

Modification of Ultra-High-Molecular Weight Polyethylene by Various Fluorinating Routes

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ABSTRACT: Chemical–physical properties of ultra-high-molecular weight polyethylene (UHMWPE) treated by direct fluorination, direct fluorination accompanied with UV irradiation, by XeF₂ and by TbF₄, were tested by FTIR spectroscopy, visible spectroscopy, ¹⁹F and ¹³C NMR, scanning electron microscopy, XRD, and EPR. Surface energy measurements were carried out. The direct fluorination of UHMWPE is a diffusion-controlled process, but treatment with XeF₂ is a kinetically controlled one. Direct fluorination and direct fluorination accompanied with UV irradiation results mainly in a formation of –CF₂– groups. On the contrary, –CHF– groups are prevailing in UHMWPE treated with XeF₂ and TbF₄.

Surface texture of UHMWPE treated with XeF₂ and with F₂ is quite different. Direct fluorination results in a higher polarity of the polymer surface when compared with treatment with XeF₂. For the case of direct fluorination, both long-lived peroxy and fluoroalkylradicals are formed. For the case of treatment with XeF₂, only fluoroalkylradicals were detected. © 2011 Wiley Periodicals, Inc. *J Polym Sci Part A: Polym Chem* 49: 3559–3573, 2011

KEYWORDS: fluorination; functionalization of polymers; halogenated; hydrophilic polymers; modification; ultra-high-molecular-weight polyethylene

INTRODUCTION Commonly used polymers not only have many advantages, such as low cost and processability, but also have a lot of disadvantages (often poor adhesion, poor printability and barrier properties, low chemical resistance, etc.). It is possible to fabricate the whole article from specialty polymers, for example, fluorine-containing polymers, which have improved commercial properties. Fluorinated polymers have a set of unique properties such as enhanced chemical stability, thermal stability, good barrier properties, and so on.^{1–18} However, practical use of specially synthesized polymers, such as fluorine-containing polymers, is restricted due to their high cost and complexity of synthesis. For example, ultra-high-molecular weight polyethylene (UHMWPE) is a very promising material to fabricate fibers combining high resistance to mechanical loading, low density, biocompatibility, chemical resistance, and electrical insulation. Industrial applications are highly developed, particularly in domains such as sport, biomedical prosthesis, and ballistic protection. However, application of these fibers as reinforcing materials

for composite applications remains limited due to its nonpolar nature, which causes the difficulty to obtain strong interactions with polymeric matrices. As a result, the constitutive fibers are not able satisfactorily to transmit the mechanical stresses imposed on the composite material. Moreover, due to a low polarity, UHMWPE has a very bad printability.

Very often application properties of polymer articles and materials are defined mainly by their surface properties. Hence, it is not necessary to fabricate articles from fluoropolymers but simpler, cheaper and more convenient to apply a surface treatment of articles made from commonly used polymers. In this case, the direct fluorination can be effectively used. Direct fluorination of polymers is a heterogeneous reaction of gaseous F₂ and its mixtures with a polymer surface. This is a method of the surface modification: for majority of glassy polymers only upper surface layer is modified (~0.01–10 μm in thickness depending on application area), but the bulk properties remain unchanged. As fluorination is one of the most effective chemical methods to

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TABLE 1 Concentration of Double Bonds and $-\text{CH}_3$ Groups in the Virgin UHMWPE

<i>Trans</i> -vinylene $-\text{CH}=\text{CH}-$	Relative Concentration of Residual Double Bonds with Respect to Amount of Moles of Elemental Units of Polymer Chain				Total Relative Concentration of Double Bonds	Amount of $-\text{CH}_3$ Groups per 1000 Carbon Atoms
	Vinylene $-\text{CH}=\text{CH}_2$	Vinylidene $\text{R}_1\text{R}_2\text{C}=\text{CH}_2$	Conjugated Diene $-\text{CH}=\text{CH}-\text{CH}=\text{CH}-$			
0	5.8×10^{-5}	0.88×10^{-5}	0.48×10^{-5}		7.16×10^{-5}	<0.01

modify and control physicochemical properties of polymers over a wide range, this process became an important tool of great interest. Direct fluorination has many advantages when used in industry. Because of a high exothermicity of the main elementary stages, fluorination proceeds spontaneously at room temperature sufficient for industrial applications rate. Direct fluorination is a dry technology. 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. These features of the direct fluorination initiated its wide industrial utilization to enhance barrier properties of automotive polymer fuel tanks and vessels for storage of toxic and volatile liquids, to enhance gas separation properties of polymer membranes, and to enhance adhesion properties and printability of polymer articles,^{1–11} and also friction coefficient can be reduced, and antibacterial properties and chemical resistance can be improved. Fluorination of UHMWPE fibers resulted in a marked reinforcement of low-density polyethylene-UHMWPE fibers composite.¹⁵

In the current research, various fluorination routes were applied to modify different physical–chemical properties of UHMWPE. It will be shown below that chemical composition, surface texture, and other properties of fluorinated UHMWPE depend on the type of fluorination route.

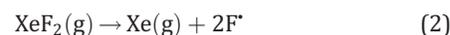
EXPERIMENTAL

Four fluorination routes were applied to fluorinate UHMWPE. Direct fluorination process using gaseous fluorine-containing mixtures and direct fluorination assisted with simultaneous UV irradiation (maximum of UV radiation from the eximer lamp practically coincided with the maximum of F_2 absorption) was performed in static conditions in closed stainless steel vessels at room temperature. Fluorination mixtures contained fluorine, helium, and oxygen. Fluorine concentration in a gaseous mixture was varied over 1–100% range. Mixtures of 10% F_2 + 90 % O_2 and F_2 -He- O_2 mixtures were used for fluorination. The fluorination duration was varied over 1 min–1 month range. In majority of the experiments, NaF pellet was introduced in a reaction vessel to remove emitted HF ($\text{NaF} + \text{HF} \rightarrow \text{NaHF}_2$). Gaseous fluorine and He had purity better than 99.9% (the main impurity was oxygen) and 99.999%, respectively. Fluorination with TbF_4 (synthesized from TbF_3 (Aldrich, 99.9%) in pure F_2 gas at 500 °C during 12 h) was performed in double-compartment chamber.^{16,17} When TbF_4 was heated to 420–500 °C, it decomposed according to the reaction



Polymer samples were placed at the second compartment, which was cooled from outside by water, so the temperature of a polymer was close to room temperature.

Fluorination using gaseous XeF_2 was performed due to the equilibrium $\text{XeF}_2(\text{s}) \rightleftharpoons \text{XeF}_2(\text{g})$.^{13,14} Xenon difluoride could be easily decomposed on the polymer surface and inside it during heating (and even at room temperature) according to the equation:



Moreover, as the vapor pressure is low at room temperature (3.8 mmHg), heating allows the XeF_2 partial pressure to be increased, and the reactivity with polymer may be then improved. Xenon difluoride is a colorless solid at room temperature, and its manipulation needs a dry atmosphere in order to prevent decomposition and sublimation. A stainless steel reactor with a capacity of 100 mL was used for the fluorination by XeF_2 . Polymer and XeF_2 were placed in a glove box under argon atmosphere. The reactor was then stored at a constant temperature during an appropriate time.

UHMWPE (molecular weight 2×10^6) was supplied by the Institute of Catalysis of the Russian Academy of Sciences (Novosibirsk, Russia). UHMWPE films were fabricated by hot pressing at 160–180 °C. Density of pressed UHMWPE films was measured by a following conventional method. Polymer film was immersed into the water- CaCl_2 solution which density was gradually changed. When the film reaches a state of weightlessness (i.e., does not go down and does not come to the surface), the density of the film is equal to the density of solution. It was found that the density of virgin UHMWPE was equal to $0.933 \pm 0.001 \text{ g cm}^{-3}$. The amount of residual double bonds and $-\text{CH}_3$ groups was determined by infrared spectroscopy^{18–20} (see Table 1). Concentrations of double bonds and $-\text{CH}_3$ groups in UHMWPE are much smaller than ones when compared with other polyethylenes.²¹

IR spectra were measured by FTIR spectrometers FT-02 (Lumex, Russia) and Nicolet 5700 (Thermo Electron). One hundred to five hundred scans at 4 cm^{-1} resolution were collected to measure one spectrum. IR spectra were processed by GRAMS software. EPR spectra were measured by EPR-21 spectrometer (USSR) and X band Bruker EMX spectrometer (France) operating at 9.653 GHz at room temperature. Diphenylpicrylhydrazyl (DPPH) was used to calibrate

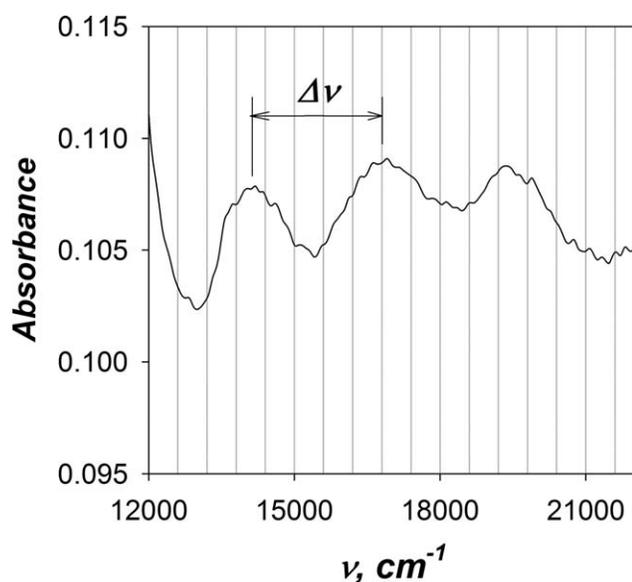


FIGURE 1 Spectrum of the fluorine treated UHMWPE film. T (%), transmission; ν (cm^{-1}), wavenumber. Treatment conditions: undiluted fluorine pressure was equal to 0.1 bar, treatment duration 6 h, treatment temperature 19 °C.

