Фторполимеры
Fluoropolymers

Collection of thesis of international conference

FLUOROPOLYMERS: RESEARCH, PRODUCTION PROBLEMS, NEW APPLICATIONS

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CONTENS

A JOURNEY FROM THE SYNTHESIS OF FUNCTIONAL 2-TRIFLUOROMETHACRYLATE MONOMERS TO THEIR RADICAL COPOLYMERIZATIONS WITH VINYLIDENE FLUORIDE, AND APPLICATIONS

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2-Trifluoromethacrylic acid (MAF) in a versatile building block for the synthesis of new functional monomers. [1] It can be homopolymerized by anionic initiation [2] but failed in the presence of any radical systems. However, its radical copolymerization with vinylidenefluoride (VDF) has been successful. This presentation reports overall strategies to synthesize novel functional 2-trifluoromethacrylate monomers and macromonomers as well as their radical copolymerization with VDF, leading to various materials such as higher thermal stable thermoplastics, [3] polymer gel electrolytes for Lithium ion batteries, [4, 5] anticorrosion6 and adhesive [7] hybrid coatings (Figure 1). [6]

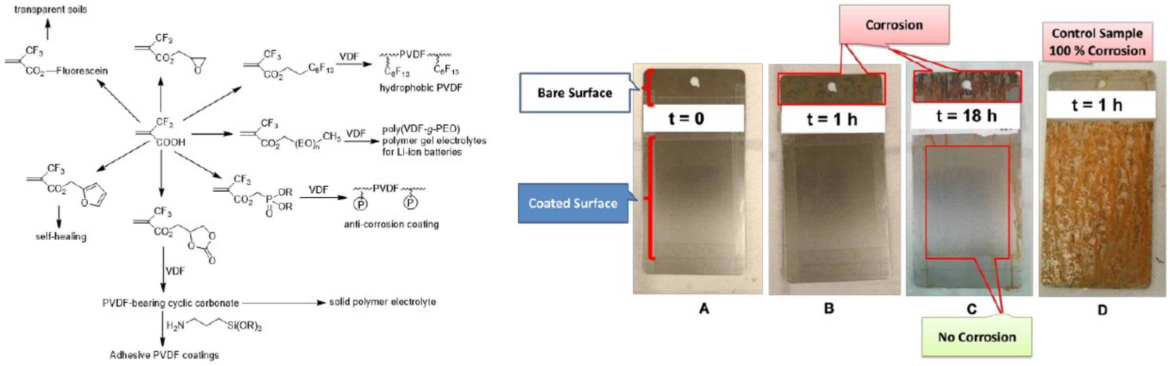
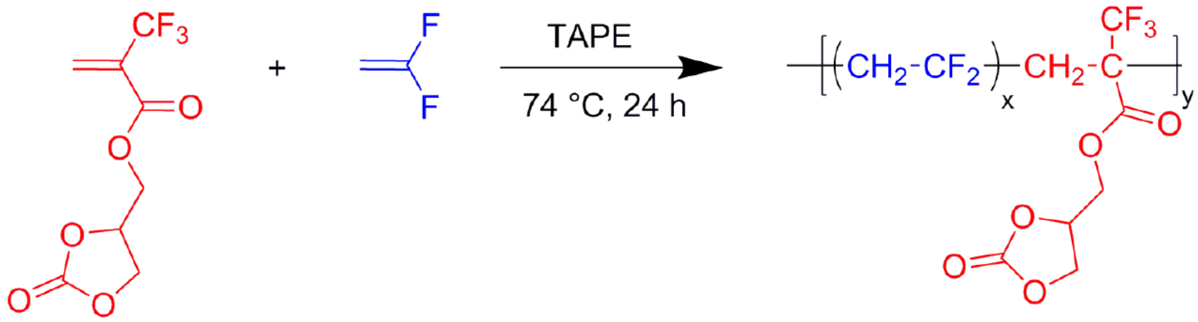


Figure 1. Overall strategies to synthesize novel functional 2-trifluoromethyl mon-omers from 2-trifluoromethacrylic acid (MAF) and their radical copolymerization with VDF (left). Steel plates coated with poly(VDF-co-MAF Phosphonate) copolymer at the beginning of the experiment (A), after 1 h (B), and after 18 h (C). (D): Uncoated steel plate as reference sample after 1 h (right).

For polymer gel electrolytes for Lithium ion batteries, an original monomer bearing a cyclocarbonate function, (2-oxo-1,3-dioxolan-4-yl)methyl 2-(trifluoromethyl) acrylate (MAF-cyCB), was prepared and copolymerized with VDF (Scheme 1)[5].



Scheme 1: Radical copolymerization of VDF with (2-oxo-1,3-dioxolan-4-yl)methyl 2-(trifluoromethyl)acrylate (MAF-cyCB) initiated by tert-amyl peroxy-2-ethylhexanoate (TAPE)5

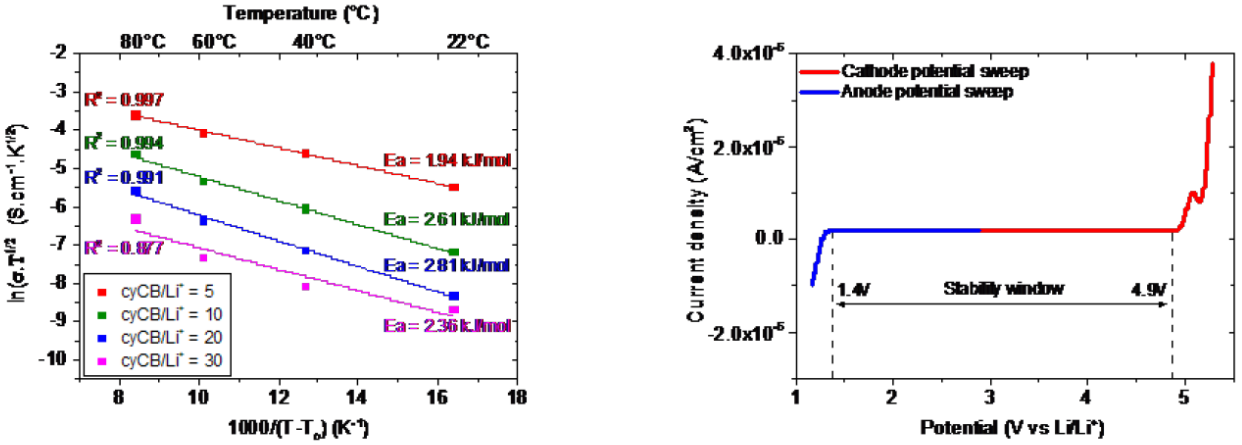


Figure 2. Temperature dependence of the ionic conductivity (left) and Linear sweep voltammetry curves of polymer electrolyte with cyCB/Li+ = 5. The scan rate is 0.5 mV/s (right) for the investigated SPEs using VTF model 5

Tosoh FineChemical Corporation (Shunan, Japan) is acknowledged for suppling MAF monomer.

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NEW METHODS OF SYNTHESIS MONOMERS FOR FLUORINATED POLIMERIC MATERIALS

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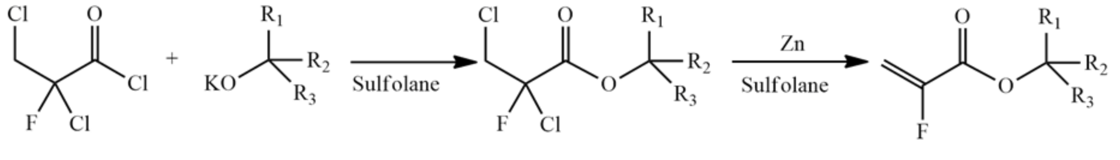
Fluorine polymeric materials due to high chemical and thermal stability, resistance to environmental, high transparency and processability, are used in various branches of science and technology.

Polymeric waveguides for optics and photonics and gas separation membranes for fuel cells are ones of the most interesting and promising areas for the use of fluorinated polymeric materials at the present.

The synthesis of monomers for fluorinated polymeric materials are often multistage and expensive, which limits the widespread use of these materials. Therefore, it is very important to develop more technologically advanced methods for the synthesis of fluorinated monomers.

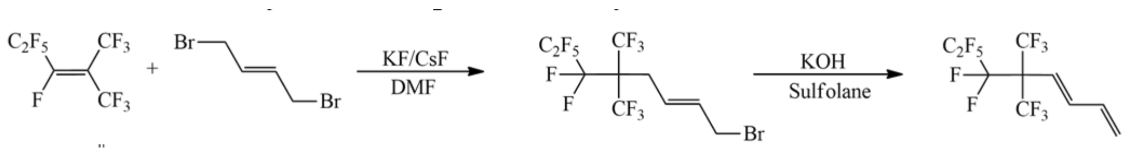
We have developed methods for the synthesis of perhalogenated acrylates and alpha-fluoroacrylates with good optical transprency characteristics due to the minimum content of C – H bonds [1].



1: $R_1 = R_2 = R_3 = CF_3$
2: $R_1 = R_2 = CF_3$, $R_3 = CF_2Cl$
3: $R_1 = R_2 = CF_2Cl$, $R_3 = CF_3$

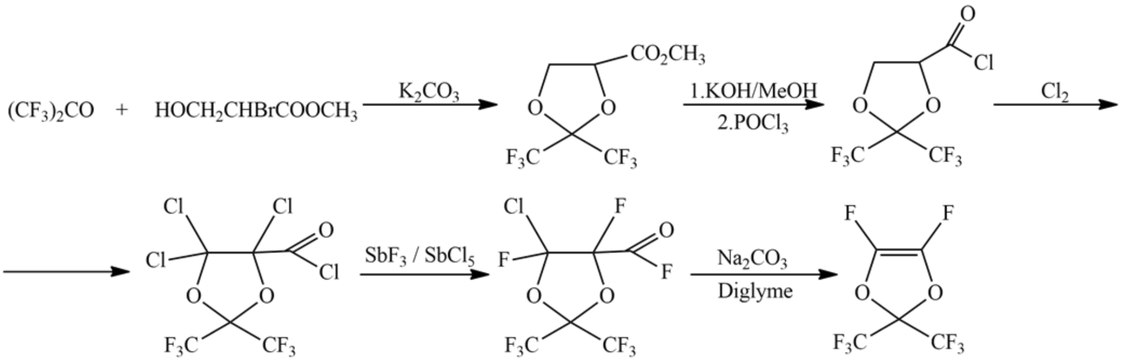
Scheme 1. Synthesis of perhalogenated tret-buthyl alpha-fluoroacrylates

We have developed a typical method for the synthesis of perfluoroalkyl-1,3-butadienes, and for the first time it was shown that when copolymerized with highly fluorinated acrylates and diacrylates, butadienes possess the necessary properties for use as polymeric optycal waveguides [2].



Scheme 2. Synthesis of perfluoroalkyl-1,3-butadienes

We have developed a new and cheaper way of producing perfluoro (1,3-dicosols), whose copolymers have exceptional transparency and gas separation properties [3].



Scheme 3. Synthesis perfluoro (1,3-dicosols)

We have also developed an industrially available method for the synthesis of 2-fluorosulfonyltetrafluoroethyl trifluorovinyl ether, which is used to obtain membranes for fuel cells [4].

$$CF_2{=}CFOCF_2CF_2Br \xrightarrow[2)Cl_2]{1)Zn,\ SO_2} CF_2{=}CFOCF_2CF_2SO_2Cl \xrightarrow{MF} CF_2{=}CFOCF_2CF_2SO_2F$$

Scheme 4. Synthesis of 2-fluorosulfonyltetrafluoroethyl trifluorovinyl ether

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RADIATION SYNTHESIS AND PROSPECTS FOR THE USE OF TETRAFLUOROETHYLENE TELOMERES WITH TERMINAL HYDROXYL AND AMINO GROUPS AND ADJUSTABLE CHAIN LENGTH

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As a result of the radiation telomerization of tetrafluoroethylene (TFE), solutions of the telomeres $R_1(C_2F_4)nR_2$ are formed in a number of solvents. The terminal functional groups R_1 and R_2 have an impact on the properties of the resulting telomers in their practical application, in particular, in the creation of composites and coatings on fiberglass and polyester fabrics. Telomerization of TFE in fluorinated solvents (freons, fluorinated alcohols) proceeds at high speeds, but the resulting telomeres have a longer chain length, which does not always allow them to be used for practical purposes. Adding small amounts of other solvents to freons, which will serve as additional chain transmitters, it is possible to obtain TFE telomeres with the required chain length and active terminal groups. These telomeres, which have active terminal groups, are capable of forming a chemical bond with the surface or filler when creating composites or protective coatings.

To obtain telomeres with terminal hydroxyl and amino groups and an adjustable chain length in the corresponding solvents is very problematic. Telomeres are formed in pure ethanol with an average chain length of only a few TFE units ($n \sim 1$–3). A similar pattern will be observed when using aliphatic amines, which are active chain transmitters. In addition, they are toxic, which complicates their use as solvents. To obtain TFE telomeres with OH and NH_2 terminal groups, it is advisable to carry out radiation synthesis in reactive telogen (for example, freon 113, freon 114B2) by introducing small amounts of ethanol and ammonia into it. These solvents, playing the role of effective additional chain transmitters, terminate a growing polymer chain and fragments of their molecules form part of the telomere. This leads to a significant reduction in the length of the telomere chain. Changing the concentration of alcohol or ammonia, you can adjust the chain length of the resulting product [1].

In this work, binary solvents are used to obtain telomeres with terminal hydroxyl and amino groups: freon113 + ethanol and freon 113+ ammonia. The kinetics of the TFE telomerization process in Freon 113 was studied by kinetic calorimetry, depending on the amount of ethanol and ammonia. TFE telomeres with OH and NH_2 terminal groups and adjustable chain length were obtained. Elemental analysis of chlorine and nitrogen allows us to estimate the chain length, which depends on the amount of ethanol or ammonia. The average length of the telomere chain for pure freon is ~300 TFE units. The chain length of telomeres with NH_2 groups varies from 45 to 20 units of TFE with an increase in the concentration of ammonia from 0.18 to 0.45 mol / l. The chain length of telomeres with OH groups is 10-30 units of TFE.

Thermogravimetric analysis indicates that the resulting telomeres are sufficiently thermostable. Minor telomere mass loss is observed at 150–200^{0}C, and weight loss at 350^{0}C is 15 and 4% for telomeres with OH and NH_2 groups. The molecular structure of the obtained telomeres was studied by IR spectroscopy. IR spectra of telomeres confirm the presence of amino and hydroxyl groups.

TFE telomeres with OH and NH_2 groups were used to hydrophobize highly porous heat-shielding materials based on quartz fibers (TZMK-10, TKV). Samples of hydrophobic TZMK-10 were obtained. Water absorption of samples decreases by 2 orders of magnitude; wetting angles exceed 100 and 1400 for telomers with OH and NH_2 groups.

This work was supported by the Basic Research Program of the Presidium of the Russian Academy of Sciences No. 32 “Nanostructures: physics, chemistry, biology, fundamentals of technologies” and the theme of the State Task No. 0089-2019-0008 using the USS «Gammatok-100».

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DEVELOPMENT OF A PROCESS FOR OBTAINING A COPOLYMER OF TETRAFLUOROETHYLENE WITH PERFLUORINATED ETHERS WITH PROPERTIES CLOSE TO IMPORTED ANALOGUES

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Fluoroplast-50 is an important representative of fluoropolymers for melt processing. According to its chemical structure, it is a fully fluorinated copolymer of tetrafluoroethylene with perfluoroalkylvinyl ether. The polymer belongs to the family of semi-crystalline resins.

Perfluoroalkyl vinyl ethers, under standard conditions, do not form homopolymers and are capable only of a copolymerization reaction. It is known that copolymerization of tetrafluoroethylene with perfluoroalkyl vinyl ether can be carried out in water, in the mass of monomers or in the medium of an organic solvent. Both organic and inorganic peroxides are used as initiators.

The properties of the copolymer is closest to PTFE. Surpasses PTFE on radiation resistance, elasticity. Does not possess the property of cold flow. The working temperature range of copolymer products is similar to that for PTFE and ranges from – 196 to + 250 °C. Fluoroplast-50 is widely used in various industries, such as nuclear power, electronics, instrument engineering, chemical industry, food industry and medical equipment.

It is processed by suitable methods for thermoplastic polymers: melt extrusion, injection molding, molding, etc. The copolymer obtained can be welded by standard methods with precise control of the heating temperature.

Due to the simplicity of the implementation of surface treatment by pressing, the copolymer is used for leveling surfaces, valves, tubes, parts in which it is necessary to comply with the requirements for heat and chemical resistance. Outstanding resistance to heating makes these polymers suitable for insulation of cables heated to a temperature of 250 – 260 °C.

On the international market, tetrafluoroethylene and perfluoropropyl vinyl ether copolymer is represented by such major companies as Chemours Company FC, LLC (Teflon ™ PFA, Teflon ™ PFA HP, Teflon ™ PFA HP Plus); Asahi Glass Company (Fluon® PFA); Daikin (NEOFLON PFA); 3M (Dyneon ™ Fluoroplastic PFA, Ultra High Purity PFA, Ultra High Purity PFA FLEX); Solvay Specialty Polymers (Hyflon® PFA P series and M series), as well as Gujarat Fluorochemicals Ltd. (INOFLON® PFA). In Russia, the copolymer is produced under experimental conditions under the name fluoroplast-50. Polymer properties of various manufacturers are shown in Table 1. Information taken from publicly available official sources.

Table 1

Properties of TFE copolymer with perfluoroalkyl vinyl ether of various manufacturers

Property	HaloPolymer	Chemours Company	Asahi Glass Company	Daikin	3M	Solvay Specialty Polymers	GFL
Release form	Granules, powder	Granules, powder	Granules	Granules, powder	Granules	Granules	Granules, powder
MFI, g / 10 min	1,0-15	1,7-42	1,0-36	1,0-32	2-25	1,5-28	2,2-15
Melting point, °C		284-317	305-315	295-310	308	300-316	310
Density, g / cm^3	2,15-2,17	2,15	2,12-2,17	2,12-2,16	2,15	2,12-2,18	2,17
Breaking strength, MPa	25-33	25-33	32-39	24,5-34,3	25-34	20-26	28-30
Relative elongation at break, %	330-400	260-360	340-410	300-450	360-400	280-300	300-350
Endurance with repeated bending, cycles		4000 – 2500000	18000 – 500000	900000	14000 – 3100000	1500 – 120000	
Shore hardness		D55-D60	D60		D60	D55-D60	

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EFFECT OF SYNTHESIS CONDITIONS ON THE STRUCTURE OF FLUOROPOLYMERS

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Researches in the field of fluoropolymers synthesis, in connection with the need for technology in these materials, had a practical orientation and, first of all, were aimed at developing methods for their production and their application in industrial production [1]. Techniques used in the synthesis process to control the particle shape of the powders of the resulting polymers were developed, however, studies on the supramolecular structure of fluoropolymers and establishing its relationship with properties remained in the background [2].

Using the example of tetrafluoroethylene-ethylene copolymer (TFE-E), we tried to establish the relationship between the synthesis conditions and the postpolymerization treatment techniques with the powder particles structure organization, which exhibits itself in particles smaller than 0.6 microns, which we called as [3] primary particles. From the studied TFE-E grades, only one has an oval shape of primary particles (Ф-40БМ), the particles of the other grades are spherical. It was not possible to determine the size and shape of the powder primary particle of a foreign grade (Tefzel 2195), since when scanning even at minimum energies, the sample was charged from the electron beam and the image had drifted. In our opinion, the structure of its primary particle is closest to the oval. Presented in the Table 1 grades of TFE-E copolymer are located at the level of the average size of the primary particle. It is shown that the primary particles in different grades have an unequal size distribution from 45 to 600 nm, while it is observed that with an increase in the size of the primary particle, the melt flow rate (MFR) increases and, in most cases, the mechanical tensile strength of test samples decreases. It appears from this that the strength depends not only on the size of the primary particles, but also on their location, a similar ambiguous relationship was established, for example, in the study of the supramolecular structure of polypropylene [4].

Some TFE-E grades do not have a flowability, estimated by the value of the melt flow rate (MFR), determined in accordance with TU 301-05-17-89 at a temperature of 300 °C, therefore, the table shows the data of MFI determined at a temperature of 305 °C and a load of 10 kg.

Table 1

General properties of studied TFE-E grades and their primary particles.

TFE-E grade	Primary particle size, nm	Primary particle form	MFI, g/10 min	Tensile strength at break, МПа	Elongation at break, %
Ф-40 П	90	spherical	0,3	40,4	266
Ф-40 М (порошок)	174÷186	spherical	1,2	36,9	344
Ф-40 ЛД	209, 302	spherical*	6,6	42.0	303
Ф-40 АМ	279, rare 160	spherical	36,2	27,0	138
Ф40 ВЭМ	rare 93÷130, 240÷290, rare 307	spherical	0,06	38,8	260
Ф-40 Д	rare 45÷60, 279÷372, rare 500-600	spherical **	28,3	20,7	254
Ф-40БМ	288x209 321x186	deformed oval***	16,2	27,5	256
Tefzel 2195	-	hard to discern****	60	40,0	360

*– different diameters of the spheres on different clusters, there are fibrils up to 20 microns thick.

