

Multiple Surface Structures in Polyolefins Formed by Modification Methods

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ABSTRACT: New methods for the formation of multiple surface structures in polyolefins were developed both at the molecular and macromolecular levels, which produced a high local nonuniformity of surface properties. In particular, I obtained varied molecular structures at the surface as a result of consecutive heterophase fluorination and sulfonation reactions of the polymers. Nonuniform macroscopic surface structures were formed with dosed thermal and deformation treatments of prefluorinated polymeric materi-

als with the partial destruction of the formed modified layer and the subsequent predominant sulfonation of the disclosed macroscopic regions of the initial nonfluorinated polymer. The kinetics of the multiplet structure formation were studied. © 2005 Wiley Periodicals, Inc. *J Appl Polym Sci* 95: 1198–1208, 2005

Key words: surfaces; fluoropolymers; functionalization polymers

INTRODUCTION

The surface modification of polymeric materials and related items have recently become an extensively developed direction of research, which has allowed for the elaboration of processes for the manufacture of novel materials with improved physicochemical properties based on well-known polymers.¹

It is common practice to uniformly modify a polymer surface so that a predominantly homogeneous molecular structure may be formed.^{2–6} In many cases, these methods make it possible to prepare novel polymeric materials with a set of useful properties.^{7–11} At the same time, the problem of obtaining nonuniform surface macroscopic structures and chain-alternating surface molecular structures based on existing polymers is currently attracting much interest. These structures enable one to implement a high gradient of surface properties and a diverse structural and molecular design.

As shown earlier,^{12,13} the continuous surface layer of a surface-modified fluorinated or sulfonated polymer may be distorted because of thermal and deformation effects; as a result, microdefects and macrodefects are formed, and the physicochemical properties of the material deteriorate. With a number of consecutive and interrelated modification procedures,¹⁴ including thermal treatment below the melting temperature of a polymer and mostly reversible tensile de-

formations, one can improve the stability of the surface layer during the service life of polymeric materials and related items.

The efficiency of using strong fluorinating and sulfonating reactants for the modification of the surfaces of various polymers was demonstrated in a number of studies.^{9–11,15–18} The transformation of the chemical structure of the polymer surface layer in the course of fluorination and sulfonation was investigated at the molecular level, whereas the structure and properties of materials with a modified surface were determined at the macrolevel.

The goal of this study was to investigate the effect of the fluorination and sulfonation of polyolefins and fluoroplastics on their surface properties; to obtain surface layers with a maximal hydrophobicity after fluorination, close to that of polytetrafluoroethylene, or hydrophilicity after sulfonation, larger than that for known polar polymers; and third, to study the formation of chemically nonuniform multiple structures with various degrees of localization.

EXPERIMENTAL

Polyolefin films were treated with elemental fluorine mixed with helium at 20°C under atmospheric pressure in a stainless steel tank. Fluorine was taken from different steel cylinders. In this study, I made no attempt to quantitatively determine the purity of fluorine. However, from previous studies,⁹ it is known that the concentration of commercial fluorine is not more than 98%, and the basic impurities are hydrogen fluoride, oxygen, and traces of water. During the prep-

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aration of the mixtures of fluorine and helium, fluorine was passed through KF to remove HF and frozen to remove traces of water. This method allowed the purity of fluorine to be significantly increased; the concentration of oxygen was reduced to 0.1–0.2%. Helium used for the preparation of the fluorine-based mixtures was characterized by a high degree of purity (99.99%) and, therefore, lacked oxygen.

Samples of the polymer films were placed in a 2-L anticorrosion steel vessel constructed with thin rods 1 mm in diameter, which formed concentric circles in cross-section. The vessel was sealed hermetically, evacuated to a residual pressure of 1 Torr, filled with helium, and evacuated once again to a residual pressure of 1 Torr. The latter operation was carried out to remove any traces of oxygen from the vessel. The quantity of fluorine in the reaction vessel was larger by a factor of 3 than the stoichiometric amount necessary for the complete fluorination of the polymer films used in the experiments. The vessel was filled with a mixture of fluorine and helium from a cylinder to a pressure of 770 Torr, and the fluorination of the polymer films was carried out for a preset time. The vessel was then evacuated to a residual pressure of 1 Torr, and the polymer films were maintained under this pressure for 30 min until fluorine and the reaction products desorbed from the film. The vessel was then filled with air up to atmospheric pressure, and the polymer films were extracted from the vessel. Unlike in a previous study,⁹ in which the fluorination of polymer films was conducted under a flow of the gas mixture, in this work the films were fluorinated under static conditions. This made it possible to achieve a much more uniform modification of the surface of the films located in various parts of the reaction vessel.

The surface of the polymeric materials was modified by elementary fluorine mixed with helium under atmospheric pressure or sulfuric anhydride under reduced pressure. In general, the treatment procedure consisted of the following stages: the loading of the material into a hermetically sealed reactor, its evacuation, the feeding of a reactant of a given concentration into the reactor, the exposure of the material in the reactor for a prescribed period of time, the evacuation of the remaining reactant and reaction products from the reactor, an increase in the pressure in the reactor up to atmospheric pressure, and finally, the removal of the modified polymer from the reactor. The degree of modification [i.e., the ratio of the weight of fluorine that reacted with the polymer or of the formed sulfo groups to the treated surface area of the polymeric material (C_A^F and $C_A^{SO_3H}$, respectively)] was controlled by elemental analysis and by a change in the weight of the tested samples.

The sulfonation of polymers was carried out in a glass desiccator at a residual pressure of 1 Torr at 50°C. The concentration of sulfuric anhydride in the

desiccator was controlled by variation of the partial pressure of the reactant in the range 10–50 Torr. After sulfonation, the samples of polymeric materials were degassed in the desiccator, removed from it, and if necessary, rinsed with distilled or running tap water. In some experiments, samples were deformed in air in a stainless steel drawing device before sulfonation, placed into the desiccator, and sulfonated in the stressed state. To compare the efficiency of the gas-phase and liquid-phase methods, some samples were treated with oleum and then rinsed with water.