the resonance frequency ($g \approx 2.0036 \pm 0.0002$). Data processing and simulations were performed using EPR-8K (Laboratory of Molecular Biophysics, National Institute of Environmental Health Sciences, NC), Bruker WIN-EPR, and SimFonia softwares. Nitroxy radical standard was used to calibrate the EPR spectrometer sensitivity. Thickness of fluorinated layer was measured by applying spectroscopy in the visible region of spectrum (UV-Visible spectrophotometer Specord M40, Karl Ceiss Jena, Germany, was used) as described in refs. 5–9. 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 (see Fig. 1). To measure the surface energy (polar and dispersion components and the total surface energy), a conventional method of contact angle measurement was applied.^{22,23} Three liquids, water, formamide, and ethyleneglycol, were used for this purpose. X-ray diffraction (XRD) patterns were measured by Philips X'Pert Pro diffractometer operating with the Cu- K_{α} radiation. NMR experiments were carried out with both Bruker Advance spectrometer (working frequency of 282.2 MHz for ^{19}F) and a Tecmag spectrometer (working frequencies for ^{13}C and ^{19}F were equal to 125.81 and 470.74 MHz, respectively). A special cross-polarization/MAS NMR probe with fluorine decoupling on a 2.5-mm rotor was applied. The $^{19}\text{F} \rightarrow ^{13}\text{C}$ match was optimized on PTFE. For ^{19}F MAS spectra, a simple sequence was used with a single $\pi/2$ pulse duration of 5.5 μs . Two magic angle spinning probes operating with 4- and 2.5-mm rotors were used for 14 and 30 kHz spinning rates, respectively. For MAS spectra, a simple sequence was performed with a single $\pi/2$ pulse length of 4 and 3.5 μs for ^{19}F and ^{13}C , respectively. Therecycle times were equal to 5 s for ^{19}F and CP spectra. ^{19}F chemical shifts were externally referenced to CF_3COOH and were referenced with respect to

CFCl_3 ($\delta_{\text{CF}_3\text{COOH}} = -78.5$ ppm vs. δ_{CFCl_3}). ^{13}C chemical shifts were referenced to tetramethylsilane (TMS). Micrographs were recorded by ZEISS Supra 55VP scanning electron microscope, using secondary electron detector (Everhart-Thornley detector). Specimens were prepared by sticking polymer films on the surface of an adhesive carbon film. The energy of electron beam was over 0.5–2.5 keV range.

RESULTS AND DISCUSSION

Rate of Formation of Fluorinated Layer on the Polymer Surface

Visible spectra of all the films modified by both the direct fluorination and the direct fluorination accompanied with UV irradiation exhibit well-defined interference features (Fig. 1). Based on such features, it is possible to come to a conclusion that the fluorinated films consist of layers of virgin (unmodified) and fluorinated (mainly or partially) polymers, which are separated by a very thin boundary (transient) layer.^{5–9,11,21} The main chemical transformations take place just inside this layer. Its thickness δ_B can be evaluated as $\delta_B \ll 0.1 \mu\text{m}$. The thickness δ_F of fluorinated layer can be calculated via following formulae:^{5–10}

$$\delta_F = (2 \cdot n_F \cdot \Delta\nu)^{-1} \quad (3)$$

where $\Delta\nu$ is the distance between two neighboring interference minima or maxima as shown in Figure 1, n_F is the refraction index of fluorinated layer. Usually, $n_F = 1.40 \pm 0.04$ as was shown in our earlier works.^{5–9}

Results of the measurements of the thickness of a fluorinated layer δ_F are shown in the Figure 2. It is evident that

$$\delta_F = At^{0.5} \quad (4)$$

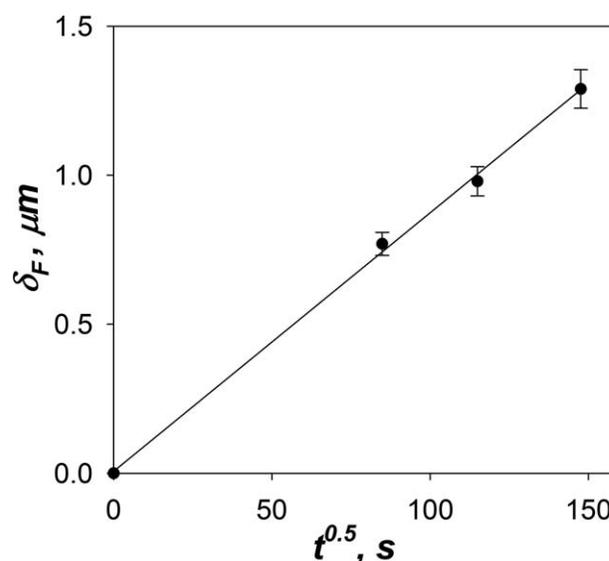
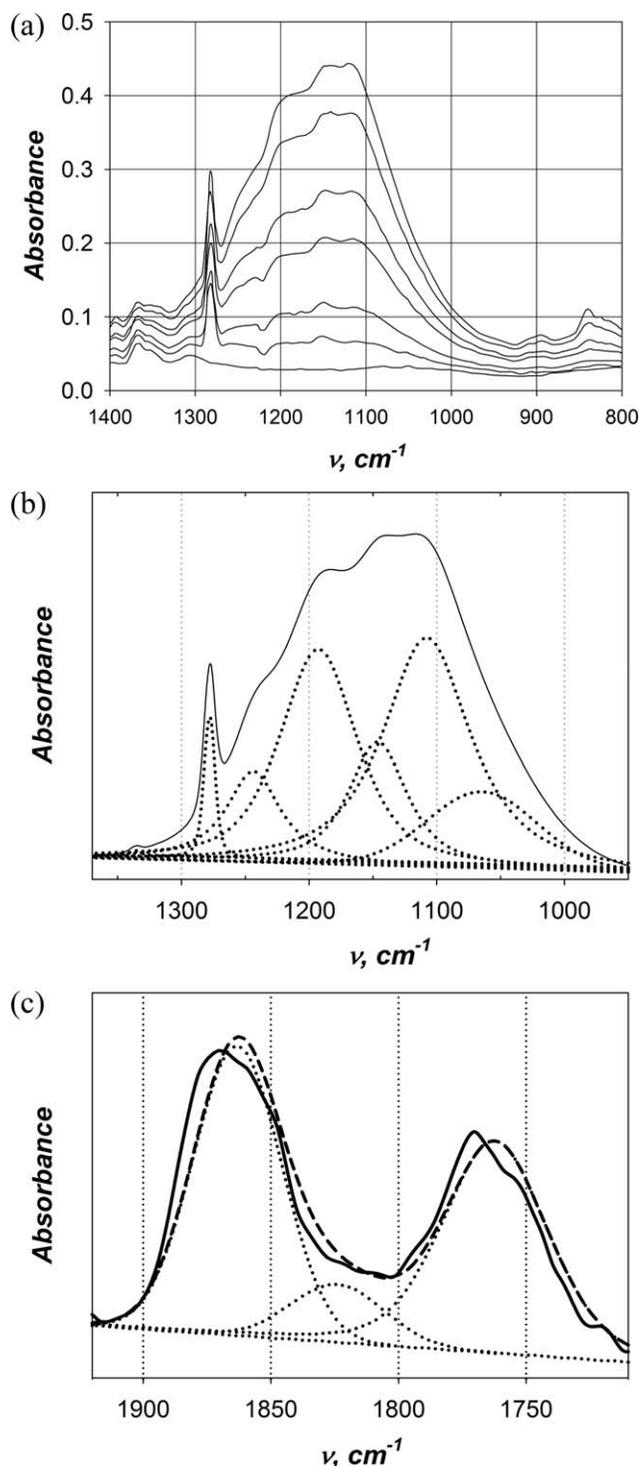


FIGURE 2 Thickness of fluorinated layer δ_F of fluorinated layer vs. fluorination duration t . Treatment conditions: undiluted fluorine at pressure 0.1 bar, temperature 19 °C.

So, interference features of the transmission spectra of a fluorinated films and linear dependence of the thickness of a fluorinated layer on square root of treatment duration reveals that (see also refs. 5–9, 11 and 21).

1. The fluorinated film consists of two layers, fluorinated and untreated layers, separated by a very transient layer where the major chemical transformations take place.
2. The rate of formation of fluorinated layer is defined by a



rate of penetration of fluorine through fluorinated layer to untreated one, that is, diffusion-controlled.

For all the films treated with XeF_2 no interference features, over $3000\text{--}20000\text{ cm}^{-1}$ range was observed. According to the well-known principles of optics, the interference features of fluorinated (by any fluorination route) polymer film may arise only when (i) the film consist of partially or totally fluorinated layers (if the film was treated from both sides) and unmodified virgin layer, (ii) thickness of the transition layer between fluorinated and unmodified layers is less (preferably much less) than the $1/4$ wavelength of probe light and (iii) surfaces of fluorinated film and unmodified layer are parallel to each to other (with accuracy of $1/4$ wavelength of probe light). It can be concluded that there is no sharp boundary between fluorinated and virgin polymer layers or at least (this conclusion can be made on the base of the basic optics principles), the thickness of that boundary is $\gg 0.3\text{--}0.6\text{ }\mu\text{m}$ ($1/4$ wavelength of probe light). Such a feature can be explained as follows. For the case of using XeF_2 , polymer is treated with a mixture of molecular F_2 and atomic F^{\bullet} fluorine. Atomic fluorine diffuses much faster inside the polymer bulk than F_2 . Also XeF_2 from the gaseous phase penetrates inside the polymer bulk and can decompose there providing atomic fluorine. So, for the case of XeF_2 , the fluorination reaction probably is not diffusion controlled but kinetically controlled.

