

Fluorinated polymers: evaluation and characterization of structure and composition

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Abstract: The proposed review represents the systematic analysis of modern methods and approaches for the characterization and structural evaluation of fluorinated polymers that have found a wide application as materials for chemical processing, chemically resistant components and coatings, pharmaceutical and electrical packaging, biomedical equipment, etc. The chemical composition of the polymers (fluorine content, its distribution inside the fluorinated materials, chemical bonds, presence of oxygen-containing groups) substantially influences on the operation properties (chemical resistance, adhesive, cohesive, optical, dielectrical, thermal, barrier, gas permeation) of the final polymeric products. Hence, it was of particularly importance to bond the emergence of specific features with the presence of fluorine in the chemical structure of polymer by means of related analytical techniques. Namely, we focused on spectral (IR, UV-VIS, NMR, XPS, EPR), chemical (elemental analysis), Secondary-ion mass spectroscopic (SIMS) and microscopic (AFM, SEM-EDX) methods emphasizing their general consideration and limitations as well as application for the in-depth characterization.

Keywords: fluorinated polymers; X-ray photoelectron spectroscopy (XPS); nuclear magnetic resonance spectroscopy (NMR); secondary-ion mass spectroscopic (SIMS); atomic force microscopy (AFM); scanning electron microscopy (SEM); energy dispersive X-ray (EDX); infrared (IR) analysis.

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Фторированные полимеры: оценка, характеристика структуры и состава

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Аннотация: Предлагаемый обзор представляет собой систематический анализ современных методов и подходов к характеристике и оценке структуры фторированных полимеров, которые нашли широкое применение в качестве материалов для химических процессов, химически стойких компонентов и покрытий, фармацевтической и электрической упаковки, биомедицинского оборудования и т.д. Химический состав полимеров (содержание фтора, его распределение внутри фторированных материалов, химические связи, наличие кислородсодержащих групп) существенно влияет на эксплуатационные свойства (химическая стойкость, адгезионные, когезионные, оптические, диэлектрические, термические, барьерные, газовая проницаемость) конечных полимерных продуктов. Следовательно, особенно важно связать появление специфических особенностей с присутствием фтора в химической структуре полимера с помощью соответствующих аналитических методов. А именно, сосредоточились на спектральных (ИК, УФ-видимая, ЯМР, XPS, ЭПР), химических (элементный анализ), масс-спектрометрических (ВИМС) и микроскопических (АСМ, SEM-EDX) методах, рассматривая их основные возможности и ограничения для углубленной характеристики фторсодержащих полимеров.

Ключевые слова: фторированные полимеры; рентгеновская фотоэлектронная спектроскопия (РФЭС); ядерный магнитный резонанс (ЯМР); вторичная ионная масс-спектрометрия (ВИМС); атомно-силовая микроскопия (АСМ); сканирующая-электронная микроскопия (СЭМ); энергодисперсионный рентгеновский анализ; инфракрасная Фурье-спектроскопия.

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1. Introduction

Fluorine-containing polymers (FPs) are popular and irreplaceable products of large-scale chemistry. World production of fluorinated polymers in 2010 amounted to more than 200,000 tons, in 2012 – 223,000 tons, while by 2022 it is predicted to double (to 405,000 tons) [1]. The high global demand for FPs is due to a unique combination of properties: chemical, electrochemical and thermal stabilities, oxygen resistance, low surface energy, low coefficient of friction, low high frequency-loss rates, low refractive indices, low permittivity etc. [1–4]. Such attractive macroscopic parameters of FPs are feasible owing to extremely high energy of C—F bond ($478 \text{ kJ}\cdot\text{mol}^{-1}$) for ordinary bonds and a lowest energy of intermolecular interactions (a solubility parameter of the perfluorinated compounds corresponds to ca. $12\text{--}13 \text{ (J}\cdot\text{cm}^{-3})^{1/2}$ whereas for the common hydrocarbons it does to $14\text{--}15 \text{ (J}\cdot\text{cm}^{-3})^{1/2}$). FPs are indispensable in many branches of science and technology: electronics [5, 6], energy [7–13], biomedical application [14, 15], membranes [16–21], coatings [22–25], – as materials for wire and cable insulation, industrial, architectural and multilayer barrier coatings, fuel tubing, hoses and fittings, seals, lighting, solar panels, automotive and mass transit cabling, optical fibers, etc. [1, 2, 26]. During the development and fabrication of the materials, it is extremely important to control the structure and composition of the resulting product. In this regard, the aim of this review is to consider and describe the methods for analysis of the structure and composition of FPs and changes associated with fluorination process. In order to maintain the operation properties of the products it is often sufficient to have a thin fluorinated layer over the material. Therefore, polymeric materials that are fluorinated by elemental fluorine in the gas- or liquid-phase regime are in the scope of the FPs under consideration. Such materials have a laminate structure with gradient of fluorine concentration along the normal to the surface. The thickness of the fluorinated layer usually is about several microns. The probing of these composite materials is also the aim of the review.