The degree of sulfonation of a polymer, defined as the ratio of the weight of sulfo groups emerged from the reaction on the sample surface, was calculated from the sulfur concentration as determined by elemental chemical analysis. The composition of the modified surface layers was studied by X-ray photoelectron spectroscopy (XPS) with an X-ray photoelectron spectrometer (XSAM-800, Kratos, Manchester, UK)⁹ and IR spectroscopy with an IRS-29 spectrometer (LOMO, St. Petersburg, Russia).

Unless otherwise indicated, fluorination was carried out under atmospheric pressure at 20°C with fluorine (15 vol %) mixed with helium, and sulfonation was performed by sulfuric anhydride (0.06 kg/m³) at 50°C and a pressure of 20 Torr.

Commercial low-density polyethylene (LDPE), high-density polyethylene (HDPE), and polypropylene (PP) films (Dorkhimzavod, Moscow) and fluoroplastic films (Plastopolimer Joint-Stock Co., St. Petersburg) were used as samples in this study.

The wetting method^{19,20} was used to investigate the surface properties of polymeric materials, including the modified ones. The contact angles of water, glycerol, and *n*-heptane drops, placed from a glass capillary onto the surface of a film (which was preliminarily cleaned with ethanol and dried at a room temperature), were measured on an optical microscope (20×). The Owens–Wendt method²⁰ was applied to calculate both the surface energy (γ) and its components, polar energy (γ^p) and dispersion energy (γ^d). The relative error in the measurements was $\pm 8\%$. In some cases, the values of γ were determined from the parachor and by the additive method.²⁰ Note that the experimental values of the contact angle obtained by different authors with different procedures may differ even for the same polymers. These facts must be accounted for by the comparison of the measurement results.

RESULTS AND DISCUSSION

Properties of films with fluorinated and sulfonated surfaces

First, I consider the effect of the degree of modification during fluorination, sulfonation, thermal treatment, and tension strain on the surface characteristics of the LDPE films.

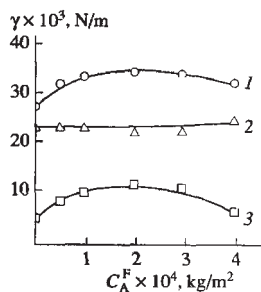


Figure 1 Dependence of (1) γ and its components, (2) γ^d and (3) γ^p , for the LDPE film (preliminarily oxidized in air) on the degree of fluorination.

Figure 1 shows γ and its components, γ^p and γ^d , plotted versus the degree of fluorination of the LDPE films. One can see that these three quantities exhibited different patterns of behavior. Although γ^d followed a straight line, the other two dependencies were curves with maxima. For their analysis, it made sense to compare my results with similar data on fluoroplastics containing different amounts of fluorine (Table I). As shown in refs. 9 and 14, the heterogeneous fluorination of LDPE is a process of consecutive substitution of hydrogen by fluorine atoms and simultaneously occurring reactions of the destruction and addition of fluorine involving an insignificant number of multiple bonds. At the same time, atomic and molecular fluorine diffuses into the material. I assumed that during fluorination, the surface layer of polyethylene (PE) underwent all the structural forms typical of fluoroplastics [from poly(vinyl fluoride) to polytetrafluoroethylene].⁹ On the basis of this assumption, I compared the surface properties of fluoroplastics (Table I) with those of the fluorinated LDPE.

It was obvious that both the dependence shown in Figure 1(1) and the change in γ as a function of the fluorine content in an elementary polymer unit (Table I) were expressed by curves with maxima. Some differences between the absolute values of γ are quite natural. Note that the absolute values of free energy calculated from the parachor (γ_p) and the dependencies of this parameter on the fluorine content in the polymer correlated fairly well with the corresponding

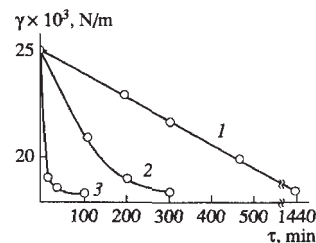


Figure 2 Dependence of free γ of the freshly prepared LDPE films on the fluorination time (τ) at concentrations of fluorine in a mixture with helium of (1) 5, (2) 15, and (3) 30 vol %.

experimental data on γ for PE and fluoroplastics. Moreover, an increase in γ^p with the degree of fluorination up to certain values of C_A^F was also due to the presence of fluoroanhydride and carbonyl groups (in addition to fluoroalkyl ones) in the surface layer.^{21,22} The formation of these groups was associated with the fact that in some experiments, I used LDPE oxidized by exposure to air rather than a freshly prepared sample. The formation of carbonyl groups is known to accompany the nonuniform oxidation of LDPE.³ Furthermore, a small amount of oxygen was also contained in the source fluorine; the presence of oxygen, to some extent, inhibits the fluorination of LDPE and contributes to the formation of fluoroanhydride groups.²³

In the case of freshly prepared LDPE film (or film after the laminate has been peeled and with no contact with air), the dependencies of γ on the time of fluorination (Fig. 2) had a shape of descending curves with saturation at the value of γ that was close to that of polytetrafluoroethylene. In this case, there was only a minimum number of fluoroanhydride groups formed, and the formation of a modified layer proceeded faster up to the values of γ typical of the corresponding fluoroplastics. Note that a value of γ of 18.5×10^{-3} N/m (which is typical of polytetrafluoroethylene) was achieved within 30 min when the polymer was treated with a mixture containing 30 vol % fluorine; after treatment with a mixture containing 15 vol % fluorine, this value was attained in 300 min; and after treatment with a mixture containing only 5 vol % fluorine, the

TABLE I
Surface Energy and its Components for LDPE and Fluoroplastics²⁰

| Polymer | Elementary unit | $\gamma^d \times 10^3$ (N/m) | $\gamma^p \times 10^3$ (N/m) | $\gamma \times 10^3$ (N/m) | $\gamma_p \times 10^3$ (N/m) ^a |
|-----------------------------|-------------------------------------|---------------------------------|---------------------------------|-------------------------------|--|
| LDPE | —CH ₂ —CH ₂ — | 33.2 | 0.0 | 33.2 | 32 |
| Poly (vinyl fluoride) | —CHF—CH ₂ — | 31.3 | 5.4 | 36.7 | 33 |
| Poly (vinyl idene fluoride) | —CF ₂ —CH ₂ — | 23.3 | 7.1 | 30.3 | 27 |
| Poly-3-fluoroethylene | —CF ₂ —CHF— | 19.9 | 4.0 | 23.9 | 24 |
| Polytetrafluoroethylene | —CF ₂ —CF ₂ — | 18.6 | 0.5 | 19.1 | 23 |

^a Calculated from the parachor.

value was attained in 1440 min. The latter proved the kinetic character of fluorination and the possibility of controlling this process by the variation of the concentration of fluorine in the gas mixture or the treatment time.