Chemical Composition of Fluorinated Layer

IR Spectroscopy

Direct fluorination strongly influences chemical composition of polymers as it can be seen from the Figure 3(a–c). UHMWPE film with $20\text{ }\mu\text{m}$ in thickness was placed inside the reaction vessel equipped with two ZnSe windows, which are stable to F_2 and HF action and are transparent over $20,000\text{--}500\text{ cm}^{-1}$ range. To remove formed in the course of fluorination HF which may inhibit the reaction a solid pellet of NaF was placed inside the reactor [$\text{NaF} + \text{HF} = \text{NaHF}_2$ (solid)]. Fluorination was carried out at fluorine pressure 0.1 bar at temperature $24 \pm 0.5\text{ }^{\circ}\text{C}$. Fluorine consumption did not exceed 10% with respect to its starting pressure. The reaction vessel was placed inside the FTIR spectrometer, and

FIGURE 3 (a) Absorption spectra of UHMWPE film over $800\text{--}1600\text{ cm}^{-1}$ range fluorinated in sequence. Spectrum at the bottom is the virgin one. Above spectra corresponds in sequence to the following fluorination duration: 2, 10, 55, 115, 270, and 424 min (from bottom to top). (b) IR spectrum of the UHMWPE film treated with fluorine during 424 min. Solid line- experimentally measured and fitted spectra (they practically coincide within the line thickness), dotted lines- separated bands with maxima at 1247 , 1197 , 1150 , 1112 , and 1068 cm^{-1} . Band at 1282 cm^{-1} does not relate to C-F absorption in a solid fluorinated film. (c) IR spectrum of the UHMWPE film treated with fluorine during 360 min: Solid line- experimentally measured, dotted lines- separated bands at 1867 , 1828 , and 1766 cm^{-1} corresponding to C=O groups with different environment, dashed line- calculated fitted spectrum.

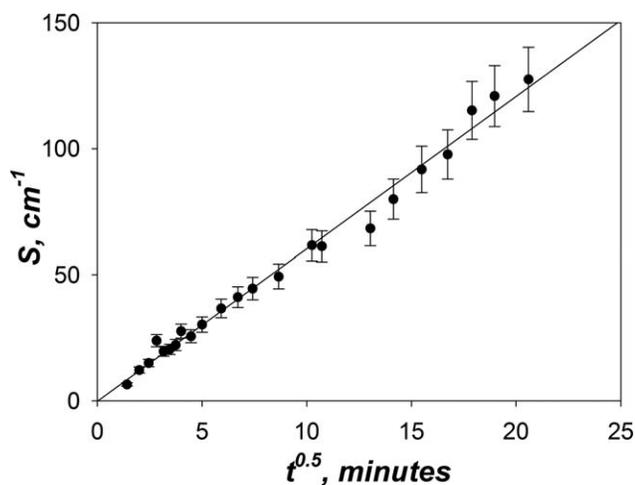


FIGURE 4 Dependence of the total area S of C–F, C–F₂, and C–F₃ bands over 850–1350 cm⁻¹ range on a square root of fluorination duration t . Treatment conditions: undiluted fluorine pressure 0.1 bar, temperature 24 ± 0.5 °C.

the IR spectra were measured continuously. During the first 10 min, 46 scans at 4 cm⁻¹ resolution were taken to obtain a single spectrum (total registration time was equal to 30 s). Then the amount of scans was increased up to 100 at 4 cm⁻¹ resolution (total registration time was equal to 65 s). The following features of fluorinated UHMWPE should be marked. Intensity of C–H absorption bands over 2850–2950 cm⁻¹ is decreased whereas intense diffuse bands corresponding to C–F_x ($x = 1, 2, \text{ and } 3$) arise over 850–1350 cm⁻¹ range. The latter one can be separated into 1247, 1197, 1150, 1112, and 1068 cm⁻¹ bands with areas ratio 1:2.9:1.4:3.8:1.2 [Fig. 3(b)], and also weaker 840 cm⁻¹ band assigned to C–F_x absorption band originates.²⁴ Carbonyl groups absorption at 1867, 1828, and 1766 cm⁻¹ (the first and the last are the most strong ones) was monitored over 1700–1900 cm⁻¹ range [Fig. 3(c)]. Band at 1867 cm⁻¹ corresponds to absorption of –C(=O)F group. Band at 1766 cm⁻¹ is probably C–O vibration in α,α' -difluoroketone –CHF–(C=O)–CHF– group.^{5–10,24} In air, the band at 1867 cm⁻¹ practically disappears due to a hydrolysis: –C(=O)F + H₂O → –C(=O)OH + HF. Band at 1282 cm⁻¹ belongs to a volatile compound, which totally disappears when fluorine is evacuated.

Computer simulation was used to calculate the total area S (cm⁻¹) of bands over 900–1400 cm⁻¹ corresponding to absorption of C–F, C–F₂, and C–F₃ bands. 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%. Dependence of the S value on a square root of fluorination duration t is shown in Figure 4. From the Figure 4, it becomes evident that

$$S = B \cdot t^{0.5} \quad (5)$$

where B is a constant value. So, S value is proportional to the δ_F value (see eq. (4): $\delta_F = A t^{0.5}$) similar to the case of

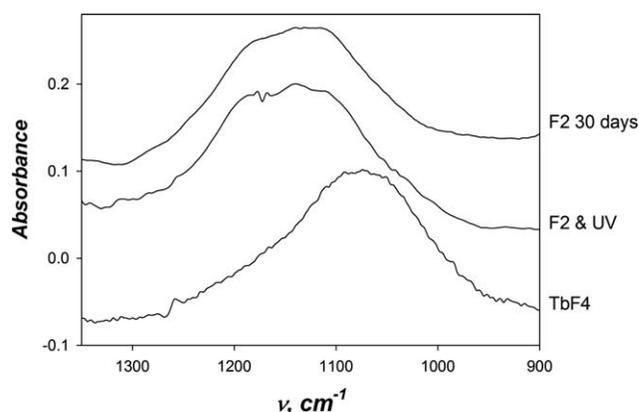


FIGURE 5 FTIR spectra of UHMWPE treated with fluorine (upper curve, fluorine pressure 1 bar during 30 days at 22 °C), with simultaneous action of fluorine and UV irradiation (fluorine pressure 0.15 bar and UV irradiation during 4 h at 20 °C; curve in the middle) and with fluorinating agent TbF₄ (curve at the bottom). All the spectra were shifted along the vertical axis to avoid overlapping.

LDPE and other polymers²¹ and HDPE.^{5,6,8} It means that the total concentration of C–F, C–F₂, and C–F₃ bonds does not depend on the thickness of fluorinated layer.

The FTIR spectrum and, hence, chemical composition of fluorinated layer depends on the fluorination route as it becomes evident from the Figures 5 and 6. IR spectra of the films treated by fluorine and by simultaneous action of fluorine and UV irradiation (Fig. 5) practically coincide and indicate that both –CHF– and –CF₂– groups exist, but the amount of –CF₂– groups is prevailing. On the contrary –CHF– groups are prevailing when UHMWPE was treated with TbF₄. For the case of treatment with XeF₂ (Fig. 6), the

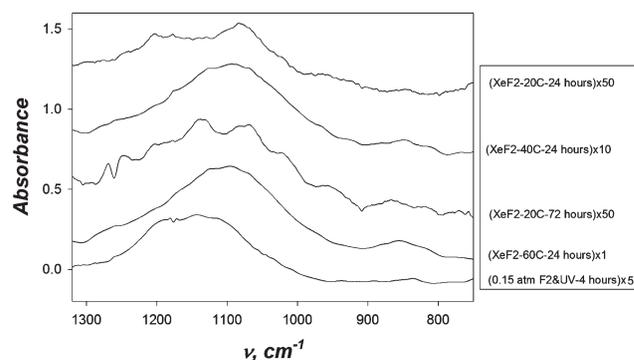


FIGURE 6 FTIR spectra (absorbance mode) of UHMWPE treated with XeF₂ during 1 day at 20 °C (upper curve, multiplied by 50), 1 day at 40 °C (second curve from the top, multiplied by 10), 3 days at 20 °C (third curve from the top, multiplied by 50) and 1 day at 60 °C (second curve from the bottom, multiplied by 1). Curve at the bottom-simultaneous treatment with fluorine pressure 0.15 bar and UV irradiation during 4 h at 20 °C (multiplied by 5). Spectra of the virgin (nonfluorinated) polymer were subtracted. All the spectra were shifted along the vertical axis to avoid overlapping.

shape of IR spectra depends on treatment conditions. It seems that at low temperature (20 °C), both $-\text{CHF}-$ and $-\text{CF}_2-$ groups are formed, but the amount of $-\text{CF}_2-$ groups is prevailing. When the temperature is increased up to 40–60 °C (and hence XeF_2 pressure and also partial pressures of atomic and molecular fluorine formed due to the dissociation of XeF_2 are increased also) mainly $-\text{CHF}-$ groups are formed, but the ratio of CF_2/CHF differs from one for the case of treatment with (i) F_2 , (ii) simultaneous action of F_2 and UV irradiation, and (iii) treatment with TbF_4 . Such conclusions are supported by the ^{19}F NMR data (see Figures 7 and 8).

