

Review

Direct fluorination—Useful tool to enhance commercial properties of polymer articles

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Abstract

Fundamental features and industrial applications of the direct fluorination of polymers are reviewed. Fundamental features of the direct fluorination of a set of polymers, such as polystyrene, polyethyleneterephthalate, poly(2,6-dimethyl-1,4-phenylene oxide), PMMA, LDPE (two types), HDPE (six types), polyvinyltrimethylsilane, poly(4-methyl-pentene-1), polyimide Matrimid 5216[®], polysulfones, polyetheretherketone, polycarbonatesiloxane, polysulphone–polybutadiene block-copolymers, polypropylene, PVF, PVDF, etc. are described. Influence of composition of the fluorinating mixture (F₂–He–N₂–O₂–HF), fluorine partial pressure, temperature and fluorination duration, on the rate of formation of the fluorinated layer and the chemical composition, density, refraction index, surface energy, gas separation properties and friction coefficient of fluorinated layer have been investigated. Processes of formation and termination of long-living and short-living radicals and grafting of acrylonitrile to fluorinated polymers have been studied. Industrial applications of the direct fluorination to enhance the commercial properties of polymeric goods, such as separation factor of polymeric membranes for gas separation, barrier properties of polymer vessels, pipes and packagings, adhesion, printability, wetting and transparency in visible and IR are reviewed.

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Keywords: Direct fluorination of polymers; Surface modification of polymers; Fluorine; Membrane separation; Adhesion

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1. Introduction

Fluorinated polymers have a set of unique properties, such as enhanced chemical stability, thermostability, good barrier properties, etc. However, practical use of fluoropolymer articles is restricted due to their high cost and

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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 simpler, cheaper and more convenient to apply a surface treatment of articles made from commonly used polymers. Direct fluorination (i.e., treatment with elemental gaseous fluorine) can be used to modify surface properties of polymers [1–9]. Usually, diluted mixtures of fluorine and nitrogen, argon, or helium are used to prevent the polymer surface from damage. Thickness of fluorinated layer can be varied over ~ 0.1 – $10 \mu\text{m}$ range. Bulk properties of fluorine-treated polymer articles remain unchanged.

There are different methods of polymer surface modification by application of fluorine and fluorocompounds. Plasma-chemical treatment has many disadvantages: complexity of the technology equipment (high vacuum and necessity of continuous initiation of a process), possible surface etching, combined action of atoms, ions, electrons and vacuum UV radiation. Application of XeF_2 as fluorine source is restricted due to its high cost.

Using elemental fluorine or its gaseous mixtures to modify polymer articles surface has many advantages. Due to the high exothermicity of the main elementary stages, fluorination proceeds at room temperature and even at liquid nitrogen temperature (77 K) and does not need initiation, heating or catalysts. Low vacuum chamber or flow reactors may be used. A controlled amount of functional groups, such as COOH , can be tailored to the polymer surface when F_2/O_2 mixtures are used for modification. Direct fluorination of polymers is a surface modification process. The thickness of a fluorinated layer can be kept well under control over 0.1 – $10 \mu\text{m}$ range. For the case of fluorination of automotive fuel tanks fabricated from polyethylene, less than 0.1% of the total fuel tank mass should be fluorinated to acquire the necessary barrier properties and the surface concentration of the bonded fluorine usually does not exceed $\sim 1 \text{ g m}^{-2}$ of the polymer article surface. Direct fluorination is a dry technology because starting reagents and point-end products are gases and solids only. Polymer articles of any shape can be treated. The process has low waste, because only the very thin upper surface layer (several micrometers in thickness, see above) is modified and there are safe, reliable and well-developed methods to neutralize (by converting into the solid phase) unused F_2 and the end-product HF .

These features of direct fluorination initiated its wide utilization to enhance various application properties of polymer articles: barrier properties, gas separation properties of polymer membranes, adhesion, printability, chemical resistance, etc. [1–9]. It is worth mentioning that treatment with elemental fluorine can be effectively used to fluorinate liquids [10]. But in this paper, only fluorination of solid materials will be considered. There exist well-developed and used modifications of a fluorination process: in static conditions and in flow reactors (for previously

fabricated polymer articles), or in the course of their fabrication at enhanced temperature (e.g. during blow molding) [2,4–7].

There are different ways to apply the direct fluorination to modify polymeric materials.

- (1) An ordinary direct fluorination, i.e., treatment of polymeric materials with fluorine or fluorine-inert gas (nitrogen, helium, etc.) mixtures. In this case, hydrogen atoms are substituted for fluorine, double and conjugated bonds are saturated with fluorine. Formation of cross-linking (formation of C–C or C–O–C bonds) and destruction of C–Si bonds depends on the polymer nature and treatment conditions. The degree of the chemical transformations in a very thin (0.001 – $0.1 \mu\text{m}$) upper layer depends on the fluorine partial pressure and treatment duration.
- (2) Oxyfluorination, i.e., treatment of polymeric materials with fluorine–oxygen mixtures. In that case, additional $>\text{C}=\text{O}$, $-\text{C}(\text{O})\text{F}$ and $-\text{C}(\text{O})\text{OH}$ groups can be inserted into the polymer structure.
- (3) Oxyfluorination accompanied with the graft polymerization. It is well known that in polymers treated with fluorine–oxygen mixtures, a controlled amount of long-living peroxy radicals is generated [11–15]. Additional modification of a polymer may be carried out by a graft polymerization of several monomers having double bonds, e.g. tetrafluoroethylene, acrylonitrile, acrylic acid and methyl methacrylate. This method of modification of polymeric goods is of the greatest interest and as to our mind, is the most prospective one because the surface properties of the modified polymer will be determined by the grafted polymer and there are much more possibilities to vary the surface properties, e.g. from hydrophobic to hydrophilic ones.

Controlled quantity of long-lived radicals (termination time around several hours) is generated inside the fluorinated layer in the course of direct fluorination of polymers. Hence, it is possible to provide graft polymerization of monomers containing double bonds from the gaseous phase. In this case, surface properties will be defined by properties of a grafted monomer. That additional modification can provide new properties of polymer surface, such as hydrophobicity or hydrophilicity, enhanced gas separation properties, enhanced adhesion and printability; moreover, bulk properties of polymer articles are not changed [2,12,16].

2. Commercial applications of the direct fluorination of polymers

Application of direct fluorination may result in a substantial financial profit in chemical, petrochemical, automotive, metallurgical, food industries, etc. [2,4–8]. There are several industrial fields of application of direct

fluorination to enhance commercial properties of polymeric articles.

At the present time, the most commercially significant application 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 [2,4–6,8,9]. Large volume (500–2000 l) HDPE tanks used to store heating fuel are fluorinated in the USA [5]. The direct fluorination of polymer containers for packaging of industrial and consumer chemicals decreases the loss of liquids that are stored [6,8]. Hence, the negative effect of petrol and toxic liquids on the environment can be substantially reduced. Direct fluorination is used also to enhance barrier properties of polymeric goods fabricated from LDPE, PVC, PP, PET, other natural and synthetic fibers, etc. [2]. At the present time, fluorination of automotive fuel tanks and containers for storage of liquids is provided on an industrial scale by a set of companies, such as “Air Products” (USA and Europe), “Fluoro-Seal Ltd.” (USA), “Fluoro Pack (Pty) Ltd.” (South Africa), “Jiangsu Rotam Boxmore Ltd.” (China), etc. Direct fluorination can be used to modify polymer films used for food storage and preservation. The permeability of oxygen can be highly decreased under treatment of polymers with fluorine and fluorine–oxygen mixtures, so the rate of food degradation can be substantially reduced [2,8,17]. As direct fluorination varies the selectivity of the separation of gas mixtures, fluorination can be used to modify the polymer packagings for food storage, such as modified atmosphere packaging (air in a pack is replaced by a mixture of different gases which composition is not controlled during storage), controlled-atmosphere packaging (composition of the gas mixture is continuously controlled during storage) and equilibrium-modified atmosphere (either the pack is flushed with the required gas mixture or the produce is sealed within the pack without no modification to the atmosphere).

