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Scientific paper

Surface Modification of Polymers Treated by Various Fluorinating Media

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Dedicated to Prof. Dr. Boris Žemva on the occasion of receiving the Zois' award for lifetime achievements.

Abstract

Fluorination processes of polymer surfaces are able to lead to drastic modifications of the surface properties without changing the bulk characteristics of the virgin material. In this paper, two types of polymers, i.e. ultrahigh molecular weight polyethylene (UHMWPE) and high density polyethylene (HDPE), are considered. The surface of these materials have been modified using two different fluorination routes, both carried out at room temperature: the direct fluorination with 10% F₂ + 90% He gaseous mixtures and the radio-frequency plasma-enhanced fluorination (PEF) using either O₂/CF₄ mixtures or c-C₄F₈. The effect of these processes on the surface of the polymer samples are compared using mostly XPS results. The different components of the C1s spectra are assigned in term of CF_x bonding, giving valuable information on the surface fluorination rate.

Keywords: F₂-gas fluorination; fluorinated rf-plasmas; UHMWPE; HDPE; surface modification; XPS; coatings

1. Introduction

Fluorination processes of polymer surfaces present many advantages. In particular, because of the high exothermicity of the involved elementary reactions, fluorination proceeds spontaneously at room temperature, which is convenient for industrial applications purposes. Fluoropolymers exhibit a set of unique properties such as high chemical and thermal stability, good barrier properties, etc.^{1–3} However a current use of fluoropolymers is restricted because of the complexity of synthesis and final high cost of the materials. Since the commercial applications of polymer items are very often defined by their surface properties, it is not necessary to use in many cases bulk fluoropolymers, and an alternative route, cheaper and more convenient, is to apply a surface treatment onto articles made of conventionally prepared polymers. Fluorination can be used as an efficient method of surface treatment, resulting in strong improvement of properties of the star-

ting polymer material, including barrier properties, adhesion, printability, gas separation properties, tribological performances with low friction coefficient, antibacterial properties, chemical resistance etc.^{4–10} Direct fluorination has many advantages when used in industry because it is a dry technology. Due to the high exothermicity of the reaction it spontaneously proceeds at room temperature, which is convenient for applications. For the majority of glassy polymers, only the upper surface layer is modified (~0.01 to several μm in thickness), and the bulk characteristics remain unchanged. Safe and reliable methods can be proposed to neutralize unused F₂ and HF end-product, by converting those gases into a solid phase (CaF₂ and NaHF₂). An important industrial development is related to the enhancement of the barrier properties of automotive polymer fuel tanks and vessels for storage of toxic and volatile liquids.^{4,5,7–12} It can be also added that, because of their very low global warming potential (GWP), reactions using gaseous F₂ have no impact on greenhouse effect.

Radiofrequency (rf) plasma technologies using fluorinated gases are also currently employed for etching or polymerization processes in microelectronics and materials sciences. Some advantages can be indeed outlined: low-temperature reaction (in many cases the treatment can be achieved at room temperature, which avoid the thermal degradation of the material), chemical modification limited to surface only (for many applications excluding enhancement of barrier properties below a few tens nanometers). These methods are able to lead to drastic modification of the surface properties without changing the bulk characteristics of the virgin material, as shown for instance in studies on high- T_C superconducting ceramics.^{13–14} The rf plasma-enhanced fluorination (PEF) of inorganic materials can be carried out with varied fluorinated gases, including NF_3 , SF_6 , F_2 , NF_3 , ClF_3 , CF_4 , CHF_3 , C_3F_8 , $\text{c-C}_4\text{F}_8$.¹⁴ Depending on the type of starting materials, the improved properties may concern wettability, adhesion, chemical stability, permeation, electrical conductivity, biocompatibility, grafting, mechanical behaviour, etc.^{5–9,11–12,15}

Two types of pristine polyethylene will be concerned in the present paper: ultrahigh molecular weight polyethylene (UHMWPE), a very prospective material to fabricate high strength fibers, and high density polyethylene (HDPE) which is a very common and cheap material used for the fabrication of car fuel tanks, bottles, etc. The former one combines high resistance to mechanical loading, low density, bio-compatibility, hydrophobicity, chemical resistance and electrical insulation. However, utilization of UHMWPE in polymer composites is restricted due to its non-polar nature. The modification of UHMWPE chemical-physical properties have been investigated depending on the type of the fluorination route, i.e. direct F_2 -gas fluorination, direct fluorination accompanied by UV irradiation, treatment with XeF_2 and by TbF_4 decomposition.¹⁶ Direct fluorination of HDPE was previously described in.¹⁷ The present study concerns the comparison of the surface modifications of UHMWPE and HDPE induced either by rf PEF fluorination or by direct F_2 -gas fluorination.

2. Experimental

2.1. Starting Polymers

UHMWPE, with $2 \cdot 10^6$ molecular weight, was prepared at the Institute of Catalysis of the Russian Academy of Sciences (Novosibirsk, Russia). The films were fabricated by hot pressing at 150–170 °C. The density of pressed UHMWPE films was measured by a conventional method and was equal to $0.933 \pm 0.001 \text{ g cm}^{-3}$. HDPE from Atofina had a density 0.949 g cm^{-3} , high load melt index 8.0g/10 min and contained ~1% of carbon black. The amount of residual double bonds was determined by IR spectroscopy to be $7 \cdot 10^{-5}$ for UHMWPE and $3 \cdot 10^{-3}$ for HDPE.

2.2. Fluorination Techniques

a) Direct F_2 -gas fluorination.