^{19}F NMR Data

^{19}F NMR spectra, recorded with magic angle spinning in order to decrease both chemical shift anisotropy and dipolar coupling, are useful for the chemical analysis of our sample, because the chemical shifts are enough different for the various possible groups in fluorinated groups. C–F, CF_2 , and CF_3 exhibit ^{19}F chemical shifts ($\delta_{19\text{F}}$) at approximately -200 , -120 , and -80 ppm with respect to CFCl_3 (Fig. 7).^{25–30} Those lines are marked with dotted lines in the Figure 7. Several Lorentzian lines were used to fit the spectra perfectly. The CHF/CF_2 ratio was estimated using the ratio of the integrated surface of the lines for CHF in the $-180/-270$ ppm range and CF_2 in the $-90/-150$ ppm one. The CHF/CF_2 ratios equal to 2.6 and 0.9 were obtained for the case of TbF_4 and F_2 , respectively, in accordance with FTIR data. Another remarkable difference concerns the position of the CHF line center. Values of -200 and -220 ppm were measured for the sample fluorinated with TbF_4 and F_2 , respectively. Such a difference is explained by different neighboring of the CHF groups; because of the shielding effect, the chemical shifts depend on the number of neighboring fluorine atoms. Considering only the closest neighboring groups, the two limit cases are $\text{CH}_2-\text{CHF}-\text{CH}_2$ and $\text{CF}_2-\text{CHF}-\text{CF}_2$. These groups exhibit chemical shifts close to -180 and -220 ppm, the lowest and highest shifts observed in this study. Higher content of CF_2 groups in UHMWPE fluorinated with F_2 explains the position of the CHF line, centered at -220 ppm. So, a preferable formation of $-\text{CHF}-$ groups when compared with $-\text{CF}_2-$ groups takes place when TbF_4 is used.

By analogy with the fluorination of nanofibres, when either TbF_4 or XeF_2 is used, atomic fluorine F^\bullet can be considered as the main reactive specie.^{31–33} ^{19}F NMR spectra of UHMWPE treated with XeF_2 are shown in Figure 8. The reaction temperature was equal to 20, 40, and 60 °C for 24 h treatment duration. At the lowest temperature (20 °C), the fluorine content is low as revealed by low signal/noise ratio of the spectrum [Fig. 8(a)] and the low relative intensity in comparison with the signal of the probe at 30 kHz [Fig. 8(c)]. Only one narrow line observed at -180 ppm was assigned to $-\text{CHF}-$ groups diluted in nonfluorinated part. As a matter of fact, in addition to the chemical shift unambiguously related to $-\text{CHF}-$, the narrow linewidth (full width at half maximum of 4000 Hz with 14 kHz spinning rate) underlines weak homonuclear $^{19}\text{F}-^{19}\text{F}$ dipolar coupling,

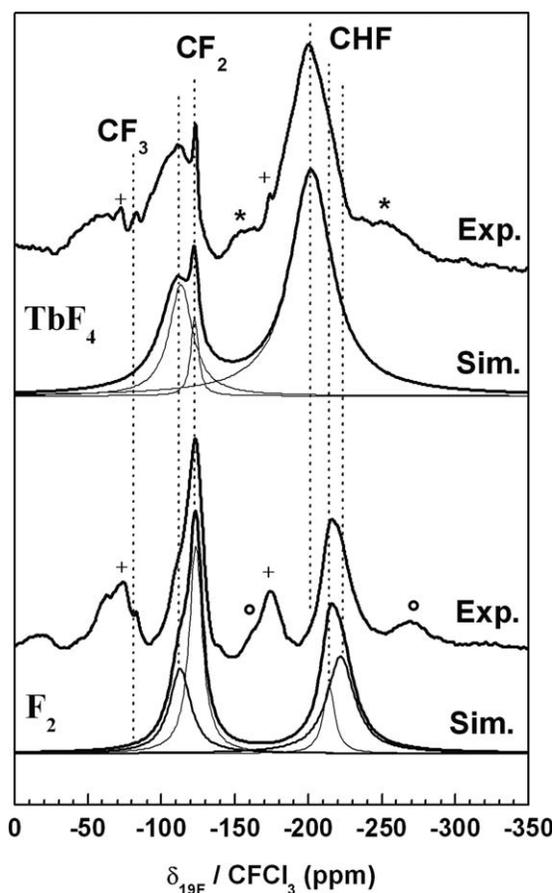


FIGURE 7 MAS ^{19}F NMR spectra (spinning speed was equal to 14 kHz) of UHMWPE fluorinated using TbF_4 (upper curve) and F_2 (1 bar pressure, lower curve). Spinning sidebands are marked by symbols *, o, and +. Thick lines, experimental results; thin hair lines, spectrum simulation.

which is explained by the dilution of ^{19}F nuclei. When the reaction temperature is increased, lines at -200 and -220 ppm appear [Fig. 8(a,c)], assigned to higher fluorine content in the neighboring of ^{19}F nuclei. The lines are broaden in accordance with the fluorine content increase. For the sample fluorinated at 60 °C, the amount of $-\text{CHF}-$ groups is higher than $-\text{CF}_2-$ one. The CHF/CF_2 ratio is equal to 1.5 using the same fitting procedure as before [see simulations in Fig. 8(b)]. The gravity center of the $-\text{CHF}-$ line for the sample treated with XeF_2 is around -200 ppm similar to the sample treated with TbF_4 showing the similitude of the fluorination mechanism, which involves atomic fluorine. Nevertheless, the CHF/CF_2 ratio is lower for the case of XeF_2 at 60 °C in comparison with TbF_4 fluorination where $\text{CHF}/\text{CF}_2 = 2.6$. Higher content of CF_2 is probably related to the reaction temperature. As a matter of fact, the CHF/CF_2 ratio is close to 2.5 when the reaction with XeF_2 is carried out at 40 °C. On the contrary, the formation of CF_2 is favored when molecular fluorine is used.

To go further in the NMR analysis, $^{19}\text{F}\rightarrow^{13}\text{C}$ cross-polarization MAS experiments were also carried out [Fig. 8(d)].

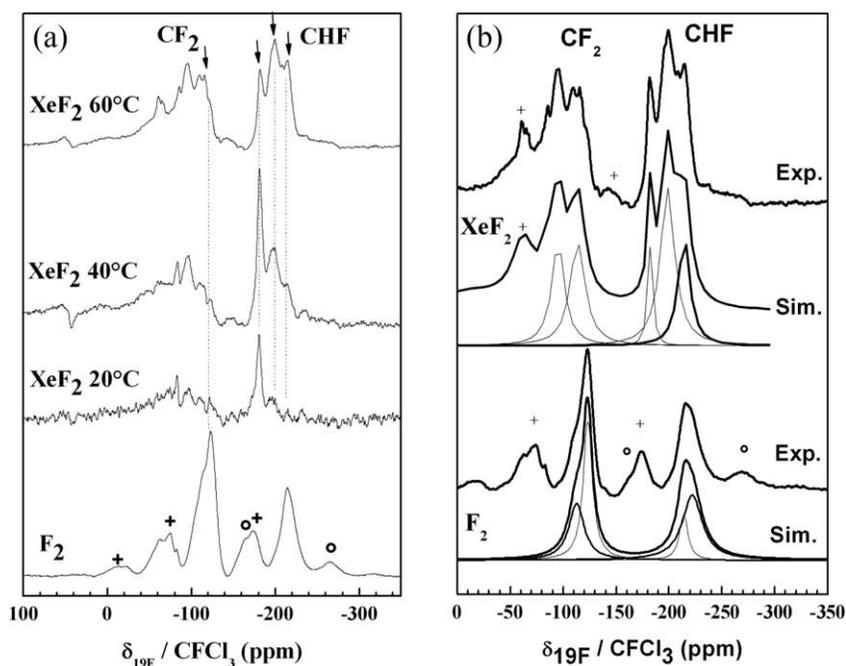
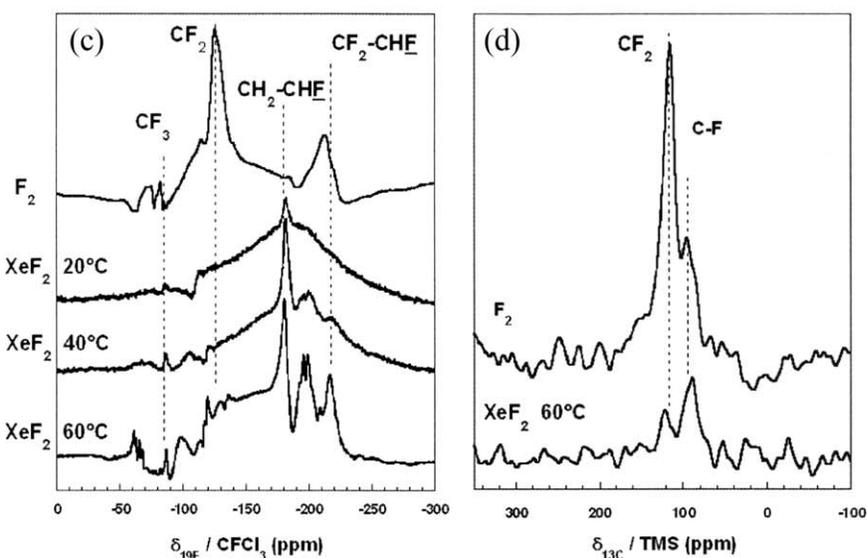


FIGURE 8 (a) Magic angle spinning ^{19}F NMR spectra (spinning frequency 14 kHz) of the UHMWPE powder treated with F_2 (1 bar pressure during 30 days at room temperature, curve at the top) and with XeF_2 : treated during 24 h at temperature 20 °C (curve at the bottom), treated during 24 h at temperature 40 °C (second curve from the bottom) and treated during 24 h at temperature 60 °C (third curve from the bottom). (b) fitting using Lorentzian lines (only isotropic lines are considered). (+ and ° are spinning sidebands), (c) MAS spectra at 30 kHz; The broad line centred at -190 ppm, which is clearly underlined for the samples obtained using XeF_2 at 20 and 40 °C, is measured without sample and is related to materials of the probe. (d) $^{19}\text{F} \rightarrow ^{13}\text{C}$ CP-MAS spectra (15 kHz) of UHMWPE fluorinated at room temperature using F_2 and at 60 °C using XeF_2 .



