

Structure and Composition of the Surface Layer in Polymers Modified by Elemental Fluorine

V. G. Nazarov

Military University of Radiation, Chemical and Biological Defense, Brigadirskii Line, 13, Moscow, 105005, Russia

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ABSTRACT: A model is proposed for the layered structure of a polymer surface modified by elemental fluorine mixed with helium. The composition of the modified surface layer has been determined, and the thermodynamic compatibility of the surface layer, transition layer, and unmodified bulk of the polymer has been studied. The thickness of the

modified layers has been calculated as a function of the fluorination conditions. © 2004 Wiley Periodicals, Inc. *J Appl Polym Sci* 95: 897–902, 2005

Key words: surfaces; fluoropolymers; polyolefins

INTRODUCTION

The methods of heterophase fluorination with elementary fluorine^{1–5} have been extensively studied and used to improve the physicochemical properties of polymers.^{6–8} The completeness of fluorination in a polymer matrix is estimated from various characteristics of the introduced functional groups, their content per unit of volume or polymer surface area, and the treatment conditions.^{1,2,9–12} Each of these parameters taken alone does not provide an adequate description of a modified polymer. The most informative characteristics of the modified surface layer are the composition of the modified layer, its thickness, the depth concentration profile, and the degree of layer modification.

The purpose of this work was to perform experiments on the fluorination of films of various polyolefins and rubbers so that the data could be analyzed and a theoretical model could be developed that described the structure of surface and transition layers in surface-modified systems.

EXPERIMENTAL

Films of polyolefins and a natural rubber were treated with elemental fluorine mixed with helium (the oxygen concentration in the mixture varied from 0.1 to 1%) at 20°C under atmospheric pressure in a stainless steel tank. Before the fluorination, the tank was evacuated as described elsewhere.¹⁰

Mixtures of fluorine and helium of various concentrations were taken from different steel cylinders. In this work, no attempt was made to determine the purity of the fluorine; however, as shown by previous studies,⁹ the concentration of commercial fluorine is not less than 98%; the basic impurities are hydrogen fluoride, oxygen, and traces of water. During the preparation of the fluorine–helium mixtures, fluorine was passed through KF for the removal of HF; the traces of water were removed by freezing. This purification technique allowed the purity of fluorine to be markedly increased: the concentration of oxygen was reduced to 0.1–0.2%. The helium used to prepare the fluorine-based mixtures was characterized by a high degree of purity (99.99%) and lacked oxygen. In some experiments, oxygen with a 99% degree of purity was added to increase its concentration from 0.1 to 1%.

The samples of the polymer films were placed in a 2-L anticorrosion steel reaction vessel made of thin rods 1 mm in diameter, which formed concentric circles in the cross section. The vessel was hermetically sealed, evacuated to a residual pressure of 1 Torr, purged with helium, and evacuated once again to a residual pressure of 1 Torr. The last operation was performed to effectively remove any traces of oxygen from the vessel.

The quantity of fluorine in the reaction vessel was three times higher than that calculated from the stoichiometric amount necessary for the complete fluorination of the polymer films used. The vessel was filled with a mixture of fluorine and helium from a cylinder until a pressure of 770 Torr was achieved, and the fluorination of the polymer films was carried out for a preset time. The vessel was evacuated to a residual pressure of 1 Torr, the polymer films were maintained under this pressure for 30 min until the fluorine and

Correspondence to: V. G. Nazarov (nazarov2@mtu-net.ru).