2. Materials and methods

2.1. Elemental analysis

The quantity of fluorine introduced to the material after direct fluorination can be estimated by combustion of sample in the Schoniger apparatus [27] and trapping of the combustion products in the absorbing solution. In the case of fluorination of polypropylene [28] and poly(*p*-phenylene terephthalamide) [29], Maity et al. absorbed those products by mixture based on Ce(III) nitrate solution and the excess of the reagent was titrated by ethylenediamine tetraacetate. Despite the simplicity of the instrumental implementation, the oxygen flask technique faces problems of incomplete decomposition of highly fluorinated polymers and formation low molecular volatile compounds (tetrafluoromethane and others) which are not trapped in absorbing solutions. Here, the chemical resistance of fluorine-containing materials that is mostly provided by high dissociation energy of C—F bond (ca. $485 \text{ kJ}\cdot\text{mol}^{-1}$) becomes their weakness. In order to improve fluorine recovery, Hruska and Lepot have decomposed the fluorinated polypropylene film with sodium peroxide [30] while Fan et al. performed the oxygen flask combustion with catalyst ($\text{WO}_3 + \text{Sn}$) [31]. Further detection of fluorine was performed by fluoride selective electrode [30, 32].

A standard CHNSO method of high temperature combustion of sample in a stream of pure oxygen can be applied for indirect estimation of fluorine in the polymers. The fluorine content in a polymer assembled from the elements (carbon, hydrogen, nitrogen sulfur and oxygen) may be calculated as a residual weight after subsequent quantitative detection of the elements. This technique is a rapid, simple and low-cost analysis and has been successfully used for investigation of surface fluorinated conventional polyolefins [33–35] and other fluorine-containing polymers [36–38]. However, it also suffers from underestimation of carbon content due to the formation of thermostable low molecular fluorinated compounds in the combustion region [39].

2.2. Spectroscopic techniques

2.2.1. IR spectroscopy

Infrared spectroscopy is a traditional routine analytical technique that allows conducting structural analysis of both surface and bulk of polymeric materials. Each functional group absorbs infrared radiation at particular frequency. Three regions (13,500–4,000 cm^{-1} (near infrared), 4,000–400 cm^{-1} (middle infrared) and 400–10 cm^{-1} (far infrared)) compose the whole infrared range. Infrared spectrum of a polymer is an individual set of specific absorption bands that can be utilized to make polymer identification in “finger print” region [40–43]. Since fluorine-containing polymers, in particular perfluorinated polymers, are often solids and weakly soluble in organic solvents, among the wide diversity of infrared analytical procedures (transmission, specular reflection, multiple internal reflection, diffuse reflection, photoacoustic etc. [43]), attenuated total reflectance technique is the most popular one and allows one to measure samples rapidly without destruction and complicated preliminary preparation. Another advantage of the procedure is ability to vary the depth d_p of penetration of IR radiation. It can be calculated as follows [44]:

$$d_p = \frac{\lambda}{2\pi n_1 \sqrt{\sin^2 \theta - \left(\frac{n_1}{n_2}\right)^2}},$$

where λ and θ are wavelength and angle of incidence of IR radiation; n_1, n_2 are refractive indices of a polymer and an ATR-crystal, respectively.