Polymeric membranes can be used for the separation 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 (i.e., productivity) often have a low gas separation factor and on the contrary membranes with high separation factor have low permeability factor (productivity) value. 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.). So the following solution should be provided to fluorinate commercially available membrane, which possesses high permeability but low selectivity. The selectivity of the membrane for (large–small size) pairs of gases will be enhanced without significant reduction of the permeability value with respect to small size molecules. The enhancement of gas separation properties of polymeric

membranes and modules treated with a fluorine mixture has been studied for the case of polyvinyltrimethylsilane, poly(1-trimethylsilylpropyne), poly(phenylene oxide), polysulfone, polycarbonatesiloxane, poly((4-methylpentene-1), polysulfone–polybutadiene block-copolymer and polyimide [18–32]. Separation factor of polyimide Matrimid[®] 5218 membrane module for He/CH₄ mixture can be increased by a factor of 20–100 (this value depends on the quality of the virgin fibers), whereas decrease of He permeability did not exceed 20% with respect to the virgin module. It should be underlined that the fluorination procedure has been applied to the membrane module made of three–five hollow fibers; hence, it can be regarded as a prototype of a semi-industrial product. For the case of treatment of flat PVTMS membranes with F₂–He mixture, the separation factor for He/CH₄ and CO₂/CH₄ pairs (biogas components) can be increased by a factor of 10 and 5, respectively, as compared with a virgin membrane. Subsequent grafting of acrylonitrile to a fluorinated PVTMS membrane resulted in an increase of the selectivity separation factor for a He/CH₄ mixture by a factor of ~35 as compared with a virgin membrane. Treatment with a F₂–O₂ mixture resulted in an increase of separation factor for He/CH₄ mixture by a factor of 100 as compared with a starting membrane. In petrochemical, chemical and energy industries, polymeric membranes treated with fluorine can be successfully used to enhance the purification of natural gas from CO₂, purification of hydrogen from CO, separation of biogas components, separation of hydrogen and helium from the natural gas, separation of hydrogen from the exhaust gases of petrochemical industry and in ethylene synthesis, etc. In metallurgy industry, fluorine-treated polymer membranes can be used as a cheaper alternative for the neon separation from the exhaust gases.

Treatment of the polymer articles used in the automotive industry (bumpers, panels, etc.) results in a great increase of the surface energy, and hence, in a substantial enhancement of adhesion properties and printability (usually primer is not necessary to apply prior to painting) ([2] and references therein, [6–8,33]). It has been shown that the direct fluorination can be successfully applied to enhance adhesion properties and printability of HDPE, LDPE, polypropylene (PP), rubber, ethylene-vinyl acetate copolymers, polyamides, polyethers, butadiene–styrene copolymers, etc. ([2] and references therein, [6–8,33]). Addition of oxyfluorinated (treated with F₂/O₂ mixtures) PP fibres to cementitious mixtures enhances properties, such as wet and dry crack control, impact resistance, water absorption, etc. [6,8]. Direct fluorination is used on the industrial scale to enhance adhesion properties of polymer articles by “Alkor GmbH Kunststoffe” (Germany) [7] and “Fluoro Pack (Pty) Ltd. Benoryn” (South Africa).

Direct fluorination can be also used to decrease the friction coefficient of polymer articles fabricated from PP and elastomers ([2] and references therein, [20]). The surface fluorinated layer becomes more stable to action of

aggressive gases and liquids and may provide protective coating. The bioresistance of polymers (PMMA, PELD, rubber) is highly enhanced under fluorination [34]. An antireflecting layer can be formed on the surface of fluorinated polymers [2]. Fluorination reduces fabric shrinkage during washing [35].

3. Fundamental features of the direct fluorination of polymers

In this paper, the main attention will be paid to the results obtained by Kharitonov et al. who have studied the direct fluorination of a set of polymers, such as polystyrene (PS) (fabricated by thermal polymerization, m.w. 10^6 , Kuskovo plant, Russia), polyethyleneterephthalate (PET) (LAVSAN[®], Russia), poly(2,6-dimethyl-1,4-phenylene oxide) (PPO) (m.w. 34,000 and 234,000, Aldrich), polyvinyltrimethylsilane (PVTMS) (m.w. 10^6 , Russia), PMMA (produced by gamma-initiated polymerization, Russia), poly(4-methyl-pentene-1), polyimide (PI) Matrimid 5218[®] (CIBA-GEYGI), low-density polyethylene (LDPE) (density 0.918 and 0.926 g cm⁻³, Aldrich), high-density polyethylene (HDPE) (industrially available with density 0.945, 0.947, 0.948, 0.946 and 0.949 g cm⁻³; first three without carbon black and latter two containing carbon black; and one from Aldrich with density 9.50 g cm⁻³), polysulfone UDel 3500, polyetheretherketone (PEEK), polycarbonatesiloxane (Carbosisil[®], Russia), polysulphone–polybutadiene block-copolymers of different composition (Seragel[®]) (Russia), PVF (Fluorochem Limited, Derbyshire, UK) and PVDF (Scientific Polymer Products Inc., Ontario, Canada) [12–15,17,19,20,23,32,36–48].

The amount of oxygen in fluorine did not exceed ~0.08%. Influence of composition of fluorinating mixture (F₂–He–N₂–O₂–HF), fluorine partial pressure, temperature and fluorination duration on the rate of formation of fluorinated layer, chemical composition, density, refraction index, surface energy, gas separation properties and friction coefficient of fluorinated layer has been investigated. Also, the processes of formation and termination of long-lived and short-lived radicals and grafting of monomers to those radicals have been studied.

There are both general and individual features of the direct fluorination of polymers. In this review, the following topics will be briefly discussed: influence of treatment conditions on chemical composition, refractive indexes and density of fluorinated layer; rate of formation of fluorinated layer, gas permeability and coefficient of friction of fluorinated layer.

Visible region transmittance spectra of fluorine-treated films exhibit interference features and consist of a set of equidistance (in wavenumber scale) maxima and minima (Fig. 1) due to the following reason: fluorine-treated polymers represent three-layer structure and consist of substantially (in many cases, practically totally fluorinated) fluorinated layer (PE and PVF are exceptions) and virgin

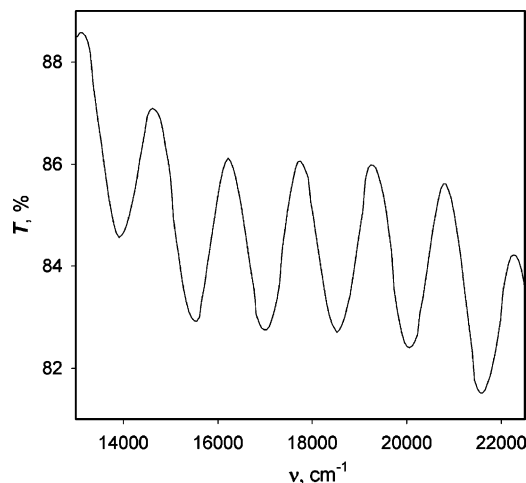


Fig. 1. Transmittance T (%) of the fluorine-treated PI film (cast and fluorinated on a sapphire substrate) vs. wavenumber ν (cm⁻¹). Thickness δ_F of fluorinated layer $\delta_F = 2.33$ μm . Film was not fluorinated through all its thickness. Reprinted from Ref. [36] with permission (Journal of Applied Polymer Sciences © 2004, Wiley & Sons, Inc.).

