Modification of surface properties of carbon-based and polymeric materials through fluorination routes: From fundamental research to industrial applications

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Abstract

The outstanding characteristics of fluorine gas, e.g., extreme reactivity and oxidizing power, and the utmost electronegativity of F^- ion, lead to very strong bonds between fluorine and most of the other elements of the periodical table. Treatments involving F_2, fluorinated gases and rf plasma-enhanced fluorination (PEF) constitute exceptional tools for modifying the surface properties of materials. Many advantages of these techniques can be indeed outlined, when compared to more conventional methods: low-temperature reactions (even at room temperature), chemical modifications limited to surface only without changing the bulk properties, possible non-equilibrium reactions. Depending on the type of starting materials and employed techniques, the improved properties may concern wettability, adhesion, chemical stability, barrier properties, biocompatibility, grafting, mechanical behavior. Several examples of surface fluorination will be given on various types of carbon-based materials, elastomers and polymers.
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1. Introduction and fluorination procedures

The outstanding reactivity of fluorine and fluorinating atmospheres has been demonstrated these last decades by the synthesis of a wide variety of inorganic fluorine-based compounds and also by the drastic modification of their surface properties [1–4].

Radiofrequency (rf) plasma technologies using fluorinated gases are now currently employed in etching or polymerization processes in microelectronics and in materials sciences. Several advantages can be indeed outlined, when compared to gas methods: (i) low-temperature reaction (in many cases the treatment can be achieved at room temperature, which avoid the thermal degradation of the material), (ii) chemical modification limited to surface only (below a few tens nanometers), (iii) possible non-equilibrium reactions. These methods are able to

lead to drastic modifications of the surface properties without changing the bulk characteristics of the pristine material, as shown for instance in studies on high-T_C superconducting ceramics [5]. The rf plasma-enhanced fluorination (PEF) of inorganic materials can be carried out with varied fluorinated gases (CF_4, CHF_3, C_3F_8, C_4F_8, NF_3, SF_6, F_2, NF_3, ClF_3) [6]. Depending on the type of starting materials and employed techniques, the improved properties may concern wettability, adhesion, chemical stability, permeation, electrical conductivity, biocompatibility, grafting, mechanical behaviour, etc. Although fluorination of graphite and carbon materials by F_2-gas has been extensively studied [7,8], only a few studies have been devoted to the treatment of their outermost surface using PEF routes.

Concerning polymeric materials, fluoropolymers have a set of unique properties such as enhanced chemical and thermal stabilities, good barrier and gas separation properties, etc. [3,4,9–13]. However, practical use of fluoropolymer items is restricted due to their high cost and complexity of synthesis. Conventional polymers have a lot of advantages, such as low cost, processability, but they also exhibit a lot of drawbacks:

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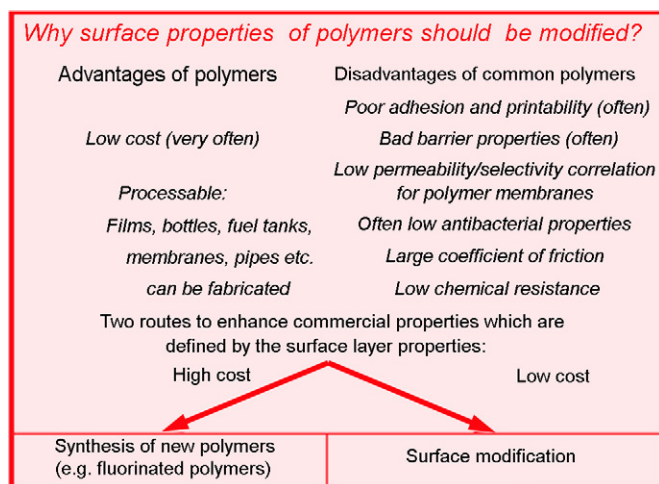khariton@binep.ac.ru (A.P. Kharitonov).

Fig. 1. Scheme presenting the advantages of surface fluorination of polymers. Reproduced from [26] under permission of L'Actualite Chimique.

often poor adhesion, printability and barrier properties, low chemical resistance, etc., as shown in Fig. 1. Very often application properties of polymer items are defined mainly by their surface properties. In many cases, it is not necessary to manufacture articles from expensive fluoropolymers because a simpler, cheaper and more convenient route is to apply a surface treatment of conventional polymers. A particularly effective approach to surface modification is the direct fluorination, because this process does not need any initiation and proceeds at practically acceptable rates at ambient temperatures. Since fluorination is one of the most effective chemical methods to modify and control physicochemical properties of polymers over a wide range, this process has become an important tool of great interest. 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 industrial problems. Due to a 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 μm thickness of the material is modified, and the bulk properties of the starting polymer remain unchanged.

As far as the surface properties are concerned, X-ray photoelectron spectroscopy (XPS or ESCA) is a particularly suitable technique to investigate changes in binding energies (BE) that occur within 1–100 nm of the material surface [14].

1.1. The fluorination procedures

1.1.1. Direct fluorination process using F_2-gas

At CNRS-University Bordeaux1 (France) the reactions were performed at room temperature in a ''fluorine line'' using handling procedures, as previously described, e.g., in ref. [1]. The samples were set in a Ni boat which had been passivated. F_2 gas 10% diluted in N_2 (air products) was used at room pressure. The reaction duration did not exceed 120 min. At the end of the experiment, F_2-gas was eliminated from the container and substituted by N_2. At Institute of Energy Problems of Chemical Physics (Russia) the reactions were performed in static conditions in closed stainless steel vessels over temperature range 77–420 K. Amount of admixtures in used fluorine (mainly oxygen) did not exceed 0.1%. Mixtures of fluorine with helium, nitrogen, oxygen, argon and hydrogen fluorine were used. Fluorine concentration in a gaseous mixture was varied over 1–100% range. Fluorine partial pressures covered range over 0.005–1 bar. The fluorination duration was varied over 1 min to several days. In majority of experiments NaF pellet was introduced in a reaction vessel to remove emitted HF.

1.1.2. Plasma-enhanced fluorination (PEF)

The experiments were carried out in a S.E. 80 Barrel Plasma Technology System. The gas was excited by a rf source at 13.56 MHz. The reactor consisted of two aluminium barrel electrodes which were coated with alumina. The inner electrode on which the sample was placed was connected to the rf source and the outer one was grounded. A primary vacuum was obtained by a 40 $m^3 h^{-1}$ Edwards E2M40-type pump equipped with a liquid nitrogen condenser which trapped any residual gases. The chamber was thermostatically controlled and maintained either at room temperature or at about 90 °C during the process. Several parameters could be tuned, in particular, inlet precursor composition, e.g., the possible presence of a second gas with the fluorinated reagent. However, due to an important etching observed when O_2 was added, the fluorinated gas was generally used alone; inlet gas flow: $8 < Q$ (ml min^{-1}) < 16; total pressure: $25 < p$ (mTorr) < 200; rf power: $40 < P$ (W) < 110.

Although different fluorinated gases have been tested (CF_4, CHF_3, C_3F_8, C_4F_8), we will deal in the following only with the results obtained with CF_4 since it is the gas which has been used with all the involved materials [15]. Taking into account previous experiments of PEF on various types of carbon materials [8,10], optimized conditions could be established with the following parameters: CF_4 gas flow rate: $Q = 8$ ml min^{-1}; total pressure: $p = 300$ mTorr; rf power: $P = 80$ W. After the fluorination treatment, the samples were generally handled and kept in a glove box under an Ar atmosphere.

2. Fluorination treatment of carbon-based materials

2.1. Starting materials and XPS characterization

The nature of C–F bonds that are formed during the reaction between the fluoro species and carbon-based materials depends on two main factors: (i) the experimental conditions of fluorination (experimental parameters of the low-pressure plasmas, nature of the fluorinated gas, etc.) and (ii) the physicochemical characteristics of the pristine material (graphitization level, coherence length of the domains, nature and amount of impurities, morphology of the particles, etc.).