The refractive indices of polymers and ATR-crystals belong to a narrow ranges of values: 1.3–1.8 for polymers, 2.2–4.0 for ATR-crystals (ZnSe 2.4, ZnS 2.2, Silicon 3.4, Ge 4.0, diamond 2.4) [44, 45]. Therefore, the variation of ATR-crystals and angle of incidence allows one to analyze polymers on the depths up to 0.7–15 μm which is comparable with the thicknesses of the fluorinated polymeric layers [46, 47].

The ATR-IR technique was applied for investigation of the most fluorinated polymers (for instance, epoxy resin [48], silicone rubber [49, 50], UHMWPE [51], LDPE, HDPE, PP, PET [52], wood samples [53], etc.). The main characteristic absorption bands for fluorine-containing polymers and composites are presented in Table 1.

IR-spectroscopy also enables to perform in situ monitoring of fluorination process by means of IR-transparent beryllium window in the reactor's wall. So, gradual conversion of $-\text{CH}_2-$ group of LDPE into $-\text{CHF}-$ and $-\text{CF}_2-$ was detected by shift of absorption band from 1,100 to 1,200 cm^{-1} [58, 63].

2.2.2. UV-Vis interferometry

Interferometry in the ultraviolet-visible region (UV-Vis) has been applied for investigation of polymers since mid-to-late XXth century [64]. The technique is based on the analysis of the interference spectrum of the UV-visible light reflected from the layers in the sample at different depths. Kharitonov et al. suggested using the procedure for estimation of depth of fluorination [65]. In the case of thin layers, the thickness of the fluorinated layer is determined via interference of the UV-Vis light having passed through the sample and reflected twice from the

Table 1. Specific absorption bands for fluorine-containing polymers and composites

Functional group	Wavenumber, cm^{-1}	Reference
C—F (general) (str*)	1,200; 1,147; 554, 509	[31, 44, 51, 52, 54–57]
$-\text{CF}_3$ (str*)	1,350–1,120	[44]
$-\text{CF}_2-$ (str*)	1,280–1,120	[44, 57]
$-\text{CF}$ (aliphatic) (str*)	1,100–1,000	[44, 57, 58]
$-\text{CF}$ (aromatic) (str*)	1,270–1,100	[44]
$-\text{C}(\text{O})\text{F}$ (str*)	1,800–1,900	[55, 59–61]
Si—F (str*)	850	[62]

* Stretch vibration.

fluorinated layer. This procedure can be realized when the fluorinated and non-fluorinated layers are separated by very thin boundary layer (not more than one fourth of light wavelength) and the boundary layer is parallel to the surface of the sample [34]. If the fluorinated polymer is not sufficiently transparent for UV-Vis light, the interference spectra can be measured in the reflection mode by changing the angle of incidence by 45°. The approach allows estimating fluorination depth from 0.1 to 50 µm and performing in situ measurements of thickness of the fluorinated layer during the fluorination process [34]. It was applied for investigation of kinetics of fluorinated layer growth for various polymers: UHMWPE [66], HDPE [47, 67], PS [34], PET, PI, PPO, PVTMS [46, 68], PTFE [46], PEEK-WC [61], etc. Refractive indices n_V^D for the conventional polymers vary in the range of 1.49–1.66 while n_F^D for the fluorinated layers of these polymers are within 1.35–1.41 (Table 2). The minimum difference between refractive indices of virgin and fluorinated layers for proper application of the technique should be higher than 0.03–0.05.

The thickness of the fluorinated layer can be calculated based on the following equation:

$$\delta_F = \frac{1}{2n_F^D \Delta\nu},$$

where $\Delta\nu$ (cm⁻¹) is an interval (a difference in wavenumbers) between neighboring maxima or minima in transmission spectra [65]. For most cases of gas-phase fluorination by elemental fluorine, the time dependence of the thickness as well as the total amount of fluorinated groups was shown to be proportional to the square root of fluorination time t_F [66]. This fact proves that (i) the fluorinated polymeric film consists of fluorinated and virgin

layers separated by very thin ($\ll 0.1$ µm) boundary where the most chemical reactions take place and (ii) the rate of generation of fluorinated layer results from diffusion of fluorine through the modified layer to the untreated one.