Although heteronuclear dipolar coupling of both ^1H and ^{19}F nuclei, which hinders the recording of the spectra, two lines are observed at 115 and 92 ppm/TMS assigned to CF_2 and CHF groups, respectively. Because of a large difference in the spectra, it can be concluded that the relative amount of CF_2 groups is larger for the case of the direct fluorination (treatment with F_2) in accordance with ^{19}F MAS measurements.

Study of the Structure and Kinetics of Termination of Long-Lived Radicals

Treatment with Fluorine-Helium Mixture

Similar to the results of authors,^{5,6,8,11,21} EPR spectra of fluorinated UHMWPE consist of a least two overlapped radicals' spectrum: peroxy RO_2 (asymmetric singlet) and diffuse very

wide spectra (15–20 mT in width) of a fluoroalkylradical (Fig. 9). Thickness of fluorinated layer ($0.34 \mu\text{m}$) was measured by applying spectroscopy in the visible region of spectrum as described in refs. 5–9 (see also Fig. 1). But the amount of peroxy radicals is prevailing. Peroxy radicals originate due to an oxygen admixture in used fluorine. Kinetics of radical termination shown in the Figure 10 can be described by the following equation:

$$R_t/R_{30} = (1.98 \pm 0.3) \cdot [1 + (0.034 \pm 0.008) \cdot t]^{-1} \quad (6)$$

where R_t is the current amount of radicals, R_{30} is the first measured amount of radicals (in 30 min after the end of fluorination), and t is the time after the end of fluorination.

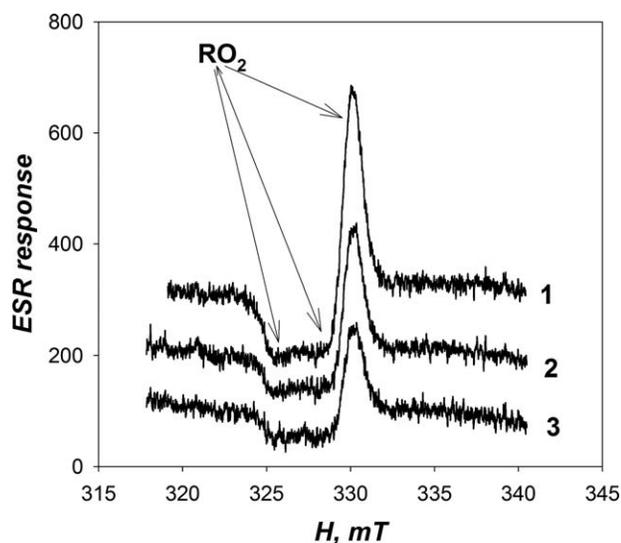


FIGURE 9 EPR spectra of fluorinated UHMWPE. Treatment conditions: fluorinating mixture composition 5% O₂ + 95% F₂, total mixture pressure 0.1 bar, fluorination duration 2 h, temperature 22 °C. Spectra 1, 2, and 3 were measured at 22 °C in 30, 90, and 180 min after the end of fluorination. Thickness of fluorinated layer was equal to 0.34 μm.

The absolute concentration of radicals measured 30 min after the end of fluorination was equal to 0.39×10^{17} radicals per cm⁻³ of a fluorinated layer. It is necessary to underline that the radical concentration was calculated with respect to fluorinated layer only, because the radicals are formed only inside fluorinated layer (necessary for calculations values of the thickness of fluorinated layer and film surface were measured). It is evident that radicals are long-lived, and their concentration is decreased by a factor of 2 in ~30 min. Applying equation (6), one can estimate the total amount of radicals at the end of fluorination ($t = 0$) as $[R_0] = 0.78 \times$

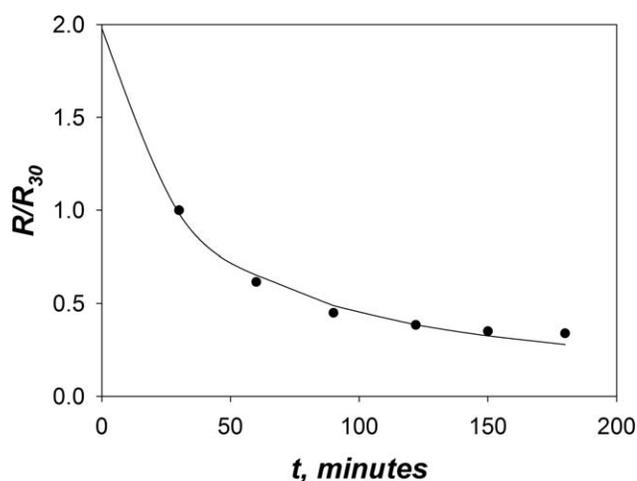


FIGURE 10 Kinetics of termination of radicals in fluorinated UHMWPE. R and R_{30} are the current amount of radicals and the amount of radicals measured in 30 min after the end of fluorination. Treatment conditions are indicated in the Figure 7.

10^{17} radical per cm³. It is quite reasonable to assume that radical termination proceeds via a bimolecular reaction $R + R = R_2$ with the rate constant k_1 . In that case, $[R]/[R_0] = (1 + 2k_1[R_0]t)^{-1}$ where $2k_1[R_0] = 0.034 \text{ s}^{-1}$, and rate constant $k_1 = 2.2 \times 10^{-19} \text{ cm}^3 \text{ s}^{-1}$. The measured k_1 value is much higher than appropriate values for low-density polyethylene and poly(phenylene oxide).^{5,6}

Treatment with XeF₂

EPR spectra of the powdered UHMWPE treated with XeF₂ differ from groups of the polymer treated with F₂-He mixture. "In situ" EPR spectra were recorded during the reaction of UHMWPE with XeF₂ at room temperature (20 °C). The sample and XeF₂ were placed together into quartz EPR tube in argon environment. The EPR tube was then sealed off. During the first 3 h, only a singlet was observed, and its intensity was decreased with time [Fig. 11(a)]. Because of its g-factor, equal to 2.020 ± 0.005 , and its evolution, we assigned this signal to defects in XeF₂ crystals. In 3 h, this signal totally disappeared and a new broad one was observed in 5 h after the beginning of fluorination. Its intensity and the resolution of the superhyperfine structure (SHFS) increased with time until 28 h. No further evolution was observed either for longer time or after exposition to air

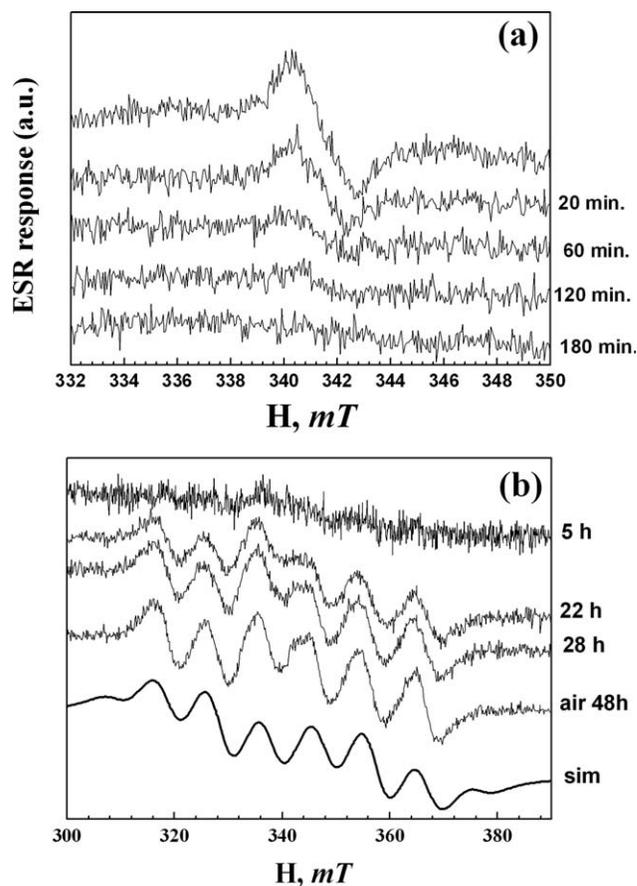


FIGURE 11 EPR spectra of UHMWPE treated with XeF₂ measured "in situ." Treatment duration is indicated at each graph: 0–3 h (a) and 5–48 h (b). Top spectrum at (a) corresponds to the starting film.

