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Surface Fluorination of Polymers Using Xenon Difluoride

GEORGY BARSAMYAN and
VLADIMIR B. SOKOLOV

15.1. INTRODUCTION

Surface engineering by means of fluorination is an effective way to change surface properties, and is used for both polymer surfaces and inorganic substrates. Polymer surface fluorination has been around a long time. The first patent we know of dates back to 1938,¹ but it was only in the 1970s that the introduction of several major industrial applications led to a rapid acceleration in development.

Surface fluorination is in popular use because most of the desirable properties of fluoropolymers are largely the result of surface phenomena. Surface fluorination enables us to modify the surface properties of a polymer while retaining others often useful bulk properties (e.g., mechanical strength, elasticity, and ease of processability).

Surface-fluorinated polymers have a number of desirable inherent properties, including:

1. Decreased gas permeability (increased barrier properties).
2. Decreased friction (decreased wear and long lifetime).
3. Enhanced wettability (better adhesion).
4. Enhanced chemical and ozone resistance.
5. Enhanced hardness.

GEORGY BARSAMYAN · Samsung Coming Co., Ltd, Dong-Suwon, Kyeongii-Do, Korea, 442-600.
Present address: Solvay S.A. Moscow Office, Moscow, 123310, Russia. VLADIMIR B.
SOKOLOV · Russian Research Center "Kurchatov Institute," Moscow 123182, Russia

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However, the fact that industrial applications of polymer surface fluorination employ a fluorine/nitrogen mixture as the fluorinating agent complicates matters because fluorine gas is toxic, may explode when brought into contact with organic substances, and causes severe burns on human tissue. Moreover, the use of fluorine requires highly qualified personnel and special safety systems.

The idea of utilizing xenon difluoride (XeF_2) as a fluorinating agent for surface engineering was first suggested in the late 1980s, based primarily on three considerations. First, direct fluorination with noble gas fluorides is a well-known, effective method used extensively in inorganic preparative chemistry. Second, direct fluorination of polymeric surfaces with a F_2/N_2 mixture has proved to be a very effective tool for modifying surface properties. Third, owing to the method of low temperature thermocatalytic synthesis developed in the Russian Research Center "Kurchatov Institute" (RRC "KI"),² the XeF_2 production process was considerably simplified and shortened, which resulted in a significant decrease in the cost of XeF_2 . Thus the general idea was to try to effect direct polymer surface fluorination using the less hazardous and less toxic solid XeF_2 instead of the conventional gaseous F_2/N_2 mixture fluorinating agent.

XeF_2 is a colorless crystalline compound stable up to 500°C , m.p. -129°C , with considerable vapor pressure for solids—4.5 mmHg (20°C). It is a linear symmetrical molecule. The mean thermochemical energy of the Xe—F bond in XeF_2 is 132 kJ/mol,³ which is less than the F—F bond energy—157.3 kJ/mol.⁴

It is appropriate at this point to recall that XeF_2 was originally considered to be exotic and was used only as laboratory chemical in very small quantities. While direct polymer surface fluorination with a gaseous F_2/N_2 mixture was already in use for several significant commercial applications.

15.2. FLUORINATION OF SUBSTANCES AND SURFACES

Fluorine was isolated by Henri Moissan at the end of June 1886 during an electrolysis of liquefied anhydrous hydrogen fluoride, containing potassium fluoride, at -23°C . The gas, produced at the anode, was fluorine. This achievement earned Moissan the 1906 Nobel prize in chemistry. Thousands of tons of fluorine are being produced today by essentially the same, albeit slightly improved, electrolytic method. Obviously, this scale of fluorine production means that fluorine chemistry has turned into an important branch of industry. This development can be understood if we look at fluorine from a chemist's point of view.

So, what is so unusual in this pale yellow highly toxic gas that condenses to a pale greenish-yellow liquid at -188°C , solidifies to a yellow solid at -220°C , has a strong ozone-like odor, and is easily detectable at concentrations about 0.1–0.2 ppm ($\approx \text{ml}/\text{m}^3$).⁵

Let us consider some notorious experimental facts. Fluorine combines readily with most organic and inorganic materials at or below room temperature. Many organic and hydrogen-containing compounds can burn or explode when exposed to pure fluorine. Owing to its extremely high oxidizing ability fluorine forms compounds with all elements except helium, neon, and argon. In all compounds fluorine always shows the same oxidation degree of -1 .

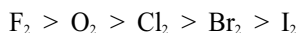
Generally speaking, direct fluorination is a well-known, effective method in the applied chemistry of fluorine. The continuing interest in inorganic fluorine chemistry is connected with the possible use of fluorine and fluorocompounds as powerful oxidants for rocket fuels and in the recovery and processing of metals such as molybdenum, tungsten, and rhenium; recovery of residual uranium from spent nuclear fuel elements by vaporizing it, forming UF_6 , and separating it; and creation of new materials with unique properties or applications, such as, e.g., SF_6 , an excellent electrical insulator used in large electrical transformers; WF_6 and ReF_6 , in production of rhenium–tungsten alloys; BF_3 , CoF_3 , CrO_2F_2 , and OsF_6 , as catalysts in organic chemistry and in processing of isotope-enriched elements and compounds; AgF_2 , CoF_3 , MnF_4 , SbF_5 , HgF_2 , ClO_3F , NO_2BF_4 , IF_5 , NF_3 , and $NOBF_4$, as fluorinating agents in organic synthesis; $LiBF_4$ and $LiPF_6$, as components for lithium batteries; NF_3 , as a source of fluorine for HF/OF high-energy chemical lasers; CF_2 , an important gas for silicon etching in microelectronics, IF_5 , an impregnating agent used in the textile industry for water- and oil-repellency; and LiF , CaF_2 , BaF_2 , and ZrF_4 , materials for ceramics and optics.⁹

