

RESEARCH AND DEVELOPMENTS IN THE FIELD OF NEW FLUOROELASTOMERS OF S. V. LEBEDEV SYNTHETIC RUBBER INSTITUTE

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Abstract. *In FSUE NIISK performed synthesis of fluororubbers with improved technological characteristics and high thermal stability, investigated chemical modifications of serial fluorocontaining rubbers, developed methods of synthesis for new fluoromonomers and new vulcanizing agents.*

Keywords: *fluorocontaining synthetic rubbers, fluoromonomers, fluoropolymers, copolymers.*

The beginning of the twentieth century had been marked by discovering the structure of one of the natural polymers - poly-2-methylbutadiene - natural rubber, which monomer was named isoprene, and also it had been marked by searching for the ways to synthesize such an elastic polymer or its analogues. In Russia in 1930-s Academician S. V. Lebedev had developed foundations and created the production of synthetic rubber - polybutadiene.

In 1940-s All-Union Research Institute for synthetic rubber (VNIISK) was established. Nowadays FSUE NIISK is the largest internationally acknowledged scientific center of fundamental and applied researches in the field of synthetic rubbers and latexes.

That period was also marked by the appearing and powerful development of fluoroorganic compounds chemistry, development of production of synthetic polymers which did not have any natural born analogues both by structure and properties, but which were necessary for carrying out the nuclear projects - fluoroplastics, fluororubbers, fluorinated oils and lubricants.

In Russia a beginning for research in the filed of fluororubbers was laid by I. M. Dolgopolsky in VNIISK about 60 years ago with the development of synthesis method and production technology of polyfluoroprene. It was obtained by emulsion polymerization of 2-fluorobutadiene, synthesis of which concluded in the fluorinating of divinyl acetylene using anhydrous hydrogen fluoride, was developed by B. A. Buzov in laboratory and implemented at pilot plant by V. Z. Ruzshinsky. However, that first fluororubber with one fluorine atom in monomer molecule could not compete with commercially produced polychloroprene.

At the same time A. L. Klebansky started researches and development of synthesis of methyltrifluoropropylidichlor silane and fluorosiloxane rubbers based on it.

V. I. Rokitiatsky's studies, which provided increasing of fluorine content in the elastomer's chain, in the 1950-s were directed at developing of the conditions for emulsion radical co-polymerization of vinyliden fluoride (M-2) with trifluorochloroethylene (M-3) and hexafluoropropene (M-6). These studies formed a foundation for development of soviet fluororubbers' SKF-32 and SKF-26 production technology - analogues of american Kel-F® and Viton®.

In the 1950-s one of the priority directions in the Institute's researches became the developments of synthesis of next generation fluorine rubbers combining advantages of first fluorine polymers - their thermal and chemical stability with frost resistance improved compare to SKF-32 and SKF-26 and in demand as by both the climate particularities of the main territories of this country and demands of aviation and space industry.

M. Dolgopolsky proved, that using of heptafluoro-3-methoxypropylacrylate in co-polymerization with vinyliden fluoride resulted in lowering the vitrification temperature for at least 20 °C [1], however

the presence acrylate fragment not containing fluorine did not provide the good resistance of rubber to aggressive medium.

The increasing of frost resistance could have been achieved at the expense of rotation freedom of chain side suspension around ether oxygen.

The necessary combination of frost resistance and resistance to aggressive medium for co-polymers based on vinyliden fluoride had been managed to obtain only after I. M. Dolgopolsky's and V. A. Gubanov's with co-workers in 1960 developed the synthesis method of new monomer - perfluoromethylvinyl ether (M-60) by pyrolysis of perfluoro-3-methoxypropionylfluoride [2] obtained by B. A. Buzov and V. V. Berenblit at electrochemical fluorination (ECF) of methyl 3-methoxypropionate [3].

Monomer M-60 had been obtained using that method in the VNIISK earlier, than it was described in the patent of DuPont company [4] based on hexafluoropropene oxide. In I. M. Dolgopolsky's laboratory its properties were characterized, and by its emulsion co-polymerization R. L. Rabinovich with co-workers obtained fluorine rubbers based on it. The production technology of new co-polymer of vinylidenfluoride with M-60 - SKF-260 with vitrification temperature of -38°C was developed [5], its characteristics are listed in Table 1. Amine vulcanization of such fluoroelastomer provided necessary properties for the rubber for aviation techniques.

In 1967 a Pilot Plant of SKF-260NT rubber [6] was run. These plant produced SKF-260NT to the end of 1990-s. In Table 1 properties of SKF-260NT are listed.

Insufficient aggressivity resistance of amine vulcanizators of fluororubbers had initiated further developments for the purpose of modification of co-polymers of vinylidenfluoride with hexafluoropropene and perfluoromethylvinyl ester.

A third co-monomer providing linkage of main chains was needed for the process of co-polymerization for bisphenol or peroxide vulcanization of fluoropolymers. Bromo-2,2-difluoroethylene which synthesis had been developed by S. V. Sokolov and D. S. Rondarev was chosen as such comonomer. It allowed A. I. Konshin and N. V. Veretennikov to obtain elastomer SKF-26B by emulsion copolymerization of vinylidenfluoride with hexafluoropropene and bromo-2,2-difluoroethylene and implement its production at Kirovo-Chepetsk Chemical Plant.

Simultaneously, at the Pilot Plant of Institute V. A. Nikitin and A. N. Frantsev had developed a production of frost resistance fluorine rubber SKF-260BPT, which properties are also listed in Table 1. The demands of space techniques demanded further increasing of frost resistance of fluorine rubbers based on vinylidenfluoride. In 1970-s S. V. Sokolov and L. A. Baranova had developed a synthesis of perfluorinated vinyl ether with two ether oxygens in alkyl chain - perfluoro-3-methoxypropylvinyl ether (M-60MP) which provided vitrification at temperature below 50°C for co-polymer.

Hexafluoropropene oxide (HFPO) was used for the synthesis of such vinyl ethers. the obtaining process of HFPO by oxidation of hexafluoropropene using hydrogen peroxide resulted in necessity to utilize large quantity of alcohol-aqueous waste, containing fluoride-ion and fluoroorganic compounds [7]. For the purpose to avoid that L. F. Sokolov had developed a technology of more safe ecological obtaining method for HFPO (M-06) by liquid-phase thermal oxidation of hexafluoropropene. That technology was developed and given to Kirovo-Chepetsk Chemical Plant for its commercial production.

In the Institute V. A. Gubanov had studied the nature of oligomerization reactions of HFPO and developed opportunities for the practical application of the products [8]. Its co-workers N. V. Veretennikov and G. M. Tulga had developed synthesis of HFPO dimer and perfluoropropylvinylether (M-100), and also HFPO trimer as a base of new fluorinated emulgators and means of fire extinguishing. Their surface active properties had been studied [9]. The developed production technologies of dimer and trimer of HFPO, and also monomers and emulsifiers based on them had been put into practice at Kirovo-Chepetsk Chemical Plant and they are used for the fluoropolymers production.

P. E. Troichanskaya had developed and put into practice the production of higher oligomers of HFPO as antifriction additives to fuels, oils and plastic anti-adhesive lubricants at Pilot Plant. That products were produced under the trade mark Foleoks according to technical conditions [10].

The production technology of M-60MP monomer due to isolation of perfluoro-3-methoxypropionyl fluoride out of ECF products and its condensation with HFPO was developed by V. A. Nikitin, V. V. Berenblit and V. I. Grachev and put into practice by B. A. Larionov at Pilot Plant.

However, linkage of vinylidene fluoride co-polymer chains with perfluoro-3-methoxypropyl vinyl ether (SKF-260MP fluororubber) by standard vulcanizing agents proved to be sterically hampered because of volume perfluoromethoxypropyl hanging.

The attempts to obtain vulcanizers of SKF-260MPD rubber obtained at dehydrofluorination of co-polymer, with necessary characteristics were not a success.

Necessary properties of vulcanizers, particularly, sufficient compression set were reached due to thermo polymerization of vinylidene fluoride and perfluoro-3-methoxypropyl vinyl ether with third monomer. D. Rondarev and L. Seniushov developed the synthesis of perfluorocyanalkyl vinyl ethers, which suited as a third monomers. The technology of isolation of difluoromalonyl difluoride and obtaining of functional cyan-containing monomer was developed and put into practice at Pilot Plant by L. N. Seniushov and A. L. Kuznetsov.

The synthesized by M. I. Bognizky 2,2-bis-3-amino-4-hydroxyphenyl-1,1,1,3,3,3-hexafluoropropane, which during the vulcanization process forms thermal resistant oxazole cycles in side chain, was used as linking agent for linkage of such fluororubber.

Table 1. Properties of Fluororubbers of SKF-260

Fluororubber characteristics	SKF-260			
		NT	VRT	MPAN
Weight loss at 120°C, % mass., no more	0,5	0,5	0,5	0,5
Weight loss at 300 °C for 3 h, % mass., no more than	0,7	0,5	2,0	2,0
Mooney viscosity 4+4 (100°C)	75-125	80-120	55-85	60-100
Vitrification temperature, °C, not above	- 38	- 38	-36	-56
Physical and Mechanical Characteristics of Vulcanizers				
Conditional tensile strength, Mpa (kg/cm ²)	12,7 (130)	17,6 (180)	8,0 (80)	6,0 (60)
Elongation at break, %, no more than	200	200	130	150
Relative residual deformation after compression by 20% (24 h x 200°C), %, no more than	24	20	45	-
Relative residual deformation after compression by 20% (24 h x 250°C), %, no more than				40
The coefficient of frost-resistance on the elastic recovery after compression at temperature -30°C, no less than	-	-	0,2	-
The coefficient of frost-resistance on the elastic recovery after compression at temperature -40°C, no less than	-	-	-	0,3

Such system of vulcanization provided the opportunity for further increasing of fluororubber frost resistance due to introduction another perfluorovinyl ether containing additional oxadifluoromethylene units in perfluoropolyoxaalkyl radical (fourth co-monomer into co-polymer).

That monomers (MFK) were obtained in the NIISK, after L. F. Sokolov had identified the structures of forming at oxidation of hexafluoropropene polyoxadifluoromethylene oligomers. V. I. Skoblikova synthesized vinyl ethers based on them, after that V. V. Berenblit and L. N. Seniushov had developed and applied production technology of such monomers at Pilot Plant.

That allowed S. V. Sokolov, A. I. Konshin and M. A. Volokova to set up the production of fourth fluororubber SKF-260MPAN at Pilot Plant, its frost resistance met the requirements of "Buran" space shuttle. Its properties are listed in Table 1.

The principles of building the structures of fluororubbers of ultra low vitrification temperatures down to -170°C due to introduction of perfluoropolyoxamethylene fragments of high thermodynamical and kinetic flexibility, into the main or side polymer chains were developed in the NIISK [12].

That ideas were put into practice for different classes of fluoropolymers - carbon-chain, triazine, polyether, fluoroacrylate and fluorosiloxane. However, chemical and thermal resistance of fluororubbers based on vinylidenfluoride is limited by their opportunity of dehydrofluorination under the influence of nucleophilic reagents or due to radical attack at thermal oxidation of methylene group.

In connection with that in recent years the demands of branches of modern techniques and first of all microelectronics had provoked the interest for perfluorinated elastomers - co-polymers of tetrafluoroethylene with perfluoroalkylvinyl ethers, resistant, particularly to plasmachemical influence at high temperatures.

Elastic characteristics of such co-polymer with perfluoromethylvinyl ether under the name of SKF-460 had been described by I. M. Dolgopolsky as far back as in 1960-s. However, then the absence of opportunity of linkage of such perfluorinated chain hampered the perfluorinated rubber from putting into practice.

The production of mechanical rubber articles made out such fluororubbers had been developed by DuPont in US only in 1980-s under the trademark of Kalrez[®] due to introduction of tertiary monomers of different structures into co-polymer. In the same years in the NIISK A. I. Konshin and M. A. Volkova had developed a radical emulsion thermopolimerization of tetrafluoroethylene with perfluoromethylvinyl ether and functional fluoromonomers with nitrile group [13].

The composition and structure of rubber called "Neoflon" had been convincingly proved by V. A. Lovchikov and U. P. Sokolov using methods of NMR ^{19}F of high definition [14]. E. A. Sidorovich had calculated the molecular mass of perfluororubbers insoluble in standard solvents out of relaxation spectra of mechanical spectroscopy based on molecular theory of elastomers viscoelastic behaviour.

Viscoelastic behaviour and phase transitions of such fluororubber within the temperature range of $-80 - +150^{\circ}\text{C}$ were studied. It had been stated, that within the range of used proportions of monomers units in chain perfluororubber was practically amorphous. Using thermogravimetric method it had been proved, that thermostability of such fluororubber was being defined content of tetrafluoroethylene. Depending on that 5% loss of mass varied within the range of $360-430^{\circ}\text{C}$ (at scanning 5°C per minute).

A. N. Kollar developed new vulcanizing agents for linkage of perfluororubbers. Perfluoroalkyl diimidoylamidines forming triazine cycles in cross-linked polymer chain at interaction of nitrile groups of third monomer [15] were used as such agents. At the Pilot Plant of FSUE NIISK M. A. Volkova, V. A. Gubanov, L. N. Seniushov and B. A. Christianchikov had set up a pilot-commercial production of perfluorinated rubber "Neoflon", which properties are listed in Tables 2 and 3.

Table 2. Properties of Fluororubber of "Neoflon"

Fluororubber Characteristics	"Neoflon"
Weight loss at 120°C , %mass., no more than	0,5

Weight loss at 300 ⁰ in 3 h, %mass., no more than	2,0
Mooney viscosity 4+4 (100 ⁰ C)	30-75
TVitrification temperature, ⁰ C, not above	- 15
Physical and Mechanical Characteristics of Vulcanizers	
Conditional tensile strength, Mpa (kg/cm ²) no less than	12 (120)
Elongation at break, %, no more than	120
Stress at 100%-strain, Mpa (kg/cm ²) no less than	4,7 (50)
Shore hardness , within	70-80
Relative residual deformation after compression by 20% (24 h x 250 ⁰ C), %, no more than	30

Table 3. "Neoflon" resistance to aggressive medium

Medium	Temperature, ⁰ C	Time	Swelling, %mass
Potassium hydroxide, 36%	120	144	1,6
Nitric acid, 67%	120	46	2,3
Ammonia gas	100	46,5	3,6
Diethylamine	25	168	3,2
Methylethylketone	25	72	4,0
Xylene	70	720	2,0
Dichloroethane	100	226	5,6
Industrial oil	80	42	0,1

In recent time M. V. Zhuravlev, N. V. Iebedev and v. A. Gubanov have been conducting the studies regarding modification of perfluororubber named "Neoflon" providing the opportunity to obtained peroxide vulcanizers.

Besides a number of different fluororubbers mentioned above, the researches and developments regarding obtaining a number of perfluorinated liquids and oils functional within temperature range of -65 to 350⁰C to create new hydraulic liquids, plastic lubricants, "liquid gaskets" and others had been conducted in the NIISK. Particularly, A. N. Kollar had created perfluoropolyoxaalkylentriazine liquid named PFT-70 [16], which was applied as an additive to high temperature lubricants efficient within the range of -65 to 300⁰C, and also PFT-100 for the temperature range of -65 - 350⁰C. At Pilot Plant

A. I. Konshin, L. D. Galiulina and E. A. Manuilova had developed and put into practice the production technologies of low-molecular liquid co-polymers of tetrafluoroethylene with perfluoroalkylvinyl ethers named SF-4100 and SF-412 used as emulsifiers or "liquid gaskets" in instrument engineering. Nowadays in the Institute the researches regarding creating new fluorinated products are continuing in the following directions:

1. Development of fluororubbers with improved technological characteristics.
2. Development of fluororubbers with improved low-temperature properties, high thermal stability and resistance to aggressive medium.
3. Chemical modification of commercial fluororubbers.
4. Development of synthesis methods for new fluoromonomers.
5. Development of synthesis methods for new vulcanizing agents.

References

- [1] Patent SU 119872, 1958. Способ получения акриловых эфиров 3- перфторалкокси-1,1-дигидроперфторпропиловых спиртов.
- [2] Мономер М-60. ТУ 38-403-286 -77; ТУ 301-14-25-90.
- [3] Patent SU 405326, 1960. Способ получения фторангидридов перфторкарбоновых кислот.
- [4] US Patent 3114778, 1963. Fluorinated Vinyl Ethers and Their Preparation
- [5] Туманова А.В., Губанов В.А., Долгопольский И.М. и др. // ЖОХ. 1964.Т. 34. N 8. С. 2802; Т. 35. N 2. с. 398.
- [6] КаучукСКФ-260НТ.ТУ 38.103431-79, ИИ1-7.
- [7] Тарант П., Стамп Е. // ЖВХО им. Д.И.Менделеева. 1970. Т. 15. N 1. С. 34.
- [8] Овчинников Е.В., Струк В.А., Губанов В.А. Тонкие пленки фторсодержащих олигомеров. Основы синтеза, свойства и применение. Республика Беларусь, Гродно, 2007. 325 с.
- [9] Хрипун М.К., Губанов В.А. // Коллоидн. Журн. 1982. N 2,С. 380.
- [10] "Фолеокс" -смазкаантиадгезионная.ТУ 6-40-00204317-34-91.
- [11] US Patent 5711037, 1998; US Patent 5736614, 1998.
- [12] Коллар А.Н., Волкова М.А., Губанов В.А. // Тезисы докладов 7-й Всероссийской конференции "Химия фтора", 2006, Москва, О-11.
- [13] Patent RU2137781, 1999. Сополимеры тетрафторэтилена и перфторалкилвиниловых эфиров для термоагрессивостойких изделий.
- [14] Sokolov Yu.P., Filippov N.N., Veretennikov N.V. i dr. Issledovanie stroeniya makromolekul metodom NMR vysokogo razresheniya / Sb. Nauchn. Tr. VNIISK. TsNIITENeftekhim, 1983. S. 45.
- [15] US Patent 7247749, 2005. Bisaminophenyl-based Curatives and Amidine-based Curatives and Cure Accelerators for Perfluoroelastomeric Compositions.
- [16] Перфторполиалкилентриазиновая жидкость ПФТ-70. ТУ 38.03.1.043-92.