atmosphere, indicating that the formed radicals are long-lived. The fitting of the SHFS using WinSimfonia software reveals two hyperfine interactions of the radical with (i) one fluorine nucleus (the coupling constant is equal to 29.0 mT) and (ii) four nuclei of either ^{19}F or ^1H , both with a nuclear spin number $I = 1/2$, the second coupling constant being equal to 9.5 mT. It results in a double-quintet signal. According to the NMR data, the more probable radical is $-\text{CH}_2-\text{C}^\bullet\text{F}-\text{CH}_2-$ but $-\text{CF}_2-\text{C}^\bullet\text{F}-\text{CF}_2-$ one cannot be excluded. The other fitting parameters were linewidth ΔH_{PP} equal to 7 mT and a g-factor equal to 2.003 ± 0.001 . Such a fitting resulted in eight lines in a good agreement with the experimental spectrum [Fig. 11(b)]. For comparison, free radicals trapped in γ -ray-irradiated PTFE have been assigned to fluoroalkyl radical ($-\text{CF}_2-\text{CF}^\bullet-\text{CF}_2-$) due the observed double quintet.³⁴

Influence of Fluorination on the Ordered Structure

X-ray diffraction patterns of virgin and fluorinated UHMWPE films (1 and 2, respectively) and virgin and fluorinated powdered UHMWPE (3 and 4, respectively) are shown in the Figure 12. The maxima of the diffractograms practically coincide (with accuracy of 0.01 Å; such a shift is constant for all the lines and lies within the experimental error of the angle value measurement), but the lines of fluorinated film and powder are widened as compared with the virgin polymer. The reason of such a widening is as follows. The fluorine-treated polymer consists of fluorinated and virgin polymers, so each line of fluorinated polymer consists of two lines corresponding to fluorinated and virgin polymers. The fitting indicates that the distance between those lines is around 0.01 Å. It means that the internal structure of UHMWPE is not practically changed under fluorination or the structure of fluorinated polymer becomes disordered.

Study of the Influence of Fluorination on the Polymer Surface Texture

To investigate the influence of fluorination on the polymer surface texture, a scanning electron microscopy was applied. The polymer samples were coated with neither carbon nor metal. The photos of the polymer surface with different magnification are represented at the Figures 13 and 14.

There are lamellar elements (fibrils) of several tens of nanometers in diameter on the surface of virgin polymer [Fig. 13(a)]. For the film treated with F_2 -He mixture, fibrils become more remarkable [Figs. 13(b,c)]. It seems that the fibril's diameters are increased, the fibrils are swollen and the surface becomes "wrinkled" and the roughness of the surface is markedly increased. It might be due to a different rate of fluorination and different fluorination degree of fibrils and other parts of the polymer surface. Previously it was shown^{5,6} that for some polymers thickness of fluorinated film exceeds thickness of the virgin film, that is, the fluorination results in a swelling of the film.

For the case of treatment with XeF_2 , the surface texture is quite different and depends on both treatment duration and temperature. For treatment during 1 day at 20 °C [Fig. 14(a,b)], the surface is coated with fibrils similar to the case

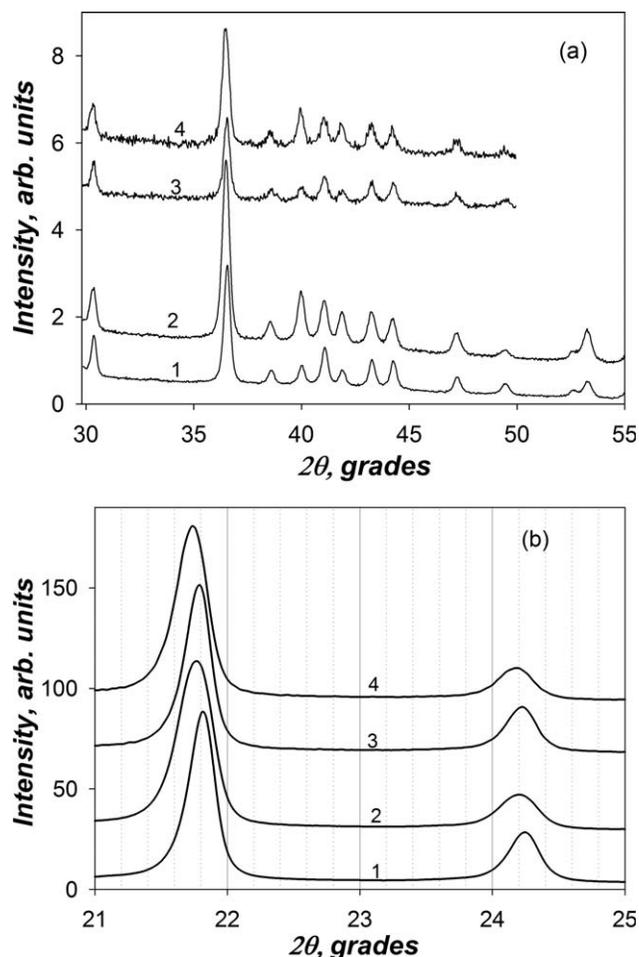


FIGURE 12 X-ray diffraction patterns of virgin and fluorinated UHMWPE film (1 and 2, respectively) and virgin and fluorinated powdered UHMWPE (3 and 4, respectively). Graph on right represents the magnified range of 21–25 range of 2θ . To avoid overlapping the diffractograms were shifted in vertical direction. Peaks over 5–20 and 55–130 range of 2θ are not shown because of a very small intensity.

of treatment with F_2 -He mixture, but fibrils are not so large, and their diameters are close to the diameters of fibrils in virgin polymer. Also some new elements such as balls (more or less round) were detected. Their size is varied over 20–1000 nm range. Ball's sequences are placed along straight line, and the sizes of balls in each sequence are close to each other. It is reasonable to propose that those ball's sequences are fluorinated polymer substances formed along the boundaries between amorphous and crystalline polymer phases where very often chemical processes are promoted. Usually similar boundaries favor the chemical reactions. When the treatment duration at 20 °C is increased up to 3 days, the lamellar structure is similar to the 1 day treatment duration, but the balls are practically uniformly distributed across the surface [Fig. 14(c,d)]. The ball's sizes become much less than for the case of 1 day treatment and varies around 50–100 nm. Larger balls are not visible. It may be due to several reasons. For example, their size should be markedly increased

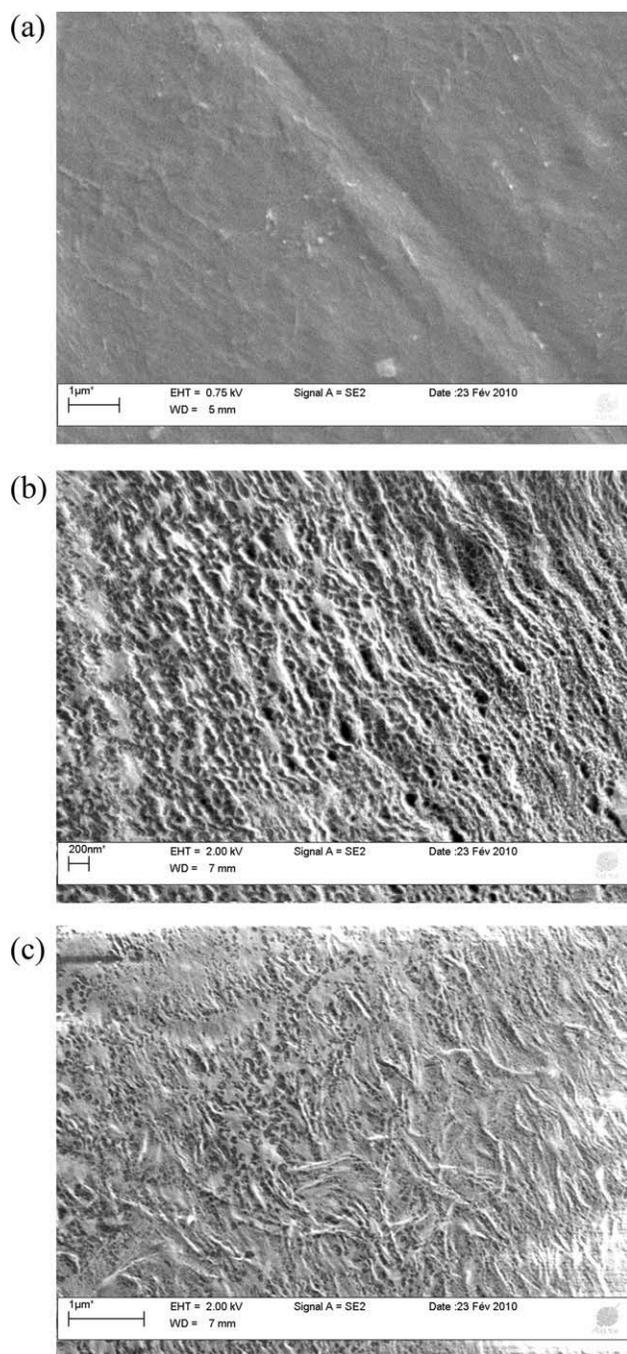


FIGURE 13 SEM images of the surface of the raw polymer (a) and treated with 10% F_2 + 90% He mixture at total mixture pressure 1 bar and temperature 24 ± 2 °C during 90 min (b and c).

with time (1 day to 3 days), they may overlap and form large (several μm or several tens μm in length and several μm in width) conglomerates. When the treatment temperature is increased to 40 °C [Fig. 14(e,f)], balls also with 50–300 nm in diameter were detected, but they were chaotically distributed across the polymer surface. But the lamellar structure is not so distinct as for the case of treatment at 20 °C. When the treatment temperature is increased to 60 °C

[Fig. 14(g,h)], the surface texture becomes more or less similar to the case of treatment with F_2 -He mixture, but the fibrils are not so distinctly marked, and the roughness of the surface is not so markedly increased as for the case of treatment with F_2 -He mixture.