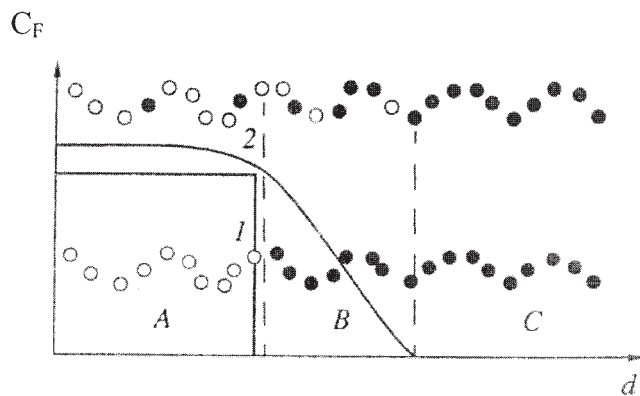


Figure 1 Schematic diagram of the concentration profiles of functional groups in the polymer film for (1) the frontal propagation of modification and (2) the diffusional propagation of modification. The hypothetical through macromolecules are also shown.

reaction products desorbed from the films, the vessel was filled with air up to atmospheric pressure, and the polymer films were extracted from the vessel. Unlike the previous study,⁹ in which the fluorination of polymer films was conducted in a flow of the gas mixture, in this work, the films were fluorinated under static conditions. This made it possible to attain a much more uniform modification of the surface of the films located in the various parts of the reaction vessel. For the fluorination experiments, commercial polyolefin films 50–100 μm thick (Dorkhimzavod, Moscow, Russia, and NPO Plastpolymer, St. Petersburg, Russia) and rubber films prepared from natural rubber 2 mm thick (NIL, Elastomer Materials and Items, Moscow, Russia) were used.

The composition of the modified surface layers was studied with X-ray photoelectron spectroscopy (XPS; XSAM-800, Kratos, Manchester, UK),⁹ IR spectroscopy (IRS-29 spectrometer, Lomo, St. Petersburg, Russia), and elemental analysis.¹³ The composition of each film as a whole was determined with elemental chemical data; the degree of modification was calculated as the weight of fluorine that reacted with the polymer (C_F) divided by the surface area of the film (A): $C_F/A = C_A^F$ (the heterophase reaction proceeded only from the surface of the film). The calculations were performed with an allowance made for the surface areas of both sides of the films.

RESULTS AND DISCUSSION

A polymer surface layer that forms upon modification should have a composition and thickness that are sufficient for the whole material to acquire the desired combination of properties. The thickness of the modified surface layer is a conditional concept, as illustrated in Figure 1. This figure shows how the concen-

tration of fluorine in a fluorinated polymer film depends on the film thickness (d). $d = 0$ corresponds to the maximum concentration ratio of fluorine in the surface layer to that in the bulk.

Depending on the regime of modification (i.e., the concentration of the fluorinating agent, the temperature, the duration, the nature of the polymer, and the ratio of the typical reaction times to the times of reactant diffusion), the depth–concentration profile of the fluorine groups incorporated into the polymer can vary from a sharp front (curve 1) to a smooth curve with a gradually decreasing value of C_F (curve 2). Figure 1 also schematically demonstrates the structure of the modified polymeric material: a fluorinated surface layer (A), with a gradually decreasing concentration of the introduced fluorine functional groups; a transition layer (B), in which the concentration of fluorine functional groups decreases rather sharply; and the unmodified polymer bulk (C). The figure also depicts a hypothetical going-through macromolecule with inhomogeneous molecular fragments located within the corresponding layers of the modified polymer. The upper hypothetical macromolecule reflects the chemical structure of various layers of a polymeric film during the diffusional development of fluorination (the fluorine-containing groups, denoted by open circles, are situated both in the surface and transition layers). The lower hypothetical macromolecule corresponds to the frontal development of fluorination (fluorine-containing groups are only in the surface layer). The frontal-type concentration profile is distinguished by a substantially uniform conversion of the chemical structure in the modified layer and a very small thickness of the transition layer. Other models of surface-modified layers have been advanced,^{14,15} but they tend to be less general.

The IR studies of the original and fluorinated low-density polyethylene (LDPE) films show a broad absorption band at 1000–1300 cm^{-1} due to the superpositioning of bands corresponding to CF , CF_2 , and CF_3 groups. Individual absorption bands observed for each of these groups in the IR region are quite close to one another, together forming a wide band.^{4,16} As the fluorination time increases, the overall intensity of this band increases because more and more fluorine accumulates in the samples (as indicated by elemental analysis).