2.2.3. NMR-spectroscopy

Nuclear magnetic resonance is a routine tool of investigation of chemical structure of polymers. The elements having magnetic momentum (for instance, ¹H, ³H, ¹³C, ¹⁵N, ¹⁹F, ²⁹Si, ³¹P and others) can be tested by NMR technique. Each atom possesses a unique chemical shift relatively to a standard, depending on electronic structure of a nucleus, atoms bonded with this atom, spatial environment, etc. Exhaustive data on the chemical structure of a polymer can be obtained on the basis of chemical shift and spin-spin coupling parameters [69–72]. A wide range of procedures of NMR are currently available but among them NMR of samples in deuterated solvents and magic angle spinning NMR (MAS NMR) are most spread. The former approach has a drawback associated with a weak solubility of fluorinated polymers in most of the solvents. While the latter (MAS NMR) allows measuring of NMR spectra of solid samples that has promoted a wide application of this technique in analysis of fluorinated polymers. Trichlorofluoromethane is often chosen as internal standard while 1,1,2-trichloro-1,2,2-trifluoroethane ($\delta(^{19}\text{F}) = -68.05, -72.20$ ppm), trifluoroacetic acid ($\delta(^{19}\text{F}) = -78.4$ ppm), C6F6 ($\delta(^{19}\text{F}) = -163$ ppm), sodium trifluoromethane sulfonate ($\delta(^{19}\text{F}) = -80.8$ ppm), PTFE ($\delta(^{19}\text{F}) = -122$ ppm) and others [53, 57, 66, 73–76] are used as external standards for correction of chemical shifts of fluorine nuclei. The NMR is a sufficiently sensitive method and enables an estimation of the fluorination degree for the fluorinated polymers via ratio of signals from different functional groups (Table 3). It also allows calculating average molecular mass of a polymer by the ratio of side functional groups to the amount of polymer units according to the corresponding chemical shifts of atom nuclei [53, 57, 58, 66, 77–81]. An example of the NMR analysis of highly fluorinated polymer is provided for long-term liquid-phase fluorination of poly(2,6-dimethylphenylene oxide-1,4) powder in pefluorodecalin (PFD) [82]. The product of the fluorination was soluble in PFD and perfluorobenzene, and was shown by standard ¹⁹F, ¹³C NMR approaches to have structure of poly(perfluorocyclohexenyl ether) [82].

Table 2. Refractive indices of virgin (n_V^D) and fluorinated (n_F^D) polymer layers estimated via UV-Vis technique

Polymer	n_V^D	n_F^D
PS [34]	1.590	1.366
PET [46,68]	1.655	1.380
Matrimid5218 [46, 68]	1.63	1.41
PPO [46, 68]	–	1.373–1.381
PVTMS [46, 68]	1.492	1.376

Table 3. Specific chemical shifts of ^{19}F and ^{13}C in various functional groups

Functional group	Chemical shift of ^{19}F , ppm	Chemical shift of ^{13}C , ppm	References
CF	-144, -138, -200	100–103	[66, 75, 76, 79]
CF ₂	-122	107.8	[53, 66, 75, 76, 79]
CF ₃	-80	118.3	
SCF ₂	-114, -118	112	[75, 76]
OCF ₂	-78, -80, -85	116.8	[75, 76, 83]
CF ₂ SO ₂ F	44–45 (from SO ₂ F group)	112–114	[83]