These experimental results could be used together with the data of other methods for the analysis of the structure and properties of modified polymers and to choose optimum treatment regimes.

The dependence of γ on the degree of sulfonation of the unoxidized LDPE (Fig. 3) is depicted by the curve with saturation. At high values of $C_A^{\text{SO}_3\text{H}}$, I achieved γ values that were substantially greater [(55–60) $\times 10^{-3}$ N/m] than those obtained for all other known polar polymers, including poly(vinyl alcohol), polyacrylonitrile, and hydrated cellulose. Provided that a sulfo group was substituted for a hydrogen atom in the ethylene unit, the value calculated from the parachor for the sulfonated LDPE amounted to $\gamma_p = 81 \times 10^{-3}$ N/m, which was also the largest for known polymers. The increasing heterogeneity of the surface with an increase in the degree of sulfonation was a typical feature, which was reflected by the more scattered character of the experimental data. The semicrystalline structure of the polymer led to different rates of sulfonation of the amorphous and crystalline regions, which may also occur due to different diffusion coefficients of a reactant.²⁴ At the initial stage of treatment, the heterogeneous polymer structure is disguised by a substantial change in the nature of the surface; at fairly large degrees of sulfonation, this effect is manifested by local carbonization of the surface.

Figure 4 presents the kinetics of sulfonation of LDPE films at various initial concentrations of sulfuric anhydride. The initial stage of sulfonation (1–3 min) was characterized by a high reaction rate, which was caused by the intensive consumption of reactive sites and a considerable heat release localized on the film surface. As soon as the surface layer containing sulfo groups was formed, the heterophase reaction occurred according to a diffusion-kinetic mechanism rather than a kinetic mechanism; its rate was determined by the sulfuric anhydride diffusion in the polymer and substantially decreased. To reduce the heat of the

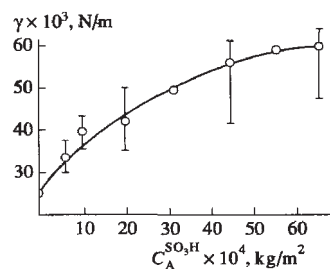


Figure 3 Dependence of free γ of the LDPE film on the degree of sulfonation.

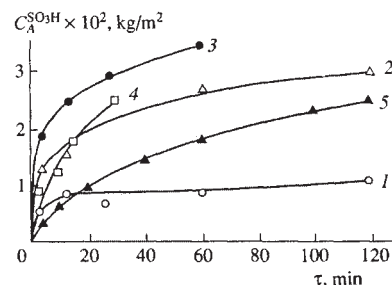


Figure 4 Kinetic dependence of the degree of sulfonation of the LDPE films at initial sulfuric acid concentrations of (1) 0.06, (2) 0.12, and (3) 0.30 kg/m^3 ; (4) at a constant concentration of 0.06 kg/m^3 ; and (5) in the liquid-phase treatment with 20% oleum ($\tau = \text{time}$).

reaction, which causes local overheating of the surface layer and thermochemical polymer destruction, I chose the following regime of sulfonation. The amount of sulfuric anhydride injected into the desiccator was either equal to or just slightly exceeded the stoichiometric amount of sulfo groups formed in the polymer. The partial sulfuric anhydride condensation on the desiccator walls ($\leq 10\%$) and the sizes of the treated samples were taken into account. In the course of sulfonation, the sulfuric anhydride concentration in the desiccator decreased, thus causing a corresponding decrease in the reaction rate. An additional reactant injection and the maintenance of its initial concentration, even at the minimum level [Fig. 4(4)], led to an increase in the sulfuric anhydride concentration and in the reaction rate.

The composition of the sulfonated surface layer was analyzed by XPS.⁹ Calibration was carried out by the right edge of the C_{1s} line with the general spectra of sulfonated LDPE samples with various degrees of modification. The following analysis of the S_{2p} line was based on the assumption that $\text{R-SO}_3\text{H}$ -type fragments with $E(S_{2p}) = 168.8$ eV (where E is the characteristic energy) predominantly formed in LDPE as a result of sulfonation, whereas $\text{R-SO}_2\text{-R}$ -type structures with $E = 167.5$ eV were not observed in the spectra. The spectra of all of the samples indicated the occurrence of some amount of calcium polysulfonates with $E = 170.4$ eV, which was caused by the washing of the sulfonated samples with running tap water. If sulfonated samples were washed with only distilled water, the corresponding peak intensity was much lower. Figure 5 shows the spectrum of sample 2 (Table II), which clearly exhibited two peaks: the peak in Figure 5(1) was the major peak at $E = 168.8$ eV, and the peak in Figure 5(2) was the minor peak at $E = 170.4$ eV. Similar spectra with somewhat different ratios of the peak areas were also obtained for other samples listed in Table II.

The analysis in Table II shows that with increasing degree of sulfonation (the sulfur content in a sample),

other things being equal, the S/C ratio characterizing the number of sulfo groups per carbon atom increased in the surface layer to 100 Å in thickness (the upper limit of sensitivity of electron spectroscopy for chemical analysis) and then insignificantly decreased. This fact that at first sight seemed abstruse with regard to the increase in the sulfur content in the samples according to the data of the elemental chemical analysis was caused by the charring of the surface layer and the regular decrease in the sulfo group concentration in it at high degrees of sulfonation. The oxygen content in the sulfonated samples was higher than its stoichiometrical amount (S:O = 1:3). This indicated the partial formation of carbonyl groups, along with sulfo groups, which was qualitatively established by the analysis of the IR spectra (1650 cm^{-1}).