To illustrate the extreme reactivity of fluorine, one can note that it is the only element that reacts directly with the heavier noble (inert) group gases, xenon and radon, to form fluorides. It is surprising that the reaction between fluorine and xenon gas occurs even at room temperature.⁶ Most noble (inert) gas compounds have been synthesized either by direct fluorination or with the help of fluorocompounds, e.g., an electric discharge in a mixture of krypton and fluorine can produce KrF_2 . In 1962 Neil Bartlett synthesized the first noble gas compound: deep red-brown PtF_6 vapor in the presence of xenon gas at room temperature produced a yellow-orange compound then formulated as $Xe \cdot PtF_6$.⁷ Within a few months of this discovery, XeF_4 was prepared as was XeF_2 . Since that time, apart from the simple fluorides mentioned above, more complex fluorides have been synthesized, including among many others, KrF_2 , $XeFSbF_6$, $KrFAuF_6$, XeF_2AsF_6 , XeO_3 , XeF_3SO_3F , $XeOF_4$, $FXeOCIO_3$, and Na_4XeO_6 .³ It is interesting to note that oxygen-containing noble gas compounds can be obtained only through reactions with xenon fluorides. Thus, because of its extreme reactivity, fluorine gave rise to new branch of chemical science—chemistry of noble gas compounds.

Another, more recent, fluorine contribution to the development of new branches of chemical science is connected with fullerenes, the first members of this family of close-caged molecules being obtained only about a decade ago. Fullerenes, having the composition C_{60} , C_{70} , C_{76} , C_{84} . . . , represent the new

(third) form of carbon. Each fullerene consists of 12 pentagonal rings and a number of hexagonal ones that have double bonds in the pentagonal rings. Nowadays only C_{60} and C_{70} are synthesized on a relatively large scale—by vaporizing graphite, followed by chromatographic extraction of the fullerene mixture. Chemically C_{60} and C_{70} behave like typical electron-deficient alkenes: the maximum number of functional groups that can be combined with C_{60} in methylation, chlorination, bromination, and other such reactions is 24, apart from the reaction with hydrogen ($C_{60}H_{36}$). By contrast, fluorination of fullerenes with F_2 , KrF_2 , or XeF_2^* forms stable derivatives with considerably larger numbers of combined functional groups: $C_{60}F_{48}$ and $C_{60}F_{60}$. Furthermore, it was shown that fluorofullerenes can react with ammonia to form fluoro-containing amines, e.g., $C_{60}F_{30}(NH_2)_{18}$.⁸ Hence, in this case, as well, the higher fluorides of fullerenes, which were obtained using noble gas fluorides, become the basic substances for new theoretical and applied directions in organic chemistry.

Thus one can draw the conclusion that there is no element in the periodic table, including other halogens and oxygen, that possesses stronger oxidizing properties than fluorine, which is really at the head of the oxidants series:



Another important conclusion is that fluorine atoms determine the chemical bonding and consequently the formation of the chemical compound. In other words the general energy apportionment in a reacting system, the rate of energy apportionment (chemical reaction rate), the direction of the chemical reaction, and the composition of the final products are determined by the oxidizing ability and reactivity of the fluorine atoms. As a radical, atomic fluorine, which has high reactivity ($F > [O] > Cl > Br > I$) over a broad temperature range (reactions occur practically without activation energy), interacts with all metals and metalloids and their compounds, with the formation of ionic salts and covalent fluorides characterized by the highest bonding strength among halogen analogues and other elements, e.g., C—F (450–500), C—Cl (340), C—Br (280), C—H (410), C—O (360), H—F (560), C—S (270), C—N (300), C—C (360), but not C=C (610), C=O (750), C≡C (840) in kJ/mol. Under certain conditions a chain reaction is initiated in fluorine/halogen, fluorine/hydrogen, and fluorine/hydrocarbon systems, which is accompanied by thermal explosion. Initiation is due to the action of the fluorine atoms.

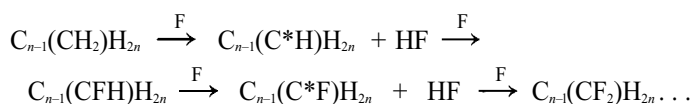
The molecules participate in the chemical reactions as “carriers” of the atoms and radicals. According to such an interpretation one can consider molecular fluorine as the simplest chemical compound of atoms—FF (like ClF,

* Fluorides of “simple” carbon are well-known: they have the general formula $(CF_x)_n$ and are widely used as cathodic material in high-energy primary batteries.

BrF, AgF, FOF, FKrF, FXeF) and its chemical properties as the result of oxidizing ability and reactivity of the fluorine atoms. The real conditions of the reaction system (temperature, pressure, agent content, reaction environment, the composition and properties of the initial agents and reaction products...) have a great influence on the chemical behavior of molecular fluorine, limiting or sharply increasing its chemical activity.