2.2.4. X-ray photoelectron spectroscopy (XPS)

X-ray photoelectron spectroscopy is a high demand technique to investigate chemical composition of polymeric surface [42, 84, 85]. The method is based on photoelectron effect when electrons are emitted from the sample due to its exposition to mild X-ray radiation of specific energy (Mg or Al K α radiation source with 2–20 keV). Analysis of the amount and energy of the photoelectrons allows estimating the content of elements (except hydrogen) and nature of their bonds since the binding energy of the electron with nucleus (i) has unique characteristic value for each element and (ii) depends on the electron environment of the element and can be shifted if it is bound to an element having different electronegativity (Table 4) [42, 86]. The signal of aliphatic carbon in the chemical group —CH₂— with energy as high as 284.5–285.0 eV is

often utilized as internal standard. The XPS technique also allows investigating the sample surface within the thickness up to 5–7 nm [86]. The depth of the layer analyzed also results from the angle of incidence of X-ray beam. So, the fluorine atom (F_{1s}, 686–689 eV) can be detected on the depths of ca. 0.8 nm (at 80°), 3.4 nm (at 45°) and 4.8 nm (at 0°) in the case of non-monochromatic anode radiation Mg K α , and on the depths of ca. 1.1 nm (at 80°), 4.5 nm (at 45°) and 6.3 nm (at 0°) in the case of monochromatic anode radiation Mg K α [86, 87]. XPS approach has high sensitivity (ca. 0.1 %) and good spatial resolution (ca. 2–5 μm) that enables element and its bonds mapping over the surface and depth of the sample [42, 84–90]. XPS was effectively applied in the series of investigations by Cheng et al. [54, 91, 92], Nazarov et al. [35, 52, 93], and other researchers [67, 81, 94–96].

Table 4. The specific binding energies of electron in carbon and fluorine atoms of F-containing functional groups

Functional piece	Chemical shift, eV
(—CHF—CH ₂ —) _n	C _{1s} : 287.91 [97, 98], 288 [99] (CF); 285.7 [97, 99] (CH ₂) F _{1s} : 686.94 [97], 689.3 [99] (F)
(—CF ₂ —CH ₂ —) _n	C _{1s} : 290.9 [97–99] (CF ₂); 286.44 [97], 286.3 [99] (CH ₂) F _{1s} : 688.15 [97]; 689.6 [99] (F)
(—CF ₂ —CF ₂ —) _n	C _{1s} : 292.48 [85, 97–99] (CF ₂) F _{1s} : 689.67 [97], 690.2 [99], 689.7 [85] (F)
(—CFH—CFH—) _n	C _{1s} : 288.4 [99, 100] (CF) F _{1s} : 689.3 (F) [100]
(—CF ₂ —CFH—) _n	C _{1s} : 291.6 (CF ₂); 289.3 (CFH) [97, 98] F _{1s} : 690.1 (F) [97]
CF ₃ —CH ₂ —O—	C _{1s} : 292.2 (CF ₃) [98]
CF ₃ —CF ₂ — (perfluorinated polymers)	C _{1s} : 295.6 (CF ₃), 291.3 (CF ₂) [98]
(—CH ₂ CH(OC(O)CF ₃)—) _n	C _{1s} : 292.65 (CF ₃) [97] F _{1s} : 688.15 (F) [97]

2.3. Microscopic methods

The AFM technique is based on monitoring of the polymeric surface by a cantilever, and detection of energy of its interaction with the surface. The method possesses high resolution along the thickness and the width of the surface that enables to perform 2D and 3D morphological analysis of the polymeric layers. Hardness, electroconductivity, adhesive and magnetic properties, roughness can be estimated in a pointwise manner. The analysis can be performed in various media (vacuum, air, inert gases, liquids) allowing to study influence of media composition on surface properties of polymer [42]. The technique was applied in investigation of surface morphology of polymers and composite materials after fluorination elsewhere [52, 101–103].

Scanning electron microscopy (SEM) is a widely applicable technique to test a surface of polymeric samples. The method is based on scanning of sample surface by a focused primary electron beam resulting in emission of secondary electrons. The intensity of secondary electrons depends on atomic number of the element: the higher the number is the larger intensity of the electrons becomes. The method allows testing the topology, morphology and crystallographic nature of the samples [104]. For instance, for the majority of polymers (UHMWPE, LDPE, PPTA, PET, PP, fir wood, etc.), an increase in roughness was observed [53, 52, 96]. By means of this technique, An et al. estimated nanoparticle size distribution and roughness of the surface of high temperature vulcanized composites made of silicone rubber and nanosilica [50].