2.1.1. Pristine carbon-based materials

The influence of the physicochemical characteristics of the starting material on the surface modification has been illustrated by the use of different types of carbon compounds: highly graphitized material, e.g., an exfoliated graphite [Papyex from Le Carbone Lorraine], various graphitic samples with size ranging between from 7 to 40 μm, furnace carbon blacks [Corax N 115, with surface area of 145 $m^2\,g^{-1}$, from Degussa] in which the coherence length of the ordered domains is limited to a few nanometers. The elastomer sample were carboxylated nitrile butadiene rubber latex (NBR) having about 40% dry rubber content and zinc oxide (1–2%). Additives included potassium hydroxide as pH control agent, accelerators, sulphur and pigments.

2.1.2. XPS characterization

XPS analysis were performed with a VG 220 i-XL ESCALAB. The radiation was a Mg non-monochromatized source (1253.6 eV) at 200 W. A 250 μm diameter area was observed on each sample, first prepared in a glove box, stored under neutral gas for transport, then quickly introduced in the fast entry air lock of the ESCA machine. Surveys and high resolution spectra were recorded, then fitted with a Eclipse processing program provided by Vacuum Generators. Each C1s component was considered as having similar full width at half maximum (FWHM), i.e. 1.3 eV. This procedure appeared to be the most reliable one, as previously proposed in investigations on fluorinated carbon blacks (see ref. [10]). A good agreement between the experimental curve and the full calculated envelope was obtained in most cases, explaining in addition subtle distinctions between the proportion of fluorinated components.

After fluorination, the modifications of the surface composition of the various materials were also investigated by transmission electron microscopy and electron probe microanalysis.

2.2. Results of fluorination treatments and discussion

2.2.1. Exfoliated graphite

The dependence of C1s and F1s XPS spectra of exfoliated graphite with the duration of plasma treatment is shown in Fig. 2. In the C1s envelope, the graphitic contribution (component 1), which is the most important component, remains almost unchanged after plasma treatment. The high BE asymmetric component could correspond to surface defects, C–H, and C–O groups. The components appearing for $285 < E_b$ (eV) < 287 can be assigned to an inductive (β) effect arising from C–F bonds: they correspond to C atoms that are not directly bound to F atoms, but that are first neighbors of CF_n groups. In the case of graphite samples, this contribution is weak because the number of reactive sites (i.e. surface defects and borders of the graphitic domains) is limited due to an important coherence length of the graphitic domains. The weak component at ca. 287 eV (component 3) can be assigned to "semi-ionic" C–F bond of F species intercalated in between two graphene layers, and those at $E_b > 288$ eV to C atoms
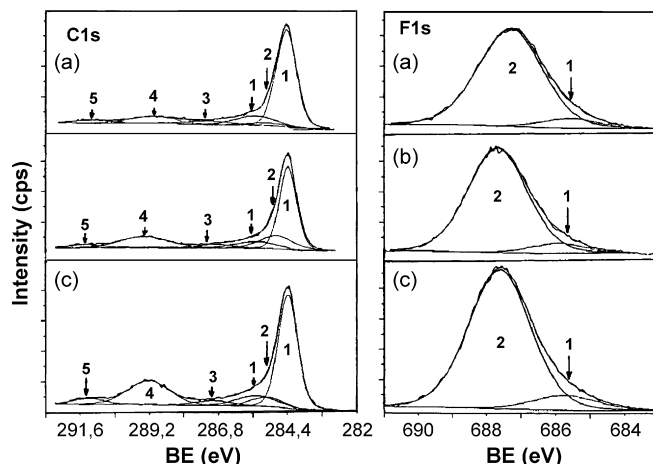

Fig. 2. C1s and F1s XPS spectra of CF_4 plasma-treated exfoliated graphite [experimental conditions: 8 $cm^3\,min^{-1}$, 200 mTorr, 80 W, 15 min (a), 60 min (b), 120 min (c)]. Reproduced from [114] under permission of Elsevier.

covalently bound to F atoms, as confirmed by the importance of component 2 in the F1s spectra. The component at ca. 289 eV (component 4) has been correlated to the fluorination of defects present at the surface of graphitic domains or in subsuperficial zones: in this case, the sp^2 configuration of C is maintained. The contribution at higher BE (component 5) may be due to different sources: fluorinated domains in which the graphene layers are buckled as in the covalent graphite fluorides $(CF)_n$, or perfluoro groups CF_n with $n = 2$ or 3, present at the peripheral border of the graphitic domains.

The PEF treatment concerns only a very thin layer of the surface of the sample, as shown by a rapid decrease of the F contribution after Ar sputtering. The types of bonds that are formed between C and F atoms are mostly covalent, only a small amount of fluorine being intercalated. Compared to F_2-gas fluorination [7,8], this method allows the formation of a covalent and insulating layer at the outermost surface of the particles.

2.2.2. Carbon blacks

Due to the complex morphology of this type of materials, ten components are required to take into account the complete envelope of the C1s envelope after PEF treatment. Details of the fitting procedure can be found in previous papers [16,17]. There are two major peaks in the C1s envelope: the peak at lower BE, located at 284.3 eV, can be assigned to the component C1s (1) which corresponds to non-functionalized sp^2 and sp^3 C atoms that are not affected by fluorination; the peak at higher BE, C1s (6), which is located at 288.6 eV is the most important component of C–F bonds and can be assigned to carbon atoms present at the surface and border of the graphitic domains. These atoms are covalently bound to fluorine atoms without any change in their sp^2 conformation (Type I structure). Between components (1) and (6) the envelope can be fitted into four components corresponding to C atoms that are not directly bound to F atoms. The shift induced by the presence of F atoms in β position of a given C atoms, has been evaluated to about 0.6 ± 0.2 eV and is roughly additive. The components C1s (i),
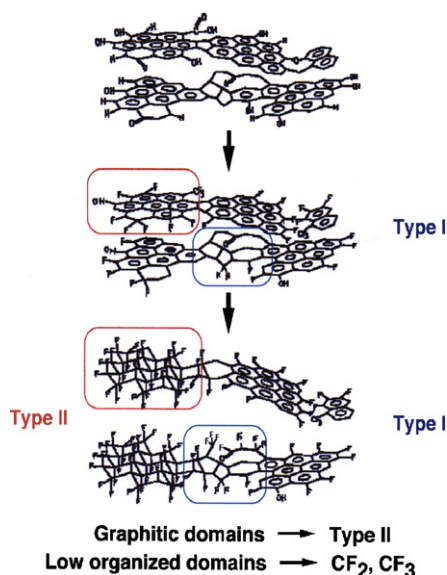
Fig. 3. Fluorination mechanism of carbon blacks.

with $i > 6$, are attributed to carbon atoms with sp^3 configuration that are covalently bound to F. The components with even higher BE, i.e. $i > 8$, can be attributed to fluorinated domains in which the charge effect is particularly important. For instance, the peak whose fitted component is located at 290.7 eV [C1s (8)] can be attributed to CF$_2$ groups of fluorinated structure of Type I, whose F atoms contribute to F1s (6), and also to C–F groups of polyalicyclic perfluorinated structures of Type II, in which sp^3 C skeleton forms puckered layers similar to those of covalent graphite fluorides (CF)$_n$ [7] (Type II structure). F atoms of this second type contribute to the component (8) of F1s envelope. For longer fluorination durations, Type I structures are progressively transformed into Type II ones, as shown in the scheme of Fig. 3.

From the analysis of the XPS spectra of fluorinated carbon blacks, it can be concluded that the fluorine atoms, fixed at the surface and in the sub-superficial zone of the particles, are covalently linked to carbon atoms. The majority of the structures of the fluorinated islands present at the surface are of Type I, a structure in which the planar (sp^2) conformation of carbon in the graphene layers is preserved; however some fluorinated islands of Type II structure also exist at the surface and their amount increases with increasing fluorination times.