**– particle edge melting

***– primary particles clusters with an increase of 32 000 times resemble "hyacinth",

****– boundaries of the primary particle are indistinguishable due to image drift, with an increase of 32 000 times.

It should be noted that polymer powders synthesized by the water-emulsion method with separation from the dispersion by freezing are larger than those by mechanical coagulated, or by suspension polymerization obtained, their size reaches 100 ÷ 250 microns. The size of the unit cell of the TFE-E crystallite is only 0.5-0.9 nm [1], therefore, we can assume that the primary particle of the nanometer-sized TFE-E copolymer, which we observe in micrographs, is a globule. The analogy of the shape and size of the primary particles that form the powder particle when producing different TFE-E grades indicates a similar molecular structure [5] that determines the type of its supramolecular formations.

The study was performed using the equipment of the MRC resource center in the field "Nanotechnology", Science Park of St. Petersburg State University.

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SYNTHESIS OF FLUOROPOLYMERS POSSESSING ION EXCHANGE PROPERTIES

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Ion exchange membranes are widely used in modern engineering and are the most modern and technologically advanced materials. Research into the membrane materials and technologies is done both in Russia and around the world [4, 8].

The Ion-exchange membrane materials are classified [1] into three large classes: high molecular weight membranes based on the functional ion-exchange groups polymers; inorganic membrane materials, and hybrid organic/inorganic materials. Perfluorinated polymer membranes containing functional groups ensuring ion exchange are used in aggressive environments. Most often, the basis of perfluorinated ion-exchange materials are copolymers of tetrafluoroethylene (TFE) and sulfonated perfluorovinyl ether.

In this study we synthesized a fluoropolymer possessing certain ion-exchange properties.

The copolymer was synthesized in 1,1,2-trifluorotrichloroethane (freon 113 or R 113), copolymerization of TFE with perfluoro (3,6-dioxa-4-methyl-7-octene) sulfonyl fluoride (FS-141) by the radical mechanism at 40–50 °C. The pressure in the reactor was kept constant at 20 kgf/cm2 through feeding the TFE during the polymerization. A similar synthesis technique is described in the patent [9]. In the experiment, the created conditions made it possible to achieve the goal. Such conditions enabled us to adjust the synthesis process. The composition of the obtained polymer was studied by means of the infrared spectroscopy.

One of the most important properties of the ion-exchange polymer membranes is their volumetric capacity. The exchange capacity should be in the range of 0.9–1.1 mEq/g.

In this case, it should be noted that the higher the exchange capacity and the lower the molecular weight, the higher the conductivity of the polymer is. On the other hand, polymers with a high exchange capacity swell too much, losing their shape and strength, and even dissolve [12]. The obtained sample has a volumetric capacity of 1 mEq/g, whichmeets the specified characteristics.

Thus, the radical polymerization method resulted in a polymer that can be used tomanufacture ion-exchange membranes.

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STUDY OF THE PROCESSES OF FORMATION OF THE STRUCTURE AND PROPERTIES IN POLYMERIC COMPOSITE MATERIALS BASED ON POLYTETRAFLUOROETHYLENE DURING EXPLOSIVE PRESSING

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The application of shock waves using the energy of explosives makes it possible to carry out a special type of mechanochemical reactions developed in polymer composite materials (PCM) at high dynamic pressures (up to 10 GPa), providing simultaneously the molding, crushing, melting, thermodynamic activation and consolidation of polymer powders and filler. powders polymers and filler. With the passage of the shock wave front at first activated states occur, and then, under conditions of mechanical and thermal fields, a new structure is created. Therefore, explosive pressing (EP) of dispersed composites based on polytetrafluoroethylene (PTFE) allows to obtain a new set of properties (high strength and hardness, wear resistance, heat and electrical conductivity, etc.) with maintaining its unique characteristics (low friction coefficient and high chemical resistance).

The regularities of the formation of the structure and properties of PCM based on PTFE under various EP conditions were studied, which made it possible to obtain compositions with heat-resistant polymers: polyimide, polyester, phenylone and metals (up to 90% by volume Al, Cu, Ni, Fe and their alloys) possessing more high strength, heat and electrophysical properties [1, 2]. Determined that at a certain power of EP (optimal parameters - pressure in the shock front P = 0.4-0.6 GPa), the structure of limiting compaction is achieved, which is characterized by plastic deformation of metal particles with their welding (when filling more than 50%) and the formation of continuous reinforcing phase - frame [1]. Wherein, metal particles are deformed along the shock front and changes occur in the fine structure of both PTFE and metals.

When the critical parameters of EP (P more than 0.6 GPa) are reached, an abrupt change in the structure is observed, accompanied by the appearance of nanoscale inclusions, which is the result of active grinding and turbulent mixing components of

PCM. To implement the critical parameters of the EP used two approaches. The first approach is based on the EP powder mixture with a low porosity (20–30%) by critical shock pressures (P = 1.0–2.5 GPa). The second approach is based on the application of critical energies to the composite system due to the high porosity of the powder mixture (40–70%) and reduced explosive power with the implementation of shock pressures P = 0.6–1.0 GPa. Due to destructive-recombination processes, intense deformation and denser packing, new structures are formed based on nanoscale components with the formation of more solid phases. Between metal particles, highly deformed PTFE particles 10 nm in size and nanofibrils are observed, which according to the EDA data [3] include metal atoms (Al, Cu, Ni, Fe), which indicates the chemical interaction between the polymer and metal phases, including the formation of carbon, oxide and fluoride compounds, as evidenced by X-ray diffraction analysis and IR spectroscopy. A spongy structure is formed after EP with a critical energy contribution, that is, nanopores with sizes ranging from 10-30 nm are formed in a monolithic metal-polymer matrix, which is a consequence of an increase in temperature before melting and evaporation of part of the material. Intensive increase in the hardness of the material confirms the formation of a new structure based on nanoscale components.

It has been revealed that with EP of powders of polytetrafluoroethylene and its compositions with polyimide or polyester with pressures of more than 1.5 GPa with an initial porosity of 30-50%, intense structural changes occur, accompanied by the orientation of the polymers along the direction of the shock front, until the formation of fibrous structures with the formation of nanofibrils thick. 20-30 nm [4]. The increase in energy impact up to 4-5 GPa leads to the development of texture due to the simultaneous deformation of ductile PTFE, which facilitates the orientation of glassy polyester or polyimide, which are significantly deformed in the direction of the shock front and become lamellar, which is due to the large effect of the explosion energy on the solid constituent of PCM. Thus traced as individual monolithic nanometer inclusion (150 - 800 nm), and agglomerates of similar size, consisting of particles ranging in size from 50 to 100 nm having a higher hardness. The formation of nanostructures is accompanied by a significant increase in hardness and a change in the fine structure of polymers.

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MORPHOLOGY OF COMPOSITE MATERIALS BASED ON MELTABLE FLUOROPOLYMERS

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The present morphology study of the fluoropolymer composite materials (FCM) based on meltable fluoropolymers was carried out to clarify ideas about their spatial-scale structure and may be useful when looking for ways to ensure ever-increasing demands on the FCM products quality. The objects of the research were: radiation-crosslinkable composition based on F-40 (ETFE) [1], green fluoride pigment concentrates based on Ф-4МБ (FEP) and on Ф-2М (PVDF), pore-forming composition on the basis of Ф-4МБ [2] produced by JSC "Plastpolymer" in the form of granules, used for the manufacture and dyeing of high-temperature insulation of wires and radio-frequency cables.

To make micrographs of granules and powders surfaces of the from which the compositions were prepared, a Zeiss Merlin scanning electron microscope with an Everhart-Thornley detector was used. To maintain the initial morphology of the objects under study, no spraying of conducting layers onto test particles was performed.

From the analyzed images it was found that the granules, which are a monolithic structure, with an increase in scale of nanometer-sized fine particles consist. That the sizes of the particles of which both the polymer powders [3, 4] and the fillers used in FCM are composed are comparable and are in the range of 0.16 ÷ 0.5 μm. For inorganic fillers (rutile structured titanium oxide, green pigment), the polydispersity of the sizes of primary particles is higher than that of polymers. At the cut of the granules, micropores of about 600 nm are observed and formations that could be called fibrils are visible inside the pores [5]. In our opinion, these fibrils are compacted spheres of primary particles of the polymer matrix composition powder. On all surfaces of the granules, aggregates are observed (from 0.1 to 0.6 μm), apparently, of inorganic powders. The pigment concentrates granules, made only on the basis of fluoropolymer powders, have a greater number of defects, such as micropores and fibrils, as compared to FCMs made with the use of fluoropolymer granules and powders.

To explain the observed phenomenon, we propose the hypothesis that the primary particles of fluoropolymers are mixed at the time of studied compositions preparing under the influence of temperature and shear deformations during extrusion and compacted with each other lose their spherical shape. In this case, the primary particles are organized in structures resembling fibrils.

The study was performed using the equipment of the MRC resource center in the field "Nanotechnology", Science Park of St. Petersburg State University.

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HYDROPHOBIZATION OF HIGHLY POROUS HEAT-SHIELDING CERAMIC MATERIALS BASED ON QUARTZ FIBERS USING FLUOROPOLYMERS

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Highly porous heat-shielding and heat-insulating materials based on quartz fibers have low specific density and thermal conductivity, can be long-term operated at temperatures up to 1200^0C, therefore they are widely in demand in various industries and in the construction of complex technical systems and structures used in extreme conditions. The disadvantage of these materials is hydrophilicity, due to the chemical composition of the fibers and highly developed porous structure, which severely limits their use in conditions characterized by high humidity. The presence of water in the interfibral space of materials, in particular, the brands TQF (thin quartz fiber) and TZMK-10, cancels their high thermal, acoustic and operational properties, and at low temperatures leads to their destruction.

In this work, we studied the process of hydrophobization of ceramic materials based on quartz fibers using solutions of radiation-synthesized telomeres of tetrafluoroethylene (TFE), having different chain lengths and different chemically active end groups, and the technology of low-temperature post-radiation grafting of tetrafluoroethylene molecules. It has been shown that treatment with TFE telomer solutions makes it possible to impart to the hydrophilic materials a highly hydrophobic state, characterized by an edge wetting angle of water of about 140 °. A comparative analysis of the effectiveness of various telomers produced in a number of solvents (acetone, butyl chloride, pentafluorochlorobenzene, freon 113 + ammonia, freon 113 + ethanol, trimethylchlorosilane) [1-3] was carried out to modify the material of the TZMK-10 brand. The most promising for hydrophobization are TFE telomeres synthesized in acetone and solvent mixtures of freon 113+ ammonia.

The technology of applying hydrophobic coatings of fluoroligomers on silicon dioxide fibers, as well as on samples of porous ceramic materials using the method of low-temperature post-radiation graft polymerization of TFE, was tested for the first time. The processing modes were selected that allow to apply coatings on the fibers, ensuring a high hydrophobicity of the materials based on them. The features of polytetrafluoroethylene coating of oxide fibers and its composition are revealed. The proposed methods for modifying highly porous heat-shielding ceramic materials based on quartz fibers significantly increase their performance characteristics and expand the possibilities of practical application as heat-shielding and heat-insulating materials.

The work was supported by the Basic Research Program of the Presidium of the Russian Academy of Sciences No. 55 “The Arctic is the scientific basis of new technologies of development, preservation and development”, the RFBR project No. 18-48-370005 and the theme of the State task No. 0089-2019-0008 using the UNU “Gammatok- 100” IPCP RAS.

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MULTIFUNCTIONAL RESOURCE-ENERGY-SAVING COATINGS BASED ON NANODISPERSED POLYTETRAFLUOROETHYLENE FORUM®

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Nanodispersed polytetrafluoroethylene (NPTFE) was first obtained in the Institute of chemistry FEB RAS Russian Academy of Sciences in 1982 year and in 1987 year a method of processing waste fluoroplastic-4 with the aim of obtaining NPTFE was recommended by the Interdepartmental Commission for implementation in the factories of the Ministry of Medium Machine Building of the USSR. The technology of production of NPTFE is based on partial thermal degradation of fluoroplast-4 in a strictly defined gas-dynamic mode [1]. Within the frames of the works devoted to creating highly dispersed fluorocarbon materials [2] and solving the problem of PTFE waste management, the process of thermal destruction of fluoroplast-4 under different gas–dynamic conditions was studied, which resulted in discovering the earlier unknown phenomenon – transfer of heavy PTFE molecules into the gas phase followed by homophase nucleation, condensation in the form of nanofilms of a thickness of up to ~ 40 nm, and subsequent packing into micro spheres of a diameter of about 1 μm and micro tubes (Fig. 1) [3].

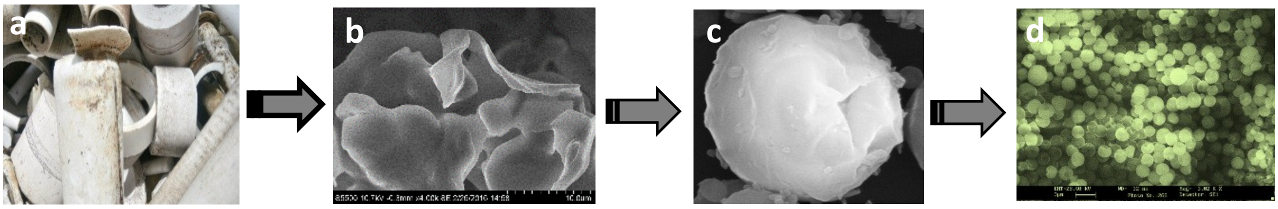

Fig. 1. PTFE waste (a), SEM-micrographs of nano films of PTFE (b), micro sphere of PTFE (c), ultra dispersed PTFE FORUM® (d).

Main approaches to studies of the processes of fraction separation of polytetrafluoroethylene of the FORUM® grade were developed. All the fractions underwent the chromatography mass-spectrometry analysis [4].

High-temperature fractions of PTFE FORUM® are applied as dry greases and antifriction, antiwear, anticorrosion, and antiscale component of coatings functioning at high temperatures. Low-temperature fractions of NPTFE FORUM® are applied in the pure form or as the main component for ski lubricants.

A specific structure of NPTFE particles is responsible for a special effect of their application in tribosystems. The most pronounced effect was achieved at application of NPTFE FORUM® as an additive to oils and plastic greases. At present, the FORUM® additive is commercially manufactured for all types of engines and transmissions of all types of vehicles.

Tests on various devices and in different modes performed using certified stands and installations and under field conditions demonstrated positive results and made it possible to recommend the antifriction and antiwear high-temperature additive to oils and greases FORUM® for the use in military equipment of federal importance.

Recently, a special attention of researchers was devoted to ecologically clean lacquer–paint materials (LPM) that are resistant to atmospheric effects, with extended operation period, fire-safe, with minimal retention of dirt and dust, and an expressed effect of protection from corrosion and anti-fouling. Due to the nano-effect, nanofilms NPTFE are easily attached to any surface, including highly dispersed materials, which facilitates application of a new material in any composite material, including LPM.

The recent trend consists in production of anti-fouling paints without biocide additives and with minimal solvent amount. As was shown in the studies, addition of 10 % NPTFE (dry content) to the LPM composition provides the anti-fouling effect as at addition into a regular iron minium as into a special anti-fouling paint with a biocide SeaForce 30 component. The most pronounced anti-fouling effect is observed in the case of mechanical deposition through rubbing of the dry NPTFE on the LPM surface or simply on the cleaned and defatted metal surface (Fig. 2.).

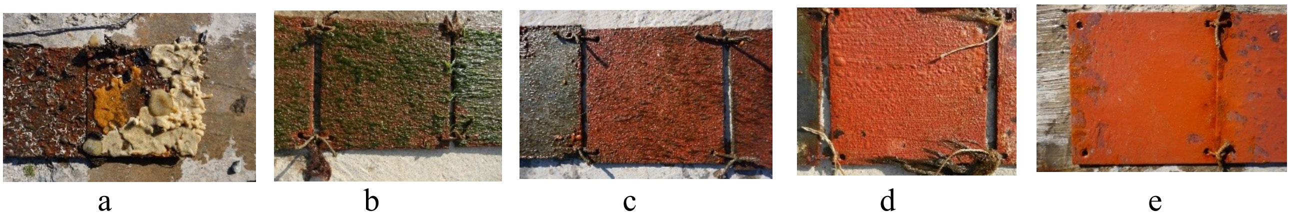

Fig. 2. Fouling of steel plates in sea water during 6 month: a – Minium MA-15 without treatment, b – SeaForce 30, c – SeaForce 30 +10% Forum®, d – Minium MA-15 coated with Forum®, e – SeaForce 30 coated with Forum®.

Hydrophobic and anti-icing properties of LPM are mutually related, so that one observes an inverse correlation between the strength of retention of the frozen-over ice and the growth of the limiting wetting angle of the drop on the surface of the tested material. Here, the LPM hydrophobicity increases maximally at complete surface covering by PTFE nanofilms, i.e., at simple rubbing by dry NPTFE powder

Physical–chemical, structural, rheological, and application characteristics of this new material were investigated by various methods in different research and manufacture facilities [5].

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SHIMADZU ANALYTICAL EQUIPMENT AND COMPLETE SOLUTIONS BY ANALIT FOR POLYMER ANALYSIS

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The unique properties of fluorinated polymers have advanced them to the leading polymer materials. Production and consumption of such polymers and derivative products are constantly expanding due to the growing demand for these materials in various industries. For the effective development of new areas and applications, it is necessary to comprehensively study the structure, properties and behavior of fluorine-containing polymers, and the existing production should control not only the performance properties of the products, but also conduct ongoing environmental monitoring of harmful emissions and wastewater generated during production. A modern and well-equipped laboratory with spectral, chromatographic, mass spectrometric and testing equipment is required for such complex analysis.

ANALIT together with its strategic partner, Shimadzu Corporation (Japan), offers a full range of equipment for research and monitoring as well as sets of dedicated certified measurement methods, licensed training and methodological support based on its own accredited laboratory. That allows us to provide complex turn-key solutions for research and production laboratories of any level.

Shimadzu is one of the world's largest manufacturers of analytical and testing equipment and produces almost the whole line of modern equipment for studying chemical, physicochemical and mechanical properties.; whereas ANALIT complements everything necessary to carry out control and R&D at all stages (equipment for sampling and sample preparation, auxiliary equipment, furniture and reagents etc.):

– spectral equipment for molecular composition and properties determiantion: spectrophotometers, FTIR spectrometers and microscopes, spectrofluorimeters. FTIR and/or Raman microscopy techniques make it possible to assess the quality of the products being made in terms of composition and homogeneity of components distribution in samples (for example, in electrical insulators), as well as to study the nature and composition of possible micro-inclusions;

– chromatographic and mass spectrometric equipment for thorough determination of molecular composition and structure: gas and liquid chromatographs (GC, HPLC, UFLC), gas and liquid chromatography mass spectrometers, MALDI mass spectrometers, as well as all necessary related equipment. The combination of the pyrolysis technique with the capabilities of gas chromatographs and mass spectrometers allows investigating processing products of fluoropolymers and studying the nature of deposits formed during the processing with high sensitivity and selectivity.

– equipment for elemental analysis in the widest range of concentrations: X-ray fluorescence spectrometers, atomic absorption spectrophotometers, ICP-OES and ICP-MS spectrometers, and all related equipment necessary for preparation of samples and reagents (including own products, such as Mobile Clean Workplace, acid purification systems, etc.), which significantly improve reproducibility and accuracy of analysis results.

– equipment for physicomechanical, thermal and thermomechanical properties evaluation: universal testing machines, hardness and microhardness testers, viscometers, equipment for thermal analysis (TGA / DTA, DSC, TMA), climatic chambers.

– equipment for determination of integral indices, studies of surface morphology, phase composition, particle size distribution: TOC-N analyzers (for rapid determination of the content of various forms of carbon and nitrogen in liquid and solid samples), X-ray diffractometers, atomic force microscopes and electron probe microanalyzers, laser analyzers particle sizes.

All the proposed equipment has been included into the State Register of Measuring Instruments, has certificates and calibration methods, as well as software and manuals in Russian.

PROBLEMS AND DEVELOPMENT PROSPECTS OF THE FLUOROPOLYMER INDUSTRY

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Despite some success in different areas, the industry continues to lose ground in the global fluoropolymer (FP) sector. Part of the russian FP decreased from 10% to more than 2 times. The main reason is the general the status of Russian industry and the lack of overall coordination industry development.

The global economic crisis has complicated the sale of raw materials, which was industry targeted. The consequence of this policy is disinterest of raw material producers in the development of FP converting technologies that create maximal surplus value.

Reducing the quality of FP and finished products. Imperfection of the current scientific and technical documentation, significant is required processing existing documentation. The lack of the qualified personnel and low production culture, absence of close connection of science with production. Previously, a system was created and worked for solving these problems, now all manufacturers and converters are “free-floating”. In this case appears a paradoxical situation: small companies interested in developing and manufacturing of new products, but as a rule, do not have the financial capabilities; large companies focused on the sale of raw materials. Examples of successful companies.