The experimental facts prove the macroscopic heterogeneity of the modified polymer surface and possible application of fluorination and sulfonation for the targeted variation of the surface characteristics of polyolefins within a wide (close to theoretical) range.

In general, the established regularities of the fluorination and sulfonation of HDPE and PP were virtually the same as those for LDPE. Differences in the kinetics and the degree of modification were due to differences in the physical structure (e.g., degree of crystallinity, density) that cause diffusion in the polymer. Thus, the average rate of fluorination [calculated as the first derivative of the degree of modification with respect to time for the initial (close to linear) portion of the kinetic curve] of a PP film at the time of modification up to 60 min was twice as high as the rate of fluorination of a LDPE film and exceeded the corresponding parameter for a HDPE film by a factor of 2.3.

Formation of microscopic and macroscopic nonuniform structures on the surface

Methods of heterogeneous fluorination and sulfonation of polymers such as PE are almost perfectly

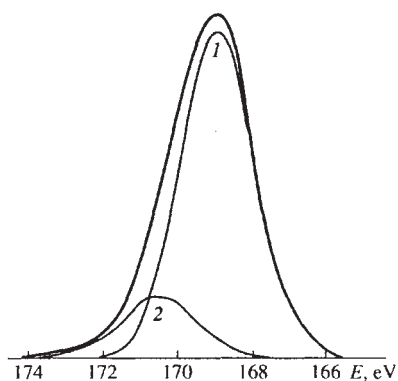


Figure 5 Photoelectron spectrum of the S_{2p} line of the sulfonated LDPE (Table II, sample 2) in the bond energy components (see text).

TABLE II
Data of the XPS and the Elemental Chemical Analysis of the Sulfonated LDPE Samples

| No. | Sulfur content (wt %) ^a | $C^{SO_3HA} \times 10^4$ (kg/m ²) ^a | Depth of analysis (Å) ^b | S/C ^b |
|-----|------------------------------------|--|------------------------------------|------------------|
| 1 | 1.0 | 6.1 | 40 100 | 0.07 0.04 |
| 2 | 1.7 | 10 | 40 | 0.08 |
| 3 | 2.2 | 13 | 40 | 0.15 |
| 4 | 2.6 | 16 | 40 | 0.13 |
| 5 | 2.9 | 18 | 40 | 0.09 |
| 6 | 3.0 | 19 | 40 | 0.09 |

^a Elemental chemical analysis, data.

^b XPS data.

suitable for the experimental reproduction of similar structures. Indeed, for a polymer whose macromolecules contain only methylene units, one may obtain chain-alternating bifunctional and polyfunctional molecular fragments²⁵ by fluorination and sulfonation, thus forming a controlled (within the macromolecule segment) chemical structure. However, one can obtain nonuniform multiple macroscopic structures with a high localization of structural fragments and intermediate transient (by polarity) surface regions by subjecting a prefluorinated polymer to thermal and deformation treatments with controlled (by size and number) disclosure of the regions of the initial untreated polymer (called further as defects of the surface layer) and by the subsequent sulfonation of these defects. The multiplicity (with respect to both size and modification degree) of such structures in a polymer may be increased by subsequent, more intense thermal deformation and other treatments in combination with modification procedures.

To form multiple surface structures, LDPE films with a moderate degree of fluorination ($C_A^F = 3 \times 10^{-4}$ kg/m²) were prepared, which demonstrated properties typical of fluorinated films.

The multiple structures were formed by several general schemes (Fig. 6). A prefluorinated film (PE_F) was thermally treated in air (T) and deformed by uniaxial stretching (ϵ), or the fluorinated surface layer was dose-destructed (DD), for example, with metal needles in accordance with a preset pattern. The top view in Figure 6 schematically shows the distortions of the continuous fluorinated layer (exhibited as the regions of the initial polymer) as a result of these effects. Subsequent sulfonation proceeded by three main routes, indicated schematically by the arrows (film sectional view); the basic route was the reaction of SO_3 with the regions of the initial polymer to give rise to sulfo groups (PE_{SO_3H}). The lower part of Figure 6 illustrates how heterogeneous surface macroscopic structures were formed by the screening of the initial polymer, fluorination, screen removal, and sulfonation.