2.2.3. Graphite samples as anodes for lithium-ion secondary batteries

The surface modification of carbon materials that constitute anodes of lithium-ion secondary batteries is of decisive interest because during the first charge of a battery, lithium ions interact primarily with chemical species present at the surface, such as hydroxyl, carbonyl and carboxyl groups, forming a solid electrolyte interphase which may decompose organic solvents present in the electrolyte. PEF treatments have been carried out on various graphite samples of size ranging between 7 and 40 μm. Surface fluorine concentrations obtained by XPS were in the range of 3–12 at.%. Raman spectroscopy has revealed

that surface disordering of graphite was induced by plasma fluorination. When PEF treated, graphites showed very high reversible capacities, higher than those of original graphites and even higher than the theoretical capacity of graphite, i.e. 372 mAh g^{-1}, without any change of the profile of charge-discharge potential curves. The increments in the reversible capacities were ∼5, ∼10 and ∼15% for graphites with average diameters, 7, 25 and 40 μm, respectively. Furthermore the first coulombic efficiencies were nearly the same as those for original graphites or higher by several percents [18].

When the anodes are constituted of high temperature HT-treated petroleum cokes it was shown by HRTEM that the external structures were formed of nanotube-like bundles. The outmost surface of these materials is mostly formed of hemispherical tips similar to those found in nanotubes. By low-temperature fluorination using CF$_4$ radio-frequency plasmas, an opening mechanism of the nanotube-like tips occurs, thus allowing an increase of Li$^+$-ion intercalation in between the graphene layers [19]. The interest for Li^i storage in Li$^+$-ion batteries has been demonstrated by capacity measurements which show an enhancement of the Li$^+$ capacity retention into the host materials.

It has been assumed that these procedures yield important electrode modifications:

- surface oxygen is reduced to some extent;
- the surface area of the electrode material is increased, with a subsequent increase of Li$^+$ intercalation and/or adsorption in the electrode. This latter property may be due to two factors: (i) an increase of the structural disorder caused by fluorination which probably diminishes the length of the graphitic domains and induces the formation of surface nanopores in which excess lithium can be accommodated [18]; (ii) an increase of the intercalation rate of Li into graphitic layers in the case of PEF fluorination of HT-treated petroleum cokes [19].

3. Fluorination of elastomers and polymers

3.1. PEF fluorination of elastomers: the case of nitrile butadiene rubber

PEF treatments of NBR-based gloves using CF$_4$ rf plasma without thermal activation do not bring important modifications of C1s spectra. The very small amount of C–F bonds which are formed can be attributable to CHF–CHF groups. However, on the other hand, 5–10% of fluorine are found at the surface. From the position of the components in the F1s spectrum, it can be assumed that the major components are ''ionic'' fluorides, in which fluorine is bound to inorganic elements that have been introduced during the fabrication process of the elastomer: CaF$_2$, ZnF$_2$ or complex fluorides. The effect of thermal activation is illustrated in Fig. 4. An important increase of the surface fluorination is noted from the elemental analysis, with a mean surface F/C ratio reaching 1.6. In these conditions, the C1s spectra Exhibit 2 clear maxima: one at a BE similar to that of the starting material, and another one with a shift of +6.8 eV.
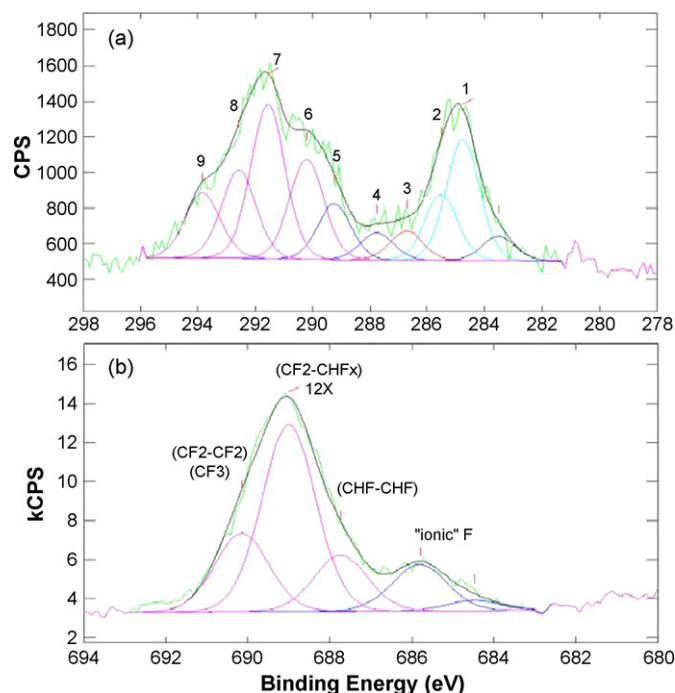
Fig. 4. C1s (a) and F1s (b) XPS spectra of NBR sample PEF-treated at 90 °C. Reproduced from [114] under permission of Elsevier.

If we take the same assignment procedure as previously used, this second maximum can be assigned to CF_2 groups with first C neighbours bound to one F atom, for instance CF_2–CHF groups. Another feature of the spectrum which is consistent with an increase of surface fluorination is the presence of two more contributions at higher BE. The contribution at +8.0 eV shift corresponds to CF_2 groups with CF_2 (or CF_3) first neighbours, or to CF_3 groups with non-fluorinated neighbours, whereas the contribution with a shift of 9.1 eV can be assigned to terminal CF_3 groups with fluorinated neighbours. The assignment and correspondence of the different components are given in Table 1. In the case of the F1s spectrum, although the amount of the ''ionic'' fluorides is more or less similar (12%), the value of the main component at 688.7 eV corresponds to CF_2–CH_2, or $CH\underline{F}$–CF_2 units. At lower BE, the CHF–CHF component at 687.3 eV is weaker (15%). A further component at 689.8 eV can be assigned to perfluorinated CF_n groups, in particular PTFE-like CF_2–CF_2 units and terminal CF_3 groups.

Table 1
Assignment of the components of C1s XPS envelope

No.	Chemical bond	Shift (eV) relative to BE = 284.5 eV
1	CH_n	–
2	$\underline{C}H_2$–CHF	0.7–1.1
3	$\underline{C}H_2$–CF_2	2.0
4	$\underline{C}HF$–CH_2 CHF–CHF	3.0–3.5
5	$\underline{C}HF$–CF_2	4.5
6	CF_x–$\underline{C}F$–CF'_x $(x, x' = 2, 3)$ $\underline{C}F_2$–CH_2	5.3–5.5
7	$\underline{C}F_2$–CHF	6.2–6.8
8	$\underline{C}F_2$–CF_2	7.8
9	$\underline{C}F_3$–CF_x	9.1

These results clearly show that the fluorination mechanism of NBR samples depends on the fluorination conditions. When the treatments are carried out at room temperature a gentle fluorination occurs and only a small amount of polymer surface is fluorinated, most fluorine reacting with inorganic cations such as Ca^{2+} or Zn^{2+}. A thermal activation yields a more massive fluorination of the surface with an opening of the butadiene double bonds that finally leads to perfluorinated (–CF_2–) groups and even terminal –CF_3 groups. In the latter conditions, the permeation properties are subsequently decreased.

3.2. Direct fluorination of polymers

3.2.1. Fundamental features of the direct fluorination of glassy polymers

The following polymers were investigated: high density and low density polyethylene (HDPE-6 varieties and LDPE-2 varieties), polyvinylfluoride (PVF), polyvinylidenefluoride (PVDF), polystyrene (PS), poly(ethylene terephthalate) (PET), polymethylmethacrylate (PMMA), poly(phenylene oxide) (PPO-2 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 region of spectra, refractometry, electron microscopy, gas-chromatographic and volumetric measurement of transport properties of polymer membranes, measurement of the surface energy and permeation rate of petrol through polymer films. Two original interference methods were developed to study the growth kinetics of the fluorinated layer ''in situ'' and density of fluorinated thin polymer layers (over 0.5–10 μm) [11,20–24].