Direct fluorination process was performed at the Institute of Energy Problems of Chemical Physics (Branch) of the Russian Academy of Sciences (Russia) using 10% $\text{F}_2 + 90\%$ He mixture at 1 bar pressure in static conditions in closed stainless steel vessels (volume 100 to 500 cm^3) at room temperature. Treatment was carried out at room temperature (22 ± 2 °C). The fluorination duration was varied from 2 to 90 minutes. In the majority of experiments, NaF pellet was introduced in the reaction vessel in order to remove emitted HF by transforming it into NaHF_2 .

b) Plasma-enhanced fluorination (PEF).

rf plasma fluorination was performed at ICMCB-CNRS (Bordeaux, France). The experiments were carried out in a S.E. 80 Barrel Plasma Technology System. The gas was excited by 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 $40 \text{ m}^3 \text{ h}^{-1}$ Edwards E2M40-type pump equipped with a liquid nitrogen condenser which trapped any residual gases. Several parameters could be tuned, in particular, inlet precursor composition, e.g., the possible presence of a second gas with the fluorinated reagent, in our case O_2 . In the following we will deal only with results obtained with O_2/CF_4 and $\text{c-C}_4\text{F}_8$, because of their different behavior. Oxyfluorinated plasmas containing CF_4 (~75%) mixed with O_2 (~25%) were used in order to get a higher amount of F radicals. It has been shown that the final reaction scheme corresponds to a strong increase in the concentration of fluorine in the gas phase.¹⁴ On the other hand, $\text{c-C}_4\text{F}_8$ molecules have a totally different process: they dissociate into neutral radicals (e.g., CF_2^* , CF_3^*) and stable molecules (e.g., C_2F_4). It has been shown that CF_2^* species are the dominant CF_x^* radicals, which further are deposited onto the treated material, forming a fluorinated layer of $(\text{CF}_2)_n$ composition. Taking into account previous experiments of PEF on various types of carbon materials,^{18–20} optimized conditions could be established with the following parameters: inlet gas flow $Q = 8 \text{ ml min}^{-1}$; total pressure: $p = 300 \text{ mTorr}$; rf power: $P = 80 \text{ W}$. After the fluorination treatment, samples were generally handled and kept in a glove box under an Ar atmosphere.

2.3. Characterization Techniques

FTIR spectrometer FT-02 (Lumex, Russia) was used to record IR spectra. 100 to 500 scans at 4 cm^{-1} resolution were collected to measure one spectrum. The thickness of fluorinated layer was measured by spectroscopy in the visible region of spectrum (UV-Visible spec-

trophotometer Specord M40, Karl Ceiss Jena, Germany) as described in.^{6–12} The visible spectra of fluorinated films exhibit interference features and the distance between interference minima/maxima can be used to calculate the thickness of fluorinated layer. Surface energy (polar and dispersion components and total surface energy) was measured by the conventional Owens-Wendt; the contact angle method was applied.²¹ Three different liquids: water, formamide and ethylene glycol, were used. X-ray diffraction (XRD) patterns were measured by Philips X'Pert Pro diffractometer operating with the Cu-K α radiation.

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 mm diameter area was investigated. The sample, first prepared in a glove box, were stored under neutral gas for transport, and 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) of 1.3 eV. This procedure appeared to be the most reliable one, as previously proposed in investigations on fluorinated carbon materials (see ref.¹⁸). A good agreement between the experimental curve and the full calculated envelope was obtained in most cases, explaining in addition subtle distinctions between the relative amount of fluorinated components. After fluorination, the modifications of the surface composition of the various materials were also investigated by XPS and atomic force microscopy.

3. Results and Discussion

3. 1. Surface Modification of PE Polymers by Direct Fluorination (F₂-gas)

3. 1. 1. Physical Chemical Characteristics of the Fluorinated Layer

3. 1. 1. 1. FTIR Spectroscopy and Composition of Fluorinated Layer

FTIR spectra of fluorinated HDPE films markedly differ from the spectra of virgin films (Fig.1). Strong diffuse band appears over the region 1400–1000 cm⁻¹. That band consists of a set of separate bands defined via computer simulation: 1125, 1194, 1240 and 1146 cm⁻¹ bands which are due to absorption of C–F_x bands. Relative intensities of the bands at 1125, 1194, 1240 and 1146 cm⁻¹ are as follows: 100 : 57 : 21 : 2.5. Also a weak band at 837 cm⁻¹ can be also assigned to C–F absorption. Several weak bands originate at 1350, 1393 cm⁻¹ and 895 cm⁻¹. Two weak bands at 1866 and 1770 cm⁻¹ can be assigned to –COF and –COOH groups. Groups –COOH arise due to a partial hydrolysis of –COF groups: –COF + H₂O →

–COOH + HF. Very weak absorption around 3450–3750 cm⁻¹ can be due to absorption of hydroxyl (–OH) and absorbed HF groups, as it was shown for the case of fluorination of polyvinyltrimethylsilane.