(unmodified) layer, which are separated by a very narrow transient reaction zone. The main chemical conversion processes proceed inside that reaction zone. But the main chemical composition changes may be followed by several post-reactions inside the fluorinated layer. Electron microscope evidence of the narrow boundary between fluorinated and untreated layers of PVTMS is shown in Fig. 2. The fluorine-treated PVTMS film was inserted into epoxy resin and after solidifying was cut in the direction perpendicular to the film surface. Then the carbon–platinum replica of the cut was obtained. It is evident from Fig. 2 that fluorinated (~0.4 μm in thickness) and untreated polymer layers are separated by a narrow boundary, and the thickness of the boundary layer is much smaller than the thickness of the fluorinated layer. This is valid when the thickness δ_F of fluorinated layer exceeds 0.1–0.2 μm . For thinner layers, such a situation was not observed. A laser interference

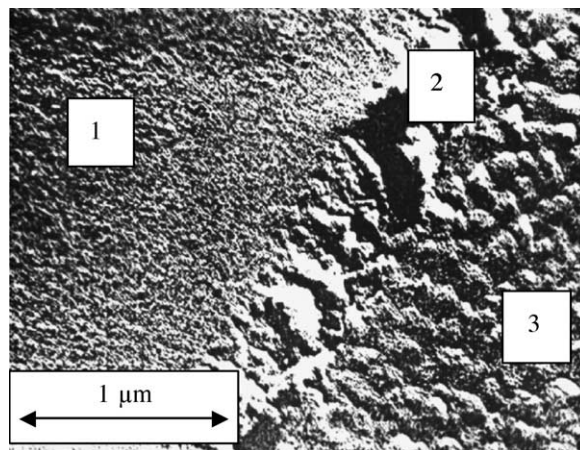


Fig. 2. Cut of fluorine-treated PVTMS film. (1) Epoxy resin layer, (2) fluorinated PVTMS, and (3) unmodified layer.

method [13,43,45–47] allowed the estimation of the dependence of the upper limit of the thickness, δ_b , of transition layer between fluorinated and untreated polymer layers: $\delta_b < 0.01 \delta_F$ (fluorinated PET), $\delta_b < 0.03 \delta_F$ (fluorinated PI) and $\delta_b < 0.004 \delta_F$ (fluorinated PS).

For all the polymers studied, direct fluorination may be regarded as a diffusion-controlled process. It means that when $\delta_F \geq 0.1\text{--}0.2 \mu\text{m}$, fluorine-treated polymers consist of practically totally fluorinated layer (PE and PVF are exclusion of a rule) and virgin (unmodified) layer, which are separated by a very narrow transient reaction zone (main chemical conversion processes proceed inside that reaction zone). The rate of formation of the fluorinated layer is limited by a diffusion of molecular fluorine through fluorinated polymer layer to the untreated one. Rate of formation of fluorinated layer depends on polymer nature, fluorine partial pressure, p_F , fluorinating mixture composition and temperature. For the majority of glassy polymers thickness δ_F of fluorinated layer depends on square root of treatment time for the case when $p_F = \text{constant}$. For some polymers (PE, PET and PMMA), slight deviations from square root dependence were observed during the initial reaction stage.

Generally, at a constant temperature

$$\delta_F(\mu\text{m}) = At^{0.5} = Bp_F^k t^{0.5} \quad (1)$$

where p_F (bar) is the fluorine partial pressure, t (s) the fluorination duration, A -value depends on fluorine partial pressure. B -values vary over a wide range (see Table 1).

To avoid chain scission and cracks, usually fluorine diluted with nitrogen (sometimes with He or Ne) is used.

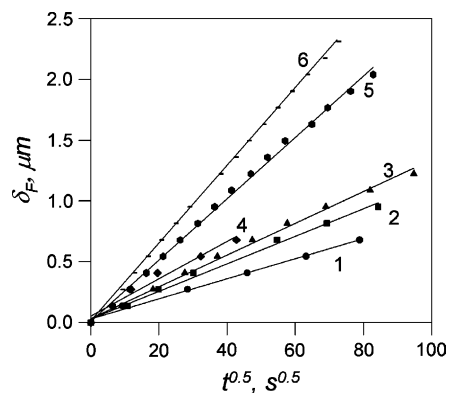


Fig. 3. Dependence of δ_F on the square root of fluorination duration t for the PVTMS film cast onto sapphire support. Treatment with undiluted fluorine at temperature $294 \pm 1 \text{ K}$. Fluorine pressure was equal to 0.02, 0.04, 0.06, 0.08, 0.12 and 0.2 bar for curves (1–6), respectively. Reprinted from Ref. [42] with permission (Journal of Fluorine Chemistry © 1999, Elsevier).

Fluorine concentration is ca. 1–10 vol.%. For the case of the abovementioned polymers, the rate of fluorination is varied over a wide range (Table 1). Treatment duration necessary to form thickness of fluorinated layer $\delta_F = 1 \mu\text{m}$ depends on a polymer nature and varies from $\sim 1 \text{ min}$ to $\sim 1 \text{ h}$ for industrially available treatment conditions. The rate of fluorination is increased with temperature [1,37,38]. Increase of treatment temperature to $60\text{--}100 \text{ }^\circ\text{C}$ can substantially (to some 10 s) decrease the treatment duration (Figs. 3 and 4).

Usually, the fluorination rate depends mainly on the fluorine partial pressure and even 10-fold dilution of fluorine with He or N_2 does not influence the rate of fluorination.

Table 1
 B - and k -values (see formula 1) for various polymers and treatment conditions

Polymer	Fluorinating mixture	Treatment temperature (K)	B ($\mu\text{m s}^{-0.5}$)	k
PS	F_2	293 ± 1	0.140	0.67
PCS	F_2	296 ± 2	0.090	0.81
PPO (m.w. 224,000)	F_2	293 ± 1	0.136	0.76
PPO (m.w. 34,000)	F_2	296 ± 2	0.0727	0.53
PVTMS	F_2	294 ± 1	0.0948	0.65
PVTMS	20% F_2 + 80%He	294 ± 2	0.0787	0.60
PVTMS	5% F_2 + 95%He	294 ± 2	0.0820	0.64
PVTMS	2% F_2 + 98%He	294 ± 2	0.0542	0.50
PI	F_2	295 ± 2	0.0733	0.41
PI	10% F_2 + 90% N_2	295 ± 2	0.0217	0.74
PET	F_2	295 ± 2	0.0796	0.454
PVA	F_2	295 ± 2	0.0247	0.484
Epoxy resin	F_2	295 ± 2	0.0695	0.524
Seragel [®] S3760/3	F_2	295 ± 2	0.0372	0.60
PMP (RT181)	F_2	295 ± 2	0.049	–
PP (20PCT)	F_2	295 ± 2	0.335	0.66
PP (40HST)	F_2	295 ± 2	0.219	0.65
LDPE (density 0.926 g cm^{-3})	F_2	293 ± 2	0.0172	0.56
LDPE (density 0.926 g cm^{-3})	9.7% F_2 + 90.3%He	295 ± 2	0.0175	0.57
LDPE (density 0.918 g cm^{-3})	F_2	293 ± 2	0.0200	0.52
Polysulfone (Udel 3500)	F_2	295.2 ± 0.2	0.0461	0.43
Sulfonated polyetheretherketone	F_2	297 ± 1	0.0568	0.70
PVDF	F_2 , F_2 -He	Over 295–430 K range	No reaction	–
PVDF	F_2 -He and UV radiation	295	No reaction	–

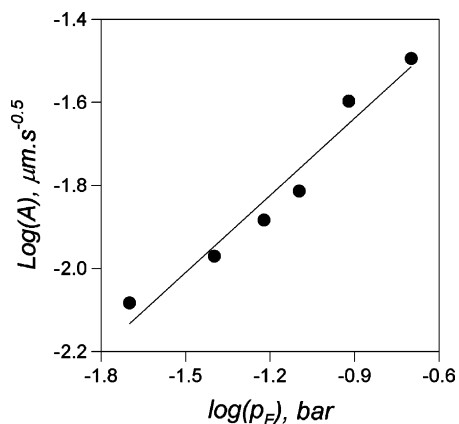


Fig. 4. Dependence of the A-value on fluorine partial pressure p_F for the curves from Fig. 3.