Promising areas of development:

1) Improving the production technology of FP, obtaining materials of high and stable quality, revision of the existing scientific and technical documentation;

2) Fuse FP converting: oversized plates and films for linings, pipes, connecting fittings for pipelines;

3) Production of long tubes F-4D and F-4DM;

4) Development and implementation of a composite production strategy, including, based on the modified F-4;

5) Specialization of manufacturing companies and converter, (pressing, tube, porous materials, rotor lining);

6) Restoring the production of traditional freons and products on their basis.

FLUORINATED THERMOSETTING RESINS FOR PHOTONICS AND MICROELECTRONICS

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The development of modular systems of resins to achieve optimized viscosity, refractive index and enhanced thermal and mechanical properties is the basic requirement for new optical polymers that can be used flexibly in many different applications.

For passive optical waveguides fluorinated acrylates and diacrylates were utilized to realize a refractive index of 1.45 (cladding) and 1.48 as well as 1.50 (core). Chlorinated acrylates and substituted styrenes were added to vary the refractive index of core and cladding material of passive optical waveguides and to achieve a refractive index contrast of 0.03 to 0.05. As third important component of all formulations Glycidylmethacrylate was used to increase the network density and thus, the thermal stability of the materials. As alternative to Glycidylmethacrylate as crosslinker a high content of di- and trifunctionalized acrylates can be used. A schematic representation of the formulation and processing of the optical polymers for wave guides is depicted in Figure 1. After processing the liquids via spin-coating and subsequent curing via UV or thermal treatment, the refractive index, the optical loss and the thermo-optic coefficient of prepared thin layers of optical polymers were analysed with a metricon prism coupler system (m-line measurement). In this case, the optical loss is determined by scanning a fiber optic probe and photodetector down the length of a propagating streak to measure the light intensity scattered from the surface of the material.

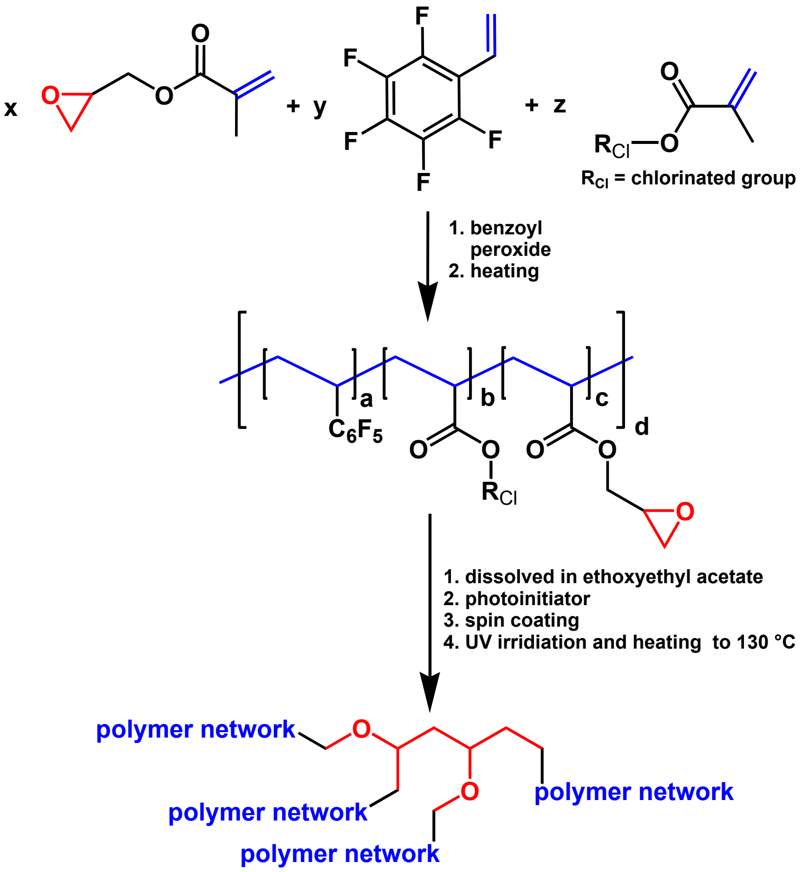

Figure 1. Reaction scheme, preparation of polymers for passive optical waveguides.

It could be shown that the refractive index can be varied between 1.45 and 1.50 easily by utilization of different contents of halogenated acrylates, that the optical loss of the layers within a wave guiding structure is below 0.5 dB/cm and that very low thermo-optic coefficients could be achieved (Figures 2 and 3).

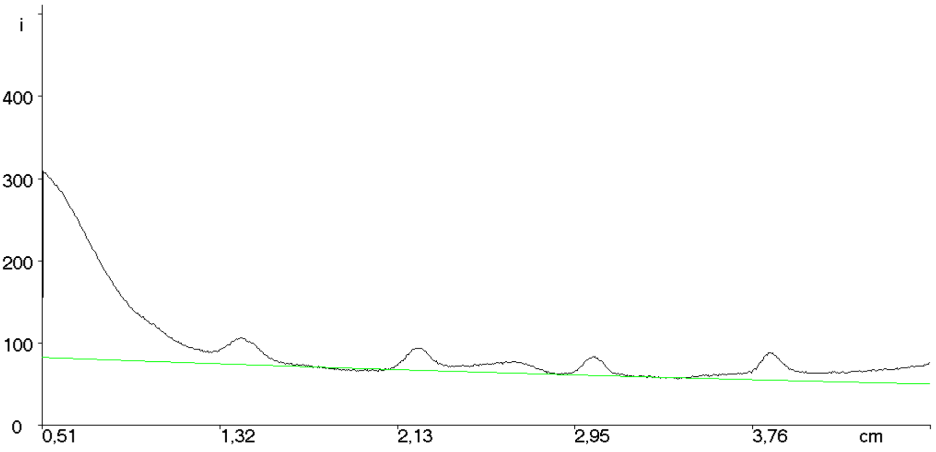

Figure 2. Determination of optical loss of core material with n=1.48 and optical loss 0.4 dB/cm.

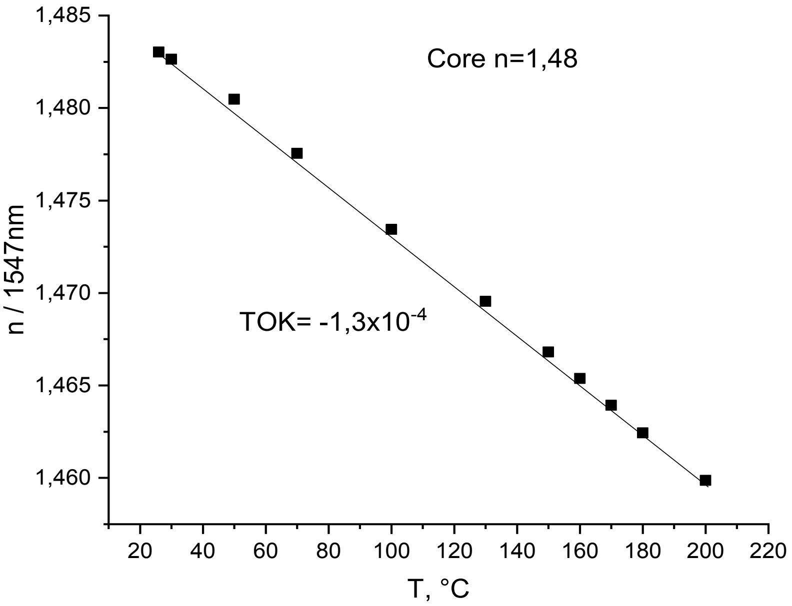

Figure 3. Determination of thermo-optic coefficient of core material n=1.48, thermo-optic coefficient -1.3×$10^{-4}$$K^{-1}$.

Finally, the newly developed materials were processed via spin-coating on a silicon waver and were structured via photolithography, yielding micro structures that can be tested for use as wave-guides in micro-optics and micro-electronics (Figure 4).

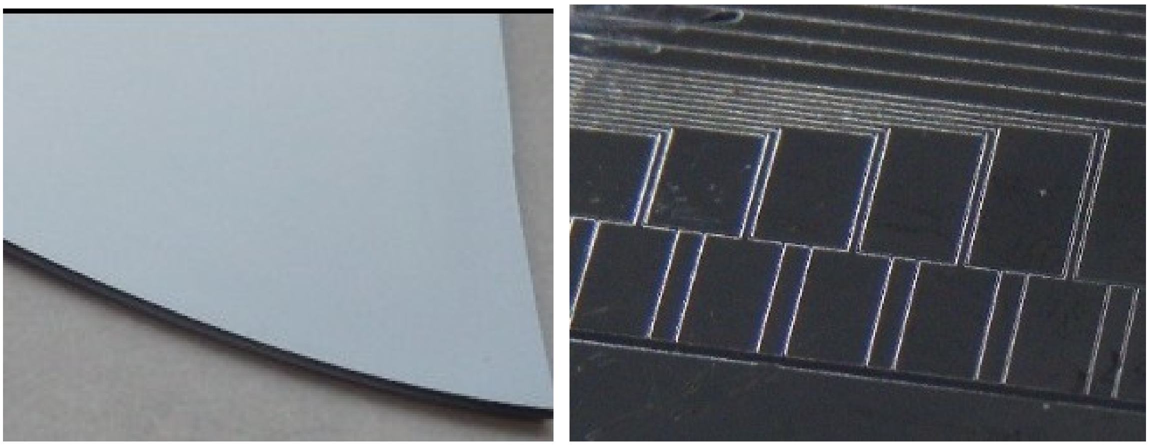

Figure 4. Left: new optical polymer on silicone, Right: micro structured optical polymer.

Based on the experience in developing materials for optical wave guides additional investigations on cladding materials for optical fibres were performed. In this case optical polymers with an extremely low refractive index of less than 1.39 are needed. Hence, only highly fluorinated monomers or oligomers can be used (Figure 5).

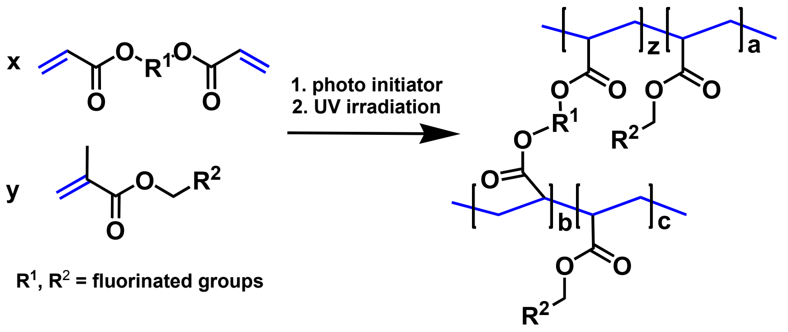

Figure 5. Reaction scheme, preparation of polymers for claddings for optical fibers.

Since commercial glass fibre drawing processes are running with a speed up to 2 000 m/min, the investigation of the curing behaviour and conversion is essentially. Hence, different formulations of acrylates including radical photoinitiators were cured with different exposure times (resulting in a different UV dose) and different UV sources (Hg-lamp and 390 nm LED). It could be shown that at high exposure times above 1 s nearly no differences between the commercial reference and the newly developed formulations occur due to saturation effect. At short exposure times still exist significant differences between curing with Hg-lamp and UV-LEDs but again only minor differences between the formulations and the reference system could be observed (Figure 6). By increasing the UV-intensity/ dose the conversion can reach nearly the value that was achieved with Hg lamps. Thus, the thermosetting polymers studied provide an excellent curing behaviour (high conversion) with both, UV-LED and Hg-lamp curing.

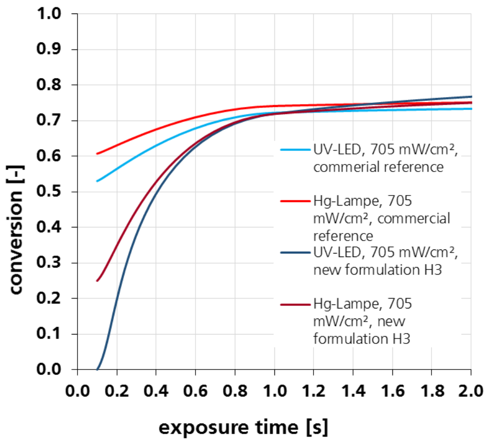

Figure 6. Dependence of conversion of UV curable resins from exposure time.

The mechanical properties of the materials are comparable to commercial reference systems but the thermal properties were improved and the coating materials can be used up to 150 °C (Figure 7). Hence, the glass transition temperature of 80 °C of the new material is approx. 20 °C higher than the glass transition temperature of the reference (60 °C).

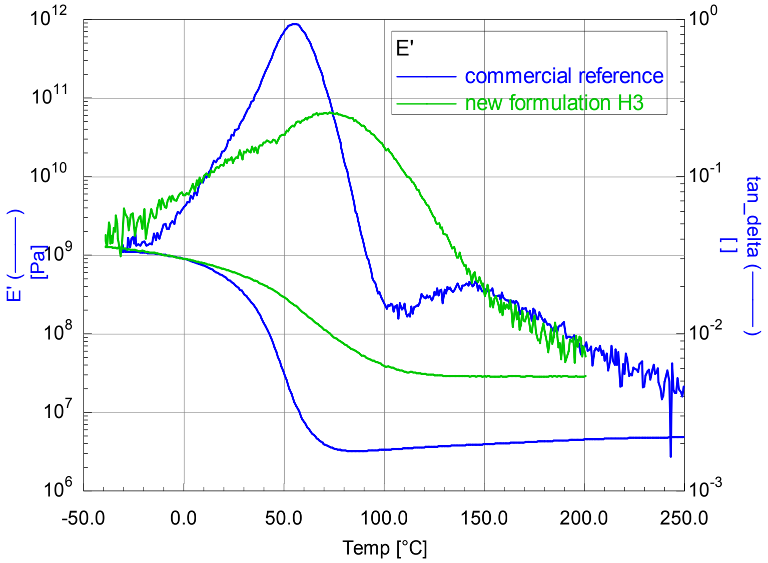

Figure 7. Dynamic mechanical analysis of two acrylate based coating materials.

Additionally, the low optical loss of the fibres allows the utilization in medical applications and materials processing. Furthermore, the developed materials are at least twenty times autoclavable and new medical fibres will become more sustainable than currently commercially available fibres since they can be reused.

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FEATURES OF STRUCTURE NANOORGANIZATION IN FLUOROELASTOMERS

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During the synthesis of polymers, their nanoorganization is formed to one degree or another, depending on the conditions of its conduct and the chemical structure of the macromolecules. Nanoorganization of polymers is a complex system of orderly constructed formations and straight chains connecting them, has a thermodynamic nature according to XRD, DSC, IR spectroscopy and diffusion method and is formed by macromolecular fragments consisting mainly of trans conformers, according to IR spectroscopy. Nanoformations are rearranged with a clear periodicity above the softening temperature of polymers (T_S), regardless of the chemical structure of the macromolecules. The temperature range of nanoorganization of polymers is primarily determined by the kinetic flexibility of macromolecules and molecular weight [1, 2]. Fluororubber, according to the authors [3], have a globular structure. Globules are formed in the process of emulsion polymerization and are microgel.

The aim of the work is to identify the features of the structure of the nano organization fluororubber.

The fluororubber FPM-26 diffractogram, along with the asymmetric angular dependence of the amorphous scattering intensity with a maximum at $2\theta = 40.43°$, contains an intense reflex with a maximum at $2\theta = 16.49°$. Similarly, on the diffractogram of fluororubber FPM-32, in addition to the amorphous halo with a maximum at $2\theta = 39.52^{o}$, an intense reflex with a maximum at $2\theta = 16.70°$ appeared.

Intensive reflexes on the FPM-26 and FPM-32 diffractograms are caused by nanoformations 4 nm and 5 nm in size (according to the Scherrer equation ($K = 0.9$)), respectively (further main reflexes of rubbers). The basis for this position are the obtained diffraction patterns of rubbers with various fillers.

The content of nanoformations with a size of 4 nm and the average d-spaces in them decreased after the introduction of zinc oxide into FPM-26 rubber. The degree of order of the nanoorganization of mixture has increased in comparison with the pure rubber due to the formation of additional ordered formations of small size. The content of large nanoformations decreased in FPM-32 rubber after the introduction of zinc oxide, but in a less degree than in the first case. Despite this, the size of large nanoformations increased to 8 nm. Various differences in the intensities the reflections of zinc oxide in diffractograms of these mixtures indirectly indicate the unequal change in the degree of order in the nanoorganization of fluororubber. The degree of orderliness of the FPM-26 nanorganization remains higher than that of FPM-32, and after the introduction of zinc oxide, which is explained by the difference in the structure of their macromolecules.

The XRD data correlate with results of analysis the EPR spectra about high content of the hard fraction in fluororubbers.

A more significant change in the structure of the fluororubber nanoorganization was found after the introduction of nanoscale modifications of titanium dioxide. Thus, in the FPM-26 rubber, nanoformations of 23 and 44 nm in size are formed along with the main ones. Under similar conditions, the degree of order of FPM-32 nanoorganization increases to a greater extent than FPM-26. The rate of change in structure of nanoorganization of fluororubber mixtures with fillers largely depends on their prehistory.

It has been established that an increased concentration of –OH and –H groups on the surface of nano-sized titanium dioxide facilitates a more effective local decrease in the flexibility of the passage chains of the fluororubber nanoorganization, which is manifested in the formation of a more perfect structure of the nanoorganization of their mixtures with filler. Accordingly, zinc oxide is a less active filler for fluororubber as compared with nanoscale modifications of titanium dioxide.

X-ray diffraction data were obtained, indicating a higher degree of orderliness of the nanoorganization of vulcanizates based on FPM-32 compared to mechanical mixtures with fillers of similar composition. In the vulcanizates, nanoformations of 40–80 nm in size have been found, which are indicated by fairly intense reflexes along with the main ones on their diffractograms.

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THE EFFECT OF LAYERED SILICATES ON THE FORMATION OF A SECONDARY STRUCTURE ON THE FRICTION SURFACE OF PTFE-BASED COMPOSITES

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It is known that the run-in stage is characterized by smoothing the irregularities and establishing the optimum surface roughness, accompanied by plastic deformation of the surface layers, loosening and amorphization of the material structure. These processes, along with the high local temperature [1], lead to the fact that a layer of secondary structure is formed on the friction surface, which differs in properties from the rest of the composite material. The properties of this layer determine the behavior of the material in the process of wear.

The goal is to study the formation of a secondary structure layer on the friction surface of PTFE-based composites.

Objects and research methods - composites based on PTFE and layered silicates (LS); tribological characteristics were studied during the period of running-in and after it according to GOST 11629-75 on the UMT-3 tribometer (CETR, USA) according to the “pin-on-disk” friction scheme at load of 2 MPa and a sliding velocity of 0.3 m/s ; structural characteristics - using the SEM method on the JSM-7800F, JEOL (Japan) with the Oxford Instruments prefix for X-ray energy dispersive analysis.

Results and discussion. A significant increase in the wear resistance of PTFE/LS composites necessitates studying the tribological characteristics of materials in accordance with the structural changes in the friction surface of these composites. The study of the tribological characteristics of materials shows a strong increase in wear resistance even when maintaining 2 wt.% LS. Preliminary mechanical activation of fillers shortens the running-in period (Figure 1).

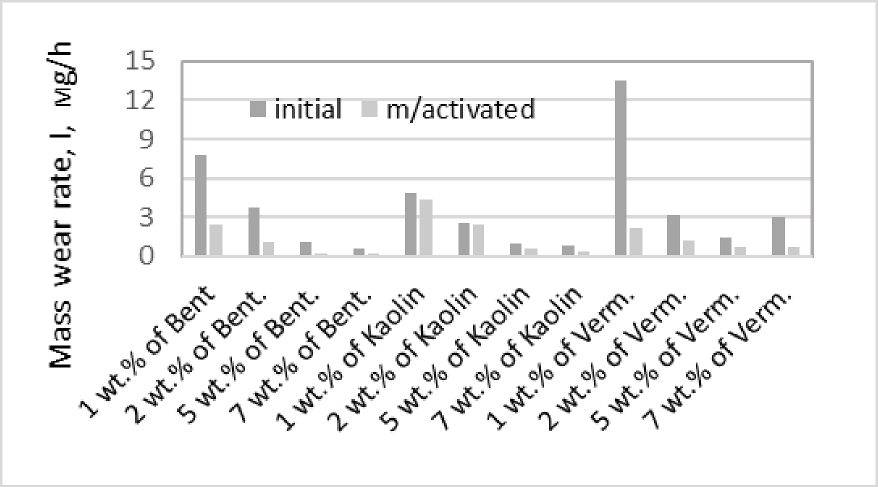
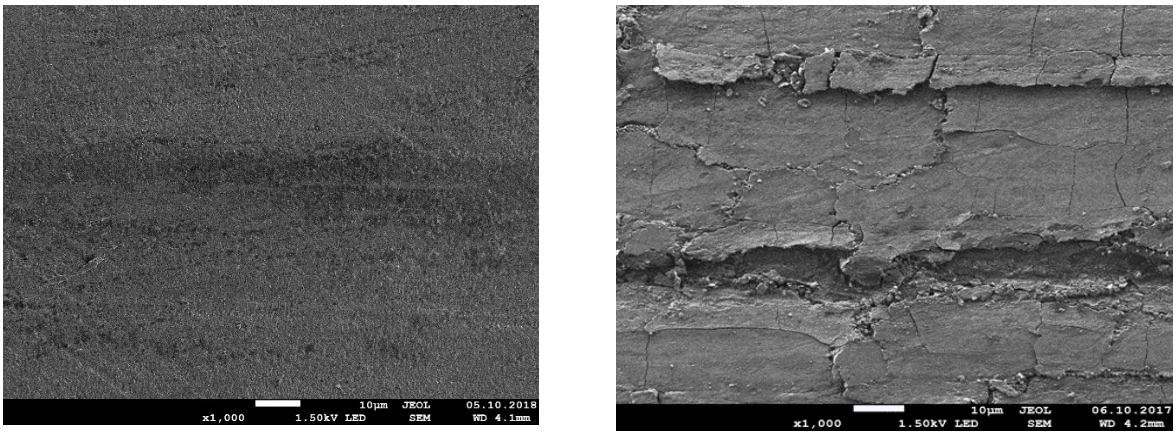


Figure1. Wear resistance of composites depending on the activation of LS during the run-in period.