FTIR spectra of fluorinated UHMWPE films markedly differ from the spectra of virgin films (Fig.1). A strong diffuse band appears over the region 1400–1000 cm⁻¹. This band consists of a set of separate bands: 1285 (very weak), 1187 (most strong), 1144, 1118 and 1079 cm⁻¹ which are due to absorption of C–F_x bands. Also two weak bands are observed at 836 cm⁻¹ and 894 cm⁻¹. A weak band occurs at 1396 cm⁻¹. Two weak bands at 1870 and 1770 cm⁻¹ can be assigned to –COF and –COOH groups. Groups –COOH arise from a partial hydrolysis of –COF groups as in the HDPE case. A very weak absorption over 3450–3750 cm⁻¹ can be due to absorption of hydroxyl –OH (hydrolysis of –COF) and absorbed HF groups. Computer simulation was used to calculate the to-

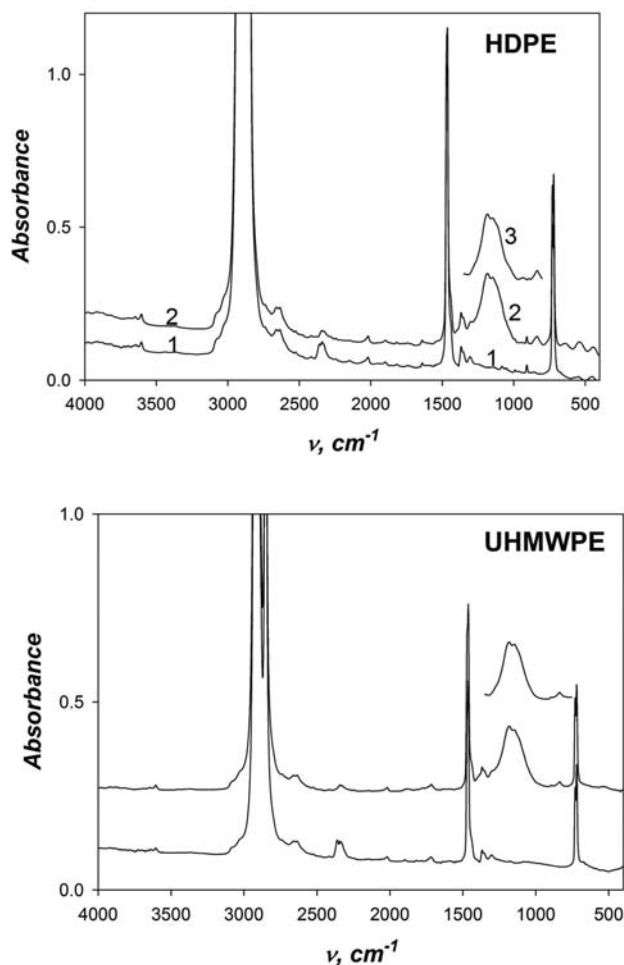


Figure 1. FTIR spectra of virgin (1) and fluorinated (2) HDPE and UHMWPE films. 3- difference spectrum, showing C–F_n (n = 1, 2 and 3) absorption bands. For both samples treatment conditions were as follows: fluorinating mixture 10%F₂ + 90% He, total mixture pressure 1 bar, treatment duration 46 minutes, treatment temperature 21 ± 2 °C.

tal area S (cm^{-1}) of bands over 900–1400 cm^{-1} range corresponding to absorption of C–F, C–F₂ and C–F₃ band. In “absorbance” mode the total amount of separate groups is proportional to the total area S of corresponding groups. Accuracy of the S value calculations can be evaluated as 5–10%. Separate bands were not extracted from a very broad diffuse band over 870–1450 cm^{-1} range because those separate bands are rather broad and are not distinctly marked. It was shown that $S = c + d \cdot t^{0.5}$ (t – fluorination duration, c and d are constant values) or, in other words, S is proportional to the δ_F value but some induction period exists. It means that the total concentration of C–F, C–F₂ and C–F₃ bonds almost does not depend on the thickness of fluorinated layer.

3. 1. 1. 2. Rate of Formation of Fluorinated Layer

Visible spectra of the fluorinated UHMWPE films exhibit well defined interference features. It can be assumed that the fluorinated films consist of layers of virgin (unmodified) polymer and fluorinated (mainly or partially) polymer which are separated by a very thin boundary (transient) layer. It was shown previously^{7,8,10} that it is the case of diffusion-controlled reaction where the rate of formation of fluorinated layer is limited by the diffusion (penetration) of fluorine through the fluorinated layer to the untreated one.

Computer simulation was used to calculate the total area S (cm^{-1}) of bands over 900–1400 cm^{-1} range corresponding to absorption of C–F, C–F₂ and C–F₃ band. In “absorbance” mode the total amount of separate groups is proportional to the total area S of corresponding groups. Accuracy of the S value calculations can be evaluated as 5–10%. Separate bands were not extracted from a very broad diffuse band over 870–1450 cm^{-1} range because those separate bands are rather broad and are not distinctly marked. It was shown that $S = c + d \cdot t^{0.5}$ (t – fluorination duration, c and d are constant values) or, in other words, S is proportional to the δ_F value but some induction period exists. It means that the total concentration of C–F, C–F₂ and C–F₃ bonds almost does not depend on the thickness of fluorinated layer.

On the basis of those data it is possible to come to a conclusion that the rate of formation of fluorinated layer is a diffusion-limited process which is limited by the rate of penetration of fluorine F₂ into untreated layer through the fluorinated layer. So at a first approach the total amount of C–F_n bonds is proportional to the δ_F value. However there is some trend of a faster increase of S with t as compared with a linear dependence. Such a deviation can be explained as follows. The main transformation of the virgin polymer into a fluorinated one takes place inside the transient reaction zone but the transformation is not complete. Then some minor post-reactions can take place inside the fluorinated layer resulting in an increase of the total amount of C–F bonds.

3. 1. 1. 3. Dependence of the Surface Energy on Treatment Conditions and Storage Duration

Surface energy (polar and dispersion components and total surface energy) was measured by the conventional Owens-Wendt method of contact angle measurement and the dependence of the changes in surface energy with storage duration in air was also investigated. Total surface energy and polar and dispersion components of fluorinated UHMWPE highly depend on the type of treatment and storage duration. The general trend is the following: the total surface energy is markedly increased (from 30 up to 45–50 mN/m) within 1–3 days after fluorination, then it decreases and reaches within 45 days a steady level around 35–42 mN/m, depending on treatment duration. Such a steady level is not markedly changed up to 120 days. It should be noted that for very short treatment durations (2 min), the increase of the polar component is more pronounced – from 10 to 41 mN/m within three days after fluorination, but then starts to decrease and reaches steady level around 21–26 mN/m which is not practically changed over 14–120 days storage.