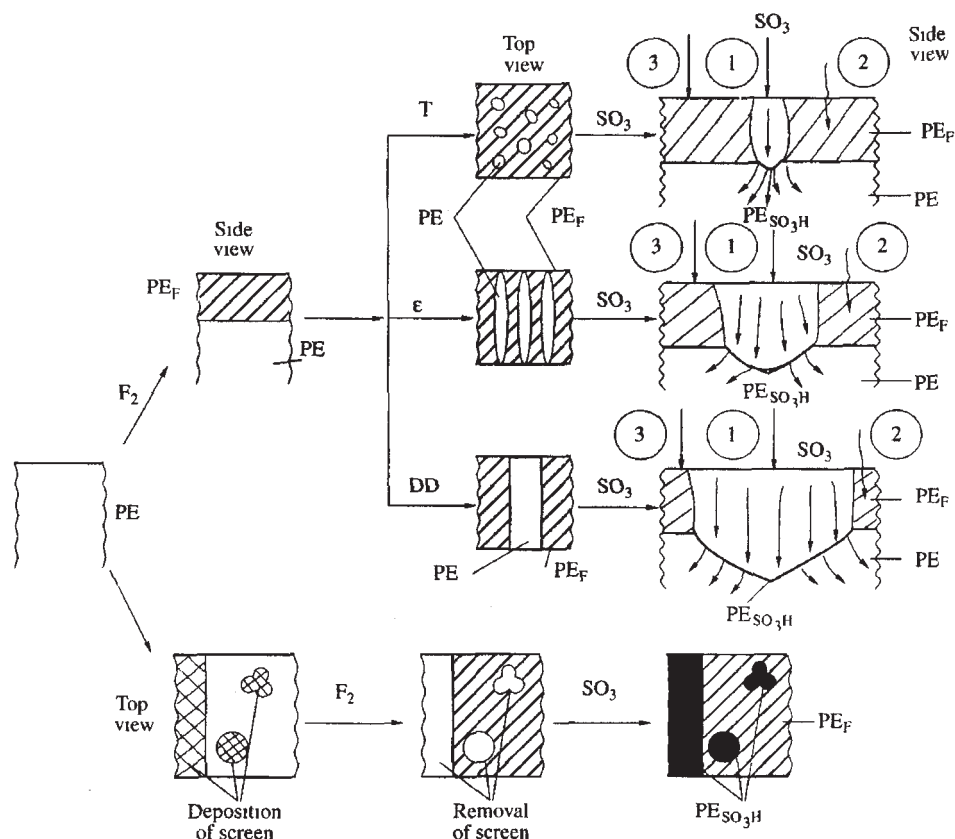


Figure 6 Layout of the formation of the multiplet surface structures (see text for explanation).

Figure 7 shows the kinetic curves for the degree of sulfonation ($C_A^{SO_3H}$) of a fluorinated LDPE film without thermal treatment [Fig. 7(1)] and on preliminary thermal treatment [Fig. 7(2)]. The sulfonation rate of the schematically prefluorinated LDPE whose surface layer was close (by its chemical structure) to that of fluoroplastics¹⁸ was 20–150 times lower than that of the initial LDPE, depending on the degree of fluorination and the sulfonation conditions. For both curves in

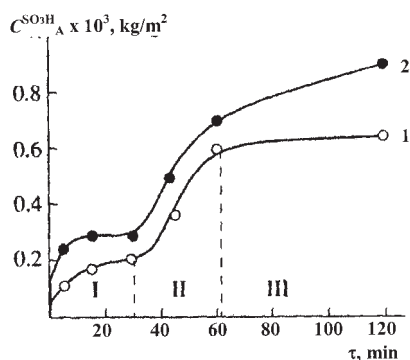


Figure 7 Dependence of the degree of sulfonation of the prefluorinated LDPE film on the treatment time (τ) with sulfuric anhydride (1) without intermediate thermal treatment and (2) after thermal treatment for 15 min at 90°C.

Figure 7, a clearly pronounced two-stage pattern was typical: at the first stage, a relatively high rate of sulfonation was followed by its subsequent deceleration; at the second stage, the rate dramatically increased, and the curves reached saturation [this is most clearly seen in Fig. 7(1)].

The sulfonation of various fluoroplastics aimed at the enhancement of their hydrophilicity (by analogy with the treatment of the fluorinated LDPE) substantiated the possibility of changing their γ due to the substitution of hydrogen atoms by sulfo groups (Table III).^{15,26} In this case, higher values of $C_A^{SO_3H}$ and $\Delta\gamma = \gamma_{mod} - \gamma_{init}$ corresponded, as a rule, to a higher content of hydrogen atoms in the repeating polymer unit, although the role of the physical structure of the polymer was also essential. It is important that the effective sulfonation of fluoroplastics is feasible only at a considerable concentration of sulfuric anhydride.

The thermal treatment (at 100°C) of the fluorinated LDPE tended to loosen the surface layer because of the occurrence of relaxation processes and tended toward the chaotic (if the film is isotropic) formation of the regions of the parent polymer, which was reflected by a decrease in the magnitude of γ [Fig. 8(1)]. The structure of the surface layer stabilized within a 20-min thermal treatment.

TABLE III
Surface Characteristics of Parent and Sulfonated Fluoroplastics

| Grade of fluoroplastic | Structural unit | $C^{SO_3H} \times 10^4$ (kg/m ²) | $\gamma_{init} \times 10^3$ (N/m) | $\gamma_{mod} \times 10^3$ (N/m) |
|------------------------|---|---|--------------------------------------|-------------------------------------|
| F-3M | (CF ₂ —CFCl)(CH ₂ —CF ₂) | 1.2 | 24 | 27 |
| F-2M | (CF ₂ —CH ₂)(CF ₂ —CF(CF ₂ H)) | 2.5 | 32 | 35 |
| F-42 | (CF ₂ —CF ₂)(CF ₂ —CH ₂) | 4.3 | 34 | 36 |
| F-26 | (CF ₂ —CH ₂)(CF ₂ —CF(CF ₃)) | 8.8 | 26 | 34 |
| F-23 | (CF ₂ —CH ₂)(CF ₂ —CFH) | 10 | 22 | 43 |

γ_{init} is the surface energy of unmodified polymer; γ_{mod} is the surface energy of modified polymer.

A similar tendency was characteristic in the more rigid and stable polymer in the thermally treated sulfonated layer [Fig. 8(2)]; however, the stabilization of γ occurred after a longer thermal treatment.

At $C_A^{SO_3H} > 1 \times 10^{-3}$ kg/m², the surface layer became so rigid that even the thermal treatment at 100°C for 15 min could not pull it apart. γ remained unchanged in this case.