Figure 2 depicts our experimental data presented as time-resolved curves of C_A^F for LDPE and natural rubber films fluorinated with gas mixtures containing various amounts of fluorine. C_A^F is an integrated parameter, equal to the amount of fluorine per unit of area of the sample surface that is added to the polymer by substitution, addition, and degradation reactions.^{4,9,17} Each of these reactions influences the modified films in a specific manner. Substitution and addition reactions give rise to the surface layer, whose

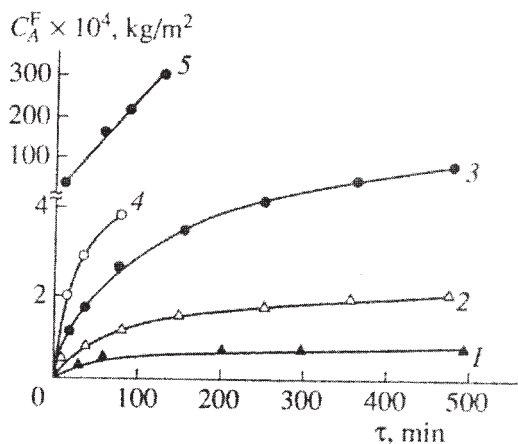


Figure 2 Kinetic curves of the fluorination of LDPE films with (1) 1, (2) 5, (3) 15, and (4) 30 vol % fluorine in the gas mixture (with He) and (5) vulcanized natural rubber with 15 vol % fluorine.

nature and properties resemble those of Teflon, whereas degradation processes should degrade the mechanical properties of the films. Indeed, when the fluorine concentration (C_{F_2}) is higher than 15 vol %, the degradation component of the reaction increases substantially, with the concomitant deterioration of the mechanical properties, especially for films less than 200 μm thick.^{4,8,10}

For LDPE, time-resolved fluorination curves taken at different concentrations of gaseous fluorine can be described by the following equation (based on our previous data^{4,8,10} and the results of this work):

$$C_A^F = 0.066 \times 10^{-4} C_{F_2}^{0.77} \tau^{0.37} \quad (1)$$

where τ is the time (min). Analyzing this equation, we can optimize the fluorination conditions as a function of the fluorine concentration and the treatment time. This experimental dependence appears to be linear for the rubbers under investigation. The reason for this phenomenon is discussed elsewhere.

The temperature dependence of the degree of LDPE fluorination plotted in semilogarithmic coordinates can be described by a straight line. This relation follows the Arrhenius law. However, at temperatures greater than 40°C, the degradation rate increases noticeably. This follows from the deterioration of the mechanical properties of the modified polymer films and a higher permeability of low-molecular-weight compounds (the diffusion probe technique). These features have been described in detail in our previous work.¹⁰

The effect of structural factors on the rate and degree of fluorination of polyolefins is illustrated by kinetic curves of C_A^F (Fig. 3) obtained for polypropylene (PP), LDPE, high-density polyethylene

(HDPE), and ultrahigh-molecular-weight polyethylene (UHMWPE). The polymers of interest are distinguished by the density (0.90, 0.92, 0.95, and 0.98 g/cm³ for PP, LDPE, HDPE, and UHMWPE, respectively), the degree of crystallinity (40–45, 40–45, 60–65, and 80–85% for PP, LDPE, HDPE, and UHMWPE, respectively),¹³ the molecular weight, and the degree of side-chain branching. These parameters affect the reactivity of the polymers with respect to fluorine. In LDPE, side branches are spaced on average at about 50 C atoms; its molecular mass is equal to 150,000, with approximately six to eight unsaturated bonds per 10,000 C atoms. For HDPE, the side branches are spaced at 200–250 C atoms, and its molecular mass is equal to 400,000, with about four to six unsaturated bonds per 10,000 C atoms. Finally, the side branches of UHMWPE are spaced at 400–500 C atoms, and its molecular mass is 2,500,000, with about one to two unsaturated bonds per 10,000 atoms.¹³ The rate of fluorination of various polyolefins is determined by both molecular factors (the number of unsaturated bonds and the number of side methyl groups) and structural factors (the degree of crystallinity and the density). This is shown well by the experimental data (Fig. 3).