Study of the Influence of the Fluorination on UHMWPE Surface Energy

It is known that the surface energy of polymers (including polyethylene) is increased under fluorination.^{3–8,35–39} There are several reasons for that increase. At first, fluorination results in a formation of polar groups ($-\text{FC}=\text{O}$, $-(\text{C}=\text{O})\text{OH}$, $-\text{CHF}-$, etc.) on the polymer surface, so the polarity of the surface is increased. There are several sources of oxygen: absorbed on the reaction vessel walls and polymers surface and dissolved in the polymer bulk oxygen and water; often oxygen is especially added to the fluorinating mixture. Second, the roughness of the polymer surface is highly increased after fluorination (see Fig. 13).

Surface energy (polar and dispersion components and total surface energy) was measured by a conventional method.^{22,23} Three liquids were used to measure surface energy: double distilled water, formamide, and ethyleneglycol. Two fluorinating mixtures were used: 10% F_2 + 90% He and 6.7% F_2 + 6.7% O_2 + 86.6% He. Polymer films were treated with total mixture 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 Tables 2 and 3 and Figures 15 and 16.

Treatment with 10% F_2 + 90% He Mixture

It is evident that the total surface energy and its polar and dispersion components highly depend on treatment and storage duration. The total surface energy [Fig. 15(a)] is markedly increased (from 30 up to 45–50 mN/m) in 1–3 days after fluorination, then it goes down but in 45 days reaches practically steady level around 35–42 mN/m depending on treatment duration. Such a steady level is not markedly changed up to 120 days. The polar component increase [Fig. 15(b)] is more pronounced for short treatment duration (2 min) from 10 to 41 mN/m in 3 days after fluorination, but then it starts to decrease and reaches steady level around 21–26 mN/m, which is not practically changed over 14–120 days storage duration range. For other treatment durations, the steady level also exceeds polar component value for the virgin polymer and is close to 16–19 mN/m (except 90-min treatment duration for which polar component drops practically to its value for the virgin polymer). The dispersion component [Fig. 15(c)] is increased from 20 mN/m to 25–23 mN/m for short treatment duration (2 and 6 min) and to 40–45 mN/m but rather quickly it drops well below its value for the virgin polymer. But in 14 days, it reaches its virgin value and remains unchanged up to 120 days storage duration.

Treatment with 6.7% F_2 + 6.7% O_2 + 86.6% He Mixture

Introduction of oxygen in fluorinating mixture results in more pronounced increase of total surface energy and its polar component. The total surface energy [Fig. 16(a)] can be

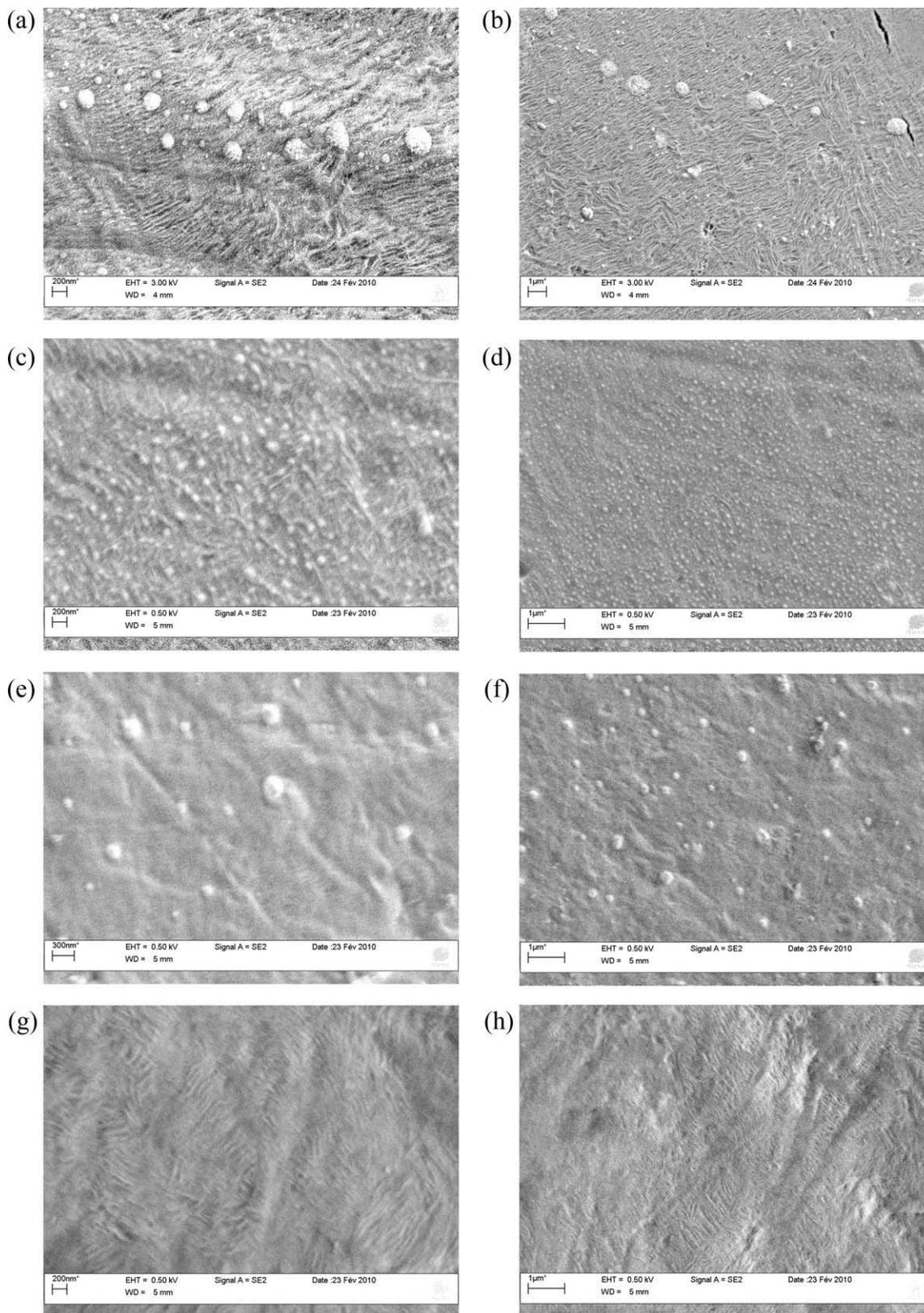


FIGURE 14 Surface of the polymer treated with XeF_2 at 20 °C during 1 day (a,b), at 20 °C during 3 days (c,d), at 40 °C during 1 day (e,f), at 60 °C during 1 day (g,h).

TABLE 2 Treatment Duration, Storage Duration, and Measured Total Surface Energy and Its Polar and Dispersion Components for the Case of Treatment of UHMWPE with 10% F₂ + 90% He Mixture

Surface energy (mJ/m ²)	Total	Polar	Dispersion												
Virgin film	29.8	10.2	19.6	29.8	10.2	19.6	29.8	10.2	19.6	29.8	10.2	19.6			
Treatment duration, minutes	2			6			21			46			90		
Storage duration, days															
1	41.9	16.9	25.0	42.0	18.8	23.0	49.8	5.2	44.6	45.4	7.2	40.4	45.8	5.4	40.4
3	48.6	41.2	7.4	35.7	23.6	12.2	43.8	29.6	14.2	37.6	11.6	33.1	42.5	9.4	33.1
7	41.6	28.9	12.7	36.4	20.5	15.9	37.8	25.0	12.7	36.9	22.9	6.8	39.7	32.9	6.8
14	39.5	20.9	18.6	38.4	16.8	21.7	33.6	15.8	17.8	34.7	16.0	21.3	31.9	10.6	21.3
45	42.7	24.8	17.9	38.2	17.1	21.1	37.7	14.1	23.5	34.4	12.2	22.2	35.0	13.8	21.2
120	41.8	26.1	15.7	38.2	17.1	21.1	37.7	14.1	23.5	34.4	12.2	21.2	35.8	12.4	23.4
700	37.4	8.7	28.7	42.0	11.7	30.3	40.7	12.9	27.8	39.8	10.0	22.3	34.0	11.7	22.3

TABLE 3 Treatment Duration, Storage Duration, and Measured Total Surface Energy and Its Polar and Dispersion Components for the Case of Treatment of UHMWPE with 6.7% F₂ + 6.7% O₂ + 86.6% He Mixture

Surface energy (mN/m)	Total	Polar	Dispersion																		
Virgin film	29.8	10.2	19.6	29.8	10.2	19.6	29.8	10.2	19.6	29.8	10.2	19.6									
Treatment duration	5 s			15 s			30 s			1 min			2 min			3 min			10 min		
Storage duration, days																					
0	29.8	10.2	19.6	29.8	10.2	19.6	29.8	10.2	19.6	29.8	10.2	19.6	29.8	10.2	19.6	29.8	10.2	19.6	29.8	10.2	19.6
1	53.2	14.0	39.1	46.9	23.4	23.5	44.2	20.2	24.0	49.8	19.1	30.7	54.2	19.3	34.9	58.7	12.1	46.6	53.7	12.9	40.8
7	56.8	48.8	8.0	45.3	25.6	19.8	52.3	38.8	13.5	44.8	26.8	18.0	47.2	27.1	20.1	45.8	28.7	17.1	47.4	28.9	18.5
14	39.4	10.2	29.2	38.0	11.1	26.9	39.4	15.3	24.1	41.8	22.1	19.5	42.6	18.0	24.6	41.2	23.6	17.6	41.3	22.5	18.9
45	35.0	17.8	17.2	35.0	15.7	19.3	41.0	23.5	17.6	37.6	13.2	24.4	43.0	14.0	29.0	40.1	12.5	26.6	42.2	19.7	22.5
120	37.1	22.2	14.8	37.3	7.8	29.4	42.5	20.3	22.2	39.9	21.9	18.0	43.0	14.0	29.0	40.1	12.5	26.6	42.2	19.7	22.5