A special feature of composites containing LS is the formation of a thin protective layer on the friction surface, which differs even visually in its consistency (Figure 2).



a b

Figure 2. The friction surface of the neat PTFE (a) and the PTFE/LS composite (x1000).

The consistency of the layer resembles a fine mass, which acts as a solid lubricant protecting the surface of the material from abrasion. The layer is formed, obviously, from the wear particles that appear in large quantities at the beginning of abrasion and fall on the friction surface [2]. Wear particles, circulating on the friction surface, undergo mechanochemical processes of dispersion, defragmentation, activation, oxidation. The forming protective layer, due to the silicate particles contained in them, has a low shear resistance, respectively, is able to slide relative to the surface of the counter body and the surface of the composite in the direction of shear. In addition, due to plasticity, the protective layer smoothest the friction surface, filling in cavities and irregularities, as well as smoothing micro-protrusions and micro-roughness.

Depending on the composition of the LS, the formation of 2 types of secondary structures on the friction surface that fit the Kostetsky description is revealed: plastic and fragile [3].

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FLUOROPOLYMER BASED SMART AND MULTIFUNCTIONAL MATERIALS AND APPLICATIONS

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Smart and functional materials offer large application potential in areas such as sensors and actuators, energy generation and storage, among others. The successful development of applications rely both in the ability to proper tailor their properties and in their application with suitable fabrication technologies. In this sense, fluoropolymer based smart materials, such as poly(vinylidene fluoride) $*\!-\!\left[\mathrm{CH_2{-}CF_2}\right]_n\!-\!*$ and poly(vinylidene fluoride-co-trifluoroethylene) (P(VDF-TrFE)) $*\!-\!\left[\mathrm{CF_2{-}CH_2}\right]_m\!-\!\left[\mathrm{CF_2{-}CHF}\right]_n\!-\!*$, and printed smart materials are areas of increasing interest due to low-cost fabrication, simple integration into devices and possibility of obtaining multifunctional materials over large and flexible areas. In this talk, an overview on the evolution of the use of smart and multifunctional materials based on fluoropolymers and their relation with the latest technology developments will be provided. Processing-morphology-functional response relationship will be discussed. Further, some relevant results, strategies and challenges in the development of specific smart and (multi)functional materials based on fluoropolymers, such as piezoelectric, piezoresistive and magnetoelectric ones, will be shown, together with some of their most interesting applications.

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ELASTOMERIC COMPOSITES BASED ON PROPYLENE OXIDE RUBBER WITH HIGH FILLING DEGREE WITH ULTRAFINE POLYTETRAFLUOROETHYLENE

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Abstract. Elastomeric composites based on propylene oxide rubber with a high filling degree (more than 10 phr) of ultrafine polytetrafluoroethylene (UPTFE) were studied. It was shown that with an increase of the fluoropolymer component content, the values of the physical and mechanical properties and frost resistance coefficient decrease. At the same time, the values of oil resistance and "surface" properties of materials, such as wear resistance and friction coefficient were improved up to 50%, 22% and 30% respectively. As shown by tribological testing of rubber containing 50 phr UPTFE, the elastomeric compo-sites operate stably under wear conditions in a wide range of loads and sliding speeds at -25 °C.

Keywords: elastomeric composites, propylene oxide rubber, ultrafine polytetrafluoroethylene, frost resistance, oil resistance, wear resistance, coefficient of friction, tribological tests.

One of the promising material for the production of frost-resistant elastomeric parts of sealing purposes for machinery operated in the North is the propylene oxide rubber (SKPO), which has unique frost resistance ($T_g = -74$ °C), ozone and heat resistance [1,2]. To meet the requirements for Arctic sealing rubbers, it is necessary to increase its oil and wear resistance. Therefore, ultrafine polytetrafluoroethylene (UPTFE) was added into SKPO based elastomeric composites. UPTFE has a low friction coefficient, operability in a wide temperature range and unique chemical resistance [3]. Addition of UPTFE in an amount of from 0.5 to 2 phr [4] led to improvement of wear resistance, decrease of swelling degree, and decrease of the compression set, which was associated with redistribution of the polymer filler between the surface and the volume of the elastomeric composites, which was detected using the method of electron microscopy. However, with the wear of surface layers with a high content of UPTFE the wear resistance of such an elastomeric material should decrease. Thus, to obtain wear-resistant materials with more reliable operability during abrasive wear, it is of interest to obtain composites based on SKPO with a high filling degree with ultrafine polytetrafluoroethylene.

Composites based on SKPO, containing from 20 to 50 phr UPTFE, were prepared in a “Brabender” plasticorder, the main technical properties were studied using standard methods: physical and mechanical properties according to GOST 270-84, swelling degree according to GOST 9.030-74, wear resistance of elastomeric composites according to GOST 426-77, frost resistance coefficient according to GOST 408-78.

Tribological testing of elastomeric composites was carried out at the Ishlinsky Institute for Problems in Mechanics of the RAS (Moscow) on a UMT-2 tribometer according to the method described in [5]. The end interaction of an annular elastomeric composite sample with a polished steel disk (Ra <0.01 μm) made of 20 x 13 stainless steel was studied. The contact pressure varied in the range from 0.1 to 0.3 MPa, the sliding velocity varied in the range from 1 to 100 mm / s, the volumetric temperature of the test samples was +22, +5, -5, -15, and -25 °C.

Studies of the physical and mechanical properties of elastomeric composites showed that as the content of UPTFE increases, there is a slight decrease in the values of tensile strength, elongation at break, and frost resistance coefficient. Such change in properties was explained by the possible containment of the highly elastic deformation of the elastomeric matrix in the presence of a rigid thermoplastic component. But it should be noted that, in general, the values do not go beyond the standard values.

Oil resistance studies of elastomeric composites were carried out in the environment of the MS-8P, SM-4,5, and MS-20 aviation oils. It was shown that addition of UPTFE leads to swelling degree decrease by 26–50% in all investigated media, which is a positive result and the values were 8-13% (Fig. 1)

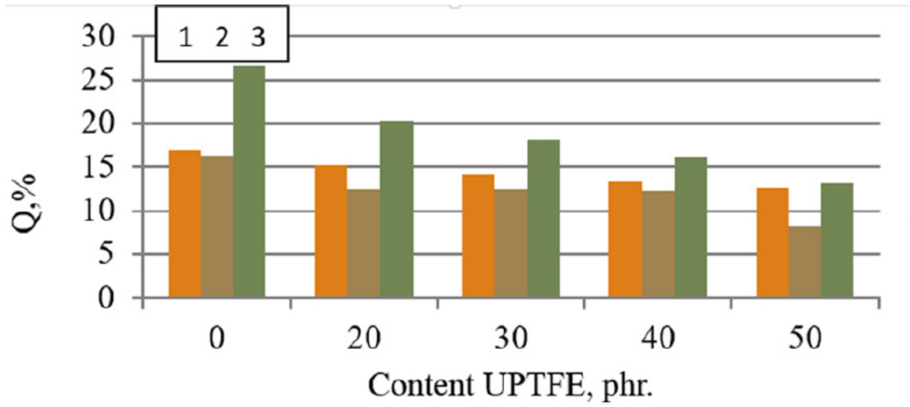

Figure 1. Swelling degree of elastomeric composites based on SKPO with different content of UPTFE in aviation oils SM-4,5 (1), MS-20 (2), MS-8P (3) (70 °C x 72 h)

Elastomeric composites with a higher degree of filling of UPTFE had lower values of volumetric wear. The lowest swelling degree and volumetric wear were observed for compositions containing 50 phr of the fluoropolymer (table 1). The decrease in the volume of the elastomeric composite containing 50 phr UPTFE compared with the initial was lower by 21%.

Table 2

The main properties of rubbers based on SKPO and UPTFE

Sample	fp, MPa	Ɛρ, %	QSM-4,5, %	QMS-20, %	QMS-8, %	ΔV, %	Км -20ºC	Км -50ºC
SKPO initial	8,8	186,6	16,96	16,3	26,65	0,907	0,8487	0,6697
SKPO+50 UPTFE	6,9	135	12,5	8,24	13,3	0,715	0,6510	0,2757

For SKPO elastomeric composites containing 50 phr UPTFE, tribological properties were studied in detail at positive and negative temperatures (Fig. 2).

The elastomeric composite showed a low friction coefficient, which was explained by the presence of UPTFE in the composition, and stable operation at all temperatures and loads. The friction coefficient of the elastomeric composites is significantly lower than for industrial rubbers based on BNKS-18 traditionally used for the production of sealing purposes rubber products. For example, the friction coefficient measured at the same conditions for industrial V-14 elastomer based on BNKS-18 rubber at room temperature varies from 1.2 to 2.4, at -25 °C from 0.9 to 1.8. All this allows us to recommend the SKPO rubber for use in cold climates to produce elastomeric sealing parts operating in conditions of intense wear.

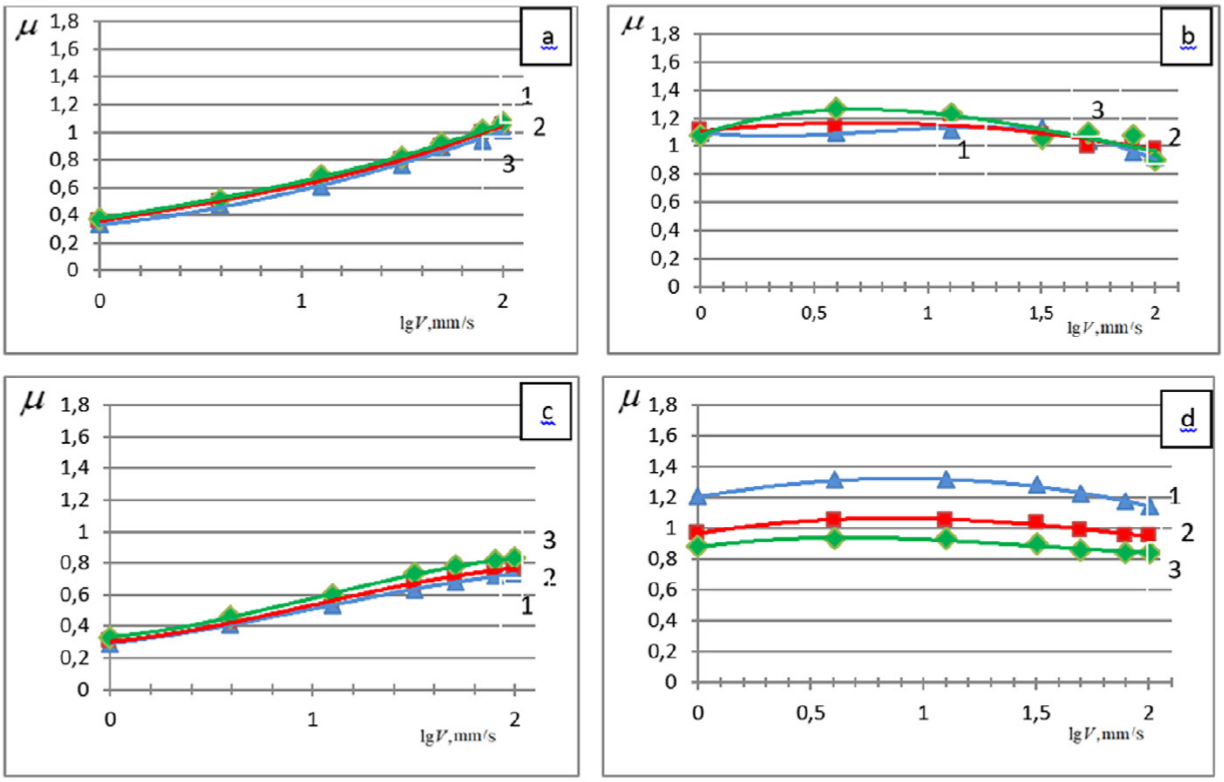

Figure 2. The dependence of the friction coefficient on the sliding speed at different temperatures and loads for the studied elastomeric composites a) SKPO (+22 ° C), b) SKPO + 50 phr UPTFE (+ 22 ° C), c) SKPO (-25 ° C), d) SKPO + 50 phr UPTFE (-25 ° C). 1- 0.1 MPa; 2 - 0.2 MPa; 3 - 0.3 MPa

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CONTROLLABLE SURFACE PROPERTIES BASED ON POLY (PERFLUORINATED METHYL METHACRYLATE)S

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Fluorinated materials have attracted considerable interest in recent years owing to their remarkable features (e.g., low surface energy; chemical/mechanical resistance; low refractive index) and their broad range of applications (e.g., self-cleaning materials; waterproof clothing; water guiding materials; anti-frosting, anti-icing, and anti-fogging agents; oil/water separation systems, etc.) 1-2. Authors have developed two relevant lines of research: i) fabrication of anti-contamination and anti-reflective films and ii) development of a simple strategy for fabrication of robust superhydrophobic surfaces. Subsequently, we aim to realize practical fluorinated polymer which can be used for cleaning applications and hydrophobic coatings. In present study, we intensively study characterization of poly fluorinated methyl methacrylate (PFMMA) focusing on surface energy, using two different methods.

The first approach is designing of chemical conformation of polymer molecule. We explore series of PFMMA homopolymers having different number of fluorine: PTFEMA (Poly trifluoroethyl methacrylate), PHFIPMA (Poly hexafluoroisopropyl methacrylate), PPFPMA (Poly pentafluoropropyl methacrylate), and PHFBMA (Poly heptafluorobutyl methacrylate). Fig. 1. shows surface energy obtained by acid-base theory and Owens-Wendt-Rabel-Kaelble method as a function of fluorine/oxygen (F/O) ratio. The surface energy decreases as F/O ratio increases, surface energy decreases; especially this difference is significant between PTFEMA and PPFPMA. Thus, it is clear that one can control wettability of PFMMA homopolymer by controlling F/O ratio. Furthermore, copolymerization is another efficient approach since we can adjust not only surface energy but other chemical/mechanical properties on demand. We designed copolymers composed of PFPMA, stearyl methacrylate (SMA), methyl methacrylate (MMA), methacrylic acid (MAA), and 2-hydroxyethy methacrylate (HEMA).

As shown in Fig. 2., surface energy is controlled more minutely by adjusting ratio of PFPMA and MMA. It is noted that, PFPMA-50 showed excellent water repellency and mechanical strength, which can be used for practical coating material for industrial use (details not shown).

The second approach is to modify the surface morphology of a material. We have developed a simple way to create a robust and efficient superhydrophobic surface via one-step spray coating of silica core/polyperfluoroalkyl acrylate shell nanoparticles (silica@PFA NPs) on epoxy-resin-coated glass slides 5. Compared to previously reported methods, our method offers several crucial advantages. It is the low surface energy after coating because of the increase in the fluorinated component, and of spontaneously generated dual-scale (micro and nano) surface roughness during spray coating as a result of higher coalescence via the soft polymeric shell binding effect. Shell binding to adjacent NPs owing to the chemical affinity of the shell significantly enhances coalescence during their deposition. Furthermore, introduction of a binding medium between the NPs and the substrate also enhances the stability of the superhydrophobic surface.

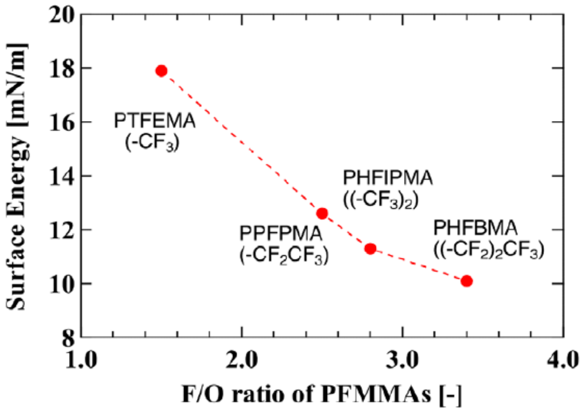

Figure 1. F/O ratio of PFMMA homopolymers and suface energy. F/O ratio is obtained by XPS O 1s and F 1s core energy measurement

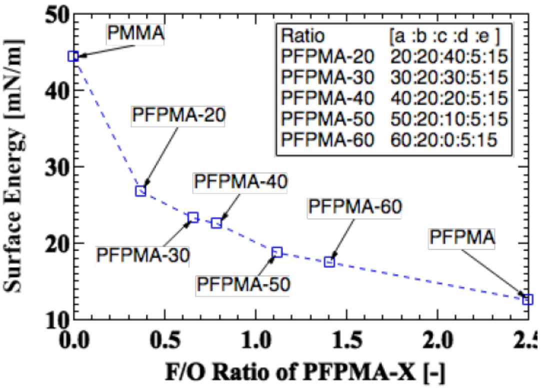

Figure 2. F/O ratio of PFPMA-X copolymers and their surface energy. X represents the nominal PFPMA content. (a: PFPMA, b: SMA, c: MMA, d: MAA, e: HEMA)

Thus, high superhydrophobicity and mechanical strength are simultaneously achieved without any expensive pre- or post- treatment process.

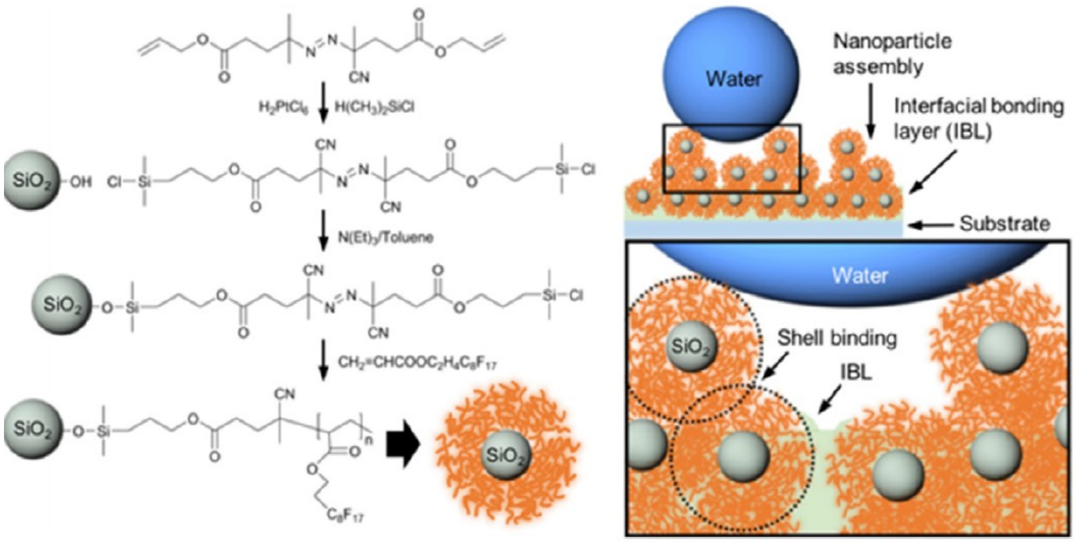

Figure 3. Schematic image of superhydrophobic surface formed by Silica@PFA NPs

In conclusion, we have conducted series of experiment controlling surface energy of PFMMAs, by controlling structure of fluorinated carbon of FMMA monomer, copolymerization, and morphological modification. The results provides practical information on designing characteristics of PMMA polymer following to requirements of the society. We expect it can be particularly interesting to researchers working to develop self-cleaning materials, anti-fouling agents, oil/water separation systems, etc.

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PVDF COATINGS: SOLVENT COMPATIBILITY AND THE EFFECT OF PLASTICISERS ON THE MORPHOLOGY, PHYSICAL AND MECHANICAL PROPERTIES OF HIGH MOLECULAR-WEIGHT PVDF

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South Africa has the world's third-largest fluorspar (CaF_2) deposits (about 41 Mt); however, up to 95% of this high-potential mineral is exported. In recent years South Africa has adopted a beneficiation strategy that encourages companies to process raw materials before exportation. One of these beneficiation strategies being explored by the Fluorochemicals Expansion Initiative (FEI) is the production and use of the fluoropolymer polyvinylidene difluoride (PVDF) locally. Several commercial opportunities for the use of PVDF have been identified with the most promising being PVDF-coated architectural fabrics.