In all the 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 (Fig. 5). When the thickness of fluorinated layer exceeds ~1 μm, the degree of fluorination is close to unity for the case of studied polymers, excluding HDPE, LDPE, PVF and PVDF. Presence of oxygen in fluorinating mixture results in a preferable formation of monofluorinated groups in the case of polyethylene (Fig. 6: the insertion of oxygen in fluorinating mixture results in a decrease of absorption of C–F_2 groups) and in a formation of controlled amount of C=O-containing groups, e.g., –COF (Figs. 6 and 7), which are transformed into –COOH groups under moisture action (Fig. 7). 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 F_2:$O_2 \sim 1$ mixture) C=O-containing groups [11,20,22–26].
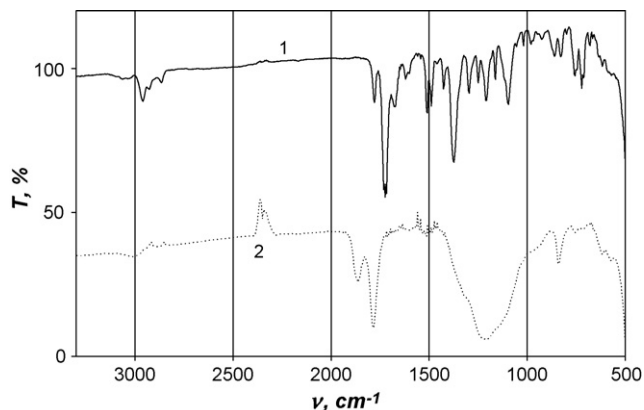
Fig. 5. (1) IR spectra of virgin polyimide Matrimid® 5218 film; (2) the same film treated with F_2:He = 1:4 mixture at total pressure 1 bar through all its thickness (spectrum was measured in vacuum; band over 2300–2400 cm^{-1} corresponds to uncompensated CO_2). Spectra are shifted along vertical axe to avoid overlapping. Reproduced from [22] under permission of Elsevier.

Fig. 7. (1) IR spectra of the film of virgin LDPE; (2) IR spectra of LDPE treated with O_2:F_2:He = 1:10:89 mixture at total pressure 1 bar during 16 h at T = 293 K, measured in 3 min after removal from the reactor; (3) spectra of the same film measured in 3 months (the films was stored in ambient atmosphere). Band over 2300–2400 cm^{-1}, uncompensated CO_2. Spectra are shifted along vertical axe to avoid overlapping. Reproduced from [25] under permission of Surface Coatings International (Oil & Colour Chemists' Association).

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 µm in thickness) transient reaction zone [11,20]. 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:

$$\delta_F = At^{0.5} = B(p_F)^k t^{0.5} + \text{const} \qquad (1)$$

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. A list of B and k values for different polymers can be found at our recent papers [11,20]. The dependence of the rate of formation of fluorinated layer on the polymer nature is illustrated at the Fig. 8. It is evident that the polymer nature highly influences the rate of fluorination: time, necessary to form fluorinated layer 1 µm in
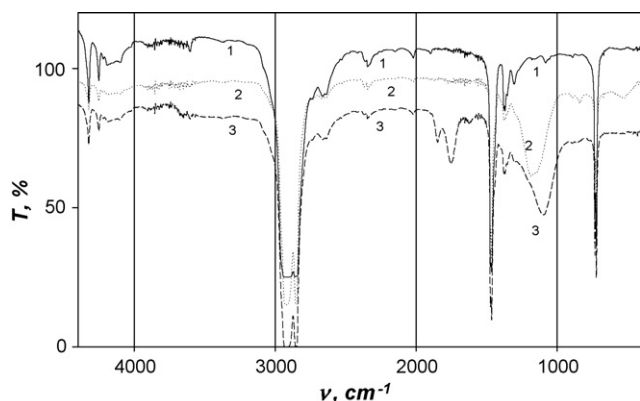

Fig. 6. IR spectra of the films of virgin and fluorinated low density polyethylene (LDPE, density 0.926 g cm^{-3}). (1) Virgin LDPE, (2) LDPE treated with undiluted F_2 at fluorine pressure p_F = 0.2 bar during 85 min at T = 293 K, (3) LDPE treated with F_2:O_2:He = 3:9:88 at total pressure 1 bar during 16 h at T = 293 K. Band over 2300–2400 cm^{-1}, uncompensated CO_2. Spectra are shifted along vertical axe to avoid overlapping. Reproduced from [25] under permission of Surface Coatings International (Oil & Colour Chemists' Association).
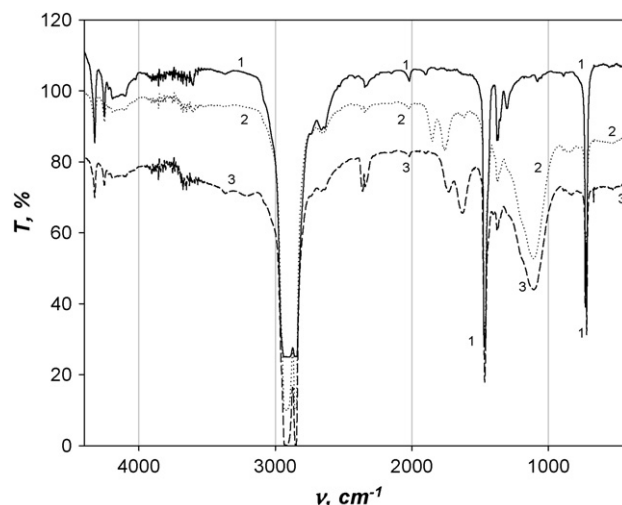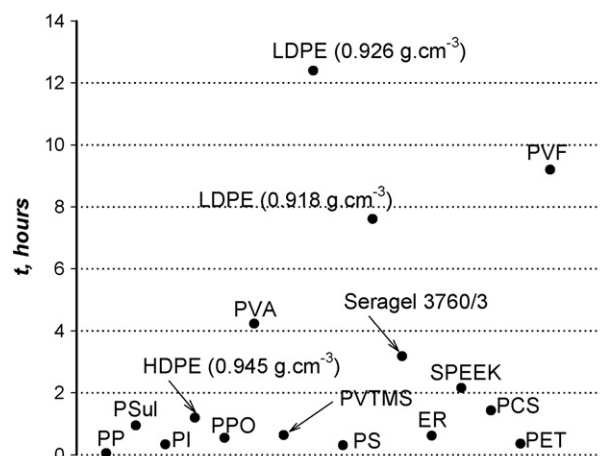

Fig. 8. Time t (h) necessary to form 1 µm thick fluorinated layer at fluorine pressure 0.1 bar and temperature 293 K on the surface of various polymers: HDPE and LDPE high density and low density polyethylene, polyvinylfluoride (PVF); PS, polystyrene; PET, poly(ethylene terephthalate); PPO, poly(phenylene oxide); PI, polyimide Matrimid® 5218; PP, polypropylene; SPEEK, sulfonated polyetheretherketone; Seragel® 3760/3, block-copolymer of sulfone and butadiene; PVTMS, polyvinyltrimethylsilane; PCS, polycarbonatesiloxane (Carbosil®); Psul, polysulfone Udel 3500; PVA, polyvinylalcohol; ER, epoxy resin.

Table 2
Density of virgin ρ_V and fluorinated 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	1.07	1.72

thickness at fluorine pressure 0.1 bar and temperature 293 K varies from ∼3 min to ∼12 h for various polymers.

O_2 and HF inhibit the rate of formation of fluorinated layer, but the presence of N_2, Ar and He in the fluorinating mixture weakly influences kinetics of fluorination. The rate of formation of fluorinated layer increases with temperature. Would the A value be represented as $A \sim A_0 \exp(-E_{act}/RT)$, the activation energy E_{act} be equal to 13.4, 28.1 and 34.2 kJ mol^{-1} for LDPE (density 0.918 g cm^{-3}), HDPE (density 0.945 g cm^{-3}) and HDPE (density 0.949 g cm^{-3}), respectively [25].