A higher degree of crystallinity (80–85% for UHMWPE, 60–65% for HDPE, 40–45% for LDPE, and 40–45% for PP) corresponds to a low degree of fluorination and a low rate of reaction during the initial stage of the process. The presence of pendant methyl groups in PP and other polyolefins apparently promotes fluorination. The occurrence of unsaturated bonds in rubbers increases the fluorination rate by 1.5–2 orders of magnitude in comparison with that of polyolefins [Fig. 2(5)].

The rate of fluorination is substantially reduced in the presence of oxygen. As a result of the fluorination of LDPE with a mixture of fluorine and helium con-

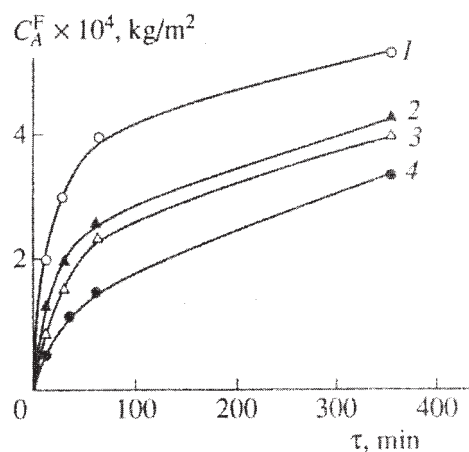


Figure 3 Kinetic curves of film fluorination: (1) PP, (2) LDPE, (3) HDPE, and (4) supermacromolecular polyethylene.

TABLE I
Characteristic XPS Binding Energies on C_{1s} of Structural Fluorine-Containing Moieties in Fluorinated LDPE

Structural moiety ^b	Binding energy (eV) ^a
—CH ₂ —CH ₂ — (1)	285.0
—CH ₂ —CH ₂ —CHF— (2)	285.8
(—CH ₂ —CH ₂ —CF ₂ —)(—CHF—CH ₂ —CHF—) (3)	286.5
—CH ₂ —CHF—CH ₂ — (4)	287.9
—CHF—CHF— (5)	289.1
—CH ₂ —CF ₂ —CH ₂ — (6)	290.7
—CF ₂ —CF ₂ — (7)	291.9

^a Determined in this and agreeing well with those determined in ref. 9.

^b Numbers in parenthesis correspond to the numbering of the curves in Figure 4.

taining a small amount of oxygen (<0.2%), a wide absorption band arises in the IR spectrum in the range of 1000–1300 cm⁻¹ (its intensity is proportional to the duration of fluorination). This is caused by the formation of CF, CF₂, and CF₃ groups due to the replacement of hydrogen atoms by fluorine atoms and the attachment of fluorine atoms to a small number of double bonds, as previously demonstrated.^{9,17}

When for LDPE the concentration of oxygen is increased, carbonyl (1650 cm⁻¹) and fluoroanhydride (COF; 1850 cm⁻¹) groups are formed along with fluorocarbon bonds, and the degree of functionality (the contents of carbonyl and COF groups) is strongly affected by the value of F₂/O₂, in agreement with previous work.¹⁸ Oxyfluorination of a linear LDPE fails to reach a sufficient chemical variety of side groups because COF groups are primarily produced via the oxidation of side or end alkyl groups rather than through the rupture of C—C bonds. Upon oxyfluorination, up to 60% of side methyl groups of PP are transformed into COF moieties.¹⁸ Moreover, the degree of LDPE film fluorination with a gas mixture containing 1% oxygen is an order of magnitude lower than that for a mixture containing 0.1% oxygen (C_A^F = 0.3 × 10⁻⁴ vs 2.8 × 10⁻⁴ kg/m²), as long as the fluorine concentration is 15% and the fluorination time is 100 min. The inhibiting action of oxygen has been taken into account for the preparation of the samples, their degassing after fluorination, the preparation of gas mixtures, and the hermetic sealing of the vessel, as noted in the Experimental section.