Substantial influence of dilution with He was observed for the case of PI when fluorine concentration was reduced to 5–2 vol.% [36].

Oxygen inhibits the fluorination rate. The inhibition effect depends strongly on the polymer nature and slightly on partial fluorine pressure (Figs. 5 and 6). As has been shown above, the rate of formation of fluorinated layer is limited by a diffusion of fluorine through fluorinated layer to untreated. Treatment of polymers with F_2 – O_2 mixtures results in a formation of C=O-containing groups [1,17,20,37,43]. But insertion of C=O groups into a polymer structure results in a strong decrease of a gas permeability. So, the reason of the inhibiting action of oxygen may be the formation of C=O-containing groups.

HF inhibits the direct fluorination of polymers. Introducing 3 vol.% of HF into the fluorinating mixture resulted in a decrease of the A coefficient (equation 1) by a factor of 1.4 for the case of PET treatment. Similar effect was monitored for the case of PS and “Seragel[®]” (copolymer of polysulfone and polycarbonatesiloxane) (Fig. 7). So, in

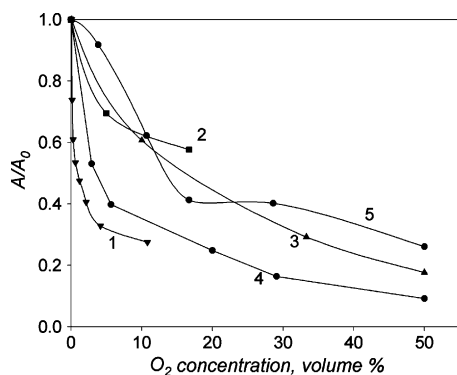


Fig. 5. Dependence of the A/A_0 -value (A_0 represents A-value for undiluted fluorine, see formula 1) on the oxygen concentration in F_2/O_2 mixture. The fluorine partial pressure was maintained constant for any polymer and was equal to 0.35 bar (1, PMMA), 0.1 bar (2, PCS), 0.2 bar (3, PPO, m.w. 244,000), 0.28 bar (4, PET) and 0.1 bar (5, PI). Treatment was carried out at room temperature.

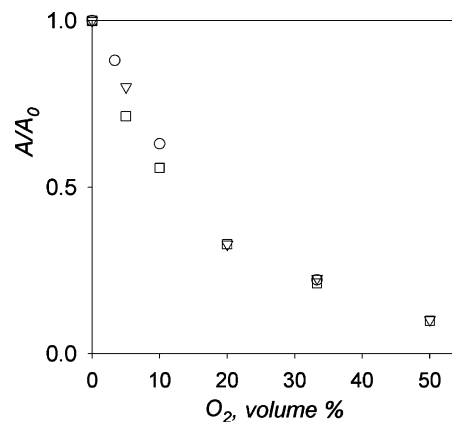


Fig. 6. Dependence of the A/A_0 -value (A_0 represents A-value for undiluted fluorine, see formula 1) on the oxygen concentration in F_2/O_2 mixture for the case of PS films. Circles, triangles and squares correspond to fluorine partial pressure p_F equal to 0.08, 0.2 and 0.48 bar, respectively. Treatment was carried out at 293 ± 2 K.

majority of experiments a pressed pellet of NaF was inserted inside the reaction volume to remove emitted HF ($NaF + HF = NaHF_2$).

The refraction indexes of polymers are substantially decreased under fluorination (see Table 2).

Fluorination influences the surface energy to a great extent. Prevailing tendency of total surface energy γ is its increase with fluorinated layer thickness δ_F (Fig. 8). γ – δ_F behaviour depends not only on δ_F value, but on the fluorine pressure also (see curves 2–4, Fig. 8). Degree of polarity (defined as ratio of polar component of the total surface energy to the total surface energy) for PVTMS is also changed in a great extent under fluorination (Fig. 9). Increase of the surface energy of polymer surfaces exposed to fluorine was reported by several authors [4,7,8,33]. There are several reasons of the surface energy increase. The main reason is probably due to a formation of acid fluoride group, such as C(O)F, which are hydrolysed to C(O)OH group

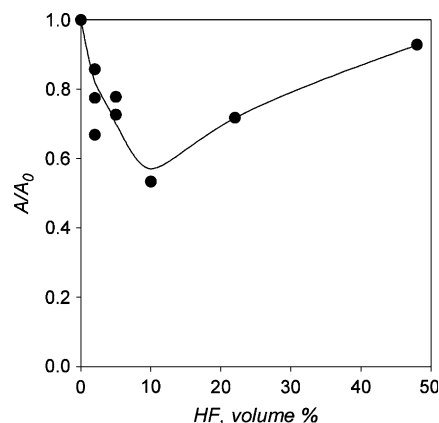


Fig. 7. Dependence of A-value on concentration [HF] of hydrogen fluoride in fluorinating mixture for the case of treatment of copolymer of polysulfone (37%) and polycarbonatesiloxane (60%) (“Seragel[®] 3760/3”) with F_2/HF mixture. Fluorine partial pressure was equal to $p_F = 0.2$ bar, treatment temperature $T = 295 \pm 2$ K.

Table 2
Refraction indexes of virgin n_V^D and fluorinated with undiluted fluorine n_F^D polymers at Na D-line (593 nm)

Polymer	n_V^D	n_F^D
PS	1.59	1.366
PET	1.655	1.38
PI	1.635	1.41
PPO (m.w. 34,000)	–	1.3730
PPO (m.w. 244,000)	–	1.3808
PVTMS	1.4915	1.376

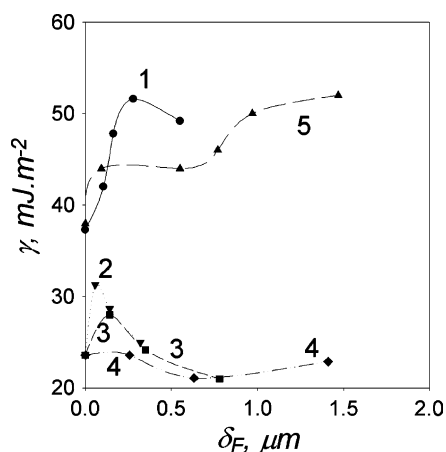


Fig. 8. Total surface energy γ vs. fluorinated layer thickness δ_F . (1) PI, treated with 2%F₂ + 98%He mixture at total mixture pressure 1 bar; (2–4) PVTMS, treated with undiluted F₂ at fluorine pressure 0.02, 0.08 and 0.2 bar, correspondingly; (5) PP, treated with different fluorine pressures. Treatment temperature: 294 ± 1 K.

(latter group has high polarity). Formation of that group proceeds due to oxygen admixture in commercially available fluorine. Another reason of the surface energy increase may take place in the case when the polymer surface treatment conditions δ_F are chosen in such a manner

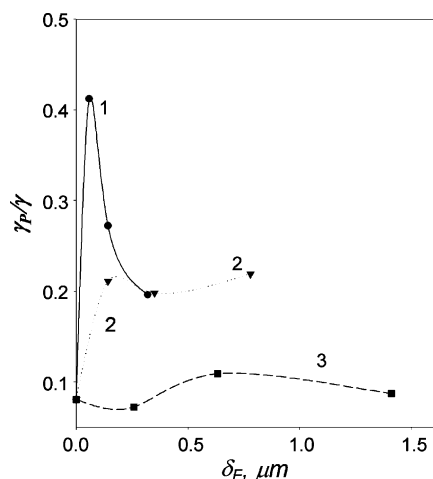


Fig. 9. Degree of polarity γ_p/γ (defined as ratio of polar component γ_p of the total surface energy to the total surface energy γ) of PVTMS vs. fluorinated layer thickness δ_F . (1–3) PVTMS films treated with undiluted fluorine at pressures 0.02, 0.08 and 0.2 bar. Treatment temperature: 294 ± 1 K.