Polyvinyl chloride (PVC) coated polyester is a common material used in flexible fabric structures. PVC/Polyester fabrics can have a structural lifespan in excess of 20 years; however, the actual lifespan of the material is based on its visual appearance. The lifespan of this material can be extended by applying a UV resistant PVDF based topcoat.

A study into the development of PVDF-containing coatings was launched by the University of Pretoria. The main aim of this study was to develop viable PVDF-based coatings that could be used to coat the locally produced PVC coated polyester fabric. At this stage the main research and development focus of FEI is to produce high molecular-weight pure PVDF. Hence, the study was limited to develop coatings based on virgin high molecular-weight PVDF.

PVDF coatings are typically applied as a lacquer during the manufacturing process. The PVDF lacquer is created by dissolving PVDF in a solvent system; once applied the fabric is heated to evaporate the solvents and set the coating. A wide variety of solvents are compatible with PVDF. The effect that several solvents have on the properties of a PVDF solution was investigated with the aim of selecting the optimal solvent to formulate the coating. The dissolution temperature effects on the colour of the solution; and the stability of the solution at room temperature were considered for the solvents listed in Table 1.

Table 1

List of PVDF solvents investigated.

Main solvents used in the dissolution temperature and solution stability experiments	Solvents investigated that produced unwanted results
Dimethylacetamide (DMA) 1-Methyl-2-pyrrolidinone (NMP) N,N-Dimethylformamide (DMF) Dimethyl sulfoxide (DMSO)	Methyl Ethyl Ketone (MEK) Toluene Tetrahydrofuran (THF)

Coatings are typically stored at room temperature. PVDF dissolution experiments were performed in order to determine the quality of the solutions when cooled down to 25 °C. The four main solvents listed in Table 1 were evaluated together with five different PVDF concentrations (5 wt%, 10 wt%, 15 wt%, 20 wt%, 25 wt%, and 30 wt%). All dissolutions were performed at 120 °C.

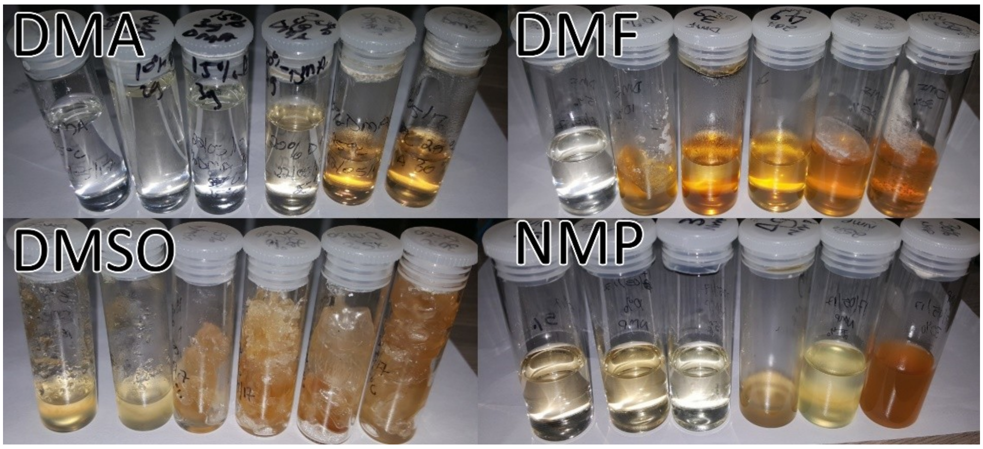

Figure 1: Solution stability results for the four main solvents. PVDF solution concentrations increase from 5 wt% at the far left to 30 wt% at the far right.

DMA and NMP produced the most stable solutions at room temperature whereas there DMSO and DMF solutions either separated or produced a solid gel, as can be seen in Figure 1. It was clear from the dissolution experiments that a PVDF weight percentage of 20 wt% was the absolute maximum recommended concentration.

The dissolution temperature effects were investigated by dissolving 10 wt% PVDF in three of the solvents (DMA, DMF, NMP) at four different temperatures: 50 °C, 80 °C, 100 °C, and 120 °C. DMA proved to be the only solvent that produced a clear non-discolour solution at any dissolution temperature.

The two most important coating properties to consider, other that the UV resistance, are coating adhesion and flexibility. Generally high molecular-weight PVDF is not inherently flexible and is incompatible with PVC (1,2) which affects the workability and film adhesion. Mention have been made in various literature to the addition of PMMA to PVDF to enhance the adhesive/compatibility properties (1,3). However, these coatings are mostly used on non-flexible materials as PMMA does not improve the flexibility due to its intrinsic stiffness. Plasticisers can be used to increase the flexibility of a PVDF coating; however very little literature data is available on the properties of films created with PVDF/plasticiser blends (4,5).

The effect of several plasticisers on the morphology, physical and mechanical properties of films created with high molecular weight PVDF through solution casting was investigated. The plasticisers included in the investigation are listed below.

Table 2

List of plasticisers investigated in this study.

P_1	2,2,4-Trimethyl-1,3-Pentanediol dibenzoate	**P_5**	Benzyl butyl phthalate
P_2	Di(Propylene glycol) dibenzoate	**P_6**	Ethylene carbonate
P_3	Dibutyl phthalate	**P_7**	Glyceryl tribenzoate
P_4	Di(ethylene glycol) dibenzoate		

Thin films were produced by dissolving PVDF in DMA, then blending the plasticiser in for about an hour. The solution was cast onto a clean glass surface and dried in the over. Solutions containing 10 wt% plasticiser (based on PVDF weight) and 50 wt% plasticiser were investigated. The following analyses were performed to characterise the films:

TGA-DTA analysis:	Melting temperature determination, PVDF degree of crystallinity analysis
FTIR analysis:	PVDF crystal phase structure analysis before and after UV exposure
DMA analysis:	Overall stiffness of material and modulus vs. time analysis
QUV artificial weathering:	UV exposure effects
SEM analysis:	Film morphology
DSC	Crystallisation temperature determination

At a plasticiser weight percentage as low as 10 wt% the melting temperature of the film was lower for all of the plasticiser except for plasticiser P6 (

Table *2*) which showed no change. At a higher plasticiser weight percentage, the melting temperature of the films was the lowest for plasticiser P3. The overall crystallinity of PVDF decreased to as low as 41 % in the presence of 10 wt% plasticiser.

As indicated in Figure 2, there are clear differences in the FTIR spectra of the plasticiser containing films compared to the film created with virgin PVDF. These differences are attributed to the change in PVDF phase structure present in the films. Preliminary analysis of the FTIR spectra indicated that the addition of plasticisers to the film favoured the formation of γ-phase PVDF.

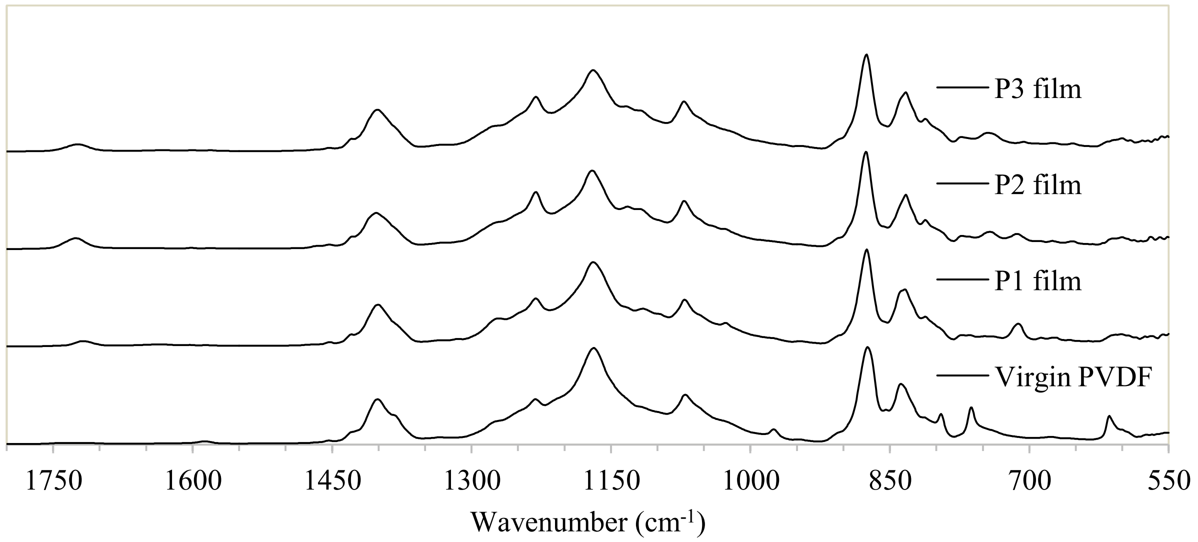

Figure 2: FTIR spectra of films created with PVDF and plasticisers (P1, P2, and P3) compared with a film created with virgin PVDF.

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PREPARATION AND APPLICATIONS OF FLUOROALKYL END-CAPPED OLIGOMERIC COMPOSITES

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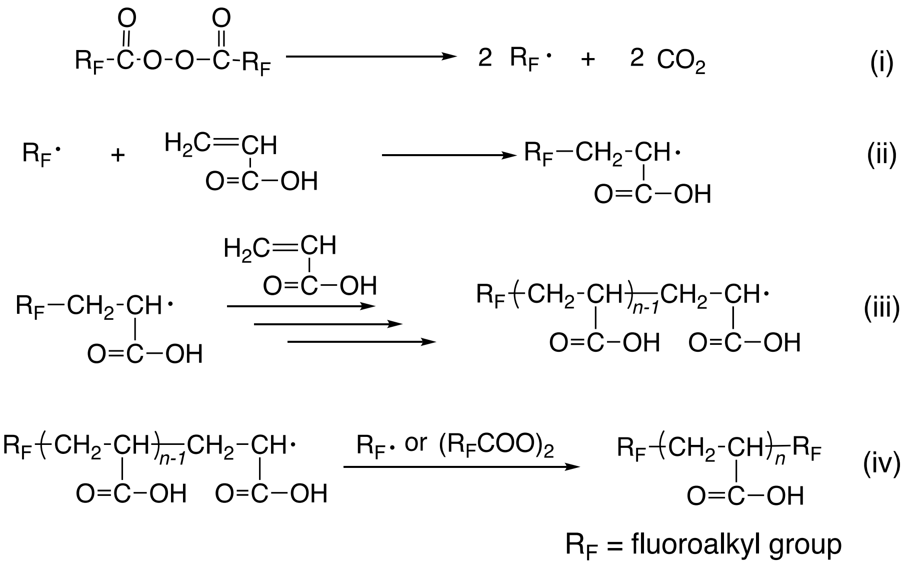
Fluoroalkanoyl peroxide [R_F-C(=O)-OO-(O=)C-R_F; R_F = fluoroalkyl group] has been hitherto well-known to be a useful radical initiator for perfluorinated monomer such as tetrafluoroethylene to produce the higher molecular weight perfluorinated polymers, due to its higher selective formation of R_F・radical through the concerted three-bond radical fission. [1] On the other hand, fluoroalkanoyl peroxide can react with the traditional radical polymerizable hydrocarbon monomers [M] such as acrylic acid as a radical initiator to produce two fluoroalkyl end-capped oligomers [R_F-$(M)_n$-R_F] through the primary radical termination of fluoroalkyl radical or radical chain transfer to the peroxide as shown in Eq. (iv) in Scheme 1. [1–3]

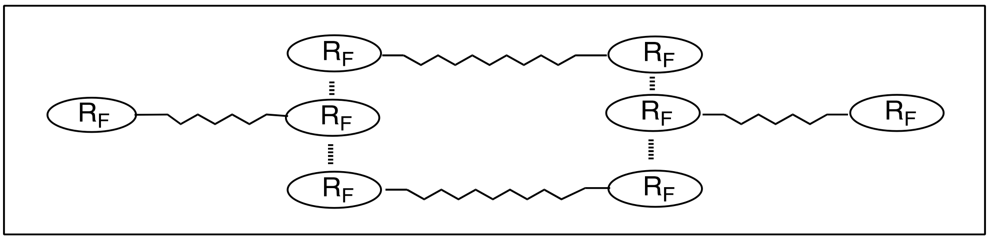
Therefore, we can obtain a wide variety of two fluoroalkyl end-capped oligomers by the use of fluoroalkanoyl peroxide as a key intermediate. [4, 5] The novel two fluoroalkyl end-capped oligomers thus obtained can exhibit unique properties, such as high solubility, surface active properties, biological activities, and nanometer size-controlled self-assembled molecular aggregates that set them apart from the corresponding randomly or block-type fluoroalkylated copolymers and non-fluorinated copolymers. [6–11]

These two fluoroalkyl end-capped oligomers [R_F-$(M)_n$-R_F] can be classified according to their structure into ABA-triblock type fluorinated polysoaps, of whose fluoroalkyl groups are directly introduced into oligomeric end-site with carbon-carbon bond formation. Thus, such two fluoroalkyl end-capped oligomers can form the nanometer size-controlled molecular aggregates with the aggregation of terminal fluoroalkyl segments in aqueous and organic media (see Figure 1). [12–15]



Scheme 1. Synthesis of two fluoroalkyl end-capped acrylic acid oligomer

Interestingly, we can observe the encapsulation of numerous guest molecules such as inorganic nanoparticles, fullerenes, carbon nanotubes, and organic dyes into these fluorinated oligomeric aggregate cores to provide the corresponding fluorinated nanocomposites. [16–25] These fluorinated oligomeric nanocomposites can exhibit a variety of unique properties, such as nonflammable characteristic [26–30], a higher photocatalytic activity [31–35], and superoleophilic/superhydrophobic, superoleophobic/superhydrophilic and superamphiphobic characteristics. [36–41] In this conference, we would like to demonstrate on the preparation and such unique properties of these fluoroalkyl end-capped oligomeric composites.



Scheme 2. Schematic model for the for the formation of fluorioalkyl end-capped oligomeric aggregates with the aggregation of end-capped fluorioalkyl groups in aqueous or organic media

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POLYMER NANOCOMPOSITES BASED ON POLYTETRAFLUOROETHYLENE FOR THE TRIBOTECHNICAL APPLICATION

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Polytetrafluoroethylene (PTFE) and polymer nanocomposites based on PTFE are widely used in engineering application. To improve the tribological properties of PTFE use different type fillers – carbon fibers (CF), layered silicates and nanoparticles of various compounds [1–3]. The combination of fibrous and nano-dispersed fillers leads to improvement of the tribological and mechanical properties of the polymer matrix [4]. The synergistic effect of improving the complex of properties due to the fact that fibrous fillers increase the mechanical characteristics, and nano-dispersed compounds intensify the processes of crystallization and structure formation in the matrix.

The purpose of the work is to study the influence of combined fillers (CF/vermiculite/ultrafine PTFE (UPTFE) and CF/kaolin/UPTFE) on the tribological properties of PTFE.

Figure 1 shows the results of study of the mass wear rate (I) of PTFE and polymer composite material (PCM). It is seen that the additional introduction of layered silicates and UPTFE in composite PTFE/CF leads an increase in wear resistance by 2.0–3.5 times. It is established that the deformation-strength characteristics during the filling of PTFE with complex fillers also increase.

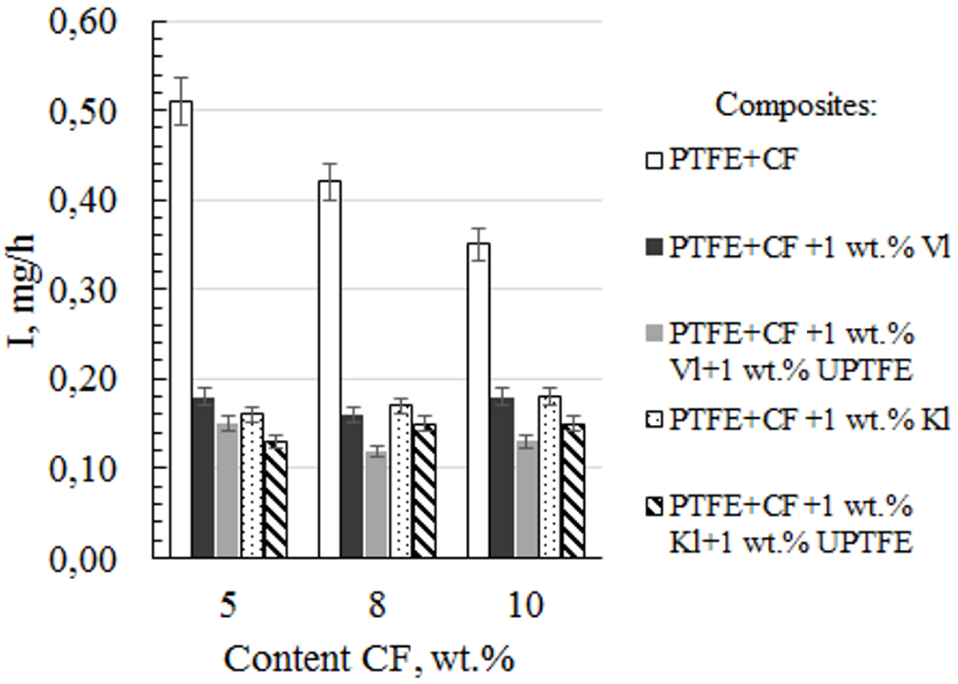

Figure 1. Results of mass wear rate of the PTFE and PCM

The SEM micrographs of worn surfaces of the composites with only CF and combined fillers (Figure 2).

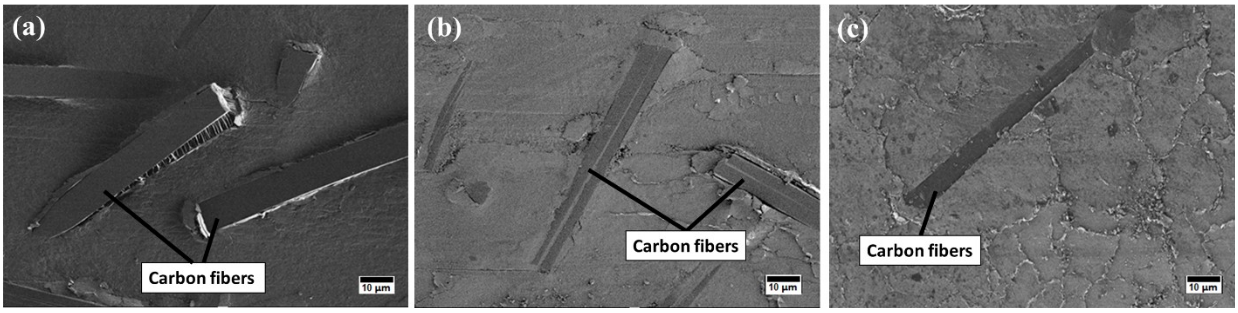

Figure 2. Typical SEM micrographs of worn surface of the PCM:
a) PTFE/CF; b) PTFE/CF/Kl; c) PTFE/CF/Kl/UPTFE

The Figure 2 shows, that additional introduction layered silicates and UPTFE to composites PTFE/CF intensifies the process of structure formation in the polymer with the formation of labile secondary structures on the friction surface. It is established that in the process of friction carbon fibers protrude above the surface of friction and localize shear deformations. This leads to a minimal destruction of polymer composites during frictional contact.

The use of combined fillers as a modifier of PTFE leads to a significant increase in wear-resistance. The developed materials can be used as a tribological materials in the friction units of machinery and technological equipment.

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SUPRAMOLECULAR STRUCTURE AND PROPERTIES OF GAMMA-IRRADIATED PTFE COMPOSITES

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Polytetrafluoroethylene (PTFE) stands out among fluoropolymers for its thermal, chemical and biological stability, anti-adhesive and anti-friction properties. The disadvantages of PTFE are related with its extremely low wear resistance under friction, high creep and low radiation stability**.** The traditional way to reduce wear and improve mechanical properties of PTFE is associated with the creation of composites on its basis. The formation of composites decreases wear by two to three orders of magnitude and makes the creep several times less. It was shown [1, 2] that γ–irradiation leads to an improvement of the adhesion of filler particles with the polymer matrix.

The goal of this work was to study the structure and properties of PTFE composites γ–irradiated above the melting point depending on the nature of filler and radiation dose.

Composites based on PTFE were prepared using traditional methods of dry bending and cold pressing followed by sintering. Inorganic and organic microsized powder particles (coke, graphite, bronze, molybdenum disulfide, cobalt oxide, chromium oxide, chopped carbon fiber and fiberglass) were used as fillers. Powder of high-molecular weight PTFE of suspension polymerization (MW $\sim 5\times10^6$) was used as polymer binder. The filler concentration was varied in the range of 2–60 mas. %.

The irradiation of composites was carried out at temperature above the melting point of PTFE crystallites (327°C) in an inert atmosphere (nitrogen) with ^{60}Co γquanta (1.25 MeV) and an absorbed dose rate of 2 kGy/h. The radiation doses were 50, 100 and 200 kGy.