The composition of the surface layer of fluorinated LDPE films has been analyzed (up to a depth of 100 Å) by XPS through the C_{1s} and F_{1s}/F_{2s} spectra with the known binding energies corresponding to specific structural fragments (Table I). As in previous work,⁹ in addition to the ground state with a binding energy of 291 eV, which has been used for spectral calibration, we introduce a C_{1s} state with a high-energy binding

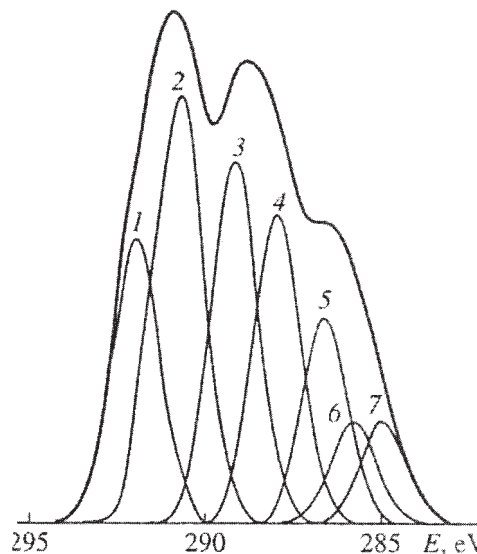


Figure 4 XPS spectra of fluorinated LDPE films. The numbers correspond to those of the fragments in Table I.

energy of 293.2–293.6 eV to describe the high-energy states of carbon. An analysis of the C_{1s} spectrum attests (Table I) to fact that the original well-resolved peak with a binding energy of 285 eV, typical of a —CH₂—CH₂— fragment, transforms after fluorination into a compound peak in the range of 285–292 eV. This fact, together with the appearance of a pronounced F_{1s} peak, indicates that the surface layer has been extensively fluorinated. Information on the composition of the fluorinated macromolecular fragments can be obtained by the resolution of the broadened C_{1s} spectrum into components with different binding energies corresponding to particular structural moieties (Fig. 4).

The contribution of each moiety to the resulting C_{1s} peak can be illustrated with an LDPE sample (C_A^F = 1 × 10⁻⁴ kg/m²). This analysis has been performed for a series of fluorinated LDPE samples, and the relevant data are presented in Table II.

These data show that the F/C ratio, which describes the degree of fluorine substitution by hydrogen,

TABLE II
Characteristics of XPS and Elemental Analysis for Fluorinated LDPE

Fluorination time (min)	C _A ^F (×10 ⁴ kg/m ² , elemental analysis)	F/C ^a	CF ₂ /CH ₂ ^b
40	0.7	1.0	0.4
60	1.0	1.1	2.8
1440	4.1	1.3	14
2880	6.8	1.5	29

^a Depth of analysis was 50 Å.

^b The relative intensity of units.

grows with the treatment time. When the treatment time is increased to 2 days, this ratio reaches 1.5 for a 50-Å-thick layer [$F/C = 2$ for poly(tetrafluoroethylene) (PTFE)]. The results indicate a fast fluorination of a thin surface (80–100-Å) layer, followed by the diffusional development of the process. As the treatment time increases, the number of CF_2 groups in the 50-Å-thick surface layer grows, as indicated by the value of CF_2/CH_2 (29) after 2 days of fluorination. Nevertheless, even after this prolonged exposure, there are still some unsubstituted hydrogen atoms in the surface layer. This, on the one hand, may reduce the physicochemical stability of the modified polymers and, on the other hand, may provide the possibility of involving the fluorinated LDPE surface in further reactions.¹⁹

