ISSN 1070-3632, Russian Journal of General Chemistry, 2009, Vol. 79, No. 3, pp. 520–526. © Pleiades Publishing, Ltd., 2009.
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Fluoropolymer Chemistry in Russia: Current Situation and Prospects

V. M. Buznik

Baikov Institute of Metallurgy and Materials Science, Russian Academy of Sciences,
Leninskii pr. 49, Moscow, 119991 Russia
phone: (+7495)1352060
e-mail: bouznik@ngs.ru

Received February 1, 2008

Abstract—The current situation in the fluoropolymer chemistry and industry in Russia was overviewed, including the fluoropolymer manufacture and market related issues. Also, the research and manufacturing cooperation in the framework of the "Fluoropolymer Materials and Nanotechnology" joint venture was discussed.

DOI: 10.1134/S1070363209030335

INTRODUCTION

Polytetrafluoroethylene, a basic polymer in the class of fluoropolymers, possesses a number of remarkable properties, including high chemical stability, insolubility in most of known solvents, high hydro- and lyophobicity, excellent insulation properties, record-level low friction coefficient, and high weather resistance. Polytetrafluoroethylene does not exhibit aging over time and is biocompatible with living tissues. All this made polytetrafluoroethylene suitable for numerous scientific, technological, industrial, medical, and everyday-life applications. Another valuable property of polytetrafluoroethylene is the preservation of performance characteristics over a wide temperature rage, from –269°C to +260°C, which is not common in polymers. This material is easily treated mechanically and thus can be processed into diversified articles by fairly simple techniques.

The above-mentioned beneficial properties are combined in polytetrafluoroethylene with a number of drawbacks that prevent it from more extensive application. These drawbacks are associated with three groups of factors: technological, environmental, and economic. The technological factors include cold flow (development of plastic strain under load at temperatures much lower than the softening point), low thermal conductivity, poor wear resistance under mechanical load, and weak adhesion to the material and article surface. Environmental factors include abundant waste generated by manufacture of polytetrafluoroethylene articles and complex character of waste processing and disposal. The economic factor (most important among those preventing more extensive application of polytetrafluoroethylene), consists in a high cost of the material compared to hydrocarbon polymers. This motivates replacement of polytetrafluoroethylene, whenever possible, by alternatives, except for cases where such replacement is functionally impossible.

Fluoropolymer Market and Manufacture in Russia

The annual production of fluoropolymers is not very high, ca. 100 thousand tons, which is under 0.1% of the overall world's polymer production. At the same time, in terms of costs, fluoropolymers occupy a significant segment of the market (over 2.5 bln US dollars), which tends to steadily grow. The major proportion (60–80%) of fluoropolymers manufactured is accounted for by polytetrafluoroethylene. The cost of fluoropolymer products broadly varies from several tens of dollars per kilogram in the case of polytetrafluoroethylene powder to 50 thousand dollars for Nafion films. The current trend in the fluoropolymer market is toward steady growth of the proportion of high-technology products. Another feature of today's market situation is the appearance of new manufacturers, in particular, those from Chinese Peoples' Republic, whose supplies of large polytetrafluoroethylene amounts at low prices, attractive for purchasers, pushes them on the foreground positions.

In Russia, the principal manufacturers of fluoropolymers are the Polymer Plant, Konstantinov Kirovo-Chepetsk Chemical Combine, Kirovo-Chepetsk, and Galogen Open Joint-Stock Company, Perm, integrated into a holding. The total annual fluoropolymer production for them is estimated at tens thousand tons. The products and articles are available in a fairly broad assortment but rank below those supplied by the main foreign manufacturers. It should be noted that these enterprises utilize thirty-year-old, and even older, technologies that have exhausted most of their innovational potential. There is a need to improve the existing technologies in terms of lower cost, higher energy and resource efficiency, and a broader assortment of products and articles, in particular, hi-tech and high-cost ones.