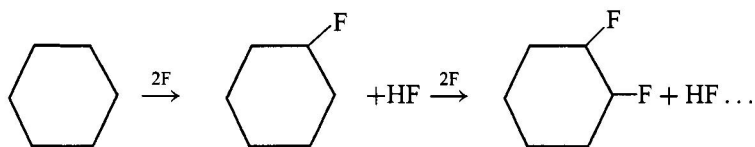
The high ("anomalously" high) oxidizing ability and reactivity of molecular fluorine in chemical reactions can be understood and explained by noting the principal properties and characteristics of fluorine, which significantly determine and characterize its chemistry, including its reactions with organic polymers, namely low energy of molecular fluorine dissociation, 157.3 kJ/mol, the highest electronegativity F of all elements, 4.10 (Ollred and Rochow scale), high electron affinity F, 350kJ/mol, high stability of C—F, H—F, and other bonds, weak polarizability of fluorine ($0.82 \times 10^{-24} \text{ cm}^3$), small atomic, covalent, and ionic radii, 0.64, 0.72, and 1.33, respectively (in Å). Standard values of enthalpy of formation and free energy of formation for atomic fluorine are: $\Delta H_{298}^{\circ}F = 75 \text{ kJ/mol}$, $\Delta G_{298}^{\circ}F = 60 \text{ kJ/mol}$.

A low dissociation energy and low activation dissociation energy (145.5 kJ/mol) indicates the presence of considerable amounts of atomic fluorine in molecular fluorine, even at moderate temperatures and pressures. A high molecular fluorine dissociation rate in combination with a low recombination velocity ensures that at every moment there is a sufficiently high concentration of atomic fluorine in the reaction system and, consequently, a high chemical reaction rate. The interaction of atomic fluorine with saturated hydrocarbons is accompanied by the formation of HF and its corresponding radical, followed by the formation of saturated polymers containing $> \text{CHF}$ and $> \text{CF}_2$ groups:



Hydrogen abstraction by fluorine is thermodynamically advantageous, since C—H bond strengths are about 410kJ/mol compared to 560kJ/mol for H—F and 450–500 kJ/mol for C—F bonding.

In contrast to saturated hydrocarbons, the unsaturated hydrocarbons react with atomic fluorine by two pathways, i.e. (atomic fluorine addition at $> \text{C}=\text{C}<$ double bond and hydrogen substitution by fluorine atoms. The reaction of fluorine with aromatic hydrocarbons proceeds with the formation of F-derivatives and hydrogen atoms break off:



It is assumed that all similar fluorination reactions proceed via an intricate radical chain-reaction mechanism. The overall reactions for the substitution of hydrogen by fluorine ($\text{RH} + \text{F}_2 \rightarrow \text{RF} + \text{HF}$, $\Delta H_{298} \approx -430 \text{ kJ/mol}$ per carbon atom) are more exothermic than the reactions for adding fluorine to the double bonds ($\text{R}_2\text{C}=\text{CR}_2 + \text{F}_2 \rightarrow \text{R}_2\text{FC}-\text{CFR}_2$, $\Delta H_{298} \approx -350 \text{ kJ/mol}$ per carbon atom). This is the reason that the carbon skeleton in the first case is often fractured ($E_{\text{C-C}} = 360 \text{ kJ/mol}$, $E_{\text{C=C}} = 610 \text{ kJ/mol}$). Thus it is necessary to minimize and control the energy of the process for successful fluorination of organic compounds,¹⁰ including organic polymers.

The principal laws for the fluorination of polymeric hydrocarbons are the same as those described above for the simple case. Direct fluorination has been used extensively in organic chemistry (but only since the early 1970s) in low-temperature methods, where the fluorine is strongly diluted with some inert gas (helium, argon, nitrogen, krypton). One can note the La Mar, aerosol-based, and liquid-phase fluorination methods.

While on the subject of fluoroorganic compounds, one cannot overstate the importance of fluoropolymers in modern industry and science. There is hardly anyone around today who has never heard of polytetrafluoroethylene (PTFE) $[\text{CF}_2-\text{CF}_2]_n$. Housewives who know nothing about fluorine use PTFE-coated frying pans or pots, and know that PTFE makes washing up easier, because virtually nothing sticks to a PTFE-coated utensil.

Nonstickiness, low friction, low wettability, and high thermal- and chemical-resistance are the major properties of PTFE, which was accidentally discovered in the DuPont laboratories in 1938, and these properties are more or less typical of other fluoropolymers that have been developed since.

In discussing fluoropolymers one has to mention also the fluororubbers, which are mostly copolymers of fluoromonomers and common rubbers. They are also much in demand by industry, owing to the fact that while they retain the traditional features of rubber—elasticity and tensile strength—they have high chemical- and thermal-resistance and low friction.

The useful properties of fluoropolymers noted above are mostly attributed to a high C—F bond strength (456 kJ/mol) and the atomic arrangement in the macromolecules. The large fluorine atoms in PTFE are so neatly packed and close to the C—C chain that it makes the carbon chain inaccessible to other atoms and molecules. Besides providing protection from chemical attack, the tightly packed nonpolarizable fluorine atoms are responsible for the PTFE's low surface energy (18.6 mN/m).¹⁰

Thus, the strong C—F bond, the special arrangement of atoms in macromolecule, and low surface energy impart some unique physical properties to PTFE and other fluoropolymers: high chemical and thermal resistance, nonstick character, low friction coefficient, and low wettability. This combination of properties

naturally makes fluoropolymers very attractive to industry and they are produced by the thousands of tons all over the world.