The reaction can spread into the bulk of the polymer because of the diffusion of the reactant in either molecular (F_2) or radical (F^*) form.¹⁷ Because the effective diameter of a fluorine molecule (3.65 Å) is much larger than that of the F^* atom (2.70 Å),²⁰ the diffusion coefficient for F_2 in LDPE (0.08×10^{-7} cm²/s, as calculated with correlation equations²¹) is less than one-tenth of that for F^* (1.0×10^{-7} cm²/s). Because of the two-component diffusion of the reactant, accompanied by the reaction with the polymer, along with a change in the diffusion parameters during the chemical transformation of the polymer and the concomitant reduction in the reactivity of the surface layer, the quantitative analysis of these systems presents a difficulty. Nevertheless, we can estimate the effective thickness of the fluorinated layer with an elemental chemical analysis of LDPE films with different thicknesses. The content of fluorine in PTFE ($C_{F,max}$) is 76 wt %. If, as a result of the fluorination of both sides of a film (with thickness d), hydrogen atoms are completely replaced by fluorine atoms in the surface layers with thickness d_F , then the thickness of the fluorinated layer can be calculated as follows:

$$2d_F/d = C_F/C_{F,max} \quad (2)$$

However, a complete layer-by-layer substitution can hardly be achieved even after prolonged fluorination. Figure 5 shows the thickness of a fluorinated layer versus the concentration of fluorine in the LDPE films, as calculated with eq. (1). There is a wide range of d_F values depending on the regime of fluorination. Figure 5 demonstrates the formation of structural fragments of polymer analogues, such as PTFE, poly(trifluoroethylene) (P3FE), poly(vinylidene fluoride) (PVDF), and poly(vinyl fluoride) (PVF), on the surface of LDPE films.

Various relationships may be obtained for more complex systems whose structure is similar to that of the surface layers being formed, such as statistical and block copolymers and layered plastics.

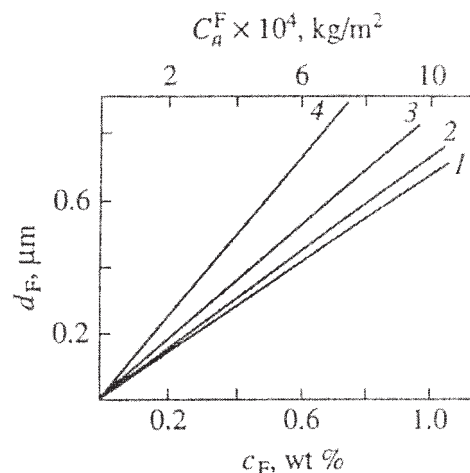


Figure 5 d_F of the fluorinated surface layer of LDPE films versus C_F and C_A^F calculated under the assumption of the formation of structures analogous to fluorinated polymers in the surface layer: (1) PTFE, (2) P3FE, (3) PVDF, and (4) PVF.

A study of the experimental data on the fluorination of various polymers leads us to conclude that relation 1 (Fig. 5) is typical of a short-time modification of low-permeable polymers (UHMWPE and HDPE) at high fluorine concentrations (15–30%). In this case, the reaction at the surface proceeds at a high rate, but a low diffusion coefficient prevents F_2 from penetrating the bulk of the polymer. For these polymers, the concentration profile is similar to curve 1 in Figure 1. Highly permeable polymers, such as poly(4-methyl-1-pentene) or membranes with a porous structure, especially at a low concentration of fluorine (<5%) and long treatment times, are typically described by dependence 4 in Figure 5. Intermediate cases of fluorination, which, in fact, are of most importance for practice, are described by profiles similar to those of curves 2 and 3 in Figure 5. These curves are close to each other because they correspond to fluorine-containing fragments of similar structures. Such a variety of structural units in the surface layer of fluorinated LDPE is also typical of other polyolefins and their copolymers.

CONCLUSIONS

The experimental data of this work show that the surface and transition layers of fluorinated polyolefins, as a rule, have a rather varied molecular design containing methylene, vinyl fluoride, and vinylidene fluoride fragments. We have suggested an approach to describing such systems that is based on an analogy to statistical and block copolymers and layered polymers. The experimental results (Fig. 5) and the calculation data are consistent with our model (Fig. 1). The chemical structure of the surface layer has been shown

to be similar to that of statistical fluorine-containing copolymers. The transition layer is the same as in a block copolymer, with fluorinated fragments adjacent to the surface layer, whereas macromolecules of the original polymer remain deeper in the polymer bulk.

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