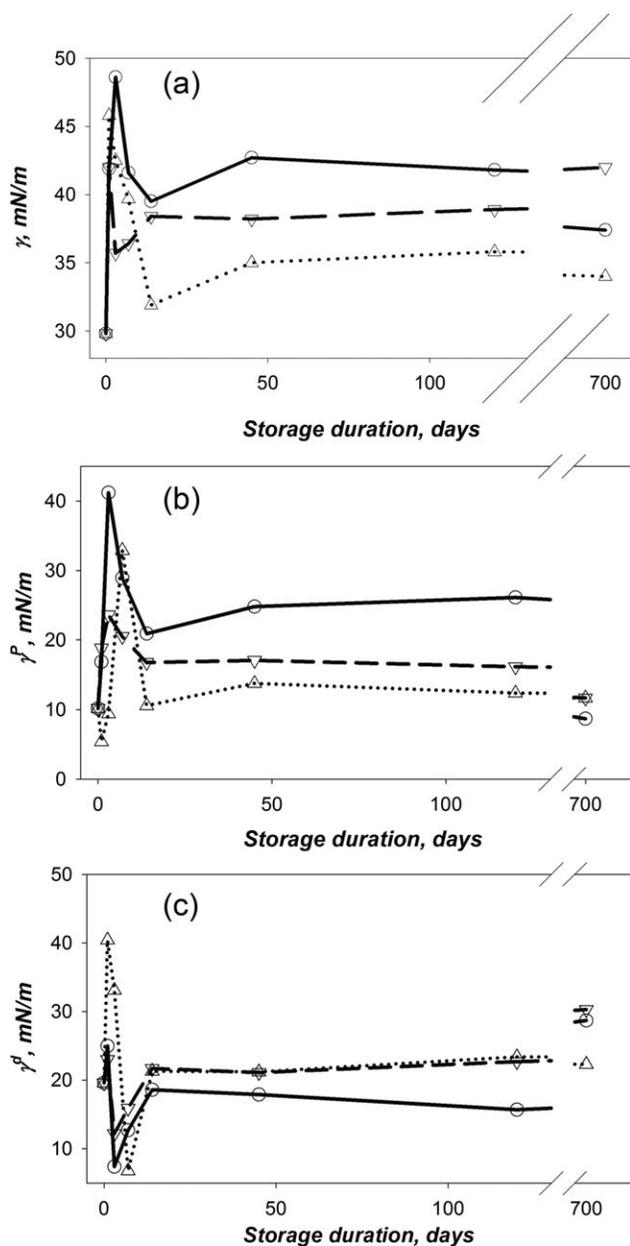


FIGURE 15 Total surface energy γ (a), polar γ^p (b) and dispersion γ^d (c) component vs. storage duration of fluorinated UHMWPE treated with 10% F_2 + 90% He mixture at 24 °C during 2 (○), 6 (▽), and 90 (Δ) min.

increased up to 59 mN/m, and it remains above 45 mN/m level at least 7 days. When the treatment duration is varied over 1–10 min range, the polar component [Fig. 16(b)] exceeds 22–28 and 18–23 mN/m level even in 14 and 45 days. But for some samples, the polar component is over 20–22 mN/m value and markedly exceeds the virgin value (~ 10 mN/m) even in 120 days. Dispersion component [Fig. 16(c)] is markedly increased after 1 day of storage by then very quickly drops down almost, but some samples has 27–29 mN/m dispersion component value even in 120 days.

Treatment with XeF_2

The samples were treated with XeF_2 during 24 h at temperature 20, 60, and 120 °C and stored inside polyethylene envelope during 40 days. The samples were taken from the envelopes 1 day before testing and were stored in open air. The surface of the sample treated at 120 °C was highly curved so the contact angles could not be measured. The measured surface energies are shown in the Table 4. It is evident that the treatment with XeF_2 results in much smaller increase of both total surface energy and its polar component when compared with the direct fluorination.

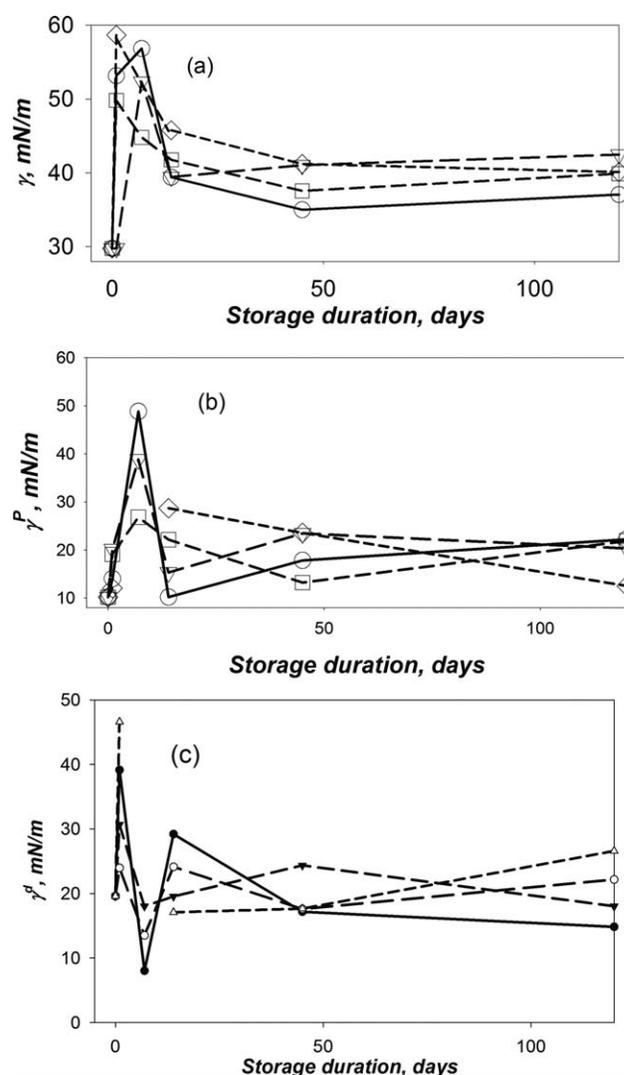


FIGURE 16 Total surface energy γ (a), polar γ^p (b), and dispersion γ^d (c) component vs. storage duration of fluorinated UHMWPE treated with 6.7% F_2 + 6.7% O_2 + 86.6% He mixture at 24 °C during 5 (○) and 30 (▽) s and 1 (Δ) and 3 (◇) min. Points at storage duration equal to zero correspond to virgin UHMWPE. Data for the treatment duration 15 s, 2 and 10 min were placed at the Table 3 to avoid overloading of the figure.

TABLE 4 The Surface Energy of the Samples Treated with XeF₂

Treatment Temperature (°C)	Time from the End of Fluorination (days)	Total Surface Energy (mN/m)	Polar Component (mN/m)	Dispersion Component (mN/m)
20	41	35.8	11.6	24.2
20	42	33.4	12.0	21.4
20	49	36.3	5.1	31.2
60	41	36.0	8.7	27.3
60	42	37.2	4.5	32.7
60	49	43.6	3.7	39.9
Untreated sample	–	29.8	10.2	19.6

CONCLUSIONS

1. Various fluorination routes, namely, direct fluorination (treatment with mixtures of F₂ and other gases), direct fluorination with simultaneous UV irradiation, treatment with fluorinating agent TbF₄, and treatment with fluorinating agent XeF₂, were applied to modify UHMWPE. Chemical composition, surface texture and other properties of fluorinated UHMWPE depend on the type of fluorination route.
2. For the case of the direct fluorination and direct fluorination with simultaneous UV irradiation, the composition of fluorinated layer is practically the same. Mainly CF₂ groups are formed, but CHF groups are formed also in smaller amount. On the contrary, treatment with TbF₄ and XeF₂ results in a prevailing formation of CHF groups, and there is some difference in chemical composition for the latter treatment routes.
3. The texture of fluorinated layer strongly depends on fluorination route. Texture distortion reaches its maximum value for the case of direct fluorination. For the case of treatment with XeF₂, the texture distortions are much less remarkable, and the texture depends on treatment temperature and treatment duration.
4. When UHMWPE is treated by direct fluorination, the formation of the fluorinated layer is diffusion-controlled that is limited by the rate of penetration of fluorine through fluorinated layer to untreated one. The thickness of fluorinated layer is proportional to the square root of treatment duration when fluorine partial pressure is kept constant. On the contrary, fluorination using XeF₂ as fluorinating agent is kinetically controlled.
5. Direct fluorination of SHMWPE results in the formation of both long-lived peroxy and fluoroalkylradicals. On the contrary only long-lived fluoroalkylradicals are formed when XeF₂ is used as fluorinating agent.
6. Both direct fluorination and treatment with XeF₂ strongly influences the surface energy, but the direct fluorination influence is much more pronounced. Addition of oxygen to fluorinating mixture provides more marked increase of the surface energy, especially its polar component.

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