To analyze these and other dependencies discussed later, it is useful to identify the possible routes of sulfonation of PE_F. The most probable were the following pathways (in descending order of intensity (see Fig. 6): (1) sulfonation of the nonfluorinated subsurface layers of the initial polymer via defects of the fluorinated surface layer; (2) sulfonation of both partially fluorinated subsurface layers and, then, of the initial polymer (by route 1) due to diffusion of sulfuric anhydride through the fluorinated surface layer; and (3) sulfonation of the fluorinated surface layer via hydrogen atoms that remained intact after fluorination.²⁷

The prevalence of a certain sulfonation pathway was attributed to C_A^F of the surface layer, the type and degree of subsequent treatment (e.g., temperature, deformation) that destroyed its uniformity, and the intensity of sulfonation. The thermal treatment of the fluorinated LDPE favored the occurrence of relaxation processes; as a result, the continuous structure of the modified surface layer was distorted, and the regions of the initial polymer became accessible. In this case, the degree of sulfonation was directly proportional to the treatment

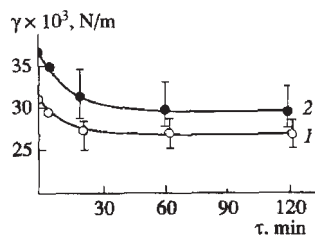


Figure 8 Dependence of γ of the (1) fluorinated LDPE film ($C_A^F = 1 \times 10^{-4}$ kg/m²) and (2) sulfonated LDPE film ($C_A^{SO_3H} = 6.5 \times 10^{-4}$ kg/m²) on the time of thermal treatment (τ) in air.

temperature (Fig. 9). General patterns of the sulfonation kinetics of the initial (Fig. 7) and heat-treated samples of a fluorinated LDPE were similar; this was explained by the fact that sulfonation occurred at 50°C (i.e., actually after the additional thermal treatment as compared to the fluorination at 20°C). Portion I (Fig. 7) was characterized by usual sulfonation kinetics (albeit extended as compared to the initial LDPE¹⁸) and a lower (by 20–150 times) degree of sulfonation associated with a much smaller number of active sites at the fluorinated polymer surface. In portion II, the sulfonation process was accelerated because of the diffusion of sulfuric anhydride into the polymer depth along the defects of the fluorinated layer formed as a result of local heating caused by the exothermic character of the polymer sulfonation. In portion III, this process was completed for the thermally untreated sample [Fig. 7(1)] because of the small defectiveness of the surface layer, whereas for the thermally treated sample [Fig. 7(2)], the sulfonation proceeded predominantly by route 1 (see Fig. 6) via sulfonated defects of the fluorinated layer due to the high affinity of sulfuric anhydride toward the sulfo groups formed. Modification performed in accordance with the third route was similar to the sulfonation of fluoroplastics containing hydrogen atoms; this speculation was proven by the close values of $C_A^{SO_3H}$ for various surface-sulfonated fluoroplastics (from 0.1×10^{-3} to 0.8×10^{-3} kg/m²²⁷) and a sulfonated surface-fluorinated LDPE.

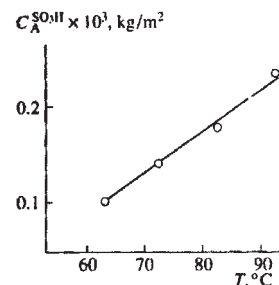


Figure 9 Dependence of the degree of sulfonation of the prefluorinated LDPE film on the temperature (T) of its intermediate thermal treatment in air for 15 min.

Multiple heterogeneous surface macroscopic structures were clearly distinguishable on the micrograph (Fig. 10) obtained with a POLAM-L211 polarization microscope (LOMO, St. Petersburg, Russia) by the phase contrast method: (1) sulfonated structures (dark in color) resulting from the effect of sulfuric anhydride on the regions of the initial polymer that became accessible on thermal treatment and (2) fluorinated structures (light in color) that remained virtually intact after sulfonation. The intensity of thermal treatment determined the dimensions of the regions of the initial polymer accessible to sulfonation. In this case, the surface picture appeared to be chaotic because the initial structure was isotropic (provided that the film was not strongly oriented initially).

An increase in the sulfuric anhydride concentration regularly resulted in an increase in the rate and the degree of sulfonation throughout the entire time interval, thus increasing the value of $C_A^{SO_3H}$ by 2–10 times. Given this, the two-stage pattern of the dependences similar to those shown in Figure 7 was more clearly defined.

Ordered large macroscopic structures were formed during ε of prefluorinated LDPE films with subsequent sulfonation (Fig. 7).

$C_A^{SO_3H}$ versus ε dependencies were expressed by straight lines whose slopes increased in the course of sulfonation. The observed proportionality between the values of $C_A^{SO_3H}$ and the magnitude of deformation was associated with the formation and development of microcracks in the fluorinated surface layer with a gradual increase in their total surface area.

The determination of the fraction of the surface area of the LDPE film with predominantly sulfonated regions was a rather complicated task because a few different sulfonation routes could have occurred (Fig. 6). Nevertheless, I could compare the degree of sul-

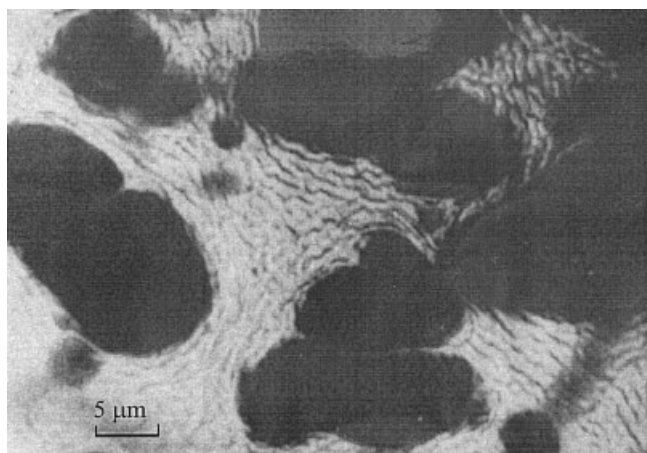


Figure 10 Phase contrast micrograph of the surface of the fluorinated LDPE film subjected to thermal treatment and sulfonation [corresponding to Fig. 7(2); sulfonation time = 60 min].

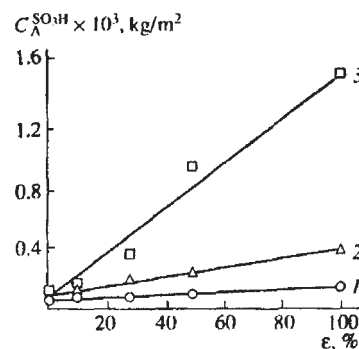


Figure 11 Dependence of the degree of sulfonation of the prefluorinated LDPE film on the uniaxial tensile deformation at sulfonation times of (1) 1, (2) 3, and (3) 5 min.

fonation for the initial and fluorinated LDPE films (in particular, for the latter case with intermediate stages of the film thermal treatment and stretching) with the data presented in Figures 7 and 11.