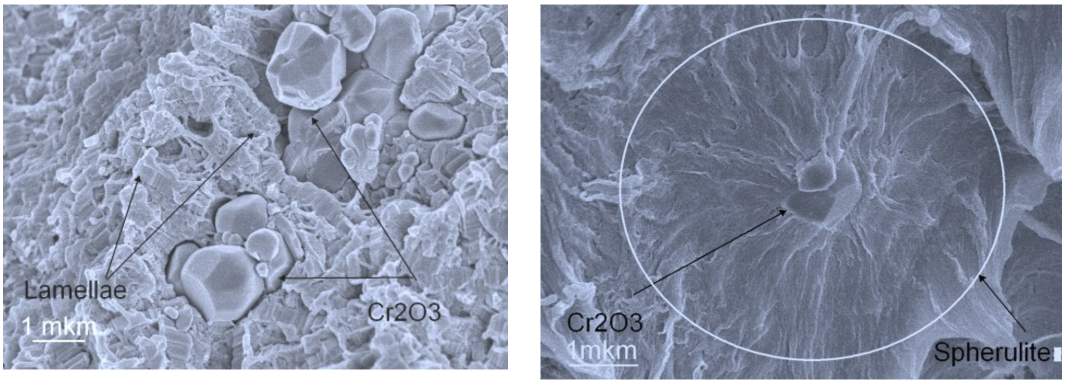
The morphology of the composites was examined by scanning electron microscopy using JSM-7500F high-resolution scanning electron microscope with a field-emission cathode (JEOL, Japan). X-ray microanalysis was used to determine the location of particles of the filler. INCA Penta FET×3 energy-dispersive analyzer (OXFORD, United Kingdom), which was supplied as part of the scanning electron microscope, was used. Mechanical and tribological properties were studied using the testing machine Instron 3365 (United States) and UMT-3 tribometer (CETR, United States). The tribological tests were carried out according to a kinematic pin-on-disc pattern under conditions of dry friction at a contact pressure of 5 MPa and a disc sliding rate relative to a fixed sample of 1 m/s. As a counterbody, a disk with a roughness of Ra = 0.3 and a hardness of HRc 45 was used.

The supramolecular structure of the polymer matrix of non-irradiated PTFE composites is characterized by the formation of lamellae 0.3–1 μm thick and up to several micrometers in length.The lamellae consist of fibrils oriented perpendicular to the large planes of lamellae. The filler particles are surrounded by polymer lamellae which are similar to the lamellae in the initial unfilled PTFE and low adhesion between the matrix and particles of organic and inorganic fillers is observed. It is manifested in the electronic images as the separation of filler particles and a polymer matrix with the appearance of an interfacial gap (fig. 1a). As a result, there is a weak interfacial interaction between the filler and the polymer matrix.

Radiation exposure leads to the disappearance of the phase separation and the formation of spherulites with the radial orientation of fibrils, in the center of which the filler particles are located. Changes in the structure are explained by an increase in interfacial interactions through the radiation grafting of macromolecules (and low-molecular-weight products) to the surface of the filler particles (fig. 1b).

The detected changes in the supramolecular structure and interfacial interaction in PTFE composites lead to significant changes in the tribological and mechanical characteristics. The linear wear rate of the irradiated composites is reduced to

50 times with respect to the non-irradiated composites, which is explained by the transition from the delamination mechanism to the abrasive one. An increase in the elastic modulus up to 3 times, an increase in Brinell hardness and stress at 10% deformation up to 50%, a decrease in irreversible deformation under static and dynamic load up to 10 times is observed.



a b

Fig. 1. SEM-images of the surface of cleavages of the PTFE composite F4CR5:
a – before radiation modification, b – after radiation modification.

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FEATURES OF STRUCTURAL CHANGES IN THE EXPLOSIVE PROCESSING OF POLYTETRAFLUOROETHYLENE

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Currently, for the modification of polytetrafluoroethylene (PTFE), for the purpose of improving its manufacturability and impart new properties, various technological methods are being developed based on the use of external high-energy impact: vibromechanic, radiation, laser, ultrasonic, shock-wave [1] processing.

Shock-wave processing is a multifactorial process, and the intensity of structural transformations can be controlled by changing the technological parameters of loading (configuration and duration of the shock pulse, the detonation rate of the explosive and the pressure of the shock wave) and the characteristics of the processed polymer powder (composition, initial porosity, dispersion) [2, 3]. The paper presents the results of a study of the structure and properties of PTFE after shock-wave processing (SWP) in a cylindrical ampoule. These conditions allow to change the loading conditions along the radius of the ampoule [2, 3], intensify the collision of polymer powder particles and their heating in the center of the ampoule, where the pressure abruptly increases due to the effect of convergence of shock waves (SW).

The dependence of the structure and properties of the polymer on the loading parameters and the initial porosity of the samples was established during the EP of the PTFE powder. Variation of the initial porosity (30 and 60 %) allowed to change the calculated pressure pulse in the pressed powder from 0.4-0.6 GPA to 1.2-1.5 GPA in the center of the ampoule at the initial porosity of the powder 30 % and above 1.5 GPA at 60 % porosity. The obtained samples were cylinders of white color, typical for solid PTFE, with well-pronounced central area of darker color. Comparative studies of the structure, thermal and strength properties of PTFE after SWP and static pressing with a pressure of 0.3 GPa were carried out using XRA, TMA, DTA and ES microscopy.

Between the peripheral and central zones there is an abrupt change in the nature of the structure. The morphology study revealed that the structure of the light-colored part of the sample (P=0.4-0.6 GPA) is characteristic of the initial PTFE, which is consistent with the data of the energy dispersive composition. In the dark central part of the sample (P=1,2-1,4 GPA) there is an elongation of fibrous structures to 5-20 microns, an increase in carbon atoms quantity according to the elemental composition, which is caused by the carbonization of PTFE as a result of its partial destruction [1]. Increasing pressure (P>1.5 GPa) in the central area of compacts leads to the formation of fibrous structures with a thickness of tens of nm, oriented in the direction of SW propagation. Supramolecular structure of PTFE, consisting of long ribbons, is transformed into a fibrous structure similar to that obtained by laser processing of PTFE and during thermomechanical stretching of polymer films [1].

X-ray diffraction studies have shown that PTFE retains an amorphous-crystalline structure, regardless of the pressure of the SWP. However, an increase in the intensity of high-energy impact is accompanied by a decrease in the degree of crystallinity from 83 to 45%, an increase in the halo area in the region of 2Θ = 30-50 °, as in the SWP of metal-PTFE composites, due to the disorientation of macromolecules due to a change in the thermodynamic regime of structure formation [4]. In the region of 2Θ = 20–30 °, a new halo appears, which is absent in the initial PTFE, the presence of which is caused by the appearance of a new disordered phase after SWP [1]. On the diffractogram of the central fibrous part (P> 1.5 GPa), a new reflex of 2Θ= 22° is observed, and the broadening (β = 7.2 mrad) of the x-ray maximum in plane 100 is caused by a decrease in the crystallite size from 29 to 21 nm and an increase in the relative deformation crystal lattice from 3.2 to 4.7 x 10-3.

Structural transformations during SWP are accompanied by a decrease in thermal deformations of the polymer during subsequent heating to the melting temperature and an increase in heat resistance to 510 °C. The formation of a fibrous structure in the central zone of pressing is confirmed by subsequent heating by an increase of 3–4 times thermal deformations (up to 12.5%) in the opposite direction along the axis of the ampoule.

Compression testing of the samples after sintering showed that toughness of polymer after SWP increases and at the degree of 20 % it equals 40 MPa, which is 25% higher than that after static pressing. This behavior of the polymer confirms appearance of structural changes after SWP that strengthen intermolecular interaction due to the diffusion of macromolecules in the boundary layers of powder particles, their setting, and also increase of defects in the structure that affects the process of the subsequent sintering samples and the toughness of the material.

Thus, it was found that varying the parameters of the SWP (P from 0.4 to more than 1.5 GPa) is accompanied by a change in the structural organization and allows to regulate the structure, interparticle interaction, thermal and mechanical properties of PTFE

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FLUORINE-CONTAINING POLYMERS FOR MEMBRANE SEPARATION

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Among membrane materials fluorine-containing and perfluorinated polymers keep a special place. Reasons for the unusual properties of them are associated with high C-F bond energy (485 kJ/mol) and low intermolecular interactions. Although the number of the monomers that are capable to form such polymers is much less than that of common organic monomers, the variation of the structures and the properties of forming polymers is relatively great. Numerous examples are known of the polymers with similar structure that include fluorine-containing groups (e.g. CF_3) or when such groups are absent. This is important for establishing of the relations between structure and properties of membrane materials and for directed search for polymers with improved properties.

Beside polymerization of the fluorine-containing monomers, there are several techniques for introduction of the fluorine to polymeric structure: namely, a direct gas-solid and gas-liquid-solid fluorination of polymers which is performed by molecular fluorine containing mixtures with inert (often He) or oxidative (O_2) gases /or perfluorinated liquids (for instance, perfluorodecaline); plasma treatment of polymer surface in the presence of fluorine-containing gases and vapors (CF_4, SF_6, C_2F_6, chlorofluorocarbons, etc.). The both techniques result mostly in so-called hydrogen-exchanged fluorination, fluorination of unsaturated (double or aromatic) bonds and cleavage of C-Si ($SiMe_3$-containing membrane polymers) and C-N (polyimides, polyamides) bonds. The peculiarity of the latter technique is mostly surface oriented or fluorination on lower thickness. In general, for both techniques during the fluorination, one observes slight decrease of permeability coefficient P for light gases (He, H_2) and significant decrease of P for heavier gases (O_2, N_2, CO_2, CH_4, …) that gives rise to higher permeability selectivities for He/CH_4, CO_2/CH_4, etc.

Fluorine-containing polymers obtained via polymerization of fluorine-containing monomers are numerous and represent various classes of high molecular compounds (polycondensation polymers, polyacetylenes, norbornene based polymers, celluloses) which are of interest for membrane separation. In total, the presence of fluorine-containing groups in macromolecules (F-, pefluoroalkyl-, perfluroaryl-, etc) also induce a more or less increase of permeability and diffusion coefficients of gases. A special consideration should be devoted to solubility coefficients of hydrocarbon and fluorocarbon and semifluorinated penetrants. There is a common dependence of representation of sorption data for a wide group of solutes (from gases to heavier paraffins) which postulates that the solubility coefficient of solute increases as the critical temperature of the solute increases [1]. However, for series of substituted fluorinated toluenes and alkanes, the rule does not work: solubility coefficients decrease from perfluorinated through semifluorinated to hydrocarbon solutes while the critical temperature of the solutes increases for the series. Other thermodynamic parameters of sorption for the penetrants have also some peculiarities that can be summarized in a deviation of interaction of C-F and C-H-containing molecules in comparison with a geometric mean rule introduced by van Laar and Lorenz [2]. However, van der Vegt et al supposed that the deviation does not take place in the fluorocarbon-hydrocarbon systems [3].

The difference in interactions of fluorine-containing compounds are expressed finally in growth of selectivity on some gas pairs, the inertness of the fluorine polymers, their oleo- and hydrophobicities and low affinity to organic vapors which make them the potential materials for diverse membrane applications such as gas separation (recovery of helium from natural gas, oxygen enriching of air, purification of natural and biogases) and different pertraction (ozonation, oxygenation, halogenation) and pervaporation processes [4].

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COMPOSITE FLUOROPOLYMER-CONTAINING COATINGS ON NON-FERROUS METALS AND ALLOYS

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Currently, non-ferrous metals, such as magnesium, aluminum and titanium alloys, are increasingly used as structural and functional materials in various industries [1]. Due to the combination of processability, low specific density, acceptable strength characteristics, these alloys have several advantages over many other structural and functional materials [2]. However, these alloys have drawbacks that significantly restrict the scope of their application. These drawbacks include the low corrosion and wear resistance of magnesium and aluminum alloys, and for titanium alloys it is the high probability of the formation of a galvanic couple of titanium with some other metals, which leads to the destruction of the latter. Additionally, these non-ferrous metals have insufficient friction characteristics. Thus, one of the most important tasks is to find ways to protect magnesium, aluminum and titanium alloys from the negative impact of an aggressive environment.

In order to solve this problem, we have developed the way to form the composite coatings on the surface of magnesium, aluminum and titanium alloys [3]. The method consists in the formation of a solid, corrosion-resistant and wearproof coating having a developed (uneven) morphology on the surface of the protected material by the plasma electrolytic oxidation (PEO). Further, various organofluorine substances, such as superdispersed polytetrafluoroethylene (SPTFE) and telomeres of tetrafluoroethylene (TFE), were impregnated in pores and deposited on the surface of the base PEO-layer by immersion in specially designed dispersions [4]. Then, heat treatment of materials was carried out, which lead to the melting of the polymer with the aim of accelerating impregnation it into the pores of outer part of the PEO-layer and forming a composite coating.

Formed coatings reduce corrosion current density by 3 orders of magnitude ($I_C = 5.4\times10^{-11}$ A/cm^2) in comparison with the base PEO-coating ($I_C = 2.5\times10^{-7}$ A/cm^2) and by 6 orders of magnitude in comparison with uncoated metal ($I_C = 5.3\times10^{-5}$ A/cm^2). The incorporation of fluoropolymer into the outer porous part of the PEO-coating reduces wear by more than 3 orders of magnitude: down to 7.6×10^{-7} mm^3/(N×m) in comparison with the base PEO-layer (1.7×10^{-3} mm^3/(N×m)).

It was found that the obtained composite coatings are resistant to atmospheric marine corrosion. No corrosive damage was observed during the three-year tests of samples with composite layers. The protective properties of composite layers are due to the impregnation of polytetrafluoroethylene into the pores of the coating, sealing of the pores and the formation of a defect-free layer on the surface of substrate materials.

Composite coatings formed using SPTFE possess the hydrophobic properties (the contact angle attains up to 140°), and coatings which formed using solution of TFE telomeres are superhydrophobic: the contact angle and the rolling angle attain up to 171° and 7°, respectively. It is shown that superhydrophobic properties are due to the multimodal hierarchical structure of the surface of the coatings formed as a result of aggregation of particles of organofluorine material with low surface energy [5].

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A NOVEL PERFLUORINATED MEMBRANE FOR FUEL CELLS

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Hydrogen fuel cells – ecologically clean sources of energy – are finding their place in modern energetics. Furthermore, possibility of obtainment of hydrogen from biomass makes them renewable, increasing their popularity. The most popular type of fuel cell uses polymer membranes as electrolyte. The widest used one is Nafion membrane. But its low conductivity at low relative humidity and high cost make it necessary to make efforts to obtain alternative membranes or modify existing ones.

The polymer was obtained by thermally initiated polymerization under high pressure of mixture of perfluoro(3-oxapent-4-ene)sulphofluoride, perfluoro-2,2-dimethyl-1,3-dioxol and perfluoropropylvinyl ether. To obtain a membrane, a casting procedure from perfluorotoluene solution was used. Then the sample was hydrolysed by NaOH water solution to obtain membrane in acid form.

Obtained membrane was characterized by different methods. Its composition was confirmed by FT-IR spectra. Water uptake at different relative humidities (RH) has been measured. At RH=95% it is 29%, which is higher than for Nafion.

Figure 1 shows results of measurement of membrane proton conductivity contacting with water. It exhibits rather high ionic conductivity – 57 mSm/cm at 21 °C, rising to 114 mSm/cm at 79 °C.

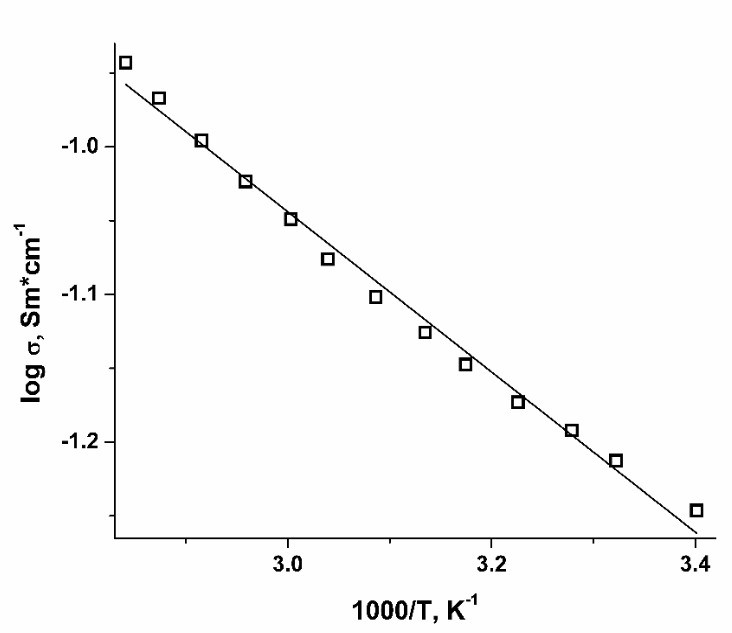

Figure 1. Protonic conductivity of the studied polymer in contact with water.

At the same time, at low RH conductivity significantly decreases down to 8,4 µSm/cm at RH=32%, becoming lower than for Nafion

Transport of anions and cations through the membrane has also been studied. Diffusion permeability of HCl solution, showing the rate of anion transport, is rather high – 9,73·10^{-7} cm^2/s.

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FLUOROPOLYMERS IN AGC

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Fluorinated organic compounds are widely used in various applications including thermoplastics, elastomers, membranes, surface coatings, and other functional materials because of their excellent physical and chemical properties. Highly or perfluorinated polymers typically have high thermal stability, high electric properties, high chemical resistance, and so on. Our company AGC Inc., which was founded more than 100 years ago, has a distinctive chemical chain which arose from raw salt (NaCl), calcium fluorite (CaF_2), and methane (CH_4) and we have continuously developed fluoropolymer products for 50 years as a downstream of chemical chain. Our products include PTFE, ETFE, PFA resins (Fluon®), FEPM (AFLAS®), ETFE film (AFLEX®), oil and water repellent coatings (Asahi Guard®), weather resistant paints (Lumiflon®), separation membranes (ForBlueTM famly), an amorphous perfluorinated transparent polymer (CYTOP®). In this article, latest development of chemicals design and modification of AGC's fluoropolymer products are reported.

AGC's melt-processable fluoropolymers ETFE and PFA are continuously modified and improved to widen their applications in various industries. Fluon+TM Adhesive resins are our latest melt-processable fluoropolymers resins with unique adhesive properties while maintaining excellent properties of conventional fluoropolymer resins. [1] The adhesiveness is introduced by incorporating third functional monomers to the ETFE or PFA backbones. Fluon+TM Adhesive resins are mainly used in applications that require strong adhesion to other polymeric substrates, such as on polyamide substrate in multilayered fuel hoses for automotive applications. In addition, Fluon+® Adhesive resins can be easily compounded with other materials. The easy processability opens the opportunity to incorporate the excellent properties of fluoropolymers such as low dielectric constant and high impact strength to other low-cost conventional materials.

Fluoroelastomer AFLAS® is tetrafluoroethylene-propylene copolymer that has been developed and commercialized by AGC since 40 years ago. AFLAS® has a better characteristics than conventional FKM fluoroelastomer that is often used for different applications. Recently, modification of polymer structures and control of characteristics were examined, and new AFLAS® grades were developed with improved crosslinking properties such as curing speed and other physical properties. Therefore, they are expected to be used in harsh environments that were difficult to apply before.

In the case of LUMIFLON® and Asahi Guard®, various monomers including both non-fluorinated and fluorinated are continuously used to modify polymer properties in order to meet our customers' demands.

FORBLUETM FLEMION is used as an ion-exchange membrane for chloralkali electrolysis process, the upstream of AGC's chemical chain. New grades have been developed and are also implemented for our customers' process. High energy efficiency membrane with low voltage operation is developed based on our technology of synthesizing unique monomers and chemically controlled polymer. FORBLUETM S-series which can be used for various electrolysis processes is recently introduced to the membrane market. Not only monomer and polymer synthesis but also membrane fabrication and reinforcement technology gained through FLEMION development are applied for S-series.

In addition, AGC has developed CYTOP®, while maintaining the conventional properties of fluoropolymers. Its monomer, perfluoro(butenyl vinyl ether), is specially designed and synthesized. CYTOP® was used for a graded index type plastic optical fiber (Fontex®), and an optical waveguide.

Furthermore, unique methods for fluoroolefin synthesis has been developed for exploring unconventional monomers, since raw materials which are commonly used to produce fluorine containing materials is limited, such as tetrafluoroethylene (TFE) and its derivatives. AGC has developed "perfluorination of an esterified compound then thermal elimination (called as PERFECT process)" as an useful fluorination method to produce perfluorinated compounds with fluorine element [2]. Moreover, olefin cross metathesis with TFE and analogous fluoroolefins has recently been found [3]. These methods are widely applicable to the organofluorine chemistry.

Fluoropolymers are expected to continuous play great roles in the future for various fields with their unique characteristics and excellent properties. As mentioned above, using monomer and polymer technology AGC has developed various fluoropolymer products, and will continue to improve their properties.