It is worth noting that SEM has been applied for estimation of depth of fluorination by preparation and analysis of cross-section of the polymeric films [48, 50, 105, 106]. Moreover, SEM is often combined with energy dispersive X-ray spectroscopy (EDXS). During the measurement, spectra of energy of X-ray emission after exposure of the sample to electron or X-ray beam are recorded. Each atom has a unique configuration of electrons and, hence, has a specific spectrum of X-ray emission. Thus, the SEM-EDXS coupling allows one to perform quantitative and qualitative elemental analysis (hydrogen excluded) of polymeric surface [107, 108]. Wirti et al. showed that surface concentration of C-F bonds achieved 2.5 % after treatment of Kevlar fibers by hydrofluoric acid [109]. A uniformity of the surface fluorination of polymers was also demonstrated elsewhere [31, 48, 51, 59, 95, 110].

2.4. Other techniques for analysis of structure of fluorine-containing polymers

The secondary ion mass spectrometry became widely used in polymer testing in the late twentieth century [111–114]. The method is based on bombardment of polymer surface by primary ions (for instance, Xe^+ , Cs^+ , Ga^+) resulting in ionization and desorption of monoatomic layers (formation of secondary ions) that allows carrying out analysis of elemental and molecular composition within thickness as large as 5 Å [86]. So, time-of-flight procedure of SIMS has detected the following molecular ions in the chemical structure of fluorinated polymers: CF_3^- , C_2F_5^- , C_3F_7^- , CHF_2 , CHOF_4^- , CH_2OF_5^- , SiF , $\text{C}_7\text{H}_2\text{F}_5^+$, $\text{C}_8\text{H}_2\text{F}_5^+$, $\text{C}_8\text{H}_4\text{F}_5^+$, $\text{C}_9\text{H}_4\text{F}_5^+$, $\text{C}_{15}\text{H}_3\text{F}_{10}$, etc [115–118]. In addition, the SIMS technique is often used for estimation of depth of fluorination, its uniformity [119–120] and distribution of fluorine-containing additives over the sample [115, 121, 122].

Oppositely, electron paramagnetic resonance (EPR) can be considered as a non-destructive method for detection of paramagnetic species (point defects, free radical, biradicals, transition metal ions, etc.) [123, 124]. For the polymers after contact with elemental fluorine, the presence of long-lived radicals was proved by EPR technique [63, 125, 126]. Peyroux et al. showed that during fluorination of LDPE the following radical structures formation took place: $-\text{CF}_2-\overset{\cdot}{\text{C}}\text{F}-\text{CFH}-$ and $-\text{CF}_2-\overset{\cdot}{\text{C}}\text{H}-\text{CF}_2-$. Their intensities decreased after the exposure to air due to attack of oxygen resulting in the formation of peroxide radicals and subsequent oxidation [58, 63, 102, 125].

A combination of the aforementioned chemical, spectroscopic, spectrometric and other techniques for estimation of chemical structure and morphology of the fluorinated materials (polymers, layers) expands the insight into the interaction of the polymers with elemental fluorine comprehensively.

3. Results and Discussion

The range of techniques, which can be applied for the characterization and structure evaluation of fluorinated polymers, highlight the complex character of surface fluorination and necessity to use various chemical and physical approaches for the study. The fluorination of surface layers determines the apparent changes in the chemical composition, morphology, spectroscopic properties and surface features. Thus, the full characterization of polymers should be provided especially in case of polymers for

the specific applications. UV-Vis spectroscopy is excellent for in situ control of thickness of the fluorinated layers and provided the general information about optic properties. The chemical and morphological analysis of cross-section and surface of the fluorinated layers can be conducted using XPS, AFM, SEM, SIMS approaches. Finally, chemical analysis can be performed by flask combustion method, CHNSO analysis, NMR, XPS, SIMS.

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5. Conflict of interests

The authors declare no conflict of interest.

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