(e.g. low fluorine partial pressure or small treatment duration) that the total replacement of hydrogen for fluorine does not proceed. For the case of PE and PP, the total replacement of hydrogen for fluorine does not proceed at industrial treatment conditions.

The density of polymers is increased greatly under fluorination and usually varies over the range ~1.6–2 g cm⁻³ [19,20,36,39,42]. To measure the density of thin (several μm in thickness) films, the following procedure was applied. Polymer films were cast on a flat surface and then removed from it. Only flat-parallel films were selected. Films were treated with fluorine from both sides. Fluorine-treated film presents a three-layer structure and consists of two layers of fluorinated polymer and of a layer of unmodified (virgin) polymer (the thickness of a transition layer between fluorinated and untreated layers is much smaller than the thickness of a fluorinated layer so, it should not be taken into account). The transmission spectrum of those films exhibited interference features in the visible region. From these data, the thicknesses of the virgin and fluorinated layers can be measured by applying a fast Fourier transformation. Combining these data with measurements of the film area and weight provides the average density of fluorinated layer (see Table 3) [42]. The density of fluorinated layer ρ_F did not depend on the thickness of fluorinated layer δ_F for the case of PET, PS, PVTMS and PPO, but dependent on δ_F for the case of PI (Fig. 10).

Fluorination influences the transparency of polymers in the near UV spectral region (Figs. 11 and 12). For the case of PS and PET, transparency in the near-UV spectral region is increased but for the case of PI and PVTMS it is decreased.

Direct fluorination results in a substantial change of the chemical composition of polymers. Due to a relatively high C–F bond energy inside fluorinated layer, most of H-atoms are replaced for F-atoms and double bonds are saturated with fluorine with formation of C–F bonds. In the case of PVTMS treated with undiluted F₂ breakage of the majority of C–Si bonds is followed by formation of C–F bonds in the polymer chain, and low-molecular weight Si-containing groups are removed from the polymer bulk. The amount of non-cleaved C–Si bonds in fluorinated PVTMS was estimated as 16 ± 4% with respect to the amount of C–Si bonds in the virgin PVTMS. For the case of PI, at least one C–N bond is cleaved with subsequent addition of fluorine atoms to the vacant position and ~15% of low-molecular weight C=O-containing fragments are removed from the polymer chain. The chemical composition of the monomeric unit of the bulk

Table 3
Density of the virgin ρ_V and fluorinated (with undiluted fluorine) ρ_F polymers

Polymer	ρ_V (g cm ⁻³)	ρ_F (g cm ⁻³)
PET	1.46	1.75
PS	1.05	2.05
PVTMS	0.85	1.73
PPO (m.w. 244,000)	1.07	1.72

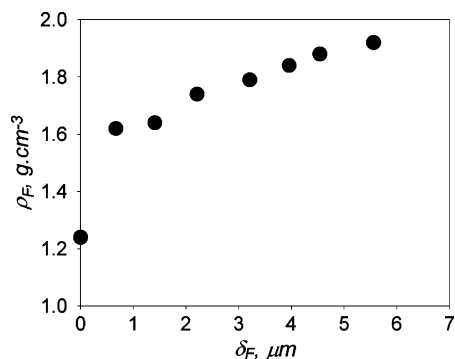


Fig. 10. Dependence of an average density ρ_F of fluorinated layer of PI film on the thickness of fluorinated layer δ_F . Treatment with undiluted fluorine at pressure $p_F = 0.2$ bar and $T = 295$ K. Reprinted from Ref. [36] with permission (Journal of Applied Polymer Sciences © 2004, Wiley & Sons, Inc.).

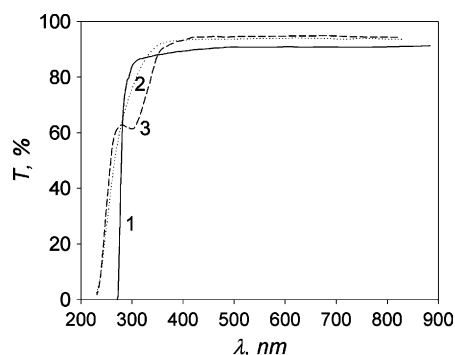


Fig. 11. Transmission T of virgin PS film (25 μm in thickness) (solid line 1), treated through all its thickness with undiluted fluorine (dotted line 2) and treated through all its thickness with 80% F_2 + 20% O_2 mixture. Absorption at 305 nm arises due to formation of $\text{C}=\text{O}$ -containing groups.

samples of PS treated through all their thickness with undiluted fluorine is $\text{C}_8\text{F}_{10} \pm 0.5$. The formula of untreated PS monomeric unit is C_8H_8 and one of the fluorinated PS still containing conjugated bonds would be C_8F_8 . If all the

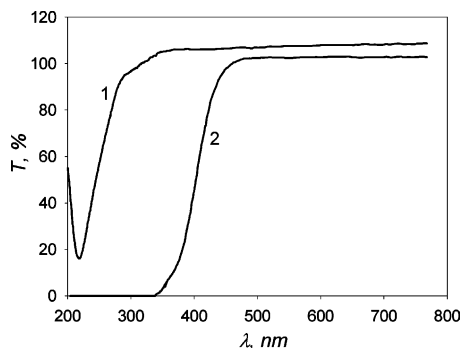


Fig. 12. Transmission spectra T of virgin PI film (1) and the same film treated through all its thickness with undiluted fluorine (2). The film was cast and fluorinated onto sapphire support. Correction to the spectrum of uncoated sapphire has been made. Refractive index of PI is close to a square root of the sapphire refractive index so PI film acts as an antireflecting coating and T -value exceeds 100%. In this case, T -value for uncoated sapphire is smaller as compared with sapphire coated with PI film. Reprinted from Ref. [36] with permission (Journal of Applied Polymer Sciences © 2004, Wiley & Sons, Inc.).

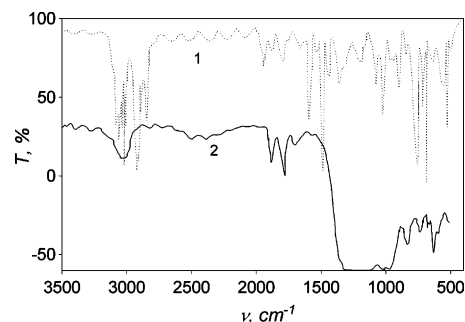


Fig. 13. IR spectra of virgin PS (20 μm in thickness) (dotted line 1) and the same film fluorinated through all its thickness with undiluted fluorine (solid line 2). Fluorine pressure 0.2 bar. Thickness of fluorinated films is equal to 30 μm .

conjugated bonds were saturated by fluorine, the content would be C_8F_{14} . It is known that under the action of fluorine, both breakdown and cross-linking take place [1]; hence, the discrepancy between the formulae (C_8F_{12} , C_8F_8 and C_8F_{14}) can be attributed to breakdown (destruction) and cross-linking of polymer chains and the number of cross-links or additional C–C bonds per each monomeric unit is 2 units more than the number of scissions. The concentration of cross-links is, therefore, equal to 1 per each monomeric unit of fluorinated PS. IR spectra of the virgin and fluorinated through all thickness PS and PI films are shown in Figs. 13 and 14. In experiments with the fluorination of PI, the change of the polymer chemical composition was monitored during fluorination by IR spectroscopy. In that case, a special reaction vessel equipped with ZnSe windows (transparent over 500–20,000 cm^{-1} spectral range and stable to fluorine action) was used to monitor IR spectra. The absorption bands were separated by computer simulation and the band areas were calculated [36].