When sulfonation was performed for 5 min under the same conditions, the results were as follows: for the initial LDPE, $C_A^{SO_3H}$ (S) = 5×10^{-3} kg/m² ($C_A^{SO_3H}$ (S) is the sulfonation degree of preliminarily fluorinated LDPE); for fluorinated LDPE, $C_A^{SO_3H}$ (F-S) = 0.1×10^{-3} kg/m² ($C_A^{SO_3H}$ (F-S) is the sulfonation degree of preliminarily fluorinated LDPE); for fluorinated, thermally treated and then sulfonated LDPE, $C_A^{SO_3H}$ (F-T-S) = 0.25×10^{-3} kg/m²; and for the intermediate stretching ($\varepsilon = 60\%$), $C_A^{SO_3H}$ (F- ε -S) = 1×10^{-3} kg/m². Under these experimental conditions, $C_A^{SO_3H}$ (F-S) for the fluorinated LDPE was about 2% of the $C_A^{SO_3H}$ (S) value for the initial LDPE, which may have been due to the involvement of the remaining hydrogen atoms in the sulfonation and the diffusion of sulfuric anhydride through the fluorinated layer with subsequent reaction in the polymer depth. The stage of intermediate thermal treatment increased the value of $C_A^{SO_3H}$ (F-T-S) compared to that of $C_A^{SO_3H}$ (F-S). The difference between these values may have been due to the sulfonation of the regions of the initial polymer that were disclosed in the fluorinated surface layer as a result of relaxation processes; this difference was equal to $\Delta C_A^{SO_3H}$ (T) = 0.15×10^{-3} kg/m². These data gave me grounds to infer that the surface area of the regions of the initial polymer that were formed during the thermal treatment and subsequently sulfonated was about 3% of the total surface area of the fluorinated film. As shown earlier, this value could be controlled by the regime of thermal treatment.

The uniaxial deformation of fluorinated LDPE films enabled me to significantly change the structure and composition of the surface layer, thus increasing the fraction of predominantly sulfonated regions because of crazing occurring in the fluorinated layer up to 20% and larger amounts with the targeted orientation of multiplet structures.

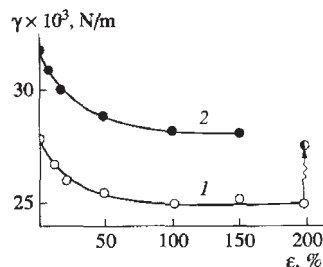


Figure 12 Dependence of free γ on the tension strain for the (1) parent LDPE film and (2) fluorinated LDPE film ($C_A^F = 1 \times 10^{-4}$ kg/m²) preoxidized in air.

Figure 12 presents γ plotted versus the relative elongation of the films of the parent and fluorinated LDPE, which supported the mechanism advanced for the formation of defects in the surface layer under tension (curve 2). According to this mechanism, the values of γ decreased to those characteristic of the parent (oxidized) LDPE. In this case, at $\epsilon > 50\%$, the values of γ appeared to be independent of the tensile strain. A similar dependence was typical of the parent LDPE; the only difference was that regions of the unoxidized polymer were formed on the surface under tension, decreasing the integrated value of γ . However, the exposure of then LDPE film (stretched up to $\epsilon = 200\%$) to air with a relative humidity of 35% for 24 h resulted, presumably, in the adsorption of moisture on the freshly formed surface with a regular increase in γ (the arrowed wavy line in Fig. 12). The rubber-like character of the deformation of both the bulk and the surface layer of a film contributed to the gradual rearrangement of the structure and the macroscopic motion of structural fragments, which was reflected by the change in the integrated macroscopic parameter γ . Despite insignificant (by their absolute value) changes in γ , the general tendency in structural rearrangement under tension was fairly clearly revealed.

Unlike the fluorinated LDPE, the value of γ for the sulfonated polymer remained constant up to $\epsilon = 100\%$ with a substantial variation in the ratio between γ^p and γ^d (Fig. 13). The effect of the surface of the parent LDPE forming in microcracks manifested itself as a linear growth in γ^d and a decrease in γ^p . In the course of film deformation, the sulfonated surface layer underwent brittle failure (at $C_A^{SO_3H} > 1 \times 10^{-3}$ kg/m² and a relative air humidity of 35%): microcracks were initially formed followed by the appearance of macrocracks. With calculations by the group contribution technique,²⁰ the glass-transition temperature (T_g) of the sulfonated layer with one sulfo group in the repeating unit of LDPE was found to be $T_g = 122^\circ\text{C}$ (cf. for LDPE, $T_g = -70^\circ\text{C}$). On the basis of these data, I inferred that this layer was highly rigid, which is typical of many high polarity polymers. This rigidity can be varied in a fairly wide range by conventional

methods, for example, by plastification with water or glycerol. The effect of plastification of the sulfonated layer was especially pronounced for the films that had been subjected to one-sided treatment. At a low relative humidity of the surrounding air, such a film spontaneously rolled up because of the effect of considerable unbalanced surface tension forces. As the humidity increased, the film gradually unrolled.

Formation of large macroscopic nonuniform structures on the surface

Still larger and reversibly strained macroheterogeneous structures were formed during dose destruction (DD) of the fluorinated surface layer as a result of the mechanical action by the scraper made of metal needles with subsequent sulfonation (Fig. 6, DD). By varying the needle diameter and creating different patterns of the destruction of the surface layer, I succeeded in forming diverse multiplet structures, characterized by a high gradient of physical and physicochemical properties during the subsequent sulfonation of these fractions. For example, it was shown¹⁸ that a difference in the values of the specific electrical surface resistance for fluorinated and sulfonated regions was as large as eight to nine orders of magnitude, whereas the values of the surface tension differed by $35\text{--}40 \times 10^{-3}$ N/m.²⁵

In addition to the proposed methods of destruction of the formed fluorinated layer, another procedure could be used to enable further reactions in the disclosing regions of the initial polymer. This procedure involved the screening of preset parts of the film surface during fluorination, as shown in Figure 6, followed by the removal of the screen and, for example, by their sulfonation with the formation of macrostructures with a desired complex shape.