An average density of fluorinated PVTMS, PS, PET and PPO does not depend on the thickness δ_F of fluorinated layer over $\delta_F = 0.5$–10 μm and markedly exceeds density of virgin polymers (Table 2). Density of fluorinated PI increases from 1.24 g cm^{-3} (virgin polymer) to ∼1.9 g cm^{-3} when δ_F rises from 0 to 5–8 μm [20,22].

Refraction indexes of fluorine-treated polymers (for the case when oxygen is not added to fluorinating mixture) are close to 1.37–1.41.

ESR spectra of long-lived radicals consisting of superimposed peroxy $RO_2{}^\bullet$ and fluororadicals spectra (Fig. 9) were observed in all the fluorinated polymers at concentrations up to 2.4×10^{20} radicals cm^{-3} of fluorinated layer (for HDPE). Radicals are placed inside fluorinated layer only. Peroxy radicals are formed due to oxygen admixture in fluorine or absorbed oxygen and water in polymer bulk and on the reaction vessel walls. Peroxy radicals terminate faster than fluororadicals.
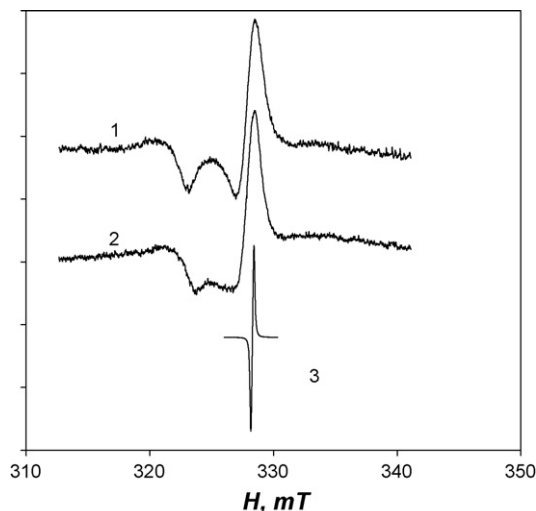

Fig. 9. ESR spectra of fluorinated LDPE (1) measured at 77 K, (2) measured at 293 K); (3) spectrum of DPPH ($g = 2.0036$). Reproduced from [25] under permission of Surface Coatings International (Oil & Colour Chemists' Association).

Kinetics of termination of radicals (both self-termination and in the course of reactions with various gases) was studied for as set of polymers (see Fig. 7 and [20,22,25–27]). It was established that the amount of radicals was decreased by a factor of 2 in several hours at room temperature in air environment (from 1 to 15 h, depending on the polymer nature). The presence of radical quenchers such as amines, NO, etc. increases the rate of radical termination [20,25–27].

The following conclusions were made. The process of fluorination of polymers is a radical chain process. Initiation of the reaction takes places via the reaction of molecular fluorine with C–H bonds or double C=C bonds and not via the dissociation of molecular fluorine. Both peroxy long-lifetime $RO_2{}^\bullet$ and fluororadicals are formed within the fluorinated layer in relatively large concentrations. The amount of peroxy radicals exceeds the amount of fluororadicals. The amount of scissions in LDPE treated under industrial conditions and measured just after fluorination is negligible.

Additional modification of a polymer surface can be achieved 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 [20,22].

3.2.2. Commercial applications of the direct fluorination of polymers

As it was mentioned above, great variety of commercial properties of polymer articles can be improved by direct fluorination: barrier properties, gas separation properties, adhesion and printability, tensile strength of polymer composites, chemical resistance, bioresistance, etc. There are various companies which are active in the field of fluorination of polymers: "Air Products" (USA and Europe), "Solvay" (Europe), "Fluoro Seal Ltd." (USA), "Fluoro Pack (Pty) Ltd." (South African Republic), Jiangsu Rotam Boxmore Ltd." (China), "Alkor Gmbh Kunststoffe"(Germany), "Interftor" (Russia), etc.

3.2.2.1. Barrier properties. At present time one of the most commercially significant applications of direct fluorination of polymeric goods is the enhancement of their barrier properties [3,11,12,20,25]. Direct fluorination creates a barrier to permeation of multiatomic molecules, e.g., hydrocarbons. This is due to several reasons. At first fluorination results in a significant increase of the specific gravity [11,20,22,24,26] and the free volume is decreased and hence the permeability of fluorinated polymers should be decreased. Also direct fluorination results in the crosslinking of polymers [9,20,28–30] so the swelling and plasticization effects under the action of hydrocarbons are suppressed and permeability values decrease. Finally the surface energy of fluorine-treated polymer surfaces in many cases is increased and hence the solubility (permeability also) of low polarity organic liquids in fluorinated polymers is decreased. There are some possible application areas where the enhancement of the barrier properties can be of commercial importance.

The fluorination of the interior of polymeric automotive fuel tanks prevents non-polar or low-polar substance (e.g., hydrocarbons) emission and reduces air pollution. According to estimates [31] the permeability value of fluorine-treated high density polyethylene (HDPE) is around 10^{-13} to 10^{-14} (cc(STP) cm cm^{-2} s^{-1}). This value is 6–7 orders of magnitude lower than one of an untreated HDPE. The main attention of investigators was paid to polyethylene (especially HDPE) [3,11,13,20,26,27,31–54]. The loss of liquids such as gasoline from polymeric fuel tanks can be reduced upon the direct fluorination by a factor of 100 [31], 10–20 [32], 100 (for Pb-free fuel [43]), 70 [48]. Spread in the above data may be due to several reasons: different treatment conditions (composition of fluorinating mixture, duration of treatment), variations in chemical structure of polyethylene, etc. The leakage of petrol/alcohol mixture can be reduced by fluorination by a factor of 18 [31]. The loss of petrol (petrol grade 0.93 octane high altitude) from HDPE pipes used between reservoirs and pumps at filling stations can be decreased upon fluorine treatment by a factor of 80 [49,50].

Direct fluorination of polymer containers for packaging of industrial and consumer chemicals decreases the loss of liquids which are stored inside the containers. Carstens [49,50] has shown that the loss of chemicals such as creosote, paints, polishes, hand cleaners, etc. from HDPE containers can be reduced upon direct fluorination by a factor of one or two orders of magnitude. Leakage of toluene from HDPE containers can be also reduced by a factor of 100 [40], 50–60 [41], 15 [53] and leakage of pentane by a factor of 100 [55]. Direct fluorination of HDPE reduces the permeability of non-polar liquids (C_7H_{16}, C_6H_6, $C_{12}H_{26}$, CCl$_4$ [45,51] and pentane, CCl$_4$, toluene, chlorobenzene [38]) through the treated polymer but do not influence the permeability of highly-polar CH$_3$OH [45]. The barrier properties of LDPE can be also improved under the direct fluorination: the loss of n-heptane and pentane can be reduced by a factor of 200 [46] and 100 [55], respectively. Direct fluorination was shown to decrease permeability of PVC, thermosetting resins, natural and synthetic fibers [56], polyurethane [37], low density polyethylene, polypropylene, PET [49,50]. Utilization of fluorine–oxygen mixtures can

increase the barrier effect in some cases [3,31,55]. Direct fluorination inhibits the migration of plasticizers from polymers and improves thermal aging resistance [57]. Rubber sheets used in sealing electrolytic capacitors become impermeable to paste and gas upon fluorination [58,59].