According to the literature, total replacement of H atoms by F atoms does not occur on the PE and PVF surface under industrially acceptable treatment conditions [49–53]. PVDF does not react with fluorine even at elevated temperature

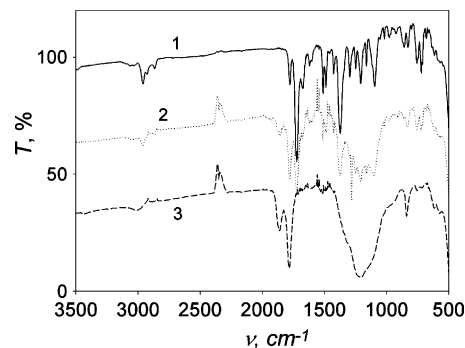


Fig. 14. IR spectra of the virgin PI film (1), the same film treated with $\text{F}_2:\text{He} = 1:4$ mixture at total mixture pressure 1 bar during 21 min at room temperature (spectrum measured in the course of fluorination) (2) and the same film treated through all its thickness (3). Band over 2300–2400 cm^{-1} belongs to uncompensated CO_2 . Reprinted from Ref. [36] with permission (Journal of Applied Polymer Sciences © 2004, Wiley & Sons, Inc.).

(420 K) or under strong UV irradiation [37,38]. When the thickness of fluorinated layer (for the case of treatment with mixtures which do not contain oxygen) exceeds 0.3–0.5 μm , the degree of fluorination of the surface polymer layer for majority of polymers reaches to unity. PE and PVF are exceptions to the rule; the fluorinated layer contains CF_3 , CF_2 , CHF and CH_2 groups.

Treatment with F_2 – O_2 mixtures results in a formation of high concentration of C(O)F groups inside fluorinated layer (up to some 10% of monomer units can be functionalized), which are hydrolysed to COOH groups under the contact with atmospheric moisture.

For the case of PE, formation of C=O-containing groups is accompanied by preferential formation of monofluorinated CHF groups. Measured as described in [43], concentrations of C=O groups in fluorinated LDPE are listed in the Table 4. Similar results were obtained by R.J. Lagow and J.L. Margrave [1]. There are two possible explanations for the formation of the C=O groups in fluorinated PE: (1) the oxyfluorination of $-\text{CH}_3$ groups (i.e., reaction between $-\text{CH}_3$ groups, O_2 and F_2) or (2) scissions of the main polymer chain. The measured amount of $-\text{CH}_3$ groups per 1000 carbon atoms was equal to 24.2 for the case of LDPE with density 0.918 g cm^{-3} . It is evident that even 0.4% of the oxygen in a fluorinating mixture results in chain scission, because the concentration of $-\text{CH}_3$ groups is far too low to explain the amount of C=O groups which are formed. It is self-evident to conclude from the results discussed above that the presence of oxygen during surface fluorination can have a significant effect via chain scission upon the final attributes of a fluorinated surface layer, such as its barrier properties. Moreover, with regard to the surface fluorination of polyethylene, it can be concluded that the presence of oxygen in a fluorinating gas mixture has a strongly negative influence upon the resulting barrier properties of surface-treated substrate material. More detail information on the chemical composition of fluorinated polymers can be found in [1,15,17–22,36–39,42,43].

The concentration $N_{\text{C=O}}$ of C=O-containing groups (i.e., amount of C=O-containing groups per one monomeric unit) practically does not depend on the fluorine partial pressure for the case of treatment with F_2/O_2 mixtures of fixed composition. The dependence of the $N_{\text{C=O}}$ value on the ratio of fluorine p_{F} and oxygen p_{O} partial pressures is shown in

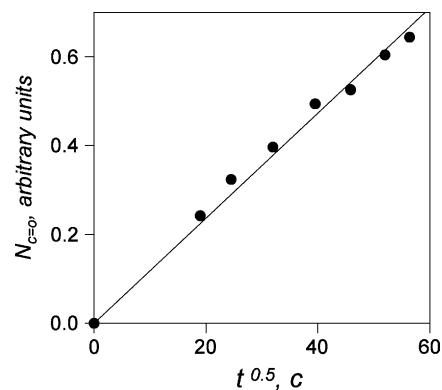


Fig. 15. Dependence of the total amount $N_{\text{C=O}}$ of C=O groups in PPO (m.w. = 244,000) treated with 20% O_2 + 80% F_2 mixture at $T = 295 \text{ K}$. Reprinted from Ref. [42] with permission (Journal of Fluorine Chemistry © 1999, Elsevier).

Figs. 15 and 16, and can be described as follows (treatment temperature $T = 295 \pm 2 \text{ K}$):

$$N_{\text{C=O}} = \frac{1.5 \pm 0.5}{1 + 0.28(p_{\text{F}}/p_{\text{O}})} \quad \text{for PS}$$

$$N_{\text{C=O}} = 0.07 + 0.19 \frac{p_{\text{O}}}{p_{\text{F}}} \quad \text{for PVTMS}$$

$$N_{\text{C=O}} = 1 \pm 0.5 \left(1 + 0.33 \frac{p_{\text{F}}}{p_{\text{O}}} \right) \quad \text{for PPO}$$

Direct fluorination of polymers is a chain-radical process. Formation of radicals has been observed even at $T = 77 \text{ K}$ for a set of polymers (PE, PP, PS, PMMA, PET, PI, etc.) [12,14,37,38]. The kinetics of formation of radicals “*in situ*” at 77 K is shown in Fig. 17. Radical formation commences immediately following the entry of fluorine into the reaction vessel, and it is clearly evident that even at the temperature of liquid nitrogen, the rate of fluorination is not insignificant. In actual experiments, the concentration of the radicals soon reaches a maximum concentration of around 10^{17} radicals per 1 g of the total sample following which, no further radical formation took place. ESR spectra are shown in Fig. 18. Spectrum 1 was measured 20 min after ingress of fluorine (fluorine pressure $\sim 0.095 \text{ bar}$ (a) and treatment temperature 77 K). Spectra 2 and 3 correspond to the same sample evacuated after fluorination and oxidized by atmospheric air and measured at 77 and 293 K, correspondingly. Spectrum 1 is a combination of absorptions

Table 4
Concentration $N_{\text{C=O}}$ of carbonyl groups in LDPE treated under different conditions

LDPE density (g cm^{-3})	Fluorinating mixture	Mixture pressure (bar)	$N_{\text{C=O}}$
0.926	$\text{O}_2:\text{F}_2:\text{He} = 1:10:89$	1	0.49
0.926	$\text{O}_2:\text{F}_2:\text{He} = 2.8:10:87.2$	1	0.48
0.918	$\text{O}_2:\text{F}_2:\text{He} = 0.4:10:89.6$	1	0.27
0.918	$\text{O}_2:\text{F}_2:\text{He} = 2:10:88$	1	0.73
0.918	F_2	0.2	0.04–0.06

Films were treated on both sides, so a double thickness of fluorinated layer was used in the calculations. The fluorine contained $\sim 0.1 \text{ vol.}\%$ of oxygen as a contaminant.