However, one should not forget that apart from the complexity of the synthesis fluoropolymers are very expensive. For example, the price of fluororubber is more than 30-fold that of an ordinary rubber such as butadiene-styrene (SBR) or ethylene-propylene (EPDM). Cost was one of the factors that gave impetus to research polymer surface fluorination, with the object of imparting the properties of fluoropolymers to the surfaces of less expensive polymers without changing their bulk properties.

The violent nature of reactions between fluorine and hydrocarbon compounds has already been noted here, and the direct fluorination of organic polymers is not an exception: it is so exothermic that if the reaction is not controlled, it generally leads to fragmentation and charring of the substrate. Moderation of the reaction rate can be effected by:

1. Diffusion control of the gas phase through the presence of diluent gases.
2. Thermal control of the gas or substrate.
3. Diffusion control in the solid phase.

It is believed that polymer surface fluorination proceeds via a free radical mechanism, where fluorine abstracts hydrogen atoms from the hydrocarbon, and fluorine atoms are substituted.¹¹ Of course, the precise conditions depend on the nature of the polymer in question and the surface properties required.

Today, controlled polymer surface direct fluorination is used in a number of specific applications. According to Annand²² there are primarily two different methods by which elemental fluorine can be applied to the surfaces of polymeric materials:

1. Postforming exposure (posttreatment).
2. Simultaneous treatment and exposure (*in situ* treatment).

These techniques differ not only in terms of their principles of operation but also in regard to economic flexibility, applicability, and the ultimate properties of the product.

In the post-treatment of films or fibers, fluorine-containing gas is continuously injected into the reactor and gaseous by-products are removed. The other type of reactor for posttreatment is the batch process reactor, which consists of a suitably sized vacuum chamber provided with means of evacuation and injection.

In-situ treatment, on the other hand, uses existing polymer processing equipment to apply the desired fluorine-containing gas to the polymer in question. Of course, there has to be some modifications of the processing equipment. The

Aeropak[®] process—simultaneous blow-molding and inner-surface fluorination of polymeric containers—is the most well-known example of an *in-situ* treatment process.

Surface fluorination changes the polymer surface drastically, the most commercially significant use of polymer surface direct fluorination is the creation of barriers against hydrocarbon permeation. The effectiveness of such barriers is enormous, with reductions in permeation rates of two orders of magnitude. Applications that exploit the enhanced barrier properties of surface-fluorinated polymers include: (1) Polymer containers, e.g., gas tanks in cars and trucks, which are produced mostly from high-density polyethylene, where surface fluorination is used to decrease the permeation of fuel to the atmosphere; and perfume bottles. (2) Polymeric membranes, to improve selectivity; commercial production of surface-fluorinated membranes has already started.¹³

While enhancing barrier properties is the most commercially significant use of direct surface fluorination it is not by any means the only example of surface modification by direct fluorination. Another example worthy of note is the change of surface energy and adhesion. It was discovered that direct surface fluorination of polyolefins generally raises the surface energy.¹⁴ Several ways have been suggested to exploit this phenomenon but it is the effect on adhesive and coating properties that has generated the greatest interest.

The resulting improvement in polymer adhesion can be significant and is being explored on a commercial scale for: (1) enhancement of the paint receptivity of molded plastic items for automotive and other applications; (2) enhanced adhesion between polyester yarn, cord, or fabric and rubber in automobile tire production; (3) increased resistance to delamination in coated flexible film; (4) improved strength in fiber-reinforced composite parts through better matrix-to-fiber energy transfer; (5) increased coating integrity on molded thermoplastic containers.¹⁵

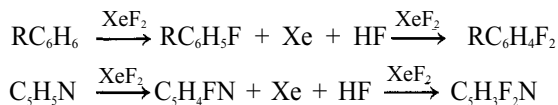
The third major application of polymer surface fluorination is improvement in tribological characteristics of rubber and rubber articles. It is commonly known that fluorination of natural or synthetic rubber creates a fluorocarbon coating, which is very smooth. Rubber articles, such as surgical gloves, O-rings, gaskets, and windshield wiper blades can be surface-fluorinated, without the bulk material losing its elastic and flexible properties.¹⁶ Fluorinated O-rings have longer lifetimes and in some cases can even be used without lubricants. Surgical gloves that have been fluorinated from the inside can be put on without talc, but the outer surface remains rough so that instruments will not slip out of the surgeon's hands.¹⁷

In closing of this general introduction it may be said that the development of the applied chemistry of fluorine, which started with fluorination of substances has led to surface fluorination of materials, which is now an effective tool in changing of surface properties.

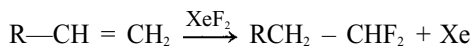
15.3. POLYMER SURFACE FLUORINATION WITH XENON DIFLUORIDE

As fluorine has such an extremely high reactivity alternative agents are being used for the fluorination of organic compounds, in particular milder XeF_2 ($\Delta H_{298}^\circ \text{XeF}_2(\text{gas}) = -108.4 \text{ kJ/mol}$; $\Delta G_{298}^\circ \text{XeF}_2(\text{gas}) = -74.7 \text{ kJ/mol}$). Furthermore XeF_2 is "pure" fluorinating agent, with its only reduction product being the noble gas xenon.