An essential component of the manufacture of polytetrafluoroethylene should be found in a technology for waste processing into commercial products. At the present time, two processing techniques are applied to this end. One of them implies thermal decomposition of waste into gaseous products which, under appropriate process conditions, form ultradispersed powders via nucleation and condensation processes. This technique is applied in production of Forum and Flurolit polytetrafluoroethylene. An alternative technique consists in mechanical treatment, specifically, jet milling, of preirradiated powdered waste; it is utilized for producing Tomflon polytetrafluoroethylene. Also, waste can be processed into commercial polytetrafluoroethylene powders by mechanical activation with disintegrators, as well as by laser ablation. In view of the fact that the waste is a by-product for fluoropolymer manufacturers, and the cost of the final product can substantially exceed that of commercial powders, these are fairly cost-effective processing methods.

Further development of fluoropolymer preparation technologies should be focused on principally new scientific and technological approaches to synthesis of these materials. An example of an efficient technique of fluoropolymer preparation can be found in the synthesis carried out in a supercritical carbon dioxide medium. This option provides certain technological benefits (continuous nature of the process, by contrast to currently used batch technologies) and prospects for preparation of new products. This line is actively attacked by DuPont; in Russia, only one team is engaged in this sphere (see relevant review in this issue). The situation in which Russia’s fluoropolymer industry has no interest expressed by manufactures in the new technology is fraught with significant lagging behind.

In this context, an important task consists in broadening the assortment of fluoropolymer-based products, in particular, composites with various fillers, including nanosize ones. In the latter case, synthesis of fluoropolymers is a fairly difficult task, since solution-based technologies are inapplicable, and high viscosity of fluoropolymer melts hinders preparation of nanocomposites with nonaggregated fillers. One way to synthesize composites and improve their properties, in particular, performance characteristics, lies in chemical and plasmochemical treatment of fillers, which allows controlling the filler–fluoropolymer matrix interaction.

New materials are often qualified as small-capacity products, whose manufacture at large enterprises could be not very efficient. This was specifically responsible for the establishment of small-sized innovation enterprises engaged in small-scale manufacture of one or more fluoropolymer products and articles. At the present time, such enterprises are engaged in manufacturing ultradispersed fluoropolymer powders by various methods, in particular, with the use of process waste from polytetrafluoroethylene manufacture (Forum, at the Institute of Chemistry, Far-Eastern Branch, Russian Academy of Sciences, Vladivostok; Tomflon, in Tomsk; and Flurolit, in Moscow). In St. Petersburg, there are Ekspress-Eko enterprise and Ekoflon Scientific and Production Company, engaged in manufacture of fluoropolymer-based filtration materials and unique implants from Flouroplastic 4D, respectively. Large enterprises or scientific institutes tend to organize small innovation enterprises to manufacture fluoropolymer-based materials and articles from the fluoropolymers supplied by the main plant of to implement the scientific and technological developments of research institutes. The world market economy experience suggests that this is a normal situation and such activities needs to be supported and made mutually beneficial for small-sized enterprises, large manufacturers, and developers of fluoropolymers. Small-sized enterprises are suitable as “testing grounds” for new technologies and new fluoropolymer products. The manufacture of new materials by small-sized enterprises favors emergence of new market segments and provides those enterprises, if successful, with an opportunity to grow into large companies or to pass the manufacture on to large enterprises.

State of Modern Russian Fluoropolymer Chemistry

Fluoropolymers belong to hi-tech products whose manufacture is typically streamlined in countries possessing high scientific and technological potentials. The manufacturers are also not large in number (no greater than twenty). Fluoropolymer technologies and manufacturing activities should be underlain by certain advances in polymer chemistry, as well as in fluorine chemistry, chemical engineering as a whole, chemical mechanical engineering, and other adjacent spheres. Such combination does not necessarily exist in every country. The high-technological nature of fluoropolymer products implies that their manufacture is closely connected to scientific researches aimed at permanent improvement of technologies; the manufacturing process and the products need continuous monitoring, and development of new products entails increased financial and technical expenses. Major fluoropolymer manufacturers typically have special analytical and research structures and also undertake active cooperation with external research and educational institutions, since covering all the abovementioned issues it is a complex task for a single entity.

As known, polytetrafluoroethylene with all its unexpected properties was discovered accidentally, which is largely due to the fact that, by contrast to hydrocarbon polymers, fluoropolymers have no natural analogs. These are typical man-made materials, and it is safe to presume that, in the future, fluoropolymer studies will bring no "accidental" discoveries. Further development of fluoropolymer manufacturing and fluoropolymer chemistry, as well as preparation of new science-intensive and high-quality products, will require in-depth basic researches in many of the chemistry and chemical engineering domains.

The fluoropolymer chemistry underlying the fluoropolymer manufacture is most highly developed in the US, where fluoropolymers were first synthesized and their manufacture was brought to commercial level. Faced by refusal to sell a license for polytetrafluoroethylene manufacturing, the Soviet Union had to manage on its own resources and undertake the relevant activities, along which line much progress was achieved. The development of fluoropolymer chem.-istry was stimulated by the need in chemically stable materials for nuclear production. To this end, extensive research activities were initiated in the middle of the XX century by a number of branch research institutes, in particular, Plastpolimer Research and Production Association, State Institute of Applied Chemistry, Karpov Research Physicochemical Institute, etc. As a result, Soviet researchers developed technologies for commercial manufacture of fluoropolymers (they were subsequently used in organizing the fluoropolymer manufacture in China). Active researches in the field of fluoropolymer chemistry were undertaken by many institutes within the Academy of Sciences: Institute of Physical Chemistry, Institute of Energy Problems of Chemical Physics, Nesmeynov Institute of Organoelemental Compounds, Topchiev Institute of Petrochemical Synthesis, etc. Also, a number of outstanding scientific schools were established, e.g., the Academician I.L. Knunyants's School (the Seventh All-Russia Conference "Fluoropolymer Chemistry" held in Moscow in 2006 was dedicated to the centennial of this school).

Today, in a respectful "age" of seventy, the fluoropolymer chemistry still has numerous issues that remain to be elucidated. In particular, the number of phase transitions in polytetrafluoroethylene and their origin are still the subject of much discussion. Reasons to this are many, and the major one is associated with a complex structure and variable self-organization of supramolecular systems such as fluoropolymers. Their structure and properties are extremely sensitive to the manufacturing technology, temperature history, and external impacts. This not only complicates synthesis, but also opens up wide prospects for innovational application of fluoropolymers, whose properties are radically modified in response to even weak external impacts.

There exist several lines in development of fluoropolymer chemistry, which are both of academic and applied significance: preparation of ultra- and nanodispersed powder materials; development of solution-based methods of application of fluoropolymer materials; synthesis of complex fluoropolymer supramolecular membrane type structures; development of composites with the use of nanosize fillers; modification of existing fluoropolymer materials by various techniques; providing a broader spectrum of functional fluoropolymers, etc.

A special sector in the market of fluoropolymer materials is occupied by polytetrafluoroethylene powders. The specific applications of the powders and the properties of articles thereof are governed by the size and shape of the powder particles. Of special interest is the preparation of polytetrafluoroethylene powder materials from process waste. Such powders are currently prepared by a number of techniques based on heat treatment and laser and radiation exposures.

There exists a technique for synthesizing powders from gaseous products yielded by pyrolytic conversion of the block polymer, which is extensively applied in manufacture of inorganic, in particular, nanosize, powders. However, the use of this technique in the case of fluoropolymer was initially prevented by a number of factors. Relevant researches conducted at the Institute of Chemistry, Far-Eastern Branch, Russian Academy of Sciences, showed that this technique is suitable in principle for preparing ultra-dispersed fluoropolymer powders, and the appropriate equipment and technologies were developed, which allowed economical manufacture of this materials on a pilot scale. The Forum products prepared from bulk process waste by this technique holds promise of extensive application. However, up to now, this material proved to be commercially successful only in the capacity of antifriction, anitwear additions to engine oils (the product has been available at the autochemistry market for over 15 years). It should be noted that this powder material is characterized by a complex self-organization hierarchy and consists of several polytetrafluoroethylene phases (low- and high-molecular-weight ones), and this is a feature that makes it essentially different from other commercial products.

The manufacture of Tomflon fluoropolymer was underlain by an alternative approach, accelerated electron irradiation of block polytetrafluoroethylene, or more precisely, of process waste. This leads to accumulation of defects, which, in turn, initiate macro- and microcracking in the polymers. Subsequent mechanical treatment (jet milling) of the material causes destruction of the particles at these defects. This yields tape-shaped particles whose molecular structure fully corresponds to that of commercial polytetrafluoroethylene samples.

One of the promising lines in development of fluoropolymer chemistry and technology consists in preparation of new fluoropolymer-based composite materials. A broad spectrum of existing fillers with different chemical compositions, as well as particle sizes and shapes, enables preparation of a multitude of composite products. However, as mentioned above, this creates a problem associated with introduction of nonagglomerated nanosize fillers. In this respect, the insolubility of fluoropolymers, being one of their merits, is a drawback at the same time: It prevents the use of solution-based technologies in various synthesis processes and in deposition of thin fluoropolymer coatings onto the surface of materials and items. It should be noted that deposition of thin controlled fluoropolymer layers eliminates the major factor limiting the extensive application of fluoropolymers, a high cost, but, importantly, the deposition technology itself should not be expensive.

In attempts to solve the problem of fluoropolymer coating deposition, researchers sought for approaches to implement solvent-based technologies, whose advantages include the simplicity and technological efficiency, as well as extensive experience of application. Also, solution-based technologies are of principal importance for deposition of fluoropolymer composite materials, since they allow introducing nanosize fillers.

To this end, several promising approaches were proposed, which were implemented so far in the research stage only. One of these approaches implies synthesis of fluoropolymers soluble in supercritical carbon dioxide, which technology can be used both in preparation of new materials and deposition of nanosize coatings. Examples can be found in Teflon AF 2400 (a copolymer of 4,5-difluoro-2,2-bis(trifluormethyl)-1,3-dioxalane and tetrafluoroethylene) available from DuPont and in a low-molecular-weight fraction of Forum. The use of these materials allows preparing thin fluoropolymer coatings with a thickness ≥ 2 nm, preserving the micro- and nanoroughness of the treated surface. This is essential for development of superhydrophobic coatings whose practical advantages include high antiadhesion and self-cleaning powers.

Specific properties of supercritical liquids make it possible, in principle, to prepare high-quality coatings. High mobility of the solvent molecules in the supercritical state and of the solute enables deposition of coatings onto inner surfaces of the materials and items having open pores, thereby modifying the adhesion properties of porous materials. Based on improved technology of preparation of supercritical CO_2, a method was developed for fluoropolymer encapsulation of paraffins. This allowed preparation of paraffin particles with the size of several hundreds of micrometers and several micrometer-thick fluoropolymer coatings. Such materials are of interest as lubricants and are also suitable for preparing polymer-polymer composites (for technology of deposition of fluoropolymer coatings in supercritical carbon dioxide, as well as for the structure of supramolecular fluoropolymer coating, see the relevant review in this issue.).

A possible limitation in deposition of coatings in supercritical carbon dioxide may be associated with the volume of the reactor used for synthesis, which will prevent deposition of coatings onto large items. An unordinary solution to this problem was found in treatment of surfaces with a jet of fluoropolymer solution in supercritical carbon dioxide, supplied from the reactor. In this version, the method can be applied for deposition of coatings on items of any shape and size. However, it was found that this technique yields loose fluoropolymer layers with poor adhesion properties. Appropriate technologies of their transformation into dense coatings possessing good adhesion properties would substantially increase the efficiency of application of fluoropolymer materials obtained with the use of supercritical liquids. In the framework of application of this method, techniques are being developed for preparation of hybrid (multocomponent) coatings from fluoropolymers with different fillers. From the academic viewpoint, it is of interest to examine the extent of degradation of the low-molecular-weight fraction of the polymer when dissolved in supercritical CO_2. This would provide an answer to the question, whether the chain macromolecules of low-molecular-weight fluoropolymer remain intact or degrade into smaller moieties. In the latter case, this method could be used for synthesizing new polymer materials from two or more soluble reactants.

Another solution-based technology of preparation of fluoropolymer coatings utilizes solutions of telomeres of tetrafluoroethylene in a liquid solvent, e.g., acetone. The method consists in the following. Gaseous tetrafluoroethylene is introduced into liquid acetone, and the resulting system is exposed to γ-rays; the induced radiation-chemical processes yield various fluorine-containing molecules (see review by Kiryukhin et al.). Quantitatively, these are mostly the $CH_3COCH_2(CF_2CF_2)_nH$ moieties with n = 5–6. Upon deposition of a telomere solution onto a surface, acetone is evaporated, leaving behind a white powdered precipitate. Heating of the latter causes the acetone terminal moieties to split off, thereby yielding macromolecules that are similar to those of polytetrafluoroethylene. This is paralleled by powder melting into a continuous coating. This technology can be used for preparation of fluoropolymer coatings both on large articles and small bulk items. The coating thickness can be controlled by the quantity of the telomere deposited, with the desired quality achieved through appropriate heat treatment. Coatings are easily deposited onto surfaces of any chemical composition (metals, ceramics, glass, wood, polymers, and fabrics and fibers, both natural and synthetic). This method is suitable, in principle, for preparation of fluoropolymer-based composite materials via mixing solutions of tetrafluoroethylene telomers with various fillers soluble in acetone.

Radiation-based techniques are suitable for preparation of graft fluorocarbon molecules and fluoropolymers on various surfaces. The relevant method implies formation of radicals both on the substrate surface and in the monomer molecules being grafted, which occur in the gas or liquid phase. The advantage offered by this method is that the fluorine-containing molecules in the coating are covalently bound to the substrate. However, the method has certain drawbacks associated with the fact that grafting proceeds in the radiation exposure zone, thereby limiting the size of the items treated and necessitating the appropriate safety measures. In this context, combinations of different technologies of fluoropolymer coating deposition seem promising, in which radiation-induced graft modification yields the first layer strongly bound to the substrate, onto which further fluoropolymer layers are deposited.

An interesting and promising approach to development of fluoropolymer materials consists in modification of hydrocarbon polymers and articles thereof via direct fluorination with gaseous products. Many of the beneficial properties of fluoropolymers are manifested on the surface level, which makes reasonable to have a hybrid material whose bulk is comprised of hydrocarbon polymers, and the surface layer, of a fluoropolymer. This is an economical procedure in which the surface of an article made of less expensive hydrocarbon polymers acquires the properties characteristic for expensive fluoropolymers. This method is beneficial in that it allows the surface film formation to be technologically controlled by varying the composition and pressure of the gaseous medium and fluorination time. This enables variation of the layer thickness, the continuous character, and the hydrophilic and hydrophobic properties of the surface, as well as the gas permeability of polymeric articles. It was shown that this method is suitable for many types of polymers and elastomers. The technology of preparation of hybrid materials was brought to the commercial scale. In particular, a small-sized Interftor innovation enterprise (Tomsk) was established, which is engaged in fluorination of polymer films with the aim to improve their adhesion properties.

The overwhelming majority of fluoropolymers are used as structural, protective, tribological, and, to a lesser extent, functional materials, except for application as insulating materials. The latter line deserves closer attention and more extensive, both basic and applied, research efforts (for some of the relevant issues, see the review by K.P. Gritsenko).

Consortium: A New Form of Cooperation of Fluoropolymer Researchers and Manufactures

The recent decades have witnessed worsening of the situation in Russia's fluoropolymer chemistry and fluoropolymer manufacture. This is associated with significant weakening of branch institutes (that had achieved much progress in these spheres) and lessened amount of the research work along these lines. The senior generation of researchers, with all the experience, knowledge, and culture of fluoropolymer production and materials science they possessed, is being replaced by younger generations. All this is taking place against the background of declining interest of the young people in scientific and industrial activities. This is largely due to the system crisis in Russia, which resulted in slackening of demand for new materials in Russia's economy. This concerns above all defense complex enterprises, the major consumers of hi-tech products. The focus of attention of Russian manufacturers of fluoropolymers shifted to exports, but foreign market of hi-tech, in particular, chemical products is highly structured and is very difficultly accessible. In this situation, the basic exported items are represented by inexpensive materials. The former monopolist on the Russian fluoroplastic market, the Russian manufacturers of fluoropolymers have to withstand severest competition both outside and inside Russia. This makes the major manufacturers of fluoropolymers change their commercial policies and improve their sales patterns. In this situation, the "DEVYATYI Element" Joint-Stock Company was established which is engaged in market promotion of fluoropolymer products. This structure can perform the dealer's functions with respect to small innovation enterprises engaged in fluoropolymer manufacture, whose limited possibilities create serious marketing problems in promotion of their products.

This situation called for new forms of cooperation between industrial enterprises and business structures, on the one hand, and scientific organizations, on the other, as well as for new approaches to cooperation among researchers. A possible form of cooperation of scientific structures and industrial enterprises can be found in a consortium. This is a temporal association of independent enterprises and organizations, engaged in coordination of their business activities. Inside a consortium, the roles are distributed in such a way that the participants are engaged in those spheres in which their respective activities have afforded the highest-level technological achievements at the lowest costs.

Several academic institutions initiated the establishment of the "Fluoropolymer Materials and Nanotechnologies" Consortium. It has a mission to promote more efficient basic and applied researches in Russia's scientific organizations engaged in the sphere of fluoropolymer materials and their manufacture and application technologies. The Consortium provides assistance in training specialists in fluoropolymer chemistry at Russian universities, as well as in promoting innovational activities of scientific organizations engaged in the fluoropolymer sphere and establishing contacts between researchers, on the one hand, and industrial enterprises and business circles, on the other.

The Consortium activities cover a broad spectrum of tasks:

– carry out joint researches on synthesis, modification, and application of fluoropolymer materials; study their properties, structures, and applications; publish the results of joint researches in scientific journals, proceedings of conferences, reviews, and monographs;

– coordinate the participants' activities aimed at innovational implementation of scientific and technological results, in particular, promote organization of small-sized innovation enterprises and manufacture of hi-tech products;

– assist the Consortium participants in getting the patent and know-how protection for the outcomes of their research activities;

– take part, on a joint basis, in tenders of innovational and initiative projects to get the funding needed for the research and innovational activity;

– raise awareness and popularize fluoropolymer materials science, fluoropolymer chemistry, and the Consortium itself;

– assist universities in training young specialists in the field covered by the Consortium activities and involve them into relevant research activities;

– provide for cooperation of academic organizations with industrial enterprises, business structures, and branch institutes engaged in fluoropolymer materials and technologies sphere both inside and outside Russia; and

– hold scientific and organizational events (seminars, conferences, symposia, round tables, etc.).

The Founders of the Consortium include: Baikov Institute of Metallurgy and Materials Science, Russian Academy of Sciences, Moscow; Institute of Chemical Physics Problems, Russian Academy of Sciences, Chernogolovka; Nesmeyanov Institute of Organoelemental Compounds, Russian Academy of Sciences, Moscow; Kurnakov Institute of General and Inorganic Chemistry, Russian Academy of Sciences, Moscow; Topchiev Institute of Petrochemical Synthesis, Russian Academy of Sciences, Moscow; and Institute of Energy Problems of Chemical Physics, Russian Academy of Sciences, Chernogolovka; and All-Russia Research Institute of Aviation Materials, State Scientific Center, Federal State Unitary Enterprise. More recently, the Institute of Chemistry, Far-Eastern Branch, Russian Academy of Sciences, Vladivostok, as well as the Institute of Metal-Polymer Systems Mechanics, National Academy of Sciences of Belarus, Gomel, and “DEVYATYI Element” Joint-Stock Company, joined the Consortium. The Consortium members include academic and branch institutes, as well as the principal Russian manufacturers of fluoropolymer products and their respective business organizations. This allows the manufacturers, businessmen, and researchers to stay in permanent contact and also facilitates their cooperation.

The “Fluoropolymer Materials and Nanotechnologies” Consortium is, in a sense, a pilot project providing a framework for implementation of new cooperation forms for researchers and manufacturers under the market conditions. The experience of the Consortium may be helpful, which makes reasonable a more detailed discussion of its organizational structure. The Consortium is a simple partnership of participating organizations, not a legal body, and has no material property in its possession. In cases of commercial and innovational implementation of joint projects the participating organizations conclude separate contracts. The Consortium integrates partners with different ownership forms; it avoids complex bureaucratic procedures associated with integration of foreign organizations and creates no property and financial threats to the participants. The Consortium activities are managed by the Coordination Council whose members are appointed by participating organizations. The Coordination Council reports to the Supervisory Council (whose members are the Directors of the participating organizations); the Supervisory Council is headed by Academician S. M. Aldoshin. The operational management of the Consortium activities is effected by Coordinator (Academician V. M. Buznik); the Coordinator is elected by and reports to the Coordination Council. The Consortium holds a seminar supervised by Academician A.R. Khokhlov. The Consortium activities are regulated by the following documents: Simple Partnership Agreement, Consortium Regulations, and Agreement on Preservation of Confidentiality of Information. The Consortium is opened for new members.