The treatment of LDPE and many other polymers with sulfuric anhydride resulted in their characteristic coloration, which varied from light brown to black. This allowed me to employ the sulfonation of the prefluorinated polymer as an effective flaw detection method. Random or targeted destruction of the fluor-

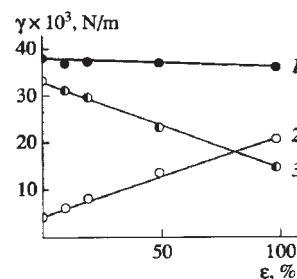


Figure 13 Dependence of (1) γ , (2) γ^d , and (3) γ^p on the tension strain for the sulfonated LDPE films ($C_A^{SO_3H} = 9 \times 10^{-4}$ kg/m²).

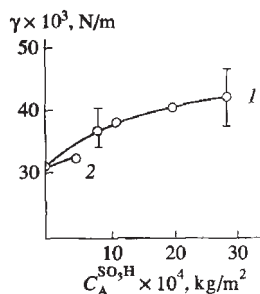


Figure 14 Dependence of γ on the degree of sulfonation for the preliminarily fluorinated LDPE films ($C_A^F = 2.5 \times 10^{-4}$ kg/m²) at concentrations of sulfuric anhydride of (1) 0.12 and (2) 0.06 kg/m³.

inated layer was adequately fixed by the contrast coloring after intense sulfonation.

The determination of γ of the polymers with the multiplet surface structure by the wetting method involved difficulty because of a considerable local heterogeneity of the surface. Nonetheless, the application of this method enabled me to assess the presence of nonuniformities in the modified surface layer. Figure 14 shows the dependences of γ on the degree of sulfonation of the preliminarily fluorinated LDPE. On the whole, these dependencies had the same pattern as analogous dependencies for a sulfonated polymer. The difference was that either a longer modification time or an increased concentration of sulfuric anhydride was needed to obtain the same values of γ . Thus, at $C_{SO_3} = 0.06$ kg/m³ and with a sulfonation time of up to 2 h, the value of γ did not change substantially [Fig. 14(2)]; however, an increase in the concentration of sulfuric anhydride up to $C_{SO_3} = 0.14$ kg/m³ led to an increase in γ , even though this effect was not so pronounced as in the sulfonation of the parent LDPE. This was associated with a barrier effect of the fluorinated layer. As a result, the sulfonation proceeded because of the two factors: first, the substitution of hydrogen atoms by sulfo groups remaining in the surface layer, which was retarded by the screening effect of fluorine atoms; and, second, the diffusion of a reactant through already present defects and defects being formed in the fluorinated surface layer. A high polarity of sulfo groups contributed to an increase in γ . A considerable scatter of the experimental data (as was the case in thermal treatment) suggested local macroheterogeneity of the surface layer.

A qualitative difference in the degree of sulfonation led to substantial distinctions in the properties of the materials as a whole. In the case of fluoroplastics, only molecular nonuniformity (or bifunctionality) involving fluorine atoms and sulfo groups could be achieved. However, in addition to this nonuniformity, macroregions composed of a predominantly fluorinated or sulfonated polymer could also be formed

when fluorinated LDPE and thermal treatment and deformation techniques were employed. Moreover, the as-modified material combined the advantages of both the parent polymer and the formed surface layers, although the sulfonated fluoroplastics acquired a set of improved physicochemical properties, such as water wettability, diminished electrical resistance, and the capability for the specific sorption of substances; in many cases, these effects also suggest an improvement in the biocompatibility of polymeric materials.²⁸

The regularities discussed previously were established for the LDPE films treated in accordance with the following scheme: Fluorination \rightarrow Intermediate partial destruction of the surface layer \rightarrow Sulfonation. However, reversing the order of fluorination and sulfonation stages (albeit with the intermediate stage) was also possible. In this case, a larger fraction of the surface became hydrophilic, whereas a smaller fraction acquired hydrophobic properties with characteristics inherent to fluoroplastics. The only limitation was the degree of sulfonation that could not exceed $C_A^{SO_3H} < 1 \times 10^{-3}$ kg/m². At higher values of this parameter, the sulfonated layer became rigid and resistant to thermal treatment and fluorination; at the same time, it could spontaneously crack (especially at low air humidity), thus complicating the targeted formation of stable multiplet structures.

CONCLUSIONS

In this study, a new technique for obtaining layered (multiplet) molecular structures in polyolefin films was developed. My method included two consecutive stages: first, the fluorination of the film surface by a mixture of gaseous fluorine and helium, and, second, the sulfonation of the polymer sample by gaseous sulfuric anhydride. The method was especially versatile for the preparation of a nonuniform, either microscopic or macroscopic, structure of a given chemical design, which is often difficult to achieve by other known techniques.

For these particular situations, I worked out a detailed sequence of stages, consisting of fluorination, thermal and mechanical treatment, and subsequent sulfonation, which made it possible to obtain polymeric materials with desired characteristics.

The effect of the degree of modification on γ of the original, fluorinated, and sulfonated films and the films with preliminarily formed multiple structures of various types was studied. I showed that structures with a low value of γ , which is typical of fluoropolymers, could be prepared by fluorination of polyolefin films. In contrast, sulfonation may have led to high values of γ , which were, in fact, greater than those for the majority of known polar homopolymers.

The concept describing the formation of the multiplet surface structures is general for the majority of

polymers and may be applied to the production of chain-alternating molecular and heterogeneous macrostructures. The most promising application fields of the procedures developed in this work are medicine, biotechnology, and electronics. Sevast'yanov and I applied the previously described procedures to prepare multiple surface structures in medicinal catheters based on PE and poly(vinyl chloride), which provided high thromboresistance.²⁸

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