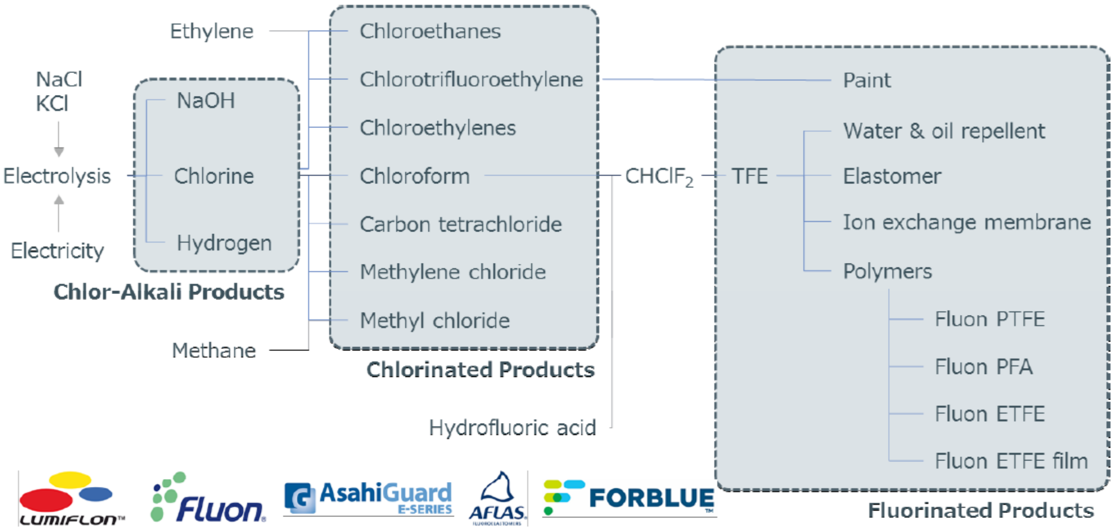

Figure 1. The AGC Group’s Chemical Chain

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ELECTRODIALYSIS IN OVERLIMITING CONDITIONS: EFFECT OF COPPER AND NICKEL HYDROXHYDROXIDES ON WATER DISSOCIATION REACTION

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Use of high-intensity current modes is a priority goal for electro-membrane technology which allow to reduce the usable expensive membranes area and create a more compact electrodialysis apparatus, resulting in lowered capital and operating outlay.

Applying of electrodialysis minimizes the eluation of toxic heavy metal compounds (THM) into the environment (the maximum permissible concentration of THM for discharge to collector is no more than 0.02 mg / l) and allows to return them to technological processes.

The aim of this research is to study the electrochemical behavior of the ion-exchange heterogeneous membranes MK-40, MA-41 (Russia) and AM-PP, SM-PP (Czech Republic) in solutions of copper sulfate, nickel and zinc chloride with a concentration of 0.01 n. Heterogeneous membranes MK-40 and MA-41 are composites containing ion-exchange resin and polyethylene as an inert binder component. Anion-exchange membranes contain quarternary ammonium basics as functional groups, and cation-exchange membranes are sulfocationic. However, membrane manufacturing techniques are different in the Czech Republic and in Russia: resin and polyethylene have different particle sizes and are manufactured by hot rolling (Czech Republic) and by hot pressing (Russia) [1, 2]. The ion transport numbers were determined by the selective polarization method [3], the concentration dependences of membrane electrical conductivity were measured by the Elins impedance meter with the release of the ohmic component. The microrelief of the membrane surface was studied by atomic force microscopy technology (AFM) using a NTegra Prima NT-MDT scanning probe microscope (Russia, Zelenograd) in a semi-contact mode on dry samples. Obtained AFM images treatment was implemented using AFM Solver P47 Pro Nova RC1 software.

Electrodialysis technology development is limited due to unsufficient data on the properties of ion-exchange membranes in solutions containing multiply charged cations. Charge increase of counterions brings to their mobility decrease and reduces the moisture content of membranes [4]. As known, the transport channels structure is important for transport processes and selective properties of membranes. It is shown that the membrane surface microrelief depends on the counterion nature. Multiply charged counterions reduce the swelling of the ion-exchange resin, bringing to the expansion of pores, cracks and microcracks on the resin and inert binder boundary. The contribution of the depth of these defects to the membrane surface brings to an increase in the microprofile height. An increase in surface roughness results in electroconvection development, the most important mechanism for mass transfer increase in dilute solutions at currents above the limit. Flowing around obstacles, solution forms vortices, bringing to a decrease in the diffusion boundary layer thickness. It enhances the role of electroconvection since this layer thickness fraction occupied by the space charge region (SCR) increases. In addition, mass transfer proceeds more intensively near the electrically inhomogeneous surface of heterogeneous membranes [4].

The presence of transition metal ions in working solutions results in the formation of sparingly soluble hydroxides on the surface of cation exchange membranes, which have catalytic activity relatively to the water dissociation reaction according to the mechanism proposed in [5]:

$$Me(OH)_2 \leftrightarrow MeOH^+ + OH^-$$
$$Me(OH)^+ + 2H_2O \leftrightarrow Me\,(OH)_2 + H_3O^+$$

It results in a significant shift in the pH of the cation exchange membrane near-membrane layer towards alkalization and causes the sparingly soluble THM hydroxides formation.

The study of electrodialysis of copper chloride solution using MA-41 / MK-40 membrane pair showed that a gradual transition to a catalytically inactive CuO oxide occurs on the MK-40 membrane surface. It is shown that despite the presipitate formation, the separation process is quite effective. Possibly, binding of OH-ions to a sparingly soluble precipitate reduces their effect on the SCR charge of cation exchange membrane and creates the conditions for electroconvection development. In case of chloride and nickel sulfate solutions, the precipitate $Ni(OH)_2$ does not change the composition and continues to catalyze the dissociation of water, bringing to a stable alkalization of the desalination chamber.

A comparison of structural parameters of MK-40 and SM-PP cation exchange membranes (Table 1) indicates that the volume fraction of the intergel solution in the SM-PP membrane is slightly less. Perhaps this is due to a slower decrease in the salt ion transport numbers with increasing current density for the SM-PP and AM-PP membranes.

Table 1

Volume fractions of the gel and intergel phases in zinc chloride solutions

Membrane	NaCl		$ZnCl_2$	
	f1	f2	f1	f2
MK-40	0.4	0.60	0.18	0.82
SM-PP	0.23	0.76	0.12	0.80

Thus, the electrochemical behavior of heterogeneous ion-exchange membranes in solutions containing multiply charged THM ions is determined by the catalytic properties of their sparingly soluble hydroxides. In conditions of possible complexation and excess of complexing anions in the phase of the anion exchange membrane, the membrane behavior is determined by the composition of the contacting solutions.

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EFFICIENT MINERALIZATION OF FLUOROPOLYMERS USING SUBCRITICAL WATER

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Owing to their high chemical and thermal stability, fluoropolymers are used in a variety of industrial applications. For example, perfluorinated ion-exchange membrane polymers, manufactured by copolymerization of tetrafluoroethylene (TFE) and a functionalized perfluorinated vinyl ether, are used in polymer electrolyte membrane fuel cells, in the production of chlorine and sodium hydroxide from brine (chlor-alkali process), in desalination to produce potable waters, owing to their specific characters such as high proton conductivity, high chemical-, mechanical-, and thermal stabilities. Furthermore, poly(vinylidene fluoride), PVDF, an engineering plastic that allows fabrication by melt processing, has been used for various applications including water-treatment membrane, lithium ion battery electrode binders and separators for electric automobiles, piping, sinks, tubing, valves, cables, films, etc., so that this specialty polymer is nowadays the second largest produced fluoropolymer after poly(tetrafluoroethylene) (PTFE). VDF-based copolymers, which enhanced the properties such as the softness and impact resistance, have also been developed and introduced in industry.

For the use of fluoropolymers with high sustainability, the establishment of waste treatment technique should be required. Incineration is the nowadays-adopted option, but this requires high temperatures to cleave the strong C-F bonds, and the released HF gas can damage the firebrick of an incinerator. Therefore, development of a non-incineration technique to decompose these polymers is strongly desired. If these polymers could be decomposed to F^- ions (i.e., undergo mineralization) by means of environmentally benign techniques, the well-established protocol for treatment of F^- ions could be used, whereby Ca^{2+} is added to the system to form CaF_2, which is a raw material for hydrofluoric acid. Thus, the development of such a method would allow the recycling of fluorine element, which faces an increasing global demand.

Subcritical water is high-pressure liquid water (the temperature ranging between 100 °C and its critical temperature, 374 °C). Reactions using subcritical water are considered environmentally benign in chemical engineering, because the water can solubilize nonpolar organic compounds and hydrolyze many organic compounds: these features can release useful products or transform undesirable compounds into environmentally compatible compounds. In the recycling processes for common plastic materials, subcritical water technology is indicated to have a smaller environmental impact than pyrolysis, whereas the energy consumption is higher.

Here we show efficient mineralization of perfluorinated ion-exchange membrane polymer (Nafion NRE-212), [1] PVDF, [2, 3] poly(ethylene-*co*-tetrafluoroethylene) copolymer (ETFE), [2] and VDF-based copolymers such as poly(vinylidene fluoride-*co*-hexafluoropropylene) [poly(VDF-*co*-HFP)] copolymer, [3, 4] poly(vinylidene fluoride-*co*-perfluoromethyl vinyl ether) [poly(VDF-*co*-PMVE)] copolymer, [4] poly(vinylidene fluoride-*co*-chlorotrifluoroethylene) [poly(VDF-*co*-CTFE)] copolymer, [3] and poly(vinylidene fluoride-*ter*-hexafluoropropylene-*ter*-tetrafluoroethylene) [poly(VDF-*ter*-HFP-*ter*-TFE)] terpolymer, [5] in subcritical water by a combination of either an oxidizing or a reducing agent. The effort to lowering reaction temperature and formation of CaF_2 in the presence of stoichiometric amount of $Ca(OH)_2$ are reported.

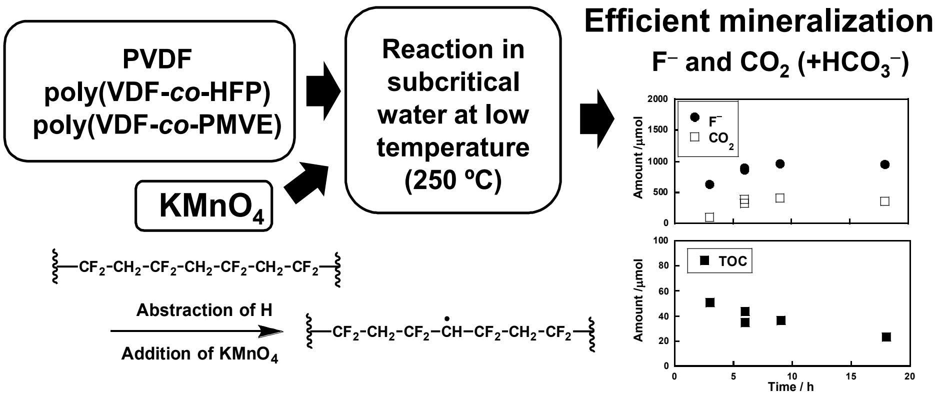

Figure 1. Schematic view for the mineralization of PVDF and VDF-based copolymers in subcritical water in the presence of $KMnO_4$. [4]

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WASTE PRODUCTION OF TETPAFLUOROETYLEN

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The composition and structure of gaseous and solid products formed during the processing of PTFE wastes by the methods of thermal destruction with exhaustive fluorination (F-4 and F-4D) and hydrothermal destruction (F-4) are determined in the work.

The gas phase released during the processing of F-4D wastes by thermal destruction with exhaustive fluorination with cobalt trifluoride consists of perfluorinated compounds of normal structure with a molecular mass above 338. Generally, solid, normal structures, perfluoroalkanes with high molecular weight are formed (Table 1).

The solid fraction is represented by spheroidal monoparticles with different chain lengths and molecular mass formed from a large number of bound blocks. Blocks are of a high molecular nature, and the elements that bind them to monoparticles are low molecular weight. Particles of the UPTFE powder (F-4D), obtained directly from the reactor, consist of plates with a particle size of 70-450 nm. Particles of the dry residue of the suspended PTFE in perfluorodecalin take the form of porous agglomerates of spheroidal shape having pores of 50-300 nm in size. Dimensions of the diagonal of the spheroids of the suspension are in the range 220-5500 nm (Figure 1).

Particles of the UPTFE powder (F-4), obtained directly from the reactor and UPTFE suspensions in perfluorodecalin, consist of plates rolled into spheroids with a diagonal of 35-950 nm and 433-1132 nm, respectively. They are combined into agglomerates having a diameter of 3-5 µm (Figure 2).

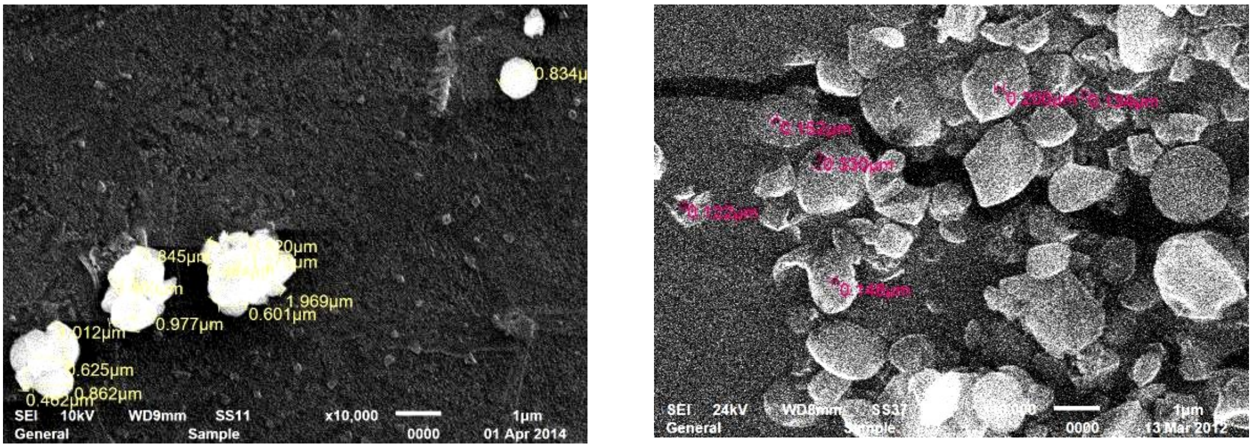
Particles of UPTFE obtained by hydrothermal destruction have a nonporous spheroidal shape with a diagonal of 4003000 nm.

Fluorinated lubricants obtained on the basis of transformer oil, copolymer of tetrafluoroethylene and ethylene, polytetrafluoroethylene, PTFE, obtained by thermal destruction with exhaustive fluorination with cobalt trifluoride, PTFE, obtained by the destruction of PTFE by hydrothermal method are investigated. UPTFE, obtained by the method of thermal destruction with exhaustive fluorination from waste fluoroplastic F-4D (Table 2), has a minimum friction coefficient of rolling. The product obtained is recommended to be used as a component of solid and consistent greases for various purposes.

Table 1

The composition of the gas fraction of the thermal destruction of PTFE waste (F-4D) with exhaustive fluorination

Exit time, min	Name of substances	Formula	Molecular weight
3,530	Perftorghexane	C_6F_{14}	338
4,887	Perfluorooctane	C_8F_{18}	381
5,663	Perfluoroseicosan	$C_{20}F_{42}$	1038



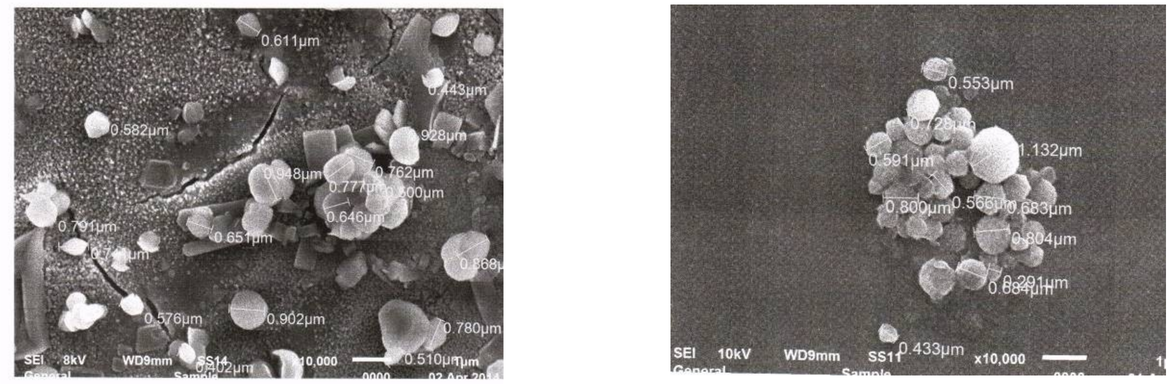
a b

Figure.1. Structure of UPTFE (F-4D). Method of thermal destruction with exhaustive fluorination: a - powder (an increase of 10000x), b - a dry residue of suspended matter in perfluorodecalin (an increase of 10000x)

Table 2

Elemental composition of UPTFE from waste F-4D

Powder from the reactor			Dry residue of suspended matter in perfluorodecalin		
Element	Weight %	Atomic, %	Element	Weight %	Atomic, %
C	19,45–19,57	27,64 – 27,81	C	31,74–54,36	41,61 – 64,02
F	80,55–80,43	72,36-72,19	F	56,48–31,35	46,80 -23,34
O			O	11,78–14,29	11,59 – 12,63
Total	100,00		Total	100,00	



a b

Figure. 2. Structure EPTFE (F-4). The method of thermal decomposition with exhaustive fluorination: a – powder, b – solids suspension in performanceline. 10000h magnification

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A MODEL-BASED CONTROL SYSTEM FOR A SMALL-SCALE PTFE RECYCLING SYSTEM FOR INDUSTRIAL PTFE WASTE MANAGEMENT

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Polytetrafluoroethylene has revolutionized the polymer industry in many ways and is still being used in numerous industries for its unique physical properties. Unfortunately, due to the same unique properties, it is not readily recycled, nor is it easy to recycle. With an increase in environmental legislation and a worldwide drive to become more environmentally friendly, PTFE has lost some of its glory in the world market.

The Fluoro-Polymer Laboratory at the University of Pretoria has been investigating various aspects of PTFE recycling over the past ten years. The thermal degradation of PTFE is well known and is essentially the same as proposed by [1]. The selectivity of the degradation process products has been investigated on a continuously fed system [2] and further developments in possible catalytic effects have been investigated [3,4]. Further, more recent, work includes the processing of waste PTFE (typically shavings from machining) to the desired particle size distribution, separation of the pyrolysis product gas by means a packed distillation column operating at sub-zero temperatures and polymerization of the product stream using various aqueous initiators [5].

An on-line qualitative analysis technique, using time-resolved FTIR analysis, has been developed and implemented to control the product stream composition by manipulating the process conditions. This technique is also employed to evaluate, and potentially control, the distillate composition. The latter is, however, a project currently under investigation.

In Figure 3; 1 is a screw-feeding system developed for both free-flowing virgin PTFE and milled waste PTFE, 2 indicates the pyrolysis reactor system with resistive furnace and, 3 is the Perkin Elmer Spectrum Two FTIR spectrometer. The hopper system (not shown) feeding the reactor has a capacity of 2 kg of polymer.

Figure 3: Pyrolysis setup at the University of Pretoria, Fluoro-Polymer Laboratory indicating pyrolysis reactor and Perkin Elmer Spectrum Two FTIR

The pyrolysis products are highly temperature and pressure dependent [1,2], with tetrafluoroethylene production favoured by low pressures (> 5 kPa abs.) and at moderate operating temperatures (650 – 700 °C) as indicated in Figure 4. Figure 4 is an example of the product selectivity mapping generated in the laboratory.

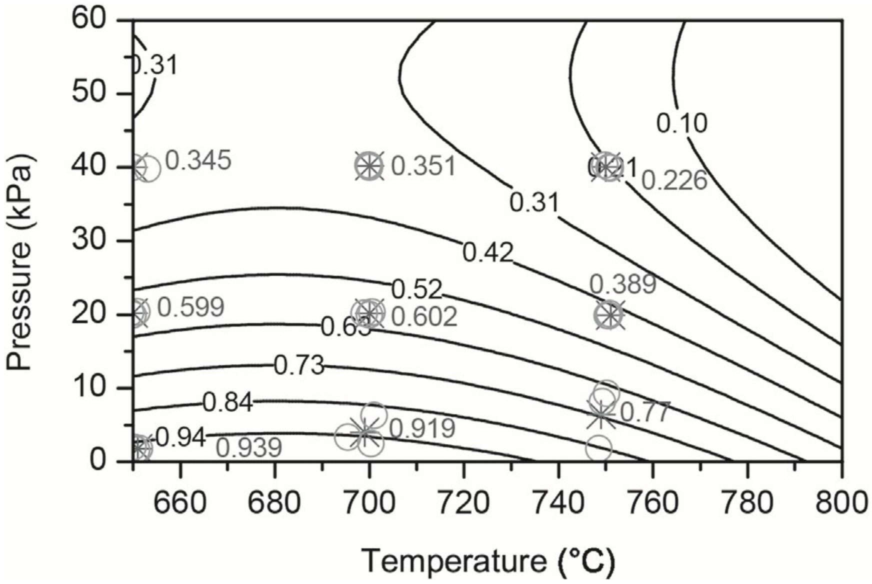

Figure 4: Model predictions of TFE fractions indicated by the contour plot and experimental values on which the model is based on (image taken from [2]).

