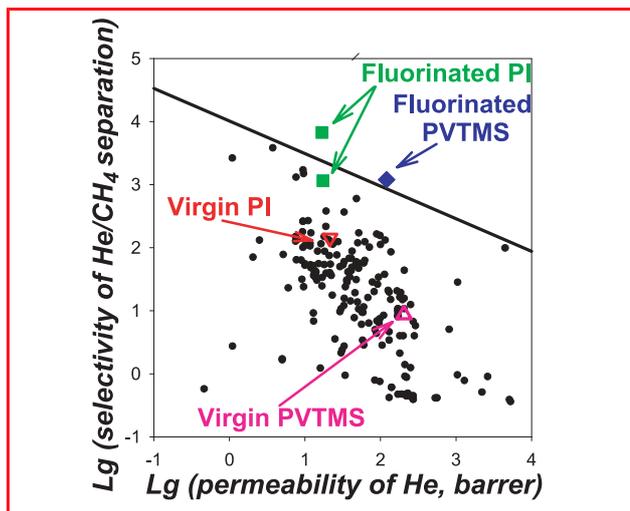


Figure 2 - Dependence of selectivity of He/CH₄ mixture on He permeability (logarithm scale).

Black points-literature data on polymeric membrane materials: ∇ - virgin polyimide hollow fiber modules; \blacksquare - fluorinated polyimide hollow fiber modules; \triangle - virgin PVTMS membrane; \blacklozenge - PVTMS membrane treated with 40%O₂ + 60%F₂ mixture.

for He/CH₄ and CO₂/CH₄ mixtures. The permeability of He was not practically changed in that case. Selectivity of separation of He/CH₄ mixture depended on the treatment conditions and was increased by a factor of 100 when F₂-O₂ mixture was used for the treatment. Hence the direct fluorination of PVTMS membranes and polyimide Matrimid 5218 hollow fiber modules provides the possibility to “over jump” the so-called “Robeson boundary” (straight line in the figure 2), which limits the correlation “permeability-selectivity” for all the previously synthesized membrane materials. It can be concluded that the direct fluorination of flat membranes and hollow fiber modules can be successfully used to enhance their gas separation properties.

The results of the described research can be used in industry to decrease the loss of alcohol-containing petrol due to its diffusion through walls of automotive polymer fuel tanks. In food and medical industry, fluorination of polymer film packaging results in a substantial decrease of the oxygen permeability and hence leads to the decrease of the rate of food and medicine degradation. In chemical and petrochemical industry, fluorinated polymer membranes can be successfully used to enhance the purification of natural gas from CO₂ and hydrogen from CO, or to enhance the separation of biogas components, of hydrogen and helium from the natural gas, of hydrogen from the exhaust gases of petroleum-chemistry industry, in ethylene synthesis and from the exhaust gases of petroleum-chemistry industry, etc. In metallurgy industry, fluorine treated polymer membranes can be used as a cheaper alternative for the neon separation from the exhaust gases.

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Surface treatment of elastomers

Interesting results have been also obtained in the case of surface treatment of elastomers, namely nitrile gloves, made

Commercial applications of the direct fluorination of polymers

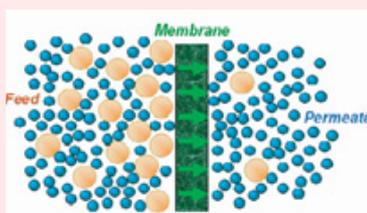
Enhancement of the barrier properties (permeability decrease)

- Automotive polymer fuel tanks
- Polymer containers and bottles for storage of volatile and toxic liquids
- Decrease of oxygen permeability of polymer films used for storage of food and medicine



Enhancement of separation selectivity

- Polymer membranes and hollow fiber modules



Enhancement of adhesion and printability

- Polymer fibers and films
- Automotive articles (bumpers, panels etc.)



Decrease of friction coefficient

Enhancement of bioresistance

Increase of the chemical resistance of a polymer surface

of carboxylated nitrile butadiene rubber latex, using either direct fluorination (10% F₂-gas diluted in N₂) or plasma-enhanced fluorination in radio-frequency cold plasmas using fluorinated gases (CF₄, CHF₃). Mechanisms of fluorination of these co-elastomers can be proposed on the basis of the assignment of the different components of the XPS spectra. Several mechanisms are observed depending on the fluorination conditions: although the modification of nitrile gloves is already effective for fluorination reactions at room temperature, an important activation is observed for experiments carried out at 90°C. When the treatments are carried out at room temperature, a gradual fluorination

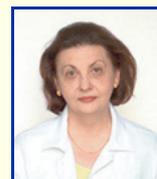
occurs: in the case of 10% diluted F₂ gas, monofluorinated C-F groups are the species most found at the surface and perfluoro groups CF_n are present in lower amount. An addition reaction takes place at the -(CH=CH)- double bonds of the polybutadiene entities, leading to -(CHF-CHF)- units. Whatever the fluorination method, thermal activation yields a more massive fluorination of the surface that finally leads to perfluorinated -(CF₂)- groups and terminal -CF₃ groups [8].

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