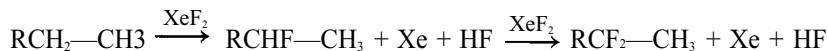
The comparative accessibility and desirable properties of XeF_2 enable its use for the synthesis of fluoroorganic compounds under "mild" conditions. As a fluorinating agent XeF_2 can be used to effect electrophilic fluorination of various organic compounds with good yield and it is a useful reagent for generating radical cations. According to Bartlett,³ in many fluorination and oxidation reactions, XeF_2 is first ionized to XeF^+ and then electron transfer gives the radical XeF^\cdot . In many cases XeF_2 is an attractive alternative to the conventional Balz-Schiemann reaction for the preparation of fluorinated aromatic compounds, e.g., fluorobenzenes (in CCl_4 , CH_2Cl_2 , CH_3CN , . . .):



Xenon difluoride reacts with carbon-carbon single, double, and triple bonds giving addition fluoroorganic compounds, e.g.,



and



In this respect XeF_2 is similar to molecular fluorine. The relatively low oxidizing ability and reactivity of XeF_2 in the same type of chemical reactions is explained by its greater dissociation energy. The activation energy of the dissociation ($\text{XeF}_2 \rightarrow \text{XeF} + \text{F}$) is 190–210 kJ/mol. The XeF radicals are very weakly bound ($E_{\text{XeF}} = 58\text{--}80 \text{ kJ/mol}$) and can be an effective source of F atoms.³

15.4. EXPERIMENTAL

The procedure was a very simple one. The sample and a certain amount of XeF_2 were placed together in a stainless steel reactor ($V = 6$ liters). The reactor

was then closed and evacuated if needed. The system was left undisturbed for some time. Owing to the high vapor pressure, the fluorination proceeded via a chemical reaction between the solid polymer surface and the gaseous XeF_2 . After a certain amount of time had elapsed the reactor was evacuated and opened, and the samples were put under a hood for 24 h for degassing.

15.5. RESULTS AND DISCUSSION

In the first stage in order to test the process of various types of polymer films were surface-fluorinated. From 1990 to 1994 it was shown that XeF_2 could be used effectively for surface fluorination of a variety of plastics. Polyethylene film and plates,¹⁸ aromatic polysulfone,¹⁹ polyvinyltrimethylsilane,²⁰ and polycarbonate,²¹ among other polymeric materials, were fluorinated successfully.

The fact that fluorination had taken place was established by various analytic methods: ESCA, IR and FTIR spectroscopy, bulk analysis, NMR, and DSC. The presence of chemically bonded fluorine in the surface layer of treated samples were uniquely determined by analysis data. Further details can be found elsewhere.²²

Here we would like to emphasize that treatment with XeF_2 fluorinates the polymer surfaces, with the depth and degree of fluorination depending upon the reaction conditions. We never observed the formation of a perfluorinated surface layer after treatment with XeF_2 . Results of XPS analysis of XeF_2 -treated polyethylene film $-(\text{—CH}_2\text{—CH}_2\text{—})_n\text{—}$ showed that the maximum degree of fluorination corresponded to the composition $-(\text{—CF}_2\text{—CH}_2\text{—})_n\text{—}$. After that, visible destruction of the polymer surface, i.e., cleavage of C—C bonds in the polymer macromolecule, would start. These results differ from those of the fluorination of polymer powders; it was reported by Lagow and Margrave in the early 1970s that polymer powders were fully converted into perfluorinated polymers under the action of a F_2/N_2 mixture.²³

Apart from the whole range of physicochemical analyses of XeF_2 -treated polymers, some other potentially interesting and useful surface characteristics were tested and measured.

First, it is interesting to note that the increased surface energy of the XeF_2 -treated polymer surfaces enhances their wettability. So, e.g., the water contact angle for polyethylene and polyurethane drops after treatment up to three- to fourfold and two- to threefold, respectively. Increased wettability can be very useful in biomedical applications; and, of course, it improves adhesion. Treated polypropylene films that were glued together showed a substantially increased adhesion strength, which was found to be greater than its cohesion strength.

Another interesting and possibly useful result of fluorination of XeF_2 -treated polymer surfaces is decreased gas permeability. For example, fluorinated poly-

vinyltrimethylsilane film showed a fourfold decrease in the CO₂ permeability coefficient, as determined by gas chromatography.

PVC tubes and pipes used in microchip manufacturing for supplying deionized water, where purity is a very important factor, were XeF₂-treated. Tests showed that the treated tubes did not contaminate the deionized water with organic compounds below 90°C. Certain types of polymers showed significant improvement in swelling in organic solvents after XeF₂ treatment. Aromatic polysulfone showed no swelling in kerosene (80°C, 7 h) while the control (untreated) sample showed a 4% increase in weight. A similar effect was found with fluororubbers. However, the most significant results were obtained with XeF₂ treatment of rubbers.

15.6. RUBBER SURFACE FLUORINATION WITH XENON DIFLUORIDE

In 1993 it was established that surface fluorination of rubbers with XeF₂ led to a significant decrease in the friction coefficient. Table 15.1 compares friction coefficients before and after treatment with XeF₂. These results generated considerable interest from the former Skega AB—one of the major producers of rubber products in Sweden, now Svedala Skega AB and Skega Seals AB. Their interest centered on the decrease in the initial friction force in small (10.3 x 2.4 mm) O-rings made from a peroxide-cured ethylene-propylene rubber (EPDM). Our joint venture lasted for two years, during which time the optimum conditions for XeF₂ surface fluorination were established and the results shown in Table 15.2 were obtained.