However, 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 such as –COF and –COOH and peroxy radicals on the polymer surface. Kinetics of formation and termination of those radicals, formed during fluorination of five varieties of industrially available polymers, was studied in refs. [20,25–27]. 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. At the end of fluorination, temperature of fuel tanks is around 55–65 °C. Since time interval available for termination of radicals cannot exceed 15–20 min the treatment technology should be a "dry" one. It was proposed [26,27] 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 h after removing of fluorine from the reaction vessel. Termination kinetics of radicals for the case of fluorinated HDPE (Finanthen®, density 0.949 g cm^{-3}) and temperatures 22 and 64 °C is shown in Fig. 10. Increase of temperature results in a significant increase of the termination rate. Additional treatment of fluorinated HDPE with triethylamine (radical quencher) 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 min, but in the case of absence of triethylamine, only by a factor of ∼2.
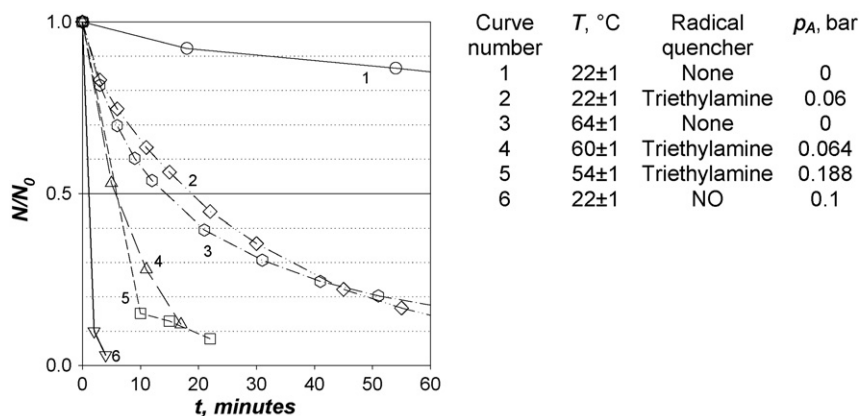

Curve number	T, °C	Radical quencher	p_A, bar
1	22±1	None	0
2	22±1	Triethylamine	0.06
3	64±1	None	0
4	60±1	Triethylamine	0.064
5	54±1	Triethylamine	0.188
6	22±1	NO	0.1

Fig. 10. Dependence of the relative amount of peroxy radicals N/N_0 in fluorinated HDPE (Finanthen®, 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.

To study the influence of treatment of freshly fluorinated
HDPE films (density 0.949 and 0.945 g cm^{-3}) with various
gases on HDPE barrier properties a set of comparative
experiments has been carried out [20,26,27]. To minimize
the amount of formed polar groups, fluorine was purified from
oxygen admixture. HDPE films were treated with undiluted
fluorine at 0.036 bar pressure and temperature $21 \pm 1\,°C$
during 125 min. Control fluorinated samples were not treated
with gaseous radical quenchers while 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
$40 \pm 0.5\,°C$. Triethylamine and nitric oxide NO were found
to be the best and most convenient 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 g cm^{-3}) by a
factor of 3.3 with respect to mixtures of 5% of methanol and
95% of petrol with respect to the case when the film were
fluorinated only but not treated additionally with triethylamine.
The same effect was obtained for the case when fluorinated
HDPE films were treated with nitric oxide NO at 0.1 bar
pressure during 10 min. It means that the post-treatment of
fluorinated HDPE with triethylamine or NO practically
eliminates negative influence of alcohol on the barrier
properties of HDPE. 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 g cm^{-3}) with triethylamine
provided the same effect as for the case of HDPE (Finanthen$^®$,
density 0.949 g 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 [27].

3.2.2.2. Membrane technologies. Polymer membranes can
be used for the separation of gas mixtures such as He–CH$_4$,
H$_2$–CH$_4$, H$_2$–CO$_2$, CO$_2$–CH$_4$, H$_2$–N$_2$, O$_2$–N$_2$, CO$_2$–H$_2$S,
CH$_4$–CO$_2$–H$_2$–He, etc. A recurrent problem is however
occurring when polymeric membranes are used: membranes
with high gas permeability have often a low separation factor
and on the contrary membranes with high separation factor
have low permeability factors (Fig. 11). Direct fluorination
results in a significant decrease of permeability of multiatomic
gases (CH$_4$, C$_2$H$_4$, etc.) as compared to diatomic and
monoatomic ones (H$_2$, He, etc.). So direct fluorination can
be used to enhance the separation factor value α of a polymeric
membrane, without any significant reduction of the perme-
ability value. For example, the gas separation value α of poly(4-
methyl-pentene-1) (PMP) membrane for a CO$_2$–H$_2$S mixture
can be increased from $\alpha = 1$ (starting membrane) to $\alpha = 4$ and
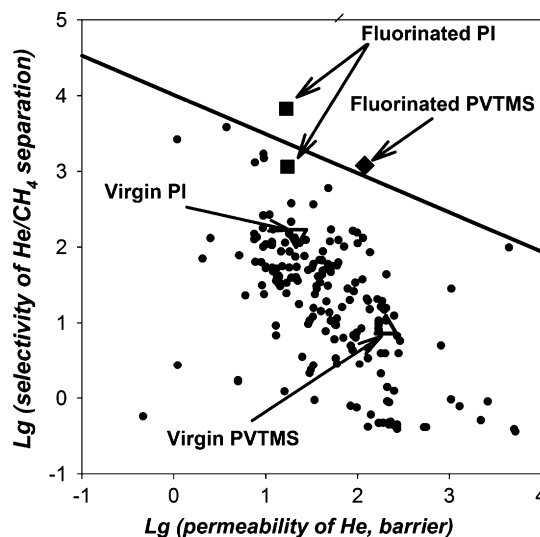moreover the permeability of CO$_2$ through the membrane is

Fig. 11. Dependence of selectivity of He/CH$_4$ mixture on He permeability
(logarithm scale). Black points: literature data on polymeric membrane materi-
als, (▽) virgin polyimide hollow fiber modules, (■) fluorinated polyimide
hollow fiber modules, (△) virgin PVTMS membrane, (◆) PVTMS membrane
treated with 40% O$_2$ + 60% F$_2$ mixture. Reproduced from [26] under permis-
sion of L'Actualite Chimique.

reduced only by a factor of 1.6 [60,61]. The value of α depends
on the thickness δ_F of the fluorinated layer and for a set of
membranes has a maximum at any δ_F value [54,55]. For
"Seragel" (polysulfone/polybutadiene block-copolymer)
homogeneous membrane (modification S-3760/3) the α value
for separation of a CO$_2$–CH$_4$ mixture continuously increases
from $\alpha = 7$ (starting membrane) to 54 when the δ_F value
increases from 0 to 1.6 μm and goes down with δ_F when the
latter is increased whereas the permeability value of CO$_2$ is
decreased by a factor 2.5–3 only when the α value reaches the
maximum value [55].

A large contribution to the modification of gas separation
properties has been made by Paul and Leroux [62–66]. They
have investigated the influence of treatment conditions
(fluorinating mixture composition, fluorination duration) on
the transport properties of polysulfone (PSF) asymmetric
membranes and films, PMP composite membranes, PVTMS
composite membranes and films and PPO composite mem-
branes. The fluorination conditions were optimized to yield an
improvement in the selectivity of the PSF membranes for the
gas pairs O$_2$–N$_2$, H$_2$–N$_2$, He–CH$_4$, H$_2$–CH$_4$ and CO$_2$–CH$_4$ with
varying decrease in the permeability of all the above gases [63–
66]. The selectivities for He, CO$_2$, Kr and Xe relative to N$_2$ and
CH$_4$ were increased upon fluorination when PVTMS mem-
brane was used, but the selectivity for the O$_2$–N$_2$ pair remained
unchanged [65]. For PPO membranes fluorination slightly
increased the selectivity of He and H$_2$ relative to N$_2$ and CH$_4$
[64]. Langsam and Anand have investigated the influence of the
treatment conditions on the gas separation properties of poly(1-
(trimethylsilyl)-propyne) (PTMSP) which has one of the
highest gas permeability coefficients among known polymers
[67,68]. But a high permeability value is associated with a
very low selectivity α value. Upon fluorination, the α values for

O_2–N_2 and He–CH_4 pairs were increased to 5.1 and 248, respectively, as compared to 1.5 and 0.41 values for the starting polymer. Similar investigations were carried out for poly(-trialkylgermylpropyne) [69]. Fluorination of PSF membrane provides hydrophilic surface properties and increases the water permeability (at 690 kPa) by a factor of 54 [70]. The α value for H_2–CH_4 and CO_2–CH_4 pairs for aromatic polyimide membranes can be increased by factors of 23 and 3.3, respectively, under fluorine treatment whereas permeability values of H_2 and CO_2 are decreased by factors of 3 and 21, respectively [71]. The α value for O_2–N_2, CO_2–CH_4 and N_2–CH_4 pairs can be increased by a factor of 2–3 upon direct fluorination of PSF, PS, polyarylate, PE, polycarbonate, ethylcellulose, styrene–acrylonitrile copolymer, poly(4-vinylanisol-4-vinylpyridine) and acrylonitrile–butadiene–styrene copolymer [72].