The presented control system uses Beer's Law in association with in-house generated spectra of all possible pyrolysis products and determines the optimal operating conditions from the temperature and pressure dependency models described in [2]. The control system can accept any reasonable combination of dominant pyrolysis products (tetrafluoroethylene, hexafluoropropylene and octafluorocyclobutane) and accurately control the process to produce the optimal product fractions.

The major advantage of the control system is to alleviate difficulties in separation the desired products (typically TFE) in the downstream distillation process. A further advantage is the direct polymerisation of pyrolysis product gas to produce fluorinated ethylene-propylene to certain specifications.

In conclusion, the proposed body of work is a component of the progress made in the Fluoro-Polymer Laboratory to efficiently recycle polytetrafluoroethylene on a scale that can service the surrounding PTFE industry. An effective control system that minimizes by-products and optimizes product specification is a large step in the responsible management of PTFE waste.

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FROM "SILENT SPRING" TO PFOA CONCERN

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Silent Spring is a brilliant and controversial book, which was written by Miss Rachel Carson and published in 1962. The Times evaluated that "Carson's book has changed the world". The book revealed that the destruction of wildlife was caused by the widespread use of pesticides. Carson aroused a public awareness of protecting the enviroment where all the livings including us exist. The book had a great influence on the government policy and brought us with ecological consciousness. The book was recognized as one of the most influential books of the twentieth century.

DDT (dichlorodiphenyltrichloroethane) with excellent insecticidal properties are not enviromental friendly, which has been extensively discussed in Silent Spring. In 2001, this compound was classified as one of persistent organic pollutants (POPs). POPs are toxic, persistent, bioaccumulative and with long range transport potential. Two important fluorinated POPs are PFOS (perfluorooctanesulfonic acid) and PFOA (perfluorooctanoic acid). PFOA are widely used in emulison polymerization. The ban of PFOA results in many alternatives because we can not live in a world without fluoropolymers.

In recent years, we focus on the enviromental evaluation on those PFOA alternatives. In this confrence, we are going to provide some of our research results for further deep discussion.

In 2017, we reported on the occurrence of a novel perfluoroalkyl ether carboxylic acid, ammonium perfluoro-2-[(propoxy)propoxy]-1-propanoate (HFPO-TA), in surface water and common carp (Cyprinus carpio) collected from the Xiaoqing River and in residents residing near a fluoropolymer production plant in Huantai County, China.[1] In 2018, we reported on the occurrences of several perfluoroalkyl ether carboxylic and sulfonic acids (PFECAs and PFESAs), including hexafluoropropylene oxide dimer and trimer acids (HFPO-DA and HFPO-TA), ammonium 4,8-dioxa-3H-perfluorononanoate (ADONA), in surface waters from China (n = 106), the United States (n = 12), the United Kingdom (n = 6), Sweden (n = 10), Germany (n = 14), The Netherlands (n = 6), and Korea (n = 6). Results showed that HFPO-DA and HFPO-TA (median = 0.95 and 0.21, respectively) were frequently detected in all countries, indicating ubiquitous dispersal and distribution in global surface waters.[2] We also investigated the effects of HFPO-TA on mouse liver following 28 days of exposure to 0.02, 0.1, or 0.5 mg/kg/d of HFPO-TA via oral gavage. Compared with previously published toxicological data of PFOA, HFPO-TA showed higher bioaccumulation potential and more serious hepatotoxicity.[3] The occurrence, tissue distribution, and bioaccumulation of hexafluoropropylene oxide trimer acid (HFPO-TA), in the black-spotted frog (Pelophylax nigromaculatus) from China were reported for the first time. The bioaccumulation factor results (HFPO-TA > PFOA) suggest a stronger accumulative potential in the black-spotted frog for these alternative substances compared to their predecessors.[4]

As novel alternatives to perfluorooctanoic acid (PFOA), perfluoropolyether carboxylic acids (multiether PFECAs, CF3(OCF2)nCOO−, n = 2−4) have been detected in various environmental matrices; however, public information regarding their toxicities remains unavailable. To compare the hepatotoxicity of multiether PFECAs (e.g., PFO_2HxA, PFO_3OA, and PFO_4DA) with PFOA, male mice were exposed to 0.4, 2, or 10 mg/kg/d of each chemical for 28 d, respectively. Results demonstrated that PFO_2HxA and PFO3OA exposure did not induce marked increases in relative liver weight; whereas 2 and 10 mg/ kg/d of PFO_4DA significantly increased relative liver weight. Furthermore, PFO_2HxA and PFO_3OA demonstrated almost no accumulation in the liver or serum; whereas PFO_4DA was accumulated but with weaker potential than PFOA [5].

Although we have done some work, we realize that the risk evaluation of PFOA alternatives is a huge task and needs more support.

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GAS-LIQUID DIRECT FLUORINATION OF POLYMER POWDER

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Using of amorphous fluorine-containing polymers as materials for gas-separating membranes is highly promising. However, widespread use of these materials encounters with difficulties because of problems with the synthesis of the corresponding fluoromonomers: multistage process, low efficiency, high cost of raw materials and solvents. A possible way for overcoming such predicaments is preparation of perfluorinated and fluorine-containing polymers via direct fluorination of polymer precursors similarly as surface fluorination of polymer films. Non-destructive hydrogen-substitution fluorination of polymer powder in a stationary thermal mode can be carried out in a gas-liquid reactor where perfluorinated organic liquid inert to F_2 is used as a solvent for gaseous fluorine.

The experiments were conducted with a powder of several oxygen-containing polymers: poly(2,6-dimethyl-1,4-phenylene oxide), cellulose acetate, and ethyl cellulose. A particle size of polymers was about 5–10 μm. Perfluorodecalin (99%) was used as the inert liquid media. The gas-liquid-solid fluorination was carried out in a bubble stainless steel reactor.

The experiments showed that an increase in partial pressure of fluorine in a gas mixture with an inert diluting gas leads to proportional increases in the amount of the reacted fluorine. Meanwhile, a growth of the reaction temperature in the range 20–90 °C does not substantially affect the rate of fluorination of polymers.

The significant destruction of the polymer is not found, but a small amount of fluorinated oligomer is formed. The fluorinated oligomer is soluble in a perfluorodecalin with admixture of hydrogen fluoride. Further destruction of a polymer is observed in a small amount: only trace amounts of tetrafluoromethane and other fluorocarbons were found.

The fluorinated polymers was investigated by FTIR spectroscopy. The hydrogen-substitution fluorination of the poly(2,6-dimethyl-1,4-phenylene oxide) was found. The fluorinated poly(2,6-dimethyl-1,4-phenylene oxide) is only partly soluble in trichloromethane while pure polymer is completely soluble in this solvent. It was found that insoluble fraction (at maximum degree of fluorination) of the fluorinated poly(2,6-dimethyl-1,4-phenylene oxide) contains at least 48 wt.% of the fluorine (or degree of substitution – 85%).

The fluorination of cellulose acetate leads to a partially destruction of the polymer (with release of acetic acid) and obtaining of fluorinated cellulose.

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MODERN STATE OF RESEARCH ON THE PTFE STRUCTURE AND PROPERTIES

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The key fact that sheds light on the relationship between the structure and properties of PTFE is the correlation of mechanical properties with shear deformation of the lamellae [1]. The essence of the correlation is the existence of polycrystalline lamellae consisting of crystalline layers separated by amorphous regions, and the possibility of these layers, called crystalline slices, relative to each other (Fig. 1). The ease of shear deformation of the lamellae explains the cold fluidity and superplasticity of PTFE, the self-lubricating properties in tribo-conjugations, the preservation of plasticity in the region of cryogenic temperatures, etc.

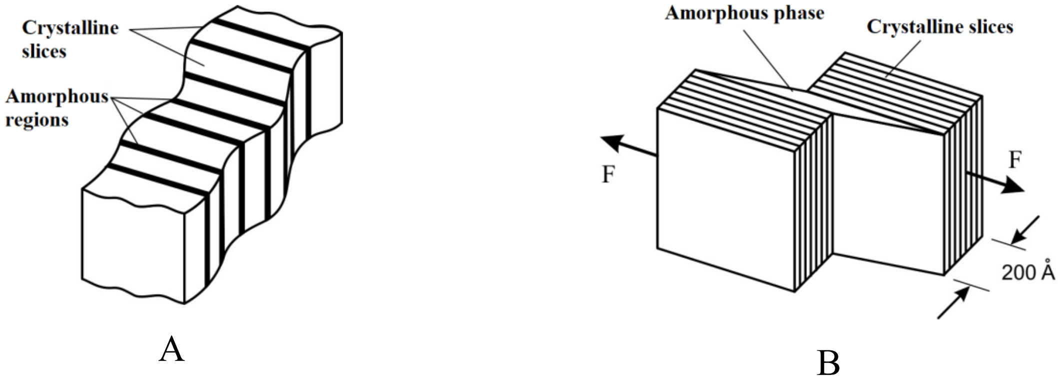

Fig. 1. Crystal lamella (A) according to electron microscopy and crystal slices in the process of shear deformation (B) [1].

Discussion questions related to the proof of the polycrystalline structure of lamellae in PTFE were considered in [2]. The model of coherent packing of fibrils in lamellae, proposed in [2], makes it possible to reconcile the data of electron microscopy, wide-angle and small-angle X-ray spectroscopy. A comparative analysis of the data of DSC, IR, densitometry and X-ray spectroscopy to study the structure of PTFE was carried out in [3].

The data accumulated in the world literature allow us to single out the main elements of the PTFE structure and, following the characteristic dimensions, arrange them in the following sequence (Fig.2) [3]: an elementary crystal cell (a ~ 0.566 nm, c ~ 1.951 nm), a fibril (diameter d ~ 15-20 nm, length l~10-30 μm), crystalline domain (in the direction (100) l ~ 100 nm), fibrillary lamella (thickness d ~ 300-500 nm, length l ~ 1-3 μm), grain mesostructures separated by regions with increased porosity (l ~ 100 μm).

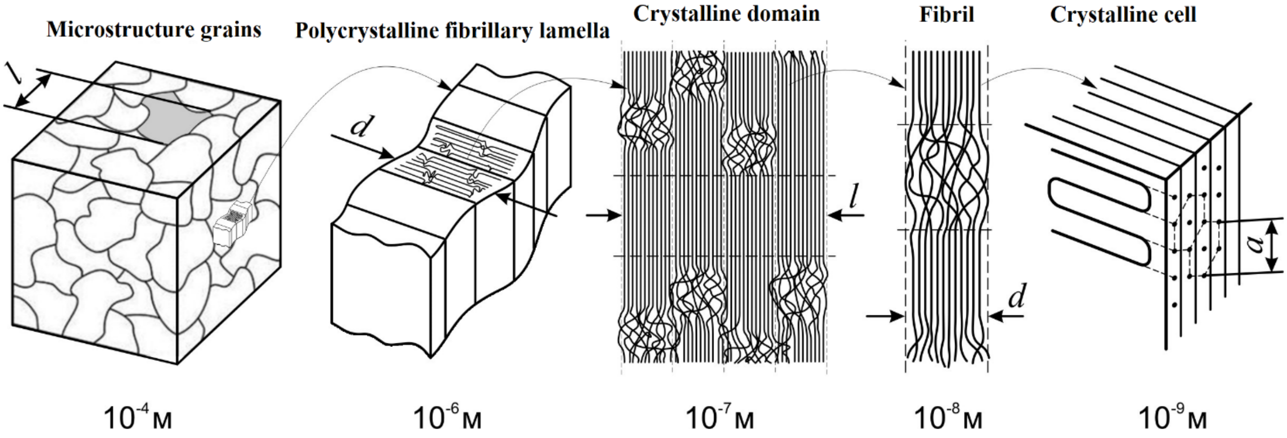

Fig. 2. Systematics of the structural elements of PTFE

The study of the laws of the effect of gamma irradiation on the structure and properties of PTFE made it possible to confirm the correlation of mechanical properties with the structure of lamellae, establish the nature of the delamination mechanism of wear and low radiation resistance, explain the mechanism of brittle fracture upon impact, etc.

One of the important results obtained recently is the development of systematics of the structural elements of PTFE irradiated above the melting point. In accordance with it, the structural elements of PTFE on the basis of characteristic size are arranged in the following sequence (Fig.3) [3]: an elementary crystalline cell (a ~ 0.566, c ~ 1.951 nm), a fibril (diameter d ~ 15-20 nm, length l ~ 10–30 μm), crystalline domain (coherence region in the direction (100) d ~ 15–20 nm), spherulite with radial packing of fibrils (diameter d ~ 50-100 μm).

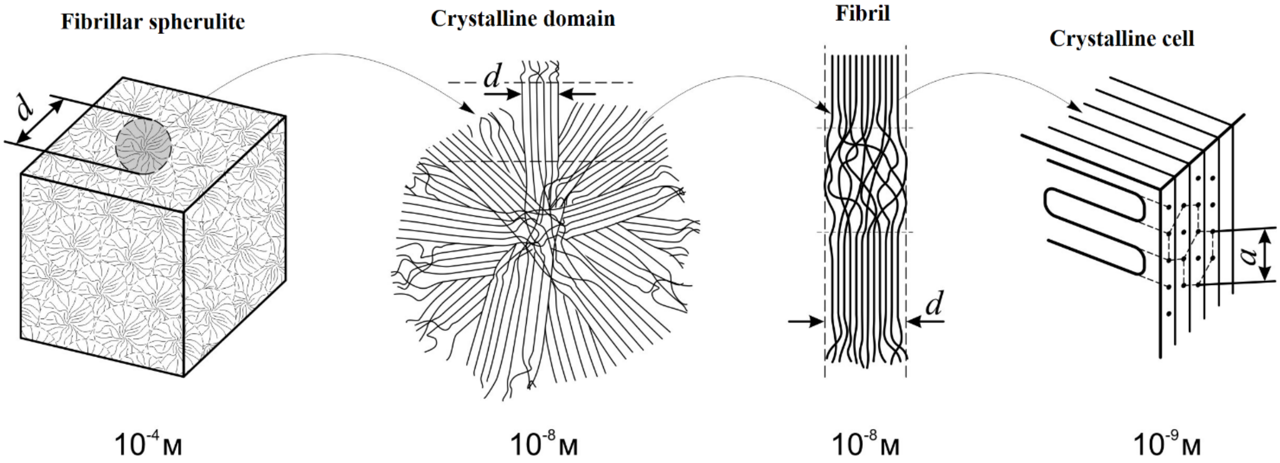

Fig. 3. Systematics of the structural elements of PTFE irradiated above the melting point.

The proposed systematics allowed us to explain the changes in the properties of PTFE irradiated in the melt, which were previously perceived as abnormal.

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X-RAY STRUCTURAL ANALYSIS OF THE GAMMA IRRADIATION EFFECT ON THE PTFE CRYSTALLITE SIZE

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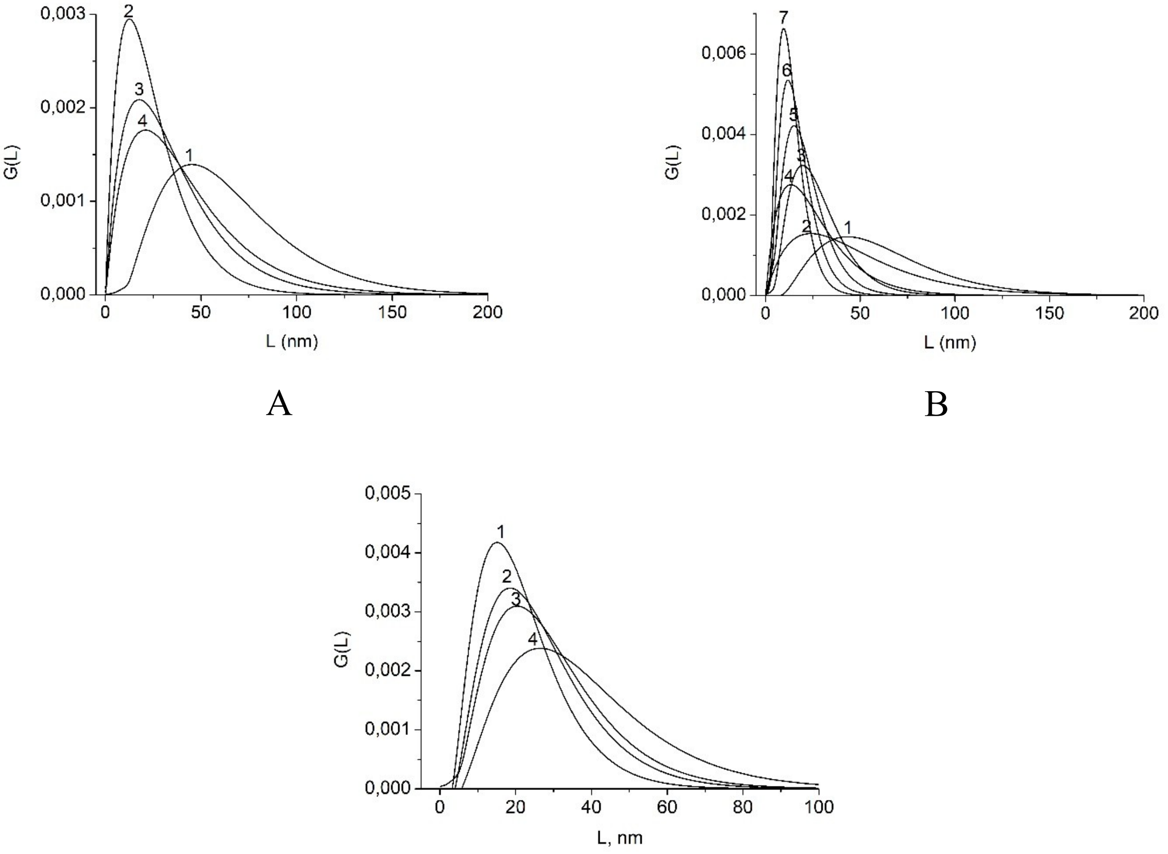
Interest in the study of the structure of PTFE has not waned since the middle of the last century and is due to its high practical significance, as well as unexpected and often not typical manifestations of physicochemical properties. The size of the crystalline domain and the influence of high-energy radiation on it still remains a controversial issue concerning the structure of PTFE.

The purpose of this work was to study the effect of gamma irradiation on the crystallite size in PTFE using wide-angle X-ray spectroscopy. The object of the study was high molecular weight PTFE (MW ~ 5×10^6) of suspension polymerization of grade PN. Block samples were made by the standard method of cold pressing 30 MPa), followed by sintering (380 °C). The samples were irradiated in an inert atmosphere with ^{60}Co gamma rays (1.25 MeV) to an absorbed dose of 2000 kGy. Diffractograms were recorded on a Bruker D-8 diffractometer in the point-to-point scanning mode in the range of 0–100° with a step of 0.01° (on a scale of 2θ) and an accumulation time of 60–90 s at each point. The average size of coherent scattering blocks $<G(L)>$ and the distribution of crystallites in size $G(L)$ were determined following the procedure proposed in [1] from the analysis of the shape of the reflection (100) at $2\theta = 18$ ° for CuK_α.

The morphology of PTFE is characterized by the formation of polycrystalline lamellae with plane-parallel stacking of fibrils (and polymer chains) perpendicular to the large planes of lamellae. Gamma irradiation above the melting point of crystallites leads to the formation of spherulite-like structures with a radial orientation of the fibrils [2]. The behavior of the function *G(L)* was studied at significantly different temperatures of gamma irradiation (at room and above the melting point), as well as for PTFE with plane-parallel and radial packing of the chains under the same irradiation conditions.



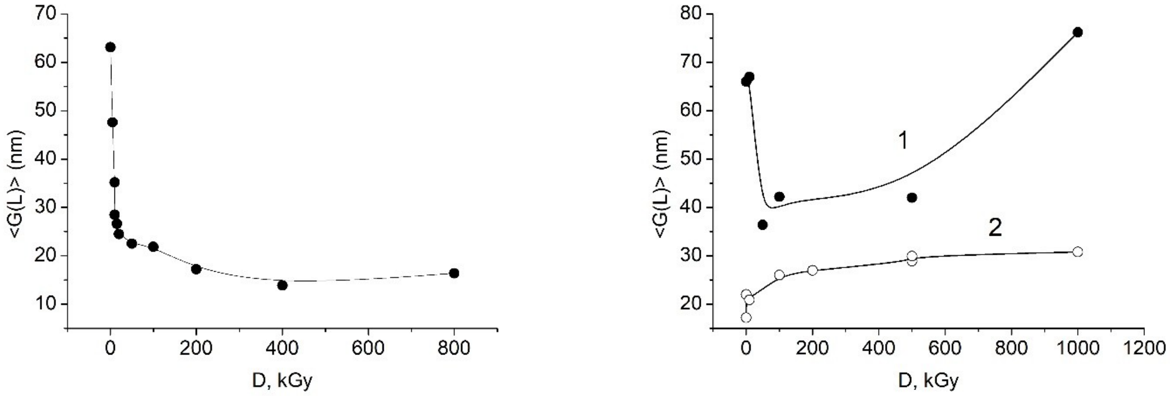
A

B

C

Fig. 1. The distribution of crystallites in size *G(L)* at various doses of radiation.
A - gamma irradiation lamellar PTFE at room temperature, *D*, