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# Direct Fluorination of Polymer Final Products: From Fundamental Study to Practical Application

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**Abstract**—The results of study of the fundamental features of the direct fluoridation of polymers, physical and chemical properties of the fluorinated layer at the surface and possible application areas of the direct fluoridation are reviewed. The influence of the composition of fluorinating mixture, the process pressure, temperature and duration on the kinetics of formation of the fluorinated layer was investigated. The fluorinated layer composition, density, refraction index and surface energy were measured at the different conditions of the surface treatment. Kinetics of termination of long-lived radicals formed inside the fluorinated layer was studied. The methods of enhancing the barrier properties of fluorinated polyethylene with respect to alcohol-containing fuel, enhancing the gas separation properties of flat membranes and hollow-fiber membrane modules and improving chemical stability of polymer pipes were developed. Possibility to use direct fluorination for reinforcement of polymer composites was demonstrated.

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## INTRODUCTION

Properties of polymer products such as adhesion capability, colorization, barrier properties, chemical stability, separating ability of polymer membranes are defined by the surface layer of the product, of the tickness from ~10 nm to a few micrometers. Therefore economically reasonable to produce the final products from a cheap and available polymer and then to modify only its surface layer. Among the methods of the surface modification the method of direct fluorination can be fairly effective [1–6].

The term "direct fluorination" commonly means the process of heterogenous reaction of gaseous molecular fluorine or its gaseous mixtures (with $N_2$, He, Ar, $O_2$ and others) with the polymer surface. The direct fluorination of polymers is specific in several aspects from the viewpoint of its practical application. The process is spontaneous at room temperature, proceeds with acceptable rate and not needs heating, UV stimulation or application of a catalyst. This process constitue the basis of "dry" technology of surface modification of polymers. Ecological safety of this technology is provided by existence of reliable and well developed methods of neutralization of the residual $F_2$ and the reaction product HF. Application of direct fluorination allows to improve some exploitation characteristics of the polymer products, in part, their barrier properties, gas separating ability, adhesion, and others [1–8]. Therewith, only thick surface layer of the product, ~0.01 nm to 10 μm thickness, is subjected to the modification while the properties of the product bulk remain intact.

Since 80th of 20 century the process of direct fluorination is applied widely at the industrial scale for improving the barrier properties of polymer fuel tanks of vehicles, but there are only fragmentary and incomplete data on the fundamental features of the process. Increased requirements to the quality of polymer products led to necessity of improving the technology of direct fluorination [3–8]. Therefore in Russia during thelast 20 years were initiated the fundamental studies of the process of direct fluorination of polymers that allowed to improve technology of this process on the laboratory scale and to formulate recommendations on practical application of the process.

In the first section of this paper are considered the basic results of the fundamental investifations of the direct fluorination process. In the second section are demonstrated the achievements in improving commercial properties of polymer products by the method of surface fluorination.

## Fundamental Characteristics of the Process of Direct Fluorination of Polymers

The following polymers were exposed to the fluorination: low-density polyethylene (two sorts), high-density polyethylene (six sorts), polyvinylfluoride, polyvinylidenefluoride, polydstyrene, polymethylmethacrylate, polyphenyleneoxide (two sorts), polyimide (Matrimid® 5218), polypropylene, butadiene – sulfone block copolymer (Seragel®), polycarbonate-syloxane (CarboSil®), polyvinyltrimethylsilane, polysulfone (Udel 3500), poly-4-methylpentene-1, epoxy resin (components: EN6, DDS and E05M), polyvinyl alcohol. As a fluorinating agent was used fluorine containing less than 0.1% of contaminants (oxygen mainly). The standard methods of surface investigation were applied: IR-FT spectroscopy, UV-VIS spectroscopy, refractometry, electron microscopy, gas chromatographc measuring of the polymer membrane transport characteristics, measuring the surface energy of polymers and measuring the gasoline penetration trough polymer films [5]. For themeasuring the kinetics of growing the fluorinated layer thickness *in situ* (without interruption of the fluorination process for a single measurement) a specal original non-destructive interfenece method was developed [5, 9, 10] that allows registration of the fluorinated layer thickness $\delta_F$ from ~0.1 μm and up to a few tens micros. The surface layer density of the layers from 0.5 to 10 μm thicknesswas also measured using the developed nondestructive procedure [5, 11].

At the fluorination of the polymers proceeds cleavage of C–H bonds and opening of double C=C bonds, including conjugate ones, with fluorine addition, and disruption of a significant part of C–N and C–Si bond (when exist) followed by adding of fluorine to carbon atom. The degree of fluorination in the polymer layers with thickness over a few micrometers, except low-density and high-density polyethylene and plyvinylfluoride, is near unity. When the fluorinating mixture contains oxygen, a controlled amount of C=O containing groups is formed, including–COF, that at the contact with atmospheric moisture are transformed into –COOH [1, 3, 4–7, 11, 14–17]. It is shown that concentration of the C=O containing groups in the fluorinated layer is constant along width and grows with the increase in oxygen content in the fluorinating mixture. For a series of polymers the value of $N_{C=O}$ that is defined as the ratio of totalnumber of C=O-containing groups to the total number of monomeric links in the fluorinated layer, can achieve the value close to ~1 [5, 17].

The transmission spectra in visible spectral region of all studied fluorinated polymer films show clear interference features that occurs both in one side fluorinated films and in those fluorinate at both sides. Such a picture can occur in the following cases: (a) the fluorinated layer and the region of nont modified polymer are separated by a narrow transition zone with thickness <<0.1 μm; (b) $n_F < n_V$, where $n_F$ and $n_V$ are refraction indices of the fluorinated and parent polymers respectively (as is actually occurs); c) The initial polymer film surface is flate enough, with the size of heterogeneities <<0.1 μm, and heterogeneity in the flourenated layer thickness is ~0.1 μm or less within whole area.

Accounting for the interference character of transmission spectra of the fluorinated polymer films and root type dependence of the fluorinated layer thickness $\delta_F$ on the fluorination duration $t$ ($\delta_F \sim t^{0.5}$, see below), one can conclude that the fluorinated surface layer and the region of the paren polymer actually are separated by a narrow transition zone with the thickness <<0.1 μm. The principal chemical transformation proceed mainly in side of the transition zone, and fluorine penetration through fluorinated layer to the not modified region of the polymer defines limiting step of the process. The existence of narrow frontier between the fluorinated layer and the region of parent polymer is confirmed also by the photos made with electron microscope of the sections of polyvinyltrimethylsilane and Seragel® films fluorinated not over whole bulk [4, 5, 18] can be seen the layers of the fluorinated an of not modified polymers.

The above mentioned interference method was used for the study *in situ* of the kinetics of grow of the fluorinated layer [4, 5, 9, 10]. For removing hydrogen fluoride (a reaction product) from the gas phase (HF inhibits the fluorination process) inall the experiment except specially mentioned to the reaction zone was added pressed sodium fluoride tablet: NaF + HF = $NaHF_2$ (solid). For all the studied polymers (ecept composite membranes based on polycarbonatsiloxane [19]) and all the mixtures used for the fluorination occurred root type dependence of the fluorinated layer thickness $\delta_F$ on the treatment duration $t$:

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

where $A$ depends on the partial pressure of $F_2$, $O_2$, He, $N_2$ and HF ($p_F$, $p_O$, $p_{He}$, $p_N$, and $p_{HF}$) and the process proceding temperature. The value of constant term (cons) can be omitted for the most polymers excluding polyethylene low-density and high-density, and polyvinylfluoride. The $B$ and $k$ values for various polymers are given in [4–6].

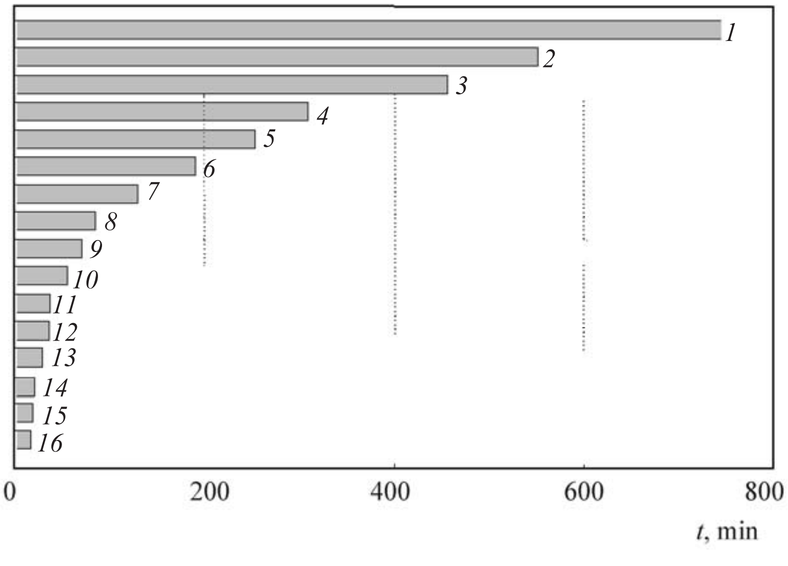
As seen in the figure that demonstrates duration of formation of 1 μm fluorinated layer at the fluorine pressure 0.1 bar at room temperature as a dependence on the polymer nature, the duration is varied in the range from 20 min to 12 h.

It is shown that presence of helium, nitrogen, argon or carbon dioxide in the commonly used in industry fluorinatingmixture little affects the fluorination rate at the constant partial fluorine pressure up to fluorine content as low as 2 vol % . For some polymers the dependence of $\delta_F$ from $p_F$ is close to the root type [Eq. (1)] that corresponds to ideal case when gas premeation through the modified polymer does not depend on the fluorinated layer thickness [5]. But in most cases occurs deviation of $\delta_F$–$p_F$ plot from the root type, that can attest that in the fluorinated layer proceeds “afterburning” reaction, that is, initially the polymer layer mass is converted to the fluorinated polymer not completely and then proceed slower processes of fluorination and those with participation of long living radicals as well.

Oxygen inhibits formation of polymer layer. The inhibition degree depends on the polymer nature [3–6]. Hydrogen fluoride also decreases the rate of fluorination. For example, at the fluorination of polyethyleneterephthalate addinfg of hydrogen fluoride 3 vol % only to fluorine diminishes $A$ coefficient [Eq. (1)] 1.4-fold [4, 5].

The rate of growing th fluorinated layer thickness increases at elevated temperature. When the dependence of $A$ coefficient is represented as $A \sim A_0\exp(-E_a/RT)$, then activation energy $E_a$ equals 13.4 kJ mol$^{-1}$ in the case of low-density polyethylene (0.918 g cm$^{-3}$ ), and 28.1 and 34.2 kJ mol$^{-1}$ in the case of high density polyethylene (0.945 and 0.949 g cm$^{-3}$, respectively) [5, 6].

The average density of the fluorinated layer of poyvinyltrimethylsilane, poystyrene, polystyreneterephthalate, and poyphenyleneoxide does not depend



Duration of formation fluorinated layer of 1 μm thickness on various polymers at the fluorine pressure 0.1 bar at room temperature. (*1*) Low-density polyethylene ($\rho$ = 0.926 g cm$^{-3}$), (*2*) polyvinylfluoride, (*3*) low-density polyethylene ($\rho$ = 0.918 g cm$^{-3}$), (*4*) polypropylene, (*5*) polyvinol, (*6*) seragel 3760/3, (*7*) sulfonated polyester, (*8*) polycarbonatesiloxane, (*9*) high-density polyethylene ($\rho$ = 0.94–0.95 g cm$^{-3}$), (*10*) polysulfone, (*11*) epoxy resin, (*12*) polyvinyltrimethylsilane, (*13*) polyphenyleneoxide, (*14*) polyethyleneterephthalate, (*15*) polyimide, and (*16*) polystyrene.

Density ($\rho_V$ and $\rho_F$) and refraction index ($n_V^D$ and $n_F^D$) of initial and fluorinated polymers

| Polymer | $\rho_V$, g cm$^{-3}$ | $\rho_F$, g cm$^{-3}$ | $n_V^D$ | $n_F^D$ |
|---|---|---|---|---|
| Poystyreneterephthalate | 1.46 | 1.75 | | |
| Poystyrene | 1.05 | 2.05 | 1.59 | 1.366 |
| Poyvinyltrimethylsilane | 0.85 | 1.73 | 1.4915 | 1.376 |
| Polypheyleneoxide, molecular weight 34000 | 1.07 | 1.72 | | 1.3730 |
| Polypheyleneoxide, molecular weight 244000 | | | | 1.3808 |
| Polyimide | | | 1.614 | 1.41 |

in its thickness in the range 0.5–10 μm and is much higher than the density of parent polymer (see the table). Density of fluorinated layer of polyimide depends on its thickness, and grows to the value ~1.9 g cm$^{-3}$ when $\delta_F$ grows to 5–8 μm [5, 16]. For comparison, the polytetrafluoroethylene density is 2.12–2.28 g cm$^{-3}$ [20].

At the fluorination at room and higher temperature of polyethylene, poystyrene, polypheyleneoxide, and poyvinyltrimethylsilane in the fluorinated polymer were detected long-living peroxide $RO_2^{\cdot}$ and fluorine-containing radicals. Their concentrations falls to a half in a few hours, depending on the polymer nature [4–6, 16, 17, 21]. The peroxide radicals are formed in account of the presence of oxygen in the fluorinating mixture or adsorbed by the polymer and the reactor walls, and water. At the fluorination of low-density polyethylene and polystyrene the radicals begin to form even at the temperature 77 K, but in the case of the low-density polyethylene their amount in a few minutes becomes stationary that obviously is connected with the presence of activation barrier in the reactions of chain propagation [5, 22].

Kinetics of radical annihilation in the fluorinated polymers was studied at room temperature and for various types of the low-density polyethylenes also at the temperature 55–65°C. The rate of radicals annihilation in the process of fluorination of the studied polymers for the period of first 5–10 h at the temperature 295±2 K can be approximated by the relation:

$$[R]/[R_0] = 1/(1 + at), \tag{2}$$

where [R] and [$R_0$] are concentrations of the radicals in the current time moment $t$ and in the initial time moment, respectively, a is calculated coefficient.

Assuming bimolecular reaction mechanism of the radical annihilation, $R^{\cdot} + R^{\cdot} \rightarrow R_2$, the rate of the radicals annihilation is expressed as:

$$[R]/[R_0]=(1 + 2k_2[R_0]t)^{-1}, \tag{3}$$

where $k_2$ is the reaction rate constant. The $k_2$ values for various polymers are listed in [5].

From the above data we conclude that the process of florination of low-density and high-density polyethylene, polyimide, poyphenyleneoxide and polyvinyltrimethylsilane follows to the chain radical mechanism. Commonly the reaction initiation is considered as dissociation of molecular fluorine, $F_2 \rightarrow F^{\cdot} + F^{\cdot}$ [1–3], but this reaction is endothermic one (163.4 kJ mol$^{-1}$ at 298 K) [1]. But there are several exothermic reactions with the fluorine participation that can be responsible for the process of initiation of fluorination of the polymers. Among them can be emphasized the exothermic reactions between the molecular fluorine and monomeric links of a polymer, e.g., with $-CH_2-$ links in polyethylene, and the reactions between the molecular fluorine and double (conjugated) C=C bonds that present in, e.g., benzene rings of polystyrene and polypheyleneoxide, or in the molecules of technological admixtures. Therefore is doubtful that the reaction of thermal fluorine dissociation can be considered as a basic reaction responsible for the initiation of the chain process at the direct fluorination of polymers.

Due to the presence in the fluorinated layer of the long-living radicals, it is possible to carry out grafting polymerization of the monomers containing double bonds. Thus, additional modification of the polymer surface is possible, and in this case the surface properties will be defined by the properties of the grafted polymer rather than the fluorinated layer [6].

## Practical Applications of the Method of Direct Fluorination of Polymers

### *Improving Barrier Properties*

The direct fluorination is used in commercial scale for improving barrier properties of polymer products, in part, of automobile fuel tanks made of high-density polyethylene and bottles for volatile and toxic liquids. Owing to protecting surface layer, environment pollution at diffusion of gasoline and other fuel through the walls of polymer fuel tanks falls up to several tens of times [2–6]. After fluorinaton the coefficients of diffusion and premeability of many multiatomic nonpolar molecules falls considerably, but unavoidable presence of oxygen in the fluorinating mixture and of oxygen dissolved in the polymer leads to formation of polar groups like –COF and –COOH on the polymer product surface. Besides, in the fluorinated layer long living peroxide radicals are generate, that are involved into the reactions leading to breaking polymer chains and formation of polar groups. This all decreases barrier properties of polymer receivers when gasoline mixed with alcohol is loaded (alcohols are added to gasoline for enhancing degree of combustion of the fuel). Hence, should be developed a method for neutralization radicals entering to the reaction proceeding after completing the fluorination.

The methods of treatment of the fluorinated fuel tanks should satisfy the following requirements: working temperature 55–65°C (that occurs to the end of fluorination of the tank surface); the time required for deleting the radicals should be less than 15–20 min; only "dry" technology is acceptable. Appropriate compound for such treatment is triethylamine. Treatment of fluorinated high-density polyethylene with the triethylamine vapor increases rate of annihilation of the radicals: even after 15–20 min treatment the content of radicals falls by order of magnitude while without triethylamine 2-fold only for the same time. Even more effective antioxidant is nitrogen monoxide NO: treatment at room temperature of fluorinated high-density polyethylene with nitrogen monoxide at the pressure 0.1 for 10 min leads to complete disappearance of peroxide radicals. Experimentally was shown that treatment under optimal parameters allows to avoid completely the negative effect of alcohol in gasoline on the barrier properties of polyethylene, that is, penetrability of freshly fluorinated polyethylene films after treatment them with triethylamine or nitrogen monoxide does not depend on the presence of alcohol in gasoline. Moreover, the advance of such improved procedure of fluorination is advantageous over the traditional one due to lack f necessity to remove oxygen and moisture traces from the reactor for fluorination. The results of these investigation are applied for European patent [21].

### *Improving the Gas Separation Properties of Polymer Membranes*

The polymer membranes are known to be used widely for the separation of gas mixtures into components. The ideal in practical sense would be a polymer membrane with high efficiency (premeability) for one of the components and high selectivity at the gas separation. However, real polymer membranes with high selectivity are of low efficiency and vice versa, selectivity of the highly productive membranes is not sufficient.

A possible solution in this situation is fluorination of the gas separating membranes that are of high productivity but insufficient selectivity. The direct fluorination of polymer membranes leads to decrease in permeability greater for large molecules ($CH_4$, $C_2H_4$, etc.) as compared with small size molecules ($H_2$, He) and respectively to increase in selectivity of the membrane on $H_2$ and He.

As the objects of investigation in this work were chosen commercially available polymers: polyimide Matrimid® 5218 and poyvinyltrimethylsilane. Were examined flat films of poyvinyltrimethylsilane and hollow fober polyimide modules [4, 5, 24, 25]. It is found that fluorination of the gas separating modules based on the hollow polyimide fiber provides considerable increase in selectivity at the separation of the mixtures $CO_2/CH_4$ and $He/CH_4$ 7-fold and 47-fold, respectively. Therewith, besides significantly improved selectivity at the separation of $He/CH_4$ and $He/N_2$ mixtures productivity of the membrane on helium does not fall. Thus, the direct fluorination of polyvinyltrimethylsilane and polyimide allows to jump over so-called Robinson frontier defining maximal ratio of permeability (productivity) and selectivity for most studied homopolymers including polyimides.

Like the case of polyimide modules, fluorination of flat poyvinyltrimethylsilane membrane results in significant increase in the selectivity of separation of the mixtures at insignificant (less than to a half) decreses of permeability by He: $He/CH_4$ by factor 138, $CO_2/CH_4$ and $He/N_2$ 19-fold**.**

In petrochemical, chemical and energetic branches of industry the p polymer ные membranes treated with fluorine can be used for the purification of natural gas from contaminating it $CO_2$ making cheaper the process of the purificayion, for correction of $H_2/CO$ ratio in the syngas, for isolation of $H_2$ and He from natural gas, for $H_2$ isolation from the exhaust gases of petrochemical plants and at the synthesis of ethylene, for purification of $H_2$ from CO (at the use of hydrogen in a fuel cell), for the separation of the components of biogas. Application of the fluorinated polymer membranes to the metallurgy will increase efficiency of neon isolation from the exhaust gases.

### *Improving Adhesion Properties and Colorability. Increasing Strength of Polymer Composite Materials*

When a mixture of fluorine and oxygen reacts with the polymer surface (fluorine pressure and treatment duration should not exceed certain level) on the surface are formed both polar groups of –CHF– type and highly polar gropups –FC(=O), which at the contact with atmospheric moisture rapidly transform into even more polar –C(=O)OH groups.This leads to a significant increase in surface energy (in the case of polyethylene above 72 mJ $m^{-2}$ ) [7, 8] and hence to considerable increased adhesion force of the polymer and its susceptibility to dyes. Note that fluorination of polymer films for better colorability is performed on industrial scale by Alkor Gmbh Kunststoffe (Germany), Fluoro Pack (Pty) Ltd (SAR) and Interfluor (Russia) enterprises.

The method of direct fluorination of Kevlar® fiber was used for enhacing thermostability and increase strength of composites based on the ethylene–propylene copolymers doped with 1.6% of Kevlar® fiber (*p*-phenyleneterephthalimide) of 10 μm diameter: the termostability increases by 36°C, the tensile strength increases simultaneously by 22% and modulus of elasticity by 89% [33].

### *Improving of Chemical Resistance of Polymer Pipes*

Fluorination at the certain conditions results in formation on the polymer product of a layer of fluoropoymer with the properties analogous to polytetrafluoroethylene. Such layer has enhanced barrier properties and resistance against aggressive liquids such as acids, alkali and solvents. Besides, enhanced hydrophoby of surface is provided, that can be important for industrial processes.

In a branch of the Institute of Enertgy Problems of Chemical Physics, Russian Academy of Sciences, in collaboration with the company “Ninth Element” has been developed a method for enchancing chemical resistance of polymer pipes. By this method can be modified either certain part of the pipe line or the line whole. This technology is not expensive. It will be scaled up to creation of a mobile installation that will allow to treat pipe lines in field conditions. Such treatment increases considerably the pipe serficelife and decreases waste adhering on the pipe walls. When allowed by temperature regime the expensive fluoroplast pipes can be replaced by cheap polyethylene, polypropylene, poystyrene and other tubes with fluorination of their internal surface after assembling the line.

## CONCLUSIONS

Let us resume the main results of the investigations on the method of direct fluorination of polymers and perspectives of its practical application.

The process of direct fluorination of a polymer surface is diffusion controlled one. The rate of thickness increase of the fluorinated layer is limited by the rate of fluorine pemeation through this layer to the layer of the parent polymer The fluorinated layer thickness depends on the partial pressure of fluorine, the treatment duration, the polymer nature and the fluorinating mixture composition. Presence of He, $N_2$ and Ar in the fluorinating mixture little affects the fluorination rate; $O_2$ and HF inhibit the process. The fluorination rate grows with temperature.

The fluorination leads to increase in density and decrease in refraction index of the fluorinated layer as compared with the parent polymer. The direct fluorination of polymer membranes improves considerably their gas separation properties.

The method of direct fluorination of polymer products can be used for improving barrier properties, enhancing adhesion and susceptibility to dyes, increasing strength of polymer composites and improving their chemical resistance.

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