Direct fluorination can be used to decrease permeability of oxygen through polymer films, envelopes and bottles used for food and medicine storage and preservation. At first the permeability of oxygen can be greatly decreased by fluorination of polymers, e.g., by a factor of 16 for HDPE films [73]. Kharitonov et al. have shown that the effect of the permeability reduction can be enhanced by incorporation of oxygen into the fluorinating mixture [20,23,74–76]. The following polymers were studied: PET, PS, PVTMS, PPO and polysulfone/polybutadiene block-copolymer. Oxygen incorporation into the fluorinating mixture can significantly reduce the gas permeability for the above polymer as compared to the case where oxygen is absent. Carstens has also shown that direct fluorination of LDPE, HDPE, PP. PS and PET results in an oxygen permeability reduction by factors of 47, 8, 18, 10 and 19, respectively [49,50]. As direct fluorination varies the selectivity of separation of gas mixtures, fluorination can be used to modify polymer packagings for food storage such as modified atmosphere packaging (air in a pack is replaced by a mixture of different gases, where the proportion of each component is fixed when introduced but is not controlled during storage), controlled-atmosphere packaging (composition of the gas mixture is continuously controlled during storage) and equilibrium-modified atmosphere (the pack is flushed with the required gas mixture) [49,50]. However, –COF groups (formed due to an oxygen admixture in a commercial fluorine) are hydrolyzed by moisture: –COF + H_2O → –COOH + HF [75–77]. It is worth to mention that fluorination of polysulfone ultrafiltration membranes results in an increase of the flux and decrease of the membrane fouling rate [78].

Polymeric membranes can be used for the separation of a set of gas mixtures, such as He–CH_4, H_2–CH_4, H_2–CO_2, CO_2–CH_4, CO_2–N_2, CH_4–N_2, H_2–N_2, O_2–N_2, CO_2–H_2S, CH_4–CO_2–H_2–He, etc. As stated before, membranes with high gas permeability have often a low gas separation factor and on the contrary membranes with high separation factor have low permeability value (Fig. 11). The best membrane materials should lie at the upper right corner of Fig. 11, but at present time no materials could be synthesized, to be lying above the straight line of Fig. 11. So the following solution should be provided: to fluorinate commercially available membranes which posses high permeability with low selectivity. Direct fluorination

results in a significant decrease of permeability of large size gases (CH_4, C_2H_6, CO_2, etc.) with respect to small size gases (H_2, He, etc.). The selectivity of the membrane for (large size-small size) pairs of gases is enhanced without significant reduction of the permeability value with respect to small size molecules. The selectivity values for He/CH_4 mixture separation are shown in the Fig. 11 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.

The influence of fluorination on the separation properties of flat membranes fabricated from polyvinyltrimethylsilane (PVTMS) and hollow fiber modules fabricated from polyimide Matrimid® 5218 (PI) is illustrated in Figs. 11 and 12 [79,80]. Fluorination of hollow fiber polyimide membrane modules results in a significant (by a factor of 47 and 7, respectively) increase of selectivity for the separation of He/CH_4 and CO_2/CH_4 mixtures. The permeability of He was practically unchanged in that case. Selectivity of separation of He/CH_4 mixture depends on the treatment conditions and is increased by a factor of 100 when F_2–O_2 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 Fig. 11), which limits the correlation "permeability-selectivity" for all the synthesized previously membrane materials. It can be conclude that the direct fluorination of flat membranes and hollow fiber modules can be successfully used to enhance their gas separation properties.

Similar effect of the selectivity enhancement was observed for the case of PVTMS membranes (Fig. 12). The effect of fluorination is most remarkable for the case of He–CH_4 pair: selectivity can be enhanced by a factor of more than 100. In all the cases the loss of He permeability did not exceed 40% with
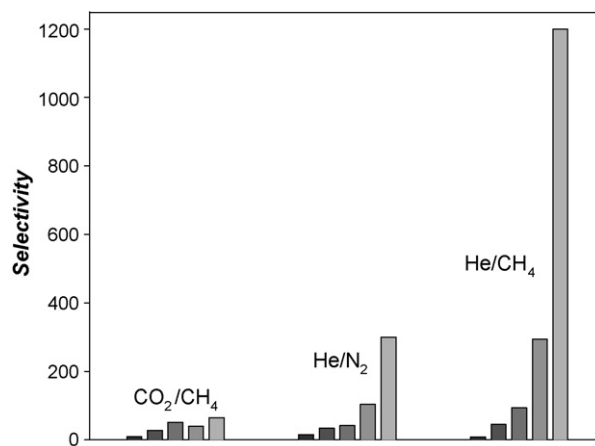

Fig. 12. Effect of treatment conditions on the selectivity of separation of CO_2/CH_4, He/N_2 and He/CH_4 mixtures. Treatment conditions (from left to right in each group at the plot): virgin PVTMS; treatment with 2% F_2 + 98% He mixture; treatment with 33% F_2 + 67% He mixture; treatment with 2% F_2 + 98% He mixture followed by a grafting of acrylonitrile; treatment with 60% F_2 + 40% O_2 mixture.

respect to the virgin membrane. Selectivity of separation of CO_2–CH_4 mixture can be increased by a factor up to 7.

Fluorinated polymer membranes can be successfully used to enhance the purification of natural gas from CO_2, 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 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.

It should be noted that the direct fluorination improves the chemical resistance of polymers. Fluorinated polystyrene and polyethyleneterephthalate cannot be dissolved in those solvents where virgin polymers can be dissolved [4,23,74,75]. So direct fluorination of polymer membranes for separation of aggressive liquids and vapours may results in improvement of their durability.

The results of the described research can be used in industry to decrease the loss of alcohol-containing petrol due to its diffusion through wall 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 CO_2, 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 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.

3.2.2.3. Adhesion and printability properties: reinforcement of polymer composites. One of the main disadvantages of polyolefins and some other polymers is a low adhesion which is due to a very low total surface energy γ and low polarity of the polymer surface (i.e. the polar component of the total surface energy γ^P is close to zero). Upon direct fluorination the polar component of the surface energy can be greatly increased [81,82]. For example, the γ^P value for PE can be increased up to 40–43 mJ m^{-2} when oxygen is introduced into the fluorinating mixture [82]. The γ^P value for PVTMS can be increased from 1.9 (starting PVTMS) up to 12.9 mJ m^{-2} upon fluorine treatment (undiluted fluorine was used) and strongly depends on treatment conditions (Fig. 13 and [11,20,24]). Direct fluorination was shown to improve adhesion of polyolefins (HDPE) [49,50,83–85], LDPE [84], ethylenevinyl acetate copolymers [86], rubber [87], polypropylene [49,50,88], polymers of aliphatic mono-1-olefins and elastomeric, resinous polymers of conjugated dienes and vinyl-substituted aromatic compounds [89], poly(arylene sulfide) [90], polyamides and polyethers [91], butadiene–styrene copolymer, PE–vinylacetate
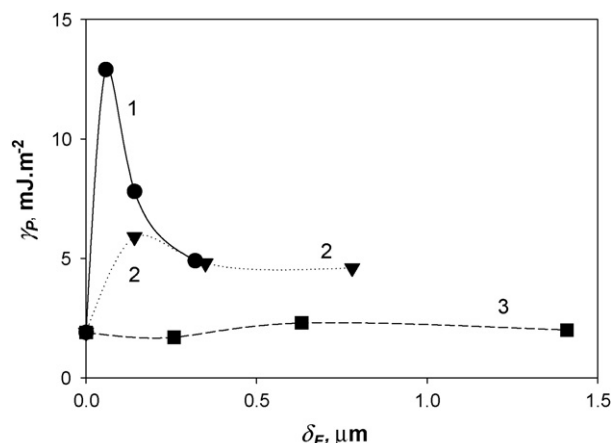

