Improvement of Performance Characteristics of Polymer Materials by Direct Fluorination

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Abstract

The fundamental features of direct fluorination of polymers and its potential commercial applications are described. The effects of the composition of the F_2 -He- N_2 - O_2 -HF fluorination mixture, fluorine pressure, temperature, and fluorination time on the formation rate and chemical composition of the fluorinated layer, as well as on the density, refractive index, surface energy, gas separation characteristics, and friction coefficient of the latter have been studied. Processes of formation and destruction of the long-lived and short-lived radicals, which are involved in the chain processes of the direct fluorination, have been investigated. A description of the commercial applications of direct fluorination to improve some performance characteristics of polymeric articles is given. Among these characteristics are the selectivity of gas separation of polymeric membranes, barrier and adhesion characteristics.

INTRODUCTION

It is common knowledge that fluorinated polymers have a number of useful properties, for example, increased reagent resistance, thermal resistance, high barrier characteristics, etc. However, applications of articles from fluorinated polymers are limited because of their high cost and complicated synthesis of fluoropolymers. In some cases, performance characteristics of polymeric articles are controlled to a large degree by their surface characteristics; therefore, manufacturing of articles from freely available polymers followed by modification of their surface with elementary fluorine to a depth of $0.1-10 \ \mu m$ often appears to be promising and convenient [1-3]. The bulk characteristics of the articles thereby remain unaffected.

There are various procedures for surface modification of polymers with fluorine and its compounds. The limitations of the plasmachemical method are sophisticated process equipment (high vacuum and continuous initiation of the process), impossibility to treat uniformly articles with a complicated shape, possible etching of the surface of the modified article, and joint action of atoms, ions, electrons, and UV radiation (including vacuum radiation) on the modified polymer. The use of xenon difluoride XeF_2 as a source of fluorine is limited because of its high cost. (One should keep in mind that XeF_2 is synthesized from expensive xenon and elementary fluorine.)

The use of elementary fluorine for surface modification of polymer articles is free from the above limitations, which are inherent in other methods. Because of the high exothermicity of the unit steps, fluorination proceeds at ambient temperature and even at the liquid nitrogen temperature (77 K), and there is no need in any initiation, specifically, any irradiation, heating, introduction of catalysts, or high vacuum. Fluorination is possible in a flow-through system at atmospheric pressure. Direct fluorination is used for surface modification of polymers; the thickness of the fluorinated layer is generally $\sim 0.1-10 \,\mu\text{m}$ and is under reliable control. This means that, for example, in the case of fluorination of automobile polyethylene fuel tanks, less than 0.1 % of the total mass of the tank subjected to fluorination is enough to attain the necessary barrier properties. The surface concentration

of bound fluorine generally does not exceed $\sim 1 \text{ g/m}^2$ of the polymer article. Articles of any shape can be modified. This is dry technology, because the initial reagents and end products of the reaction are gases and solids.

In view of the above features, direct fluorination is widely used to improve some performance characteristics of polymer articles: selectivity of gas separation of polymer membranes, barrier characteristics, adhesion, susceptibility to dyes, *etc.* [2-7]. Various fluorination procedures have been worked out and are now widely used in industry under static conditions and in flow-through systems (for ready-made polymer articles), or directly during moulding of polymer articles at elevated temperatures [2, 4, 5, 7]. A brief description of practical applications of direct fluorination in industry to improve performance characteristics of polymer articles is given below.

Modification of the polymer surface seems to be the most promising direction. During fluorination, a controlled quantity of long-lived radicals (whose lifetimes are of the order of 1-10 h) are formed in the surface layer of the polymer. This time is quite enough to carry out graft polymerization of monomers with double bonds from the gas phase. This additional modification imparts new properties to the polymer surface, for example, hydrophilicity or hydrophobicity, improves gas separation characteristics and increases the adhesive power and susceptibility to dyes, while the bulk properties of the polymer remain unaffected [2, 8, 9].

It should be emphasized that the suggested direct fluorination method complies with the sustainable development concept in both ecological and economical aspects. First, the process is free from liquid solvents; second, a very thin (micron-sized, see above) surface layer of the polymer articles is modified, and there are well-proven and reliable methods of comprehensive utilization (*i.e.* transfer to a nontoxic solid) of unchanged fluorine and gaseous fluorine hydride as a reaction product.

The application of the direct fluorination method can lead to significant economic benefits in a number of branches of Russian industry including chemical, petrochemical, automobile, iron and steel, food-processing industry, *etc.* [2, 4, 5]. Fluorination of polymer tanks for storage of hydrocarbon fuel (for example, automobile polymer fuel tanks) and toxic liquids leads to a substantial reduction of product losses from evaporation through the tank walls, due to which the detrimental effects of fuel (petrol, etc.) and toxic compounds on the environment abate. Treatment of the surface of polymer articles applied in automobile industry with fluorinated mixtures improves the adhesion and susceptibility to dyes; therefore, the priming operation can be eliminated. In petrochemical, chemical, and power industries, polymer membranes treated with fluorine may e used for reducing the price of processes for natural gas (methane) decontamination from CO_2 impurities and for hydrogen decontamination from CO impurities. They may also be used to separate hydrogen and helium from natural gas, to separate hydrogen from off-gases at petrochemical plants, and are useful for ethylene synthesis and separation of biogas components. In iron and steel industries, fluorinated polymer membranes may offer a means to reduce the price of neon separation from off-gases at metallurgical plants. In foodprocessing industry, fluorination of polymer films used for storage of perishable food decreases gas permeability (including oxygen permeability) of packing materials and, accordingly, increases the shelf-life of perishable food. In addition, fluorinated polymer films show significantly enhanced adhesion to dyes, due to which inscriptions made on them are less subject to wipe-out.

FUNDAMENTAL FEATURES OF DIRECT FLUORINATION OF POLYMERS

Direct fluorination of some polymers is reported in [9–19]. These polymers include polystyrene (PS), polyethyleneterephthalate (PETP), poly(2,6-dimethyl-1,4-phenylene ether) (PPE), polyvinyl trimethylsilane (PVTMS), poly(methylmethacrylate) (PMMA), poly (4-methylpentene-1), polyimide (PI) Matrimid 5218, low-density polyethylene (LDPE) (2 kinds), high-density polyethylene (HDPE) (5 kinds), polysulphones, polyetherketone, polycarbonatesiloxane, block copolymer of polysulphonate and polybutadiene of varying composition, poly(vinyl fluoride) (PVF), and poly(vinylidene fluoride) (PVDF). The fluorine used in this work contained ~0.08 % oxygen as an admixture. The effects of the composition of the fluorination mixture (F_2 -He-N₂-O₂-HF), fluorine pressure, fluorination temperature, and fluorination time on the rate of fluorinated layer formation, its chemical composition, density, refractive index, surface energy, gas separation characteristics, and friction coefficient have been studied. Formation and destruction of the long- and short-lived radicals have been investigated.

Direct fluorination of polymers is characterized by the general regularities and specific features. Experimental data are given below for fluorine pressure and treatment time acceptable under commercial conditions.

For all polymers under study, after the thickness $\delta_{\rm F}$ of the modified layer during fluorination has reached $0.1-0.2 \,\mu\text{m}$, the modified polymer consists of practically completely fluorinated and initial (non-modified) polymer layers (polyethylene (PE) and PVF being exceptions) separated by a very narrow transient reaction zone, which is the site of the basic chemical transformations. The rate of the fluorinated layer formation is limited by the diffusion rate of molecular fluorine through the layer of the fluorinated polymer to the initial polymer, and depends on the nature of the polymer, partial pressure of fluorine $p_{\rm F}$, composition of fluorination mixture, and temperature. For the majority of polymers the thickness of the fluorinated layer $\delta_{\rm F}$ at a constant partial pressure of fluorine increases with time by the square root law; however, for some polymers (PE, PMMA) the deviations from the square root law are observed during the initial period of time. Generally, $\delta_{\rm F}(\mu {\rm m}) = B p_{\rm F}^{\ k} t^{0.5}$, where $p_{\rm F}$ is the partial pressure of fluorine, bar; t is a fluorination time, s; *B* is the coefficient, $\mu m s^{-0.5}$. The power index k for the above polymers varies in the range 0.4-0.8, and the coefficient B is from 0.34 to 0.017. It takes typically from 1 min to 1 h (which depends on the nature of the polymer) for a 1 µm thick fluorinated layer to form at ambient temperature and at industrially applied compositions and pressure of the

fluorination mixture. When the temperature is increased to 100-150 °C, this time may decrease to several dozens of seconds.

Introduction of He and N2 into the fluorination mixture has minor influence on the rate of the fluorinated layer formation even in the case when the partial pressure of He and N_2 is 10 times higher than the partial pressure of fluorine. Oxygen and HF arising during fluorination are process inhibitors. A practically completely fluorinated layer is formed for the majority of polymers on their surface, *i.e.* nearly all hydrogen atoms are replaced by fluorine, the double and conjugated bonds being saturated with fluorine. During PVTMS fluorination, the majority of C-Si bonds break to form C-F bonds. During PI fluorination, at least one C-N bond breaks with the subsequent attachment of the fluorine atom at the breaking point, and ~15 % of the low-molecular fragments with C=O groups are eliminated from the polymer chain. However, full replacement of hydrogen atoms by fluorine is not evidenced on the PE and PVF surface; PVDF does not react with fluorine even at a temperature of 420 K and under UV irradiation. After oxygen has been introduced in the fluorination mixture, COF groups are formed in the fluorinated layer in great quantities (several dozens percent of monomer units can be modified). These groups are converted to COOH by their interaction with atmospheric moisture.

Refractivities of polymers decrease significantly during fluorination and are equal (after treatment with fluorine without oxygen additions) to 1.37–1.42 in the range 500–700 nm.

The total surface energy γ tangibly changes on fluorination: it grows with an increase in $\delta_{\rm F}$ (Fig. 1). In addition, the kind of relationship between γ and $\delta_{\rm F}$ is influenced for example by the fluorination mixture composition and treatment time (curves 2–4). The degree of polarity, which is defined as the ratio of the polar component of energy to the total surface energy, can also vary over a wide range (Fig. 2).

To measure the mean density of thin $(0.5-5 \ \mu m)$ fluorinated polymer layers, a nondestructive procedure described in [13] was used. For PS, PETP, PPE and PVTMS, the mean density ρ_F of the fluorinated layer is practically



Fig. 1. Total energy γ vs. thickness of the fluorinated layer $\delta_{\rm F}$ (T = 294 K): 1 - PI after its treatment with a mixture of 2 % F₂ + 98 % He at a total pressure of 1 bar for the mixture; 2-4 – PVTMS upon its treatment with non-diluted fluorine at a fluorine pressure of 0.02, 0.08, and 0.2 bar, respectively; 5 – polypropylene (20PCT) fluorinated under various conditions.

independent of $\delta_{\rm F}$ and is 2.05, 1.75, 1.72, and 1.73 g/cm³ respectively (for initial polymers, 1.05, 1.46, 1.07, and 0.85 respectively). In the case of PI, $\rho_{\rm F}$ depends on $\delta_{\rm F}$; when $\delta_{\rm F} > 5 \,\mu\text{m}$, the density increases to 1.92 g/cm³ (1.24 for initial PI) [9].



Fig. 2. Polarity (ratio of the polar component of the surface energy to the total energy) vs. thickness $\delta_{\rm F}$ of the fluorinated layer of PVTMS: 1--3 – PVTMS films treated with fluorine at a pressure of 0.02, 0.08, and 0.2 bar, respectively, and at $T = (294 \pm 1)$ K.

Fluorination affects the transparence of polymers in the near UV region of the spectrum: transmission increases for PS and PETP, but decreases for PI and PVTMS.

Direct fluorination of polymers is a radicalchain process. A controllable quantity of longlived radicals (mostly perfluoroalkyl radicals for PVTMS and both perfluoroalkyl, and peroxide (RO₂) radicals for PI, PS, PPE, and LDPE) are generated in the fluorinated layer. Immediately after fluorination, the concentration of the radicals in the fluorinated layer of PI, PS, PPE, and LDPE polymers is high, $(3-5) \ 10^{19} \ g^{-1}$, and decreases by a factor of two in 4-15 h; for PVTMS, this time is 1 h. Therefore, additional modification of the polymer surface can be made by grafting monomers with double bonds. The surface properties thereby will be substantially controlled by the properties of the graft polymer. Studies on graft polymerization of acrylonitrile (AN) with fluorinated PI from the gas phase demonstrated that the effective thickness of the graft AN layer δ_{gr} may amount to ~7.5 % of δ_F [9].

APPLICABILITY OF DIRECT FLUORINATION OF POLYMER ARTICLES TO INDUSTRY

A detailed description of application of direct fluorination in industry is given in [2]. The present contribution gives only a brief review. At present, direct fluorination is most widely used by a number of companies from the USA, Europe, and the republic of South Africa for improving the barrier properties of automobile fuel tanks from HDPE. Losses of petrol caused by diffusion through the tank walls can be reduced more than hundredfold by treatment of fuel tanks with fluorine [4-6]. USA has started fluorination of 500-2000 l HDPE tanks for storage of fuel used for house heating [5]. Direct fluorination of polymer containers designed for storage of liquid chemical compounds substantially reduces the loss of liquids. It improves the barrier properties of not only HDPE, but also of LDPE, PVC, polypropylene (PP), PETP, natural and synthetic filaments, etc. [2].

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Polymer membranes can be used to advantage for separating gas mixtures such as He-CH₄, H₂-CH₄, H₂-CO₂, CO₂-CH₄, CO₂- N_2 , CH_4-N_2 , H_2-N_2 , O_2-N_2 , CO_2-H_2S , CH_4-N_2 CO_2 -H₂-He, *etc.* However, gas separation using polymer membranes gives rise to the following problem: highly effective membranes exhibit low selectivity of gas separation, while highly selective membranes show minor productivity. After direct fluorination, permeability of small molecules and atoms (He, H₂) decreases much more significantly compared to larger molecules $(CH_4, C_2H_6, CO_2, etc.)$. Therefore, fluorination is especially effective when used for separating He-CH₄ and He-hydrocarbon type mixtures, the selectivity of gas separation being considerably increased without a tangible drop in productivity by helium. Figure 3 shows the effect of fluorination on the selectivity of separation of a He/CH₄ gas mixture and on permeability of He (natural gas component) through a module of hollow fibre PI fibres [9, 20]. Points for the best materials should have been plotted in the top right area, but these materials have not yet been found. The selectivity of separation depends on the quality of initial fibres and on the fluorination conditions and may be increased 20- to 100fold (depending on the quality of initial fibres) while the productivity by helium drops by no more than 20 %. The tested modules are made of 3-5 hollow fibres and hence can be considered as pilot samples. During fluorination of flat membranes from PVTMS by an F_2 -He mixture, the selectivity of separation of He/CH_4 and CO_2/CH_4 mixtures (biogas components) increased by a factor of 10 and 5 respectively compared with the selectivity of the initial membranes. The grafting of AN to the fluorinated PVTMS allowed the selectivity of separation of the He/CH₄ gas mixture to increase by a factor of 35, and treatment of membranes with an F_2/O_2 mixture, by a factor of more than 100 [9, 20].

After fluorination, oxygen permeability of PS, HDPE, LDPE, PP, and PETP polymer films used for packing foodstuffs decreases substantially (by a factor of 8-47), which increases the shelf-life of the latter [21].

The low adhesive power, one of the basic limitations of polyolefins, is related to the low



Fig. 3. Selectivity of separation of He/CH_4 mixture *versus* permeability of He for the various polymeric membranes: circles – literature data for various polymers, triangle – initial PI modules, squares – fluorinated PI modules; the arrows indicate the direction of increased selectivity of gas separation after fluorination.

values of their total surface energy γ and its polar component γ_{p} . After fluorination, γ and $\gamma_{\rm p}$ increase drastically (see Fig. 1, 2). Introduction of oxygen into the fluorination mixture results in substantial growth of adhesion compared to the case when theF₂- N_2 mixture is used. For example, γ for PE (~0 for the initial PE) increases to 12 mJ/m² with the use of the F2-N2 mixture, and to 40-43 mJ/m² upon treatment with F_2 -O₂ mixture (see references in [2]). The instances of the commercial use of fluorination to improve the adhesion properties of polymeric articles are described in [2, 6, 7]. It has been demonstrated that direct fluorination enhances adhesion of HDPE, LDPE, rubbers, PP, polyamides, polyesters, etc.

Direct fluorination causes the friction coefficient of some elastomers (ethylenepropylene, acrylonitrile-butadiene copolymers, *etc.*) to decrease (see references in [2]). The process goes without deterioration of the strength properties of polymer articles. After direct fluorination of PP, its static friction coefficient decreases appreciably (by a factor of 1.68) and the dynamic friction coefficient (Fig. 4) decreases to a lesser degree (by a factor of 1.37) [9].



Fig. 4. Static (1) and dynamic (2) friction coefficients vs. thickness δ_F of the fluorinated PP layer.

CONCLUSIONS

Application of direct fluorination may involve a substantial economic benefit in a number of branches of Russian industry; among them are chemical, petrochemical, automobile, iron and steel, food-processing industry, etc. Upon fluorination of polymeric tanks to store hydrocarbon fuel (for example, automobile polymeric fuel tanks) and toxic liquids, the losses of products by means of evaporation through the tank walls substantially decrease, in consequence of which the detrimental effects of fuel (petrol, etc.) and toxic compounds on the environment abate. Treatment of the surface of the polymeric articles applied in automobile industry with the fluorinated mixtures brings about an improvement of adhesion and susceptibility to dyes; thus the priming operation can be eliminated. In petrochemical, chemical, and power industries, the polymeric membranes treated with fluorine may offer a means to reduce the price of processes for natural gas (methane) decontamination from CO_2 impurities, for hydrogen decontamination from CO impurities. They may be used to separate hydrogen and helium from natural gas, to separate hydrogen from off-gases of the petrochemical plants, and also during ethylene synthesis and separation of biogas components. In iron and steel industry, once the fluorinated polymeric membranes are applied, the process of neon separation from off-gases of the metallurgical plants becomes less expensive. In food-processing industry, fluorination of polymer films used for storage of perishable

food causes the gas permeability (including oxygen permeability) of packing materials to reduce, and accordingly, the shelf-life of perishable food increases. In addition, fluorinated polymer films show a significantly enhanced adhesion to dyes, in consequence of which the inscriptions made on them are less subject to wipeout.

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