It can be quoted that fluorination of poly(ethylene-*alt*-tetrafluoroethylene) copolymer into PTFE was recently characterized using Raman spectroscopy, although these materials strongly differ from HFPE and UHMWPE.²²

3. 1. 1. 4. Influence of Fluorination on UHMWPE Surface Energy

Surface energy (polar and dispersion components and total surface energy) of virgin and fluorinated UHMWPE were evaluated by the Owens-Wendt method of contact angle measurement.²¹ Polymer films were treated with 10% F₂ + 90% He mixture at total pressure 1 bar at temperature 24 ± 2 °C. Dependence of the surface energy on storage duration in air was also investigated. The results are shown in the Figure 2. Data for treatment durations of 21 and 46 minutes are not shown in order not to overload the figures. It is evident that the total surface energy and its polar and dispersion components highly depend on the type of treatment and storage duration. The total surface energy is markedly increased (from 30 up to 45–50 mN/m) within 1–3 days after fluorination, then it decreases and reaches a steady level around 35–42 mN/m within 45 days, depending on treatment duration. Such a steady level is not markedly changed up to 120 days. For a very short treatment duration (2min) the increase of the polar component is more pronounced – from 10 to 41 mN/m within three days after fluorination, but then starts to decrease and reaches steady level around 21–26 mN/m which is not practically changed over 14–120 days storage. For other treatment durations the steady level of the polar component also exceeds the value of the virgin polymer and is close to 16–19 mN/m after 14–120 days storage, except for 46–90 min treatments where the polar component drops practically to its initial value after

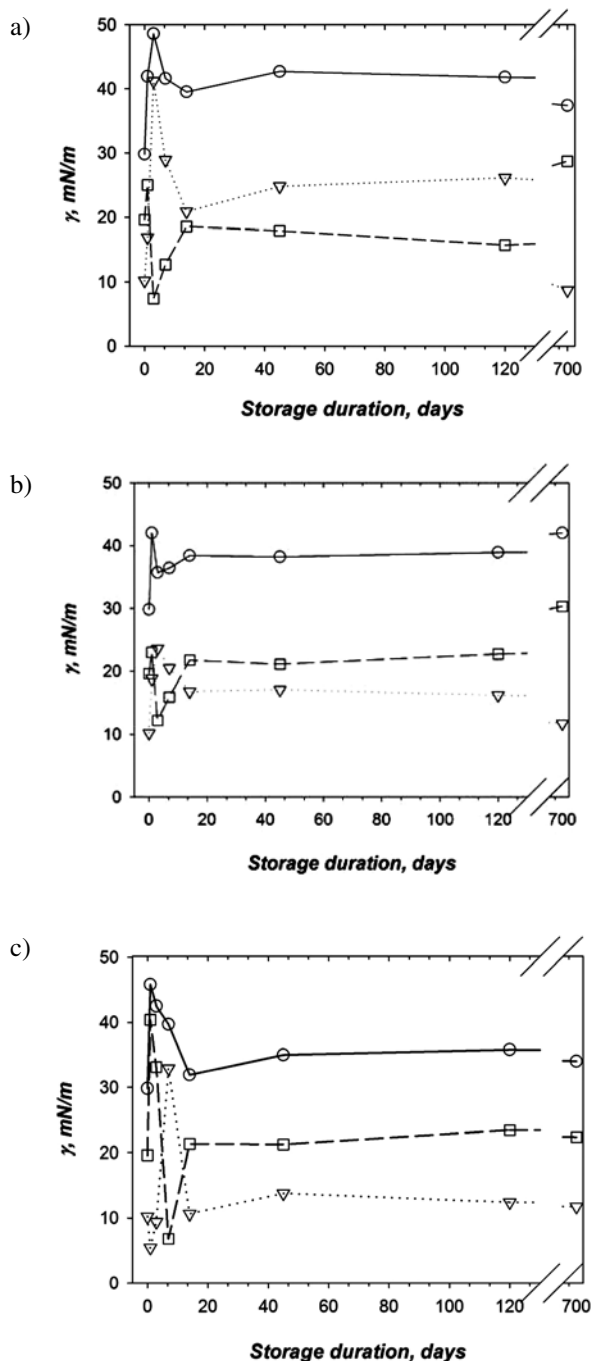


Figure 2. Total surface energy γ (circles \circ), polar component γ^p (triangles ∇) and dispersion component γ^d (squares \square) vs storage duration of fluorinated UHMWPE treated with 10%F₂ + 90% He mixture at 24 °C during 2 (a), 6 (b) and 90 (c) minutes.

45–120 days storage. The dispersion component is increased from 20 mN/m up to 25–23 mN/m within the first day for short treatment durations (2 and 6 minutes) and up to 40–45 mN/m for longer treatment durations (21–90 min). After 7 days storage, this component quickly decreases to a minimum well below its initial value, but after 14 days a value more or less close to the initial value

is reached and remains unchanged up to 120 days storage.

3. 1. 2. Determination of Surface Composition by XPS

Surface composition of F₂-treated polyethylene samples are given in Table 1 and illustrate the large amount of fluorine present on the utmost surface. In order to know the penetration depth of fluorine, the sample was etched by an Ar beam and the chemical composition was measured by XPS: a 20 nm depth can be evaluated for fluorine. The surface characteristics of two types of PE have been compared. For both types of materials, the amount of surface fluorine increases with the fluorination duration and in the same time, the amount of oxygen diminishes.²³ It can be assumed that the oxygen level in the starting materials is due to the fabrication process: hot pressing at 150–170 °C in air, where some oxidation could take place. On the other hand fluorination treatments with F₂-gas have a highly improving effect (Table 1). This effect is further increased when O₂ + CF₄ PEF is performed (see Table 3), because of a large amount of very reactive F radicals which are created under these conditions.

Most information about the type of C–F bonding are obtained through fitted C1s envelopes which are given in Fig. 3 for virgin and F₂-treated (2 and 90min) samples. In the virgin materials, the contributions of non-functionalized sp² and sp³ C atoms occur at lower binding energies (BE). The asymmetric shoulder toward higher BEs could correspond to surface defects, C–H, and C–O groups. After fluorination, the position of the components relative to nonfluorinated C atoms remains unchanged, but other numerous contributions occur at higher BEs. The C1s envelopes have been fitted using a method proposed for fluorinated C-based materials.¹⁸ The assignment of the different components is given in Table 2.

Table 2. Assignment of the XPS C1s components.

Chemical Bond	Shift (eV) relative to the CH _n component at 284.5eV
CH _n	–
<u>CH</u> ₂ –CHF	0.7–1.1
<u>CH</u> ₂ –CF ₂	2.0
<u>CHF</u> –CH ₂	3.0–3.5
CHF –CHF	4.5
<u>CHF</u> –CF ₂	4.5
CF _x – <u>CF</u> –CF _x (x,x' = 2,3)	5.3–5.5
<u>CF</u> ₂ –CH ₂	6.2–6.8
<u>CF</u> ₂ –CHF	7.8
CF ₂ –CF ₂	9.1
<u>CF</u> ₃ –CF _x	9.1

The components appearing for 285 < Eb (eV) < 287 can be assigned to an inductive effect arising from the pre-

Table 1. XPS surface analysis (atomic %) of F₂-treated HDPE and UHMWPE. [X-ray source: non-monochromatized Mg Ep = 20 eV; Scofield correction; relative error: 5–10%].

Origin of PE sample	Concentration, atomic %				
	C	O	F	N	Others elements
HDPE (pristine)	89.0	8.9	–	–	Si <1
HDPE (treatment with 10% F ₂ + 90% He mixture during 2 min)	47.0	6.4	44.1	0.6	Na :1.9
HDPE (treatment with 10% F ₂ + 90% He mixture during 90 min)	42.4	4.4	53.1	–	–
UHMWPE (pristine)	88.3	7.6	–	2.9	Ca, Na <1
UHMWPE ((treatment with 10% F ₂ + 90% He mixture during 2 min)	43.0	7.0	50.0	–	Na <1
UHMWPE ((treatment with 10% F ₂ + 90% He mixture during 90 min)	40.6	4.4	55.0	–	–

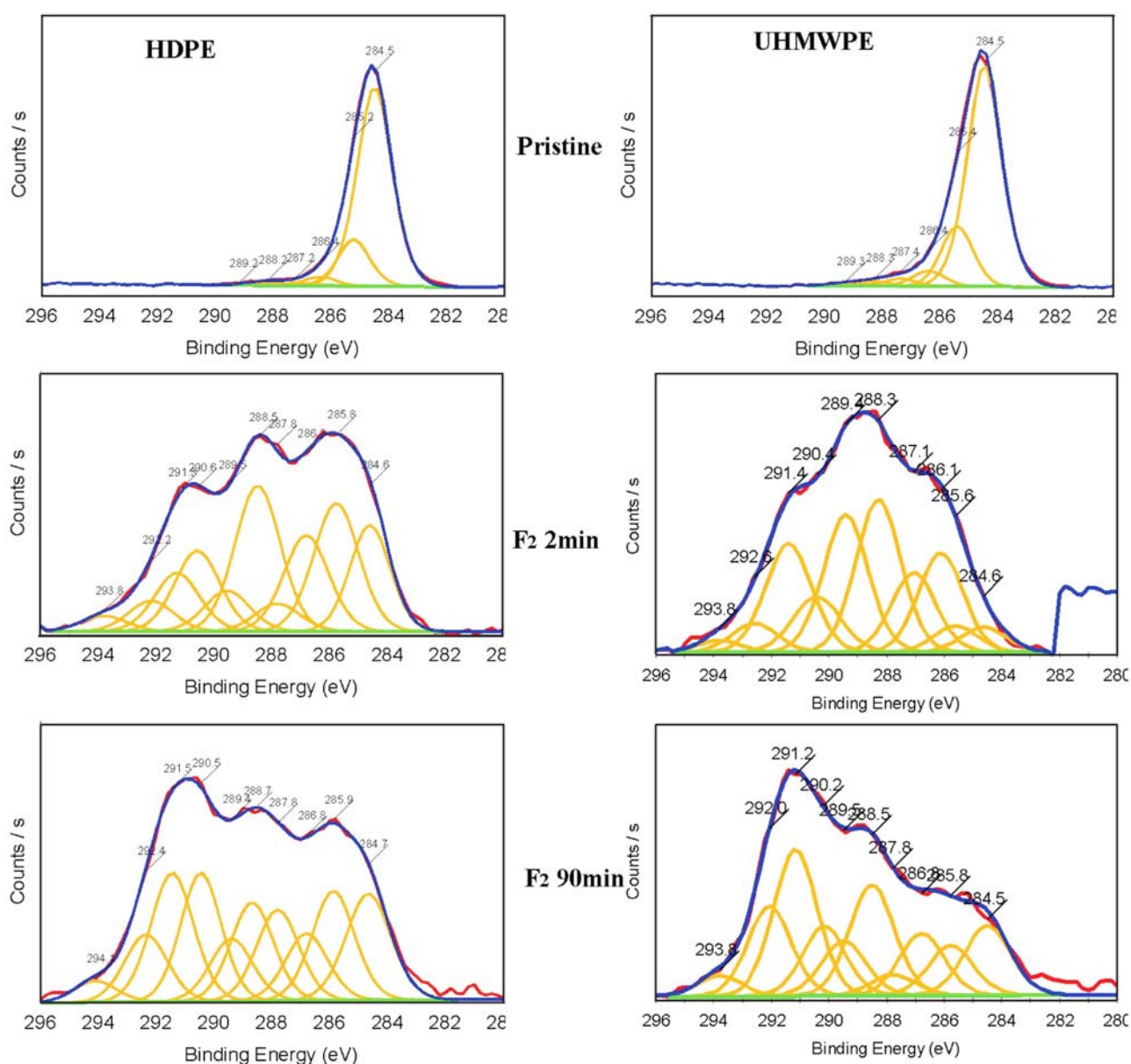


Figure 3. Fitted C1s XPS spectra of virgin and treated with 10%F₂- + 90% He mixture HDPE and UHMWPE samples (treatment duration was equal to 2 and 90 min).

sence of fluorinated C atoms: they correspond to C atoms that are not directly bound to F atoms, but that are first neighbours of CF_n groups. The bonds located at $\text{BE} > 288$ eV can be assigned to C atoms covalently bound to F atoms, as confirmed by the position of F1s maximum. If we take the same assignment procedure as previously used, the maximum observed around 291 eV for 90 min F_2 fluorinations can be assigned to CF_2 groups with first C neighbours bound to one F atom, for instance $\text{CF}_2\text{-CHF}$ groups. Another feature of the spectrum which is consistent with a strong increase of surface fluorination for 90min fluorination durations is the presence of two more contributions at higher BEs, corresponding respectively to PTFE-type groups $\text{CF}_2\text{-CF}_2$ at 292 eV, or at ~ 294 eV to CF_3 groups located at the border of the polymer domains or on lattice defects.

In the case of the F1s spectra, the value of the main component at ~ 688 eV corresponds to $\text{CF}_2\text{-CH}_2$, or CHF-CF_2 units. At lower BE the CHF-CHF component is weaker. Further component at higher BEs can be assigned to perfluorinated CF_n groups, in particular PTFE-like $\text{CF}_2\text{-CF}_2$ units and terminal CF_3 groups. The thickness of these highly fluorinated layers has been evaluated to less than 20 nm for both fluorination conditions.

During the direct fluorination of polymers some cleavage can take place when undiluted fluorine is used at high pressure (close to 1 atm) But the use of diluted fluorine mixtures lowers the level of polymer chains destruction.²⁴ Usually both cleavage and crosslinking of polymer chains take place, but it was shown previously²⁵ that in polystyrene and poly(ethylene terephthalate) treated with fluorine, amount of cross links markedly exceeds amount of cleavages. Unfortunately, the comparison of melt indexes of virgin and fluorinated PE cannot be carried out in our case because the thickness (and respectively mass) of fluorinated layer for all the samples is less than 1% with respect to the total thickness of polymer samples and the total mass of fluorinated polymer does not exceed several mg.

3. 2. Surface Modification of PE Polymers by rf Plasma-enhanced Fluorination (PEF)

In a first step the results obtained with $\text{O}_2 + \text{CF}_4$ rf-plasma treatments have been compared with F_2 -gas fluorination, since in these plasma conditions, F^\bullet radicals are the major species which are formed during the decomposition process.¹⁴ The experiments have been carried out for 1h at room temperature on both HDPE and UHMWPE virgin samples. Surface composition (atomic %) of $\text{O}_2 + \text{CF}_4$ rf-plasma PE treated samples are given in Table 3. The important level of surface fluorination is accounted by the high values of F %, together with the decrease of the oxygen content. Fitted C1s are compared in Fig. 4 for 1h $\text{O}_2 + \text{CF}_4$ PEF treated HDPE and UHMWPE samples. The C1s envelopes exhibit one maximum centered at

292eV, together with a contribution of pristine carbon species at 284.5 eV.

When compared with the F_2 -fluorinated samples (Fig. 3), in which a wide variety of components were observed, it appears that the plasma-treatment mostly yields the formation of fluorinated species with main compositions $\text{CF}_2\text{-CHF}$ and $\text{CF}_2\text{-CF}_2$. The presence of -CHF- monofluorinated groups should be reinforced by the presence of oxygen in the fluorinating mixture. F1s envelope can be fitted into 2 components, the shape of the peak depending on the ratio of CF_n contributions. When the surface is mostly composed of CF_2 groups at $\text{C1s} = 292$ eV, the F1s peak at 687eV becomes indeed the majority component.

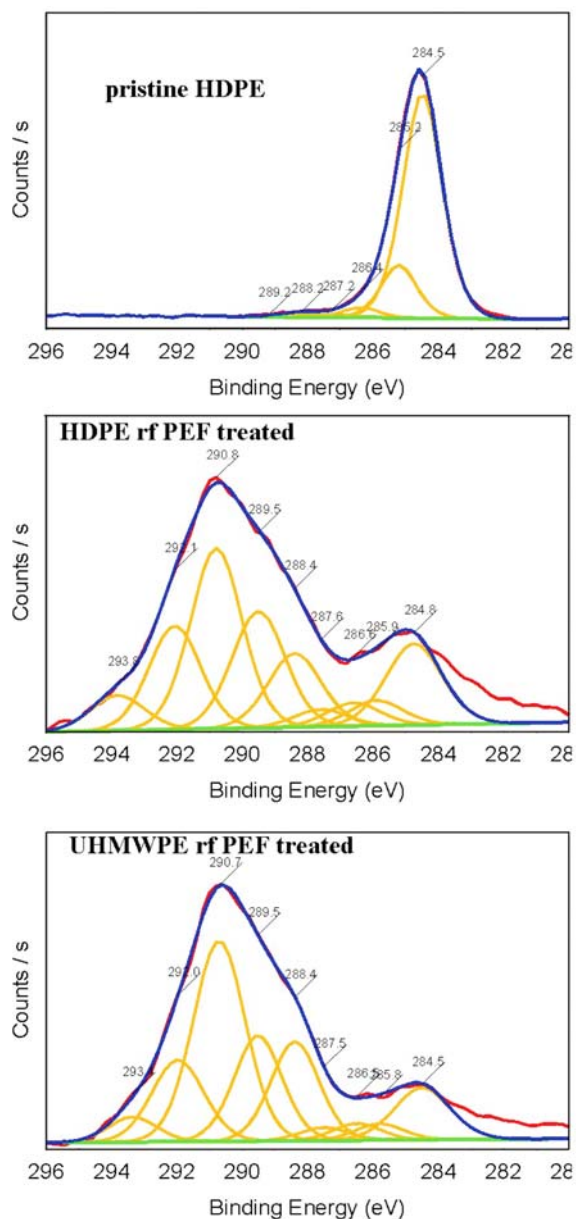
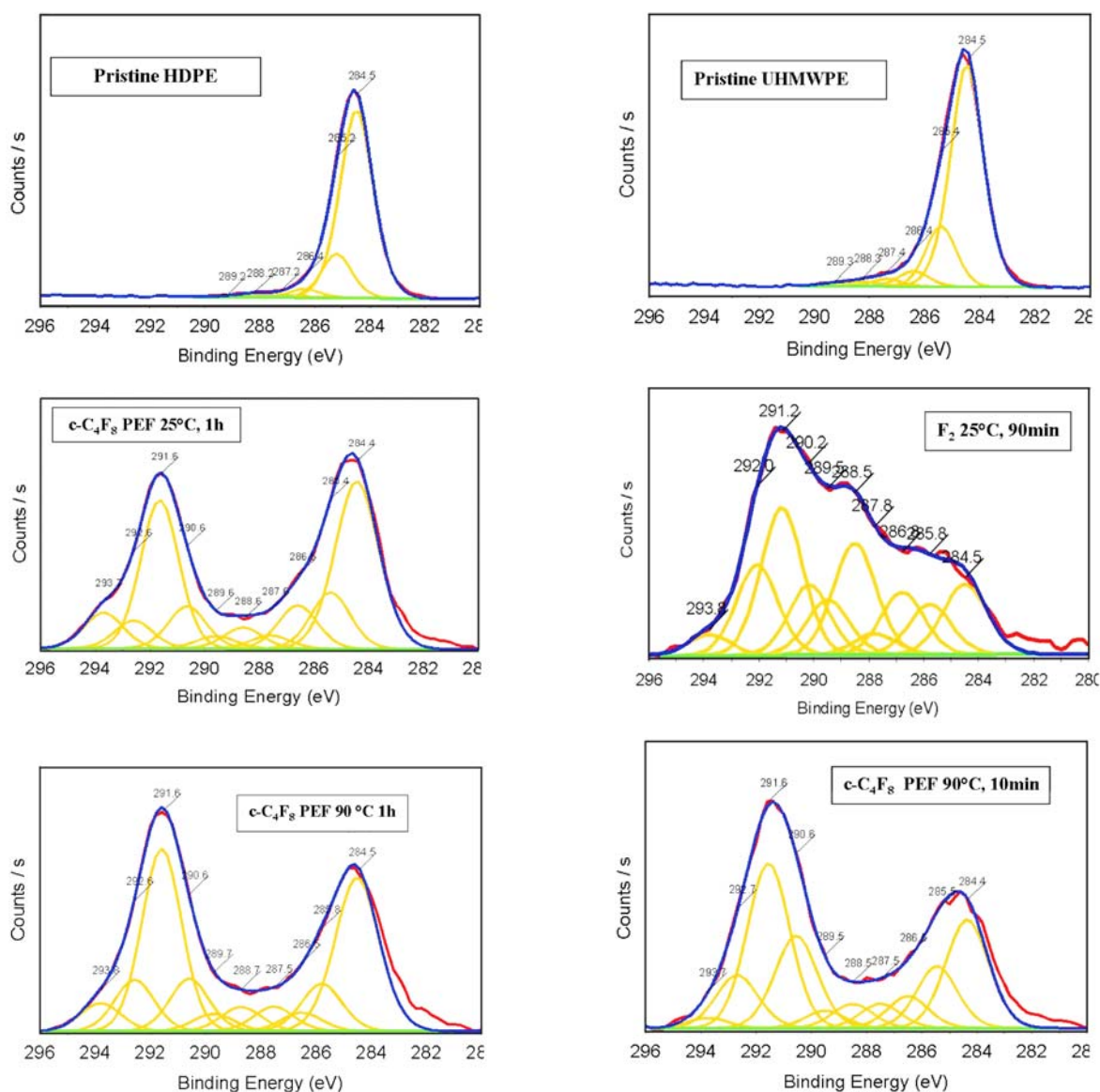


Figure 4. C1s XPS spectra of HDPE and UHMWPE samples rf PEF treated (1h, 25 °C) using $\text{O}_2 + \text{CF}_4$ mixtures, illustrating the formation of highly fluorinated surface

Table 3. Surface composition (at.%) of rf-PEF treated polyethylene samples.

Treatment conditions (fluorination duration and temperature)	C	O	F
HDPE (pristine)	89.0	8.9	–
HDPE (O ₂ + CF ₄ PEF, 1h, 25 °C)	32.6	1.7	65.6
HDPE (O ₂ + CF ₄ PEF, 1h, 90 °C)	30.6	2.4	67.0
HDPE (c-C ₄ F ₈ PEF, 1h, 25 °C)	38.3	3.3	58.4
HDPE (c-C ₄ F ₈ PEF, 1h, 90 °C)	35.1	3.3	61.6
UHMWPE (pristine)	88.3	7.6	–
UHMWPE (O ₂ + CF ₄ PEF, 1h, 25 °C)	31.0	1.2	67.8
UHMWPE (O ₂ + CF ₄ PEF, 1h, 90 °C)	38.0	1.3	60.7
UHMWPE (c-C ₄ F ₈ PEF, 1h, 25 °C)	40.9	7.0	52.1
UHMWPE (c-C ₄ F ₈ PEF, 1h, 90 °C)	33.3	2.4	64.3

Concerning c-C₄F₈ gas rf-plasma, it has been shown that the treatment leads mostly to a deposition of (CF₂)_n species.^{26,27} Table 3 illustrates the surface composition (at.%) of c-C₄F₈ PEF-treated HDPE and UHMWPE samples. The C1s envelope of the c-C₄F₈ plasma treated polymers is clearly composed of two components: the one of C–H pristine bonds and a component at 292eV, which can be clearly assigned to CF₂–CF₂ groups, accounting for a deposition of PTFE-type species. By tuning the experimental conditions, it is possible to get onto the surface mostly the latter species as shown in Fig.5 for both HDPE and UHMWPE samples. The components arising from pristine C species at 284.5 eV at room temperature PEF are decreased in 90 °C conditions (Fig. 5a). Fig. 5b compares F₂-gas treatment with c-C₄F₈ rf-plasma treatment of

**Figure 5.** Fitted C1s XPS spectra illustrating the deposition of (CF₂)_n species ^{a)} onto HDPE sample after c-C₄F₈-PEF treatments (1h at 25 and 90 °C), ^{b)} onto UHMWPE sample after either F₂-gas fluorination (90min at 25 °C), or c-C₄F₈-PEF treatment (10 min at 90 °C).

an UHMWPE sample. Using the plasma route, the surface of the polymer sample is fully coated with a “Teflon –like” layer, composed of $\text{CF}_2\text{-CF}_2$ groups. Whereas F_2 treatment the surface leads to a large variety of CF_x components, CF_2 groups are mostly present at the surface after the PEF treatment. By coupling these two fluorination techniques, it is therefore possible to form fluorinated layers, each of 10–20 nm thickness, with different and successive compositions at the surface of the pristine polymer sample.

4. Conclusions

The outmost surface of HDPE and UHMWPE polymers can be conveniently modified using two different fluorination routes, both carried out at room temperature: rf plasmas with fluorinated gases and the direct fluorination with F_2 diluted in He-gas. In the PEF case, drastic differences are observed depending on the type of reactive gases, that is O_2/CF_4 mixtures or $\text{c-C}_4\text{F}_8$. Whereas the use of O_2/CF_4 mixtures leads to a large variety of CF_x ($x = 1$ to 3) species present at the surface, a “Teflon –like” layer, composed of $\text{CF}_2\text{-CF}_2$ groups, is deposited onto the surface of the materials when using $\text{c-C}_4\text{F}_8$ rf plasmas. The two types of fluorination routes, that is direct F_2 -gas and fluorinated plasmas, can be conveniently coupled, and the treatment by a $\text{c-C}_4\text{F}_8$ rf-plasma of a HDPE sample previously fluorinated by F_2 -gas, shows that it is possible to form at the surface of the polymer sample successive fluorinated layers, each of 10–20 nm in thickness, with different compositions. In the case of the direct fluorination, the physical chemical modifications of the surface layers have been characterized using FTIR and visible spectroscopy, atomic force microscopy, XRD, XPS and surface energy measurement. From the study of the visible spectra a diffusion-controlled mechanism of formation of fluorinated layer has been confirmed. The dependence of the surface energy values on storage duration has brought information about the stability of the treated films in air. The surface compositions have been deduced from XPS results. The chemical composition, texture and the roughness of the polymer surface strongly depend on the treatment method and conditions. The composition of the fluorinated polymers was measured with depth when the films were etched by argon beam. It was shown that the fluorine concentration depends on the depth from the polymer surface.

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Povzetek

Proces fluoriranja površine polimera lahko vodi do znatnih sprememb na površini, brez da bi se spremenile osnovne karakteristike izhodnega materiala. V članku obravnavamo dva tipa materialov: ultra visoko molekularni polietilen (UHMWPE) in polietilen z visoko gostoto (HDPE). Za modifikacijo površine materialov smo uporabili dva postopka fluoriranja, ki sta potekala pri sobni temperaturi: direktno fluoriranje z mešanico plinov 10 % F₂ in 90 % He in fluoriranje z radiofrekvenčno plazmo, pri katerem smo uporabili mešanico O₂/CF₄ oziroma c-C₄F₈. Učinke procesov na površino uporabljenih materialov smo primerjali z uporabo rezultatov analiz XPS. Različne komponente C1s spektrov so opisane v povezavi CF_x iz česar lahko sklepamo o stopnji fluoriranja površine.