Fig. 13. Polar component γ_P of the surface energy versus thickness of fluorinated layer δ_F of PVTMS. (1–3) PVTMS films treated with undiluted fluorine at pressure 0.02, 0.08 and 0.2 bar, respectively. Treatment temperature: 294 ± 1 K.

copolymer [85] and other polymers [92]. Wettability (printability), hydrophility and hydrophobicity of polymers can also be modified [91,93,94]. A review of the influence of fluorination on the adhesion and surface energy can be found in ref. [3]. The possible commercial applications of the adhesion improvement include: enhancement of adhesion of PET cord (fabric) to rubber, improvement of paint receptivity of polymer goods, reinforcement of polymer composites, increased resistance to delamination in coated flexible films [3,49,50]. Direct fluorination of fibrous plastics was used to strengthen and reinforce composite materials, such as cementitious and metal components [95–98]. Fluorination was found to be very effective in improvement of the adhesive bonding of various polymers, such as polypropylene, poly-butyleneterephthalate and its blends, polyetheretherketone [99,100]. Authors of [101] have shown that oxyfluorination results in a good adhesion of even waterborne coatings to polypropylene and those changes of the surface properties are long-lasting. Equipment to improve adhesion of polymers by direct fluorination is described in refs. [3,102,103].

The influence of fluorination of one of the components of polymer-fiber composite can be demonstrated by the following example [104]. Short-fiber reinforced polymeric composites gain importance due to the advantages in outstanding mechanical properties, processing, and low cost. One of the most important synthetic polymeric fibers, *p*-phenylene terepthalamide (i.e. Kevlar®), is very much well known for high performance composite applications, because of its high specific strength, high modulus with a high thermal resistance and chemical inertness, and low electrical conductivity when compared to metallic or carbon glass fibers. However, the use of Kevlar® fiber for reinforcement exhibits several drawbacks. The most important of these drawbacks is a poor interfacial adhesion because of its chemical inertness and low surface energy, which affects the chemical and thermal properties of the composites. Thermal and mechanical properties of composites fabricated from Kevlar® fiber, modified by direct fluorination and oxyfluorination, and ethylene–propylene (EP) co-polymer

Table 3
First decomposition temperature, weight loss at the first decomposition temperature, tensile strength and tensile modulus of virgin and fiber-reinforced EP co-polymers

Composite	First decomposition temperature (°C)	Weight loss at first step (%)	Tensile strength (MPa)	Tensile modulus (GPa)
Virgin EP	233.0	69.2	27	0.36
EP + Kevlar	245.0	32	20	0.40
EP + fluorinated Kevlar	254.4	39	30	0.56
EP + oxyfluorinated Kevlar	269.0 (+36 °C as compared with virgin EP)	54	33 (+22%)	0.68 (+89% as compared with virgin EP)

were studied in ref. [104] (see Table 3). Kevlar® fibers were fluorinated and oxy-fluorinated by 5% F_2 + 95% He mixture (for fluorination) and 5% F_2 + 1% O_2 + 90% He + 4% N_2 (for oxyfluorination), respectively, under 0.8 bar pressure for 30 min at 17 °C. Ethylene polypropylene (in 100%) was mixed with 1.43% of original, fluorinated, and oxyfluorinated Kevlar® fibers differently in Brabender mixer with 60 rpm at 200 °C for 10 min. Then the mixtures were cured in hydraulic press at 200 °C and at 10 MPa pressure for 10 min. It was shown, that the thermal and mechanical properties of composite material based on ethylene–propylene copolymer reinforced with Kevlar® fibers can be markedly enhanced under oxyfluorination of Kevlar® fibers. Addition of only 1.4 wt% of oxyfluorinated Kevlar® fibers to ethylene–propylene copolymer results in increase of the first decomposition temperature of the composite material by 36 °C, tensile strength by 22% and tensile modulus by 89%.

3.2.2.4. Friction coefficient. Direct fluorination was found to decrease the friction coefficient of polymers [105–108]. The main attention was paid to elastomers [105–107]. It was found that direct fluorination can be applied to reduce the static and dynamic friction coefficient and to improve the wear life of elastomeric articles made of copolymers of ethylene–propylene, acrylonitrile–butadiene, vinylidene fluoride–hexafluoropropylene, tetrafluoroethylene–propylene, isopropylene–isobutylene, ethylene–methyl acrylate and of poly-(chlorobutadiene) and chlorosulfonated PE [106,107]. The modification proceeds without promoting degradation of the tensile properties of the article. According to [20,108,109] both static and dynamic friction coefficients of polypropylene films can be reduced by the direct fluorination.

3.2.2.5. Antireflecting coating, reduction of UV radiation. - Fluorinated polymers have reduced refractive indexes over 1.36–1.4 range. Also fluorinated and untreated polymer layers are separated by a very thin boundary layer (in thickness much less than one quarter of the wavelength of the visible light). So an antireflecting layer (in the visible and IR regions of spectra) can be formed on the polymer surface during the direct fluorination. For this reason fluorine partial pressure and treatment duration are chosen to form the fluorinated layer having thickness $\delta_F = \lambda/(4n_F)$, where λ is the wavelength for which the transparency should be enhanced. Enhancement of sunlight transmission by fluorine treatment has been obtained for PP, poly(acrylonitrile), PE, polyesters, polycarbonate,

poly(4-methyl-pentene-l) [110]. The influence of direct fluorination on optical properties in the visible region was studied for PS, PMMA and polycarbonate [111]. Direct fluorination can be used to produce a protecting coating which decreases the transparency of UV light through polymer articles [112].

3.2.2.6. Bioresistance improvement. The direct fluorination of polymethylmethacrilate, low density polyethylene and rubber results in improvement of their bioresistance [12,113]. Durability of polymer articles in hard climatic conditions (high temperature and humidity) can be therefore enhanced.

4. Conclusions

We have shown above with some examples that is possible to change drastically the nature of the some physical and chemical properties of various materials by tuning the nature of the fluorinated film which is formed on the surface of the carbon materials. These modifications can be obtained either by acting on the nature of the host material or on the characteristics of the fluorination conditions; direct F_2 gaseous fluorination or rf low-temperature plasma.

In the case of carbon-based materials, several physical properties can be improved [114], e.g., electrical conductivity of graphitised carbons and high-temperature treated carbon fibres; reversible capacities of lithium-ion secondary batteries with treated carbon anodes; electrical permittivity of carbon blacks, because of the formation of a fluorinated insulating layer on the surface of the particles, with a subsequent increase of the repulsion effect.

In the case of fluorinated polymers, the range of applications is very wide. Fluorinated polymer containers and bottles better fit to storage of toxic and volatile liquids and allow decreasing the loss of alcohol-containing petrol due to its diffusion through wall of automotive polymer fuel tanks. In food and medical industry fluorination of polymer film packaging results in a substantial decrease of the oxygen permeability. Hence the rate of food and medicine degradation can be decreased and the durability can be increased. In chemical and petrochemical industry fluorinated polymer membranes can be successfully used to enhance the purification of natural gas from CO_2, 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 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. Fluorination of ultrafiltration and microfiltration porous membranes results in increase of the flux, decrease of the fouling rate and durability of membranes. The direct fluorination highly improves adhesion and printability of polymer articles and thermal and mechanical properties of polymer composites. The direct fluorination results in a decrease of the friction coefficient (both static and dynamic) and in improvement of the bioresistance of polymer articles.

Acknowledgments

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