Friction force measurements at Skega AB were carried out by the following procedure. A piston/cylinder type of test ring was used. The O-ring being tested was greatly stretched over the piston and fitted into the seal groove. The cylinder was carefully wiped and dried with a clean cloth before the piston was put into the

*Table 15.1. Friction Coefficient Decrease
in Russian-Made Rubbers after XeF₂
Treatment*

Rubber type	Friction coefficient	
	Initial	After treatment
SBR	2.40	0.23
IR	2.00	1.48
Revertex	1.88	0.60
NBR	0.60	0.16

Table 15.2. Mean Values of Friction Force Decrease in EPDM O-Rings after XeF₂ Treatment

Type	Friction force (F), N	$F_{\text{fluorinated}}/F_{\text{initial}}$
Initial (nonfluorinated)	127.00	—
Fluorinated, mode 1	17.40	0.14
Fluorinated, mode 2	99.06	0.78
Fluorinated, mode 3	28.00	0.22
Fluorinated, mode 4	10.31	0.08
Fluorinated, mode 5	5.56	0.04
Fluorinated, mode 6	6.14	0.05

cylinder bore. The test ring was then placed in the compression test machine (L&W TCT 50) and the piston was pushed into the cylinder to a distance of approximately 17 mm at a constant speed of 400 mm/min. three tests were made on each O-ring. After each test the piston was removed from the cylinder and the bore was carefully cleaned as described above.

It is very important to know how surface fluorination affects the stability of tribological characteristics. In the case of Russian-made rubbers we used a standard friction machine (SMT), where abrading was done with a stainless steel instead of a conventional brass grid so that the test would be more rigorous. The results obtained are shown in Table 15.3.

The friction force endurance of EPDM O-rings after XeF₂ treatment in optimum mode can be illustrated by a graphic presentation of friction force measurements during 50 cycles in the compression test machine (L&W TCT 50) (Figure 15.1).

To validate our idea that treating rubber products with gaseous XeF, causes them to become surface-fluorinated, i.e., that chemically bonded fluorine atoms are incorporated in the surface layer, we did ESCA analyses of the samples treated in various modes. The results are shown in Table 15.4.

Table 15.3. Times to the Initial Values of the Friction Coefficients of XeF₂-Treated Samples^a

Rubber type	Time, h
SBR	4.5
NBR	5.2
IR	2.4
Revertex	1.8

^aThe nontreated rubber samples began losing the initial friction coefficient value during this test after 0.5 h

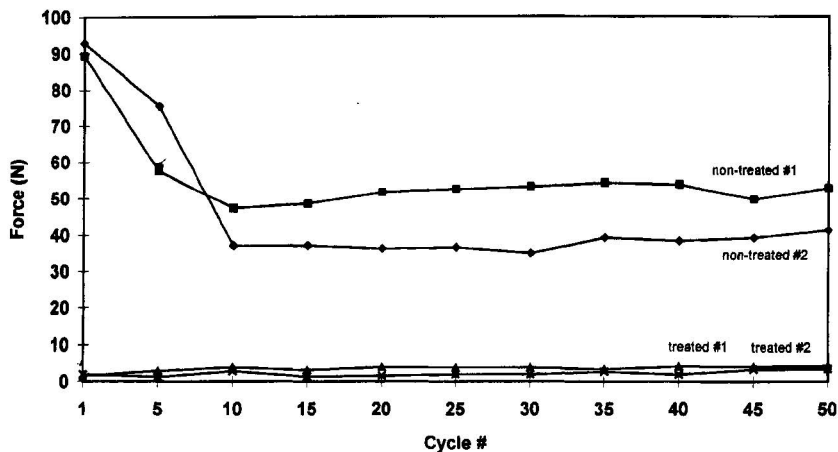


Figure 15.1. Friction force endurance of EPDM O-rings.

Although we made no attempt to elucidate the mechanism of friction decreases in rubbers after surface fluorination, it seems to us that apart from the substitution of H atoms to F in the polymer macromolecule, which forms a fluoropolymer on the surface, there is another phenomenon that makes a significant contribution to the friction decreases, i.e., fluorination of carbon black, which is used in rubber recipes for reinforcement. It appears that when the carbon black in the surface of the rubber is fluorinated it produces a lubricating effect, followed by “blooming” on the surface of the treated rubber while it is under a friction load. So, in our opinion, two effects contribute to friction decrease of carbon-filled rubbers: fluorination of the rubber macromolecules and fluorination of the carbon black; rubbers that do not contain carbon black show a much smaller decrease in friction after XeF_2 treatment.

Rubber (NBR) samples treated with XeF_2 in an optimum mode, i.e., showing the lowest friction force while retaining all the other bulk properties of NBR

Table 15.4. ESCA Analysis Results of the Rubber (SBR) Samples Treated in Different Modes

Sample No.	Elemental composition, at. %		
	Carbon	Oxygen	Fluorine
1	82.9	15.5	1.6
2	82.5	15.0	2.5
3	82.7	15.2	2.1

rubber, were analyzed in Sweden to detect surface-incorporated fluorine and the depth of fluorination with scanning electron microscope (SEM) equipped with EDS. The samples were vacuum-treated before they were sputtered with gold.

In Figure 15.2 Pictures 1.1 and 2.1 are SEM images of nonfluorinated (reference) material and fluorinated samples (Batch 15A20PR7), and Pictures 1.2 and 2.2 are the corresponding X-ray spectra. The EDS spectrum shows that Batch 15A20PR is fluorinated, since a fluorine peak can be seen in the left part of the spectrum (Picture 1.2).

Figure 15.3 shows the results of the second SEM analysis designed to give a qualitative determination of the depth of fluorination. A carefully prepared cross section of the O-ring was analyzed using the so-called "mapping technique." The light streak across Picture 3.2 shows where the fluorine is concentrated. With the aid of the microscale shown it can be estimated that the fluorination is approximately 5 μm deep.

15.7. INDUSTRIAL APPLICATION OF RUBBER SURFACE FLUORINATION WITH XENON DIFLUORIDE

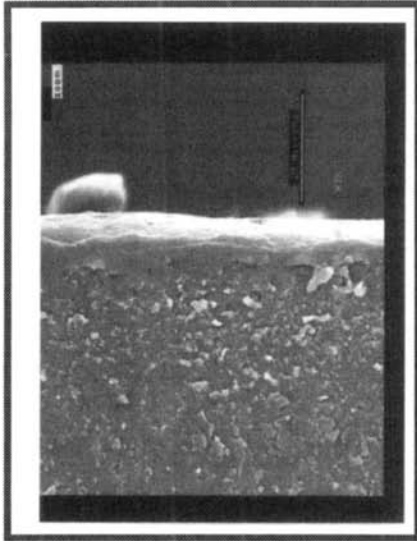
After two years of extensive research and testing, in 1955 Skega AB placed an order with the RRC Kurhatov Institute for a specially designed plant for XeF_2 treatment with a capacity of 5000 O-rings per shift. The design of the plant is very simple and it was not expensive to build. The plant has been installed at Skega Seals AB and is operating successfully.

The simple calculations presented below will show that surface fluorination of rubbers with XeF_2 is economically advantageous as compared with fluororubbers. The amount of XeF_2 needed for batch treatment of 5000 O-rings made from EPDM rubber (diam. 10.2×1.5 mm) is approximately 20 g. That means that the cost of the XeF_2 needed for one batch treatment, is $20 \times \$1.5 = \30 for 5000 O-rings or about \$0.0006 each. It should be kept in mind that, as mentioned above, the price for fluororubber is thirty times that of EPDM.

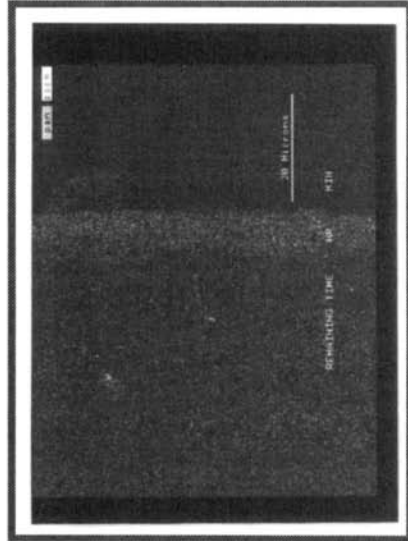
Although we have no specific data on the economics of rubber surface fluorination with the traditional F_2/N_2 mixture, in our opinion the following facts make the XeF_2 technique very attractive for rubber manufacturers:

1. Low cost, based on the quantity of XeF_2 .
2. Equipment and technique are simple and inexpensive.
3. Unlike using traditional methods there are no health, explosion, or fire hazards.

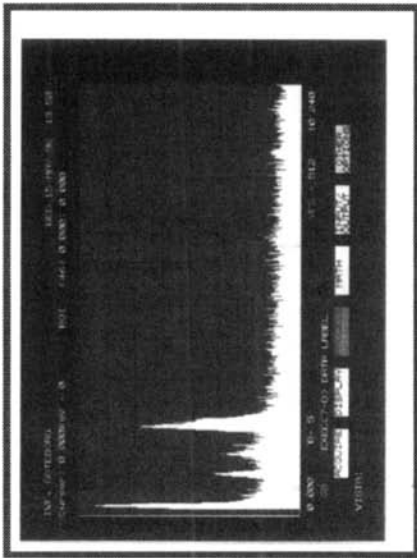
Another argument in favor of the XeF_2 method is the evidence that since 1995 it has been used by a manufacturing company that had no previous experience with direct fluorination or fluorine at all.



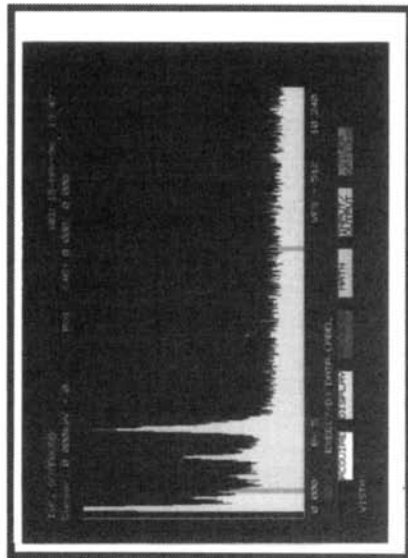
Picture 3.1
Cross-section



Picture 3.2
"Mapping"



Picture 3.3
EDS-spectrum
Bulk



Picture 3.4
EDS-spectrum
Surface

Figure 153. SEM images reflecting the depth of fluorination.