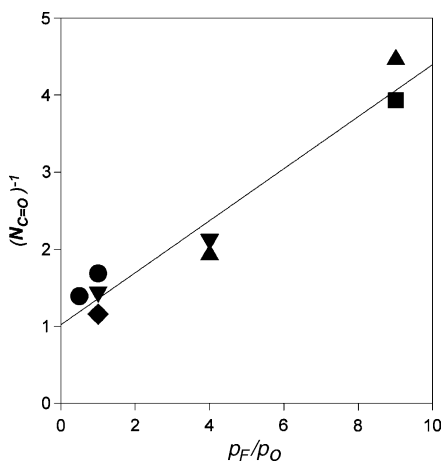


Fig. 16. Dependence of the concentration $N_{\text{C=O}}$ of C=O-containing groups in PPO (m.w. 244,000) treated with O_2/F_2 mixture at $T=295$ K on the ratio of fluorine p_{F} and oxygen p_{O} partial pressures. p_{O} -value was equal to 0.02 (squares), 0.04 (triangles corner up), 0.1 (triangles corner down), 0.2 (diamonds \blacklozenge) and 0.4 (circles) bar. Reprinted from Ref. [42] with permission (Journal of Fluorine Chemistry \copyright 1999, Elsevier).

originating from the peroxy species RO_2^\bullet and another radical which resembles the allyl $-\text{CH}_2-\text{CH}^\bullet-\text{CH}=\text{CH}-\text{CH}_2-$ radical [54] rather than the secondary alkyl radical $-\text{CH}_2-\text{CH}^\bullet-\text{CH}_2-$. Therefore, it can be concluded that, during the initial stages of fluorination of technical polyethylene, allyl radicals are formed and that these radicals initiate the subsequent fluorination of the polymer. However at $T=77$ K, further reactions do not proceed. Spectra 2 and 3 in Fig. 18 are those of the same sample measured at 77 K and 293 K respectively. It is evident from the spectra, which show typical asymmetric singlet absorptions, that all the radicals initially formed were transformed into peroxy RO_2^\bullet radicals. Similar results were obtained for flat LDPE films treated with undiluted fluorine for $t=100$ min at $T=293$ K and 0.072 bar fluorine partial pressure (see Fig. 19). The asymmetric singlet in the ESR spectrum (g -factor:

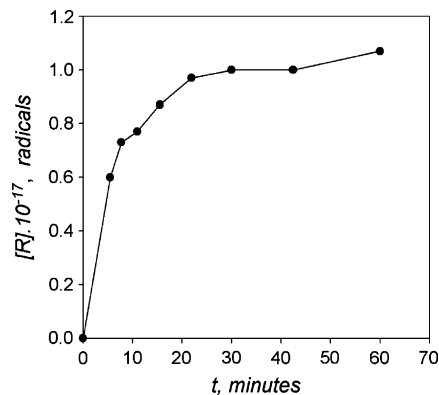


Fig. 17. Total radicals amount $[\text{R}]$ in a fluorinated LDPE vs. the square root of the time of fluorination t as measured “*in situ*” at $T=77$ K. LDPE (density 0.918 g cm^{-3}). Reprinted from Ref. [37] with permission (\copyright 2003, The Paint Research Association (PRA)).

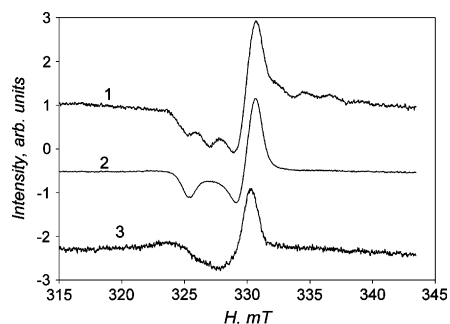


Fig. 18. (1) ESR spectrum of a LDPE sample in the form of a “cotton wool” as measured 20 min after the insertion of fluorine into the reaction vessel. The reaction was carried out at $T=77$ K. (2 and 3) Spectra of the same sample, which was evacuated after fluorination and oxidized. Spectra (1 and 2) were measured at 77 K, spectrum (3) at 293 K. The spectra were corrected with respect to the absorption of the sample before fluorination. Reprinted from Ref. [37] with permission (\copyright 2003, The Paint Research Association (PRA)).

$g_{\perp}=2.0022$, $g_{\parallel}=2.0356$) corresponds again to the RO_2^\bullet radical. Remarkably, the ESR spectra recorded at 77 K and at room temperature virtually coincides. The latter result can be readily explained by the formation of secondary or ‘middle’ peroxy RO_2^\bullet radicals, such as $\sim\text{CHOO}^\bullet\sim$ or $\sim\text{CFOO}^\bullet\sim$ and terminal species, such as $\sim\text{CH}_2\text{OO}^\bullet$, $\sim\text{CHFOO}^\bullet$, or $\sim\text{CF}_2\text{OO}^\bullet$. The spectra of ‘middle’ and ‘end’ radicals measured at a temperature of 77 K should be similar because of ‘frozen’ (restricted) rotation around the polymer chain and the g -factor components are thus also similar (see Figs. 17 and 18). However, when measured at room temperature, the spectra of ‘middle’ and ‘end’ radicals should differ from each other because unrestricted rotation of the ‘end’ RO_2^\bullet radical around the C–O bond, and the axis of the polymer chain should result in an averaging of the anisotropy of the g -factor, and hence, should result in a totally symmetric singlet spectrum. However, rotation of the ‘middle’ RO_2^\bullet radical around a C–O bond and axis of a

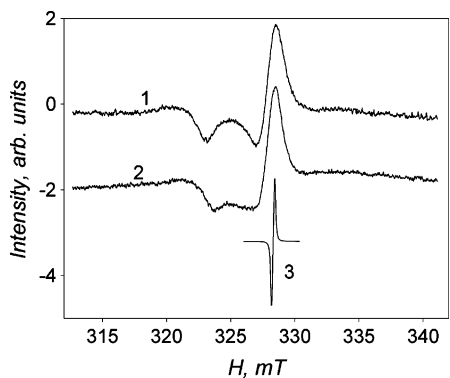


Fig. 19. ESR spectra of LDPE samples in the form of a flat film fluorinated at room temperature. Treatment conditions: undiluted fluorine, $p_{\text{F}}=0.072$ bar, fluorination time $t=100$ min at $T=293$ K. Spectra (1 and 2) were measured at 77 and 293 K, respectively. (3) DPPH spectrum ($g=2.0036$). The spectra were corrected with respect to the absorption of the sample before fluorination. Reprinted from Ref. [37] with permission (\copyright 2003, The Paint Research Association (PRA)).

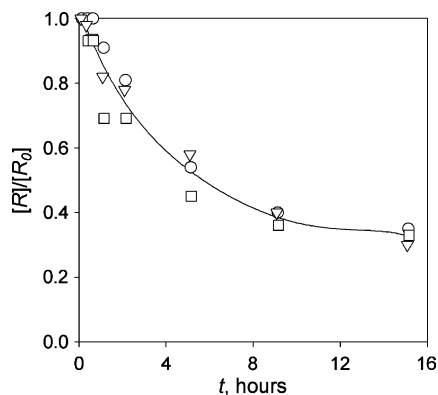


Fig. 20. Ratio $[R]/[R_0]$ ($[R]$ concentration of radicals at time t , $[R_0]$ starting concentration of radicals) vs. storage time t for the case of LDPE (density 0.926 g cm^{-3}). Treatment conditions: fluorine pressure $p_F = 0.1 \text{ bar}$, $T = 295 \text{ K}$. Treatment duration: 15 min (circles), 30 min (squares) and 60 min (triangles). Reprinted from Ref. [37] with permission (© 2003, The Paint Research Association (PRA)).

polymer chain will be restricted, the g -factor will be averaged only partially and the spectrum should be an asymmetric singlet. The detailed examination of the spectrum measured at room temperature leads to the conclusion that the majority of the radicals are ‘middle’ radicals, and hence, disruptions of the polymer chain in LDPE treated under conditions similar to that of industrial ‘off-line’ processes are practically absent. The same experiment (insertion of fluorine into the reaction vessel at $T = 77 \text{ K}$) was carried out at a lower fluorine pressure (i.e., $\sim 0.011 \text{ bar}$) and again a mixture of peroxy and alkyl/allyl radicals were detected. Subsequent heating of the reaction vessel to room temperature resulted in termination of the peroxy radicals in less than 15 min. This can be regarded as confirmation that those peroxy radicals have a carbon–hydrogen character (i.e., $-\text{CH}_2-\text{COO}^\bullet-\text{CH}_2-$ or similar) because fluorocarbon peroxy radicals are known to have significantly greater lifetimes [12,20,36–39]. The radicals formed in fluorinated polymers are long-living ones; their amount is decreased by a factor of 2 in several hours at room temperature (from 1 to 15 h for the case of PS, PET, LDPE, HDPE, PI [12,17,20,36–39]) (see Fig. 20).

An additional modification of a polymer surface may be carried out by a graft polymerization of monomers having double bonds to the long-living radicals located inside fluorinated layer. In this case, the grafted polymer will influence the surface and gas separation properties of a modified polymer [2]. Gas-phase graft polymerization of acrylonitrile (AN) to freshly fluorinated PI films and PVTMS flat membranes has been provided [20,21,36,39] (see figure). It has been shown that the maximum effective thickness of AN layer grafted to PI film was equal to $\sim 7.5\%$ with respect of the δ_F value [9] (Fig. 21).

The initiation stage of the direct fluorination of polymers, i.e., the formation of carbon–hydrogen radicals, proceeds even at liquid nitrogen temperature. This implies that the initial reaction step proceeds with almost zero activation

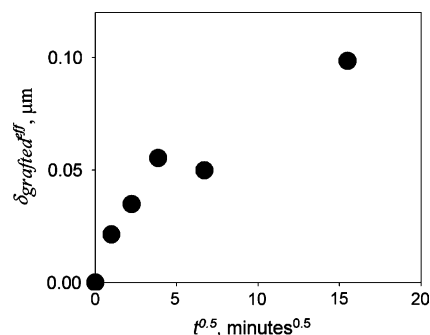
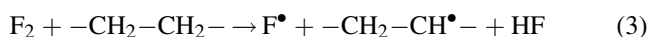


Fig. 21. Dependence of an effective thickness $\delta_{\text{grafted}}^{\text{eff}}$ of a grafted polyacrylonitrile layer on a square root of grafting duration t . Reprinted from Ref. [36] with permission (Journal of Applied Polymer Sciences © 2004, Wiley & Sons, Inc.).

energy. The commonly proposed [1] initiation reaction involving the dissociation of molecular fluorine,



a reaction which is endothermic by $\sim 146 \text{ kJ mol}^{-1}$, does not fulfil this important requirement. However, there are a number of exothermic reactions involving molecular fluorine, which are more appropriate candidates for the initial reaction step. Among these reactions, exothermic branching reactions between C=C bonds (conjugated bonds in the phenyl ring, i.e., in PS, or double bonds in industrial or pre-processed polyethylene which molecular structure deviates more or less significantly from a very regular $-\text{CH}_2-\text{CH}_2-$ structure of ideal polyethylene chain) or a slightly exothermic branching reaction between F_2 and $-\text{CH}_2-$ monomer units may predominate, i.e.,



The presence of a high concentration of $-\text{CH}_2-$ groups in PE probably favours the reaction (3) as initiation step over other theoretically possible initial step reactions. More detailed discussion of the mechanism of elementary stages of the direct fluorination of PS and PE can be found in [13,37,43].

The influence of direct fluorination on the gas separation properties of a hollow fiber module (fabricated from PI Matrimid[®] 5218) is illustrated in Fig. 22, where dependence of a separation factor of He/CH₄ mixture (components of a natural gas) on permeability of He for various polymeric membranes is represented on the basis of literature data by filled circles. The best membrane materials should be placed in the upper right corner of the figure but at present time there exist no materials lying above the solid black line. Open triangle (corner down) corresponds to the starting PI module, open squares to PI hollow fiber module after direct fluorination. Separation factor for He/CH₄ mixture could be increased by a factor of 20–50 (this value depends on the quality of virgin fibers and on treatment conditions), whereas decrease of He permeability did not exceed 20%

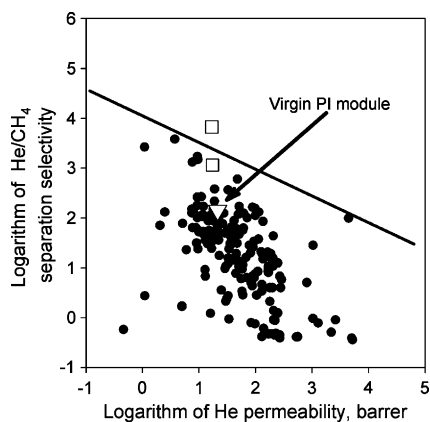


Fig. 22. Separation factor of He/CH₄ mixture vs. permeability of He for various polymer membranes. Filled points: literature data. Open triangle (corner down) and open squares correspond to the virgin and fluorinated PI Matrimid[®] 5218 hollow fiber module, respectively.

with respect to the untreated module. The fluorination procedure has been applied to the membrane module made of 3–5 hollow fibers; hence, it can be regarded as a prototype of a semi-industrial product [18]. For the case of treatment of flat PVTMS membranes with F₂–He mixture separation factor for He/CH₄ and CO₂/CH₄ pairs (biogas components) can be increased by a factor of 10 and 5, correspondingly, as compared with a virgin membrane. Subsequent grafting of AN to fluorinated PVTMS membrane resulted in increase of selectivity separation factor for He/CH₄ mixture by a factor of ~35 as compared with a virgin membrane. Treatment with a F₂–O₂ mixture resulted in more than 100-fold increase of separation factor for He/CH₄ mixture as compared with a starting polymer [2,20,21,32].

Direct fluorination of biaxially oriented PP resulted in a remarkable (by a factor of 1.68) decrease of a static coefficient of friction and less remarkable (by a factor 1.37) decrease of a kinetic coefficient of friction (see Fig. 8 from [20]). The modification proceeds without promoting degradation of the tensile properties of the polymer articles [20,39].

4. Summary

- (1) Direct fluorination of studied polymers is a diffusion-controlled process of the polymer surface modification. Fluorine-treated polymer consists of mainly fluorinated layer and unmodified layer, separated by a very thin transition layer. Rate of formation of fluorinated layer is limited by a rate of penetration of fluorine through fluorinated layer to untreated one and increases with fluorine partial pressure and treatment temperature. The rates of fluorination were measured for a set of polymers. Presence of N₂ or He in fluorinating mixture slightly influences the rate of fluorination.
- (2) Direct fluorination results in increase of a polymer density and decrease of a refraction index. Chemical

composition of fluorinated polymers is changed. C–H bonds are replaced with C–F bonds, conjugated and double bonds are saturated with fluorine, disruption of majority of C–Si and C–N bonds is followed by fluorine atoms addition to disrupted sites.

- (3) Presence of oxygen in fluorinating mixture results in a formation of C=O (COF) containing groups, which are hydrolysed by moisture to COOH groups. Even small (at the level of 0.5%) oxygen contamination results in a chain scission in PE.
- (4) The direct fluorination is chain-radical process. It proceeds via a chain branching mechanism and is initiated via a reaction of molecular fluorine with C–H or C=C bonds, but definitely not via a thermal dissociation of molecular fluorine.
- (5) Controlled amount of long-living radicals (termination time from 1 to 15 h) are generated inside fluorinated layer. Additional modification of a polymer can be arranged via graft polymerization of monomers having double bonds.
- (6) Direct fluorination (treatment with F₂/He and F₂/O₂ mixtures) of polyvinyltrimethylsilane membranes and hollow fiber modules fabricated from polyimide Matrimid[®] 5218 and subsequent grafting of acrylonitrile to fluorinated polyvinyltrimethylsilane membranes results in a significant increase of selectivity of separation of He/CH₄ and CO₂/CH₄ mixtures accompanied with a small decrease of He permeability. This is mainly due to a drastic decrease of CH₄ permeability.
- (7) Total surface energy and its polar and dispersion components can be substantially changed. Such a change would result in an enhanced adhesion.
- (8) The direct fluorination of biaxially oriented polypropylene results in a remarkable decrease of both static and dynamic friction coefficients.

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