15.8. RECENT DEVELOPMENT OF THE XENON DIFLUORIDE METHOD

An interesting advance in XeF_2 polymer surface fluorination was made in 1995. Polyethylene (PE) film was treated with XeF_2 . The reaction chamber was evacuated and blown with argon, after which a fluoromonomer—tetrafluoroethylene (TFE) (C_2F_4) was added to the reaction chamber. This second stage formed a new surface layer on the PE film. The IR spectrum of the treated PE film shows the presence of a C—F bond, but differs a lot from PE samples treated just with XeF_2 , which also show the C—F bonding. One of the most reasonable assumptions here is postpolymerization of TFE on the XeF_2 -activated PE film surface. The potential of this method is evident and needs no comment. Another very attractive idea is to substitute TFE for another perfluoromonomer compound that is easier to handle.

Recent research indicates that the XeF_2 /TFE method can also be used for inorganic surfaces,²⁴ which would be a very important development.

15.9. CONCLUSIONS

1. Xenon difluoride has proved to be an effective fluorinating agent for surface fluorination of polymers.
2. The technique of surface fluorination with XeF_2 is much less sophisticated, expensive, and hazardous than the conventional F_2/N_2 treatment.
3. The XeF_2 polymer surface fluorination technique can be easily applied at manufacturing companies that have no experience in dealing with fluorine.
4. The laboratory results that have been obtained point to several interesting possible applications of XeF_2 /TFE method.

15.10. REFERENCES

1. J. Soll, US. Patent 2,129,289 (1938).
2. B. B. Chaivanov, V. B. Sokolov, and S. N. Spirin, Preprint IAE-4936/13, Moscow, Atominform, 1989.
3. N. Bartlett and F. O. Sladky, in *Comprehensive Inorganic Chemistry*, Pergamon Press, Oxford and New York (1978).
4. R. E. Banks and J. C. Tatlow, in *Organofluorine Chemistry: Principles and Commercial Applications* (R. E. Banks, B. E. Smart, and J. C. Tatlow, eds.), Plenum Press, New York (1994), p. 16.
5. M. Howe-Grant (ed.), *Fluorine Chemistry: A Comprehensive Treatment*, Encyclopedia Reprints Series, John Wiley and Sons, New York (1995), p. 2.
6. A. B. Neiding and V. B. Sokolov, *Usp. Khim.* 12, 2146–2194 (1974).

7. Kirk-Othmer *Encyclopedia of Chemical Technology*, 4th Ed., Vol. 13, John Wiley and Sons, New York, (1995), p. 38.
8. V. B. Sokolov and G. Barsamyan, *Proceedings of XI European International Symposium on Fluorine Chemistry*, Bled Slovenia, 1995, pp. 132–135, 181–182.
9. R. E. Banks, D. W. A. Sharp, and J. C. Tatlow (eds.), *Fluorine: The First Hundred Years (1886–1986)*, Elsevier Sequoia, Lausanne and New York (1986).
10. N. Isikava (ed.), *Soedineniya Flora*, Mir, Moscow (1990), p. 16.
11. A. Kharitonov and Yu. L. Moskvina, in *Proceedings of the Second International Conference on Fluorine in Coatings*, Salford England 28–30 Sept. 1994.
12. M. Annand J. P. Hobbs, and I. J. Brass, in *Organofluorine Chemistry: Principles and Commercial Applications* (R. E. Banks, B. E. Smart, and J. C. Tatlow, eds.) Plenum Press, New York (1994), pp. 469–480.
13. V. Frolov, V. V. Teplyakov, and A. P. Kharitonov, in *Proceedings of the Second International Conference Fluorine in Coatings*, Salford, England 28–30 Sept. 1994.
14. W. J. Koris, W. T. Stannett, and H. B. Hopfenberg, *Polym. Eng. Sci.* 22, 738 (1982).
15. M. Annand J. P. Hobbs, and I. J. Brass, in *Organofluorine Chemistry: Principles and Applications* (R. E. Banks, B. E. Smart, and J. C. Tatlow, eds.), Plenum Press, New York (1994), p. 474.
16. R. J. Lagow and J. L. Margrave (to DAMW Associates), Canadian Patent 1,002,689 (Dec. 28, 1976).
R. J. Lagow and J. L. Margrave (to DAMW Associates), U.S. Patent, 440,605 (Oct. 20, 1976).
17. R. B. Badachhane, C. Homsy, and J. L. Margrave (to Vitek Inc. and MarChem, Inc.), U.S. Patent 3,992,221 (Nov. 16, 1976).
18. G. B. Barsamyan, V. B. Sokolov, B. B. Chaivanov, and S. N. Spirin, *J. Fluorine Chem.* 54,85 (1991).
19. G. B. Barsamyan, V. B. Sokolov, and B. B. Chaivanov, *J. Fluorine Chem.* 58 (N2–3), 220 (1992).
20. G. B. Barsamyan, N. A. Vargasova, S. D. Stavrova, and V. B. Zubov, *Zhurnal Prikl. Khimii* 67,610–612 (1994).
21. G. B. Barsamyan, V. B. Sokolov, and B. B. Chaivanov, in *Proceedings of XI European International Symposium on Fluorine Chemistry*, Bled Slovenia, September 1995.
22. G. B. Barsamyan, K. C. Belokonov, N. A. Vargasova, V. B. Sokolov, B. B. Chaivanov, and V. P. Zubov, Preprint IAE-J748/13 (1994).
23. J. L. Margrave and R. J. Lagow, *J. Polym. Sci. Polym. Lett. Ed.* 12, 177 (1974).
24. Korean Patent Application 96–47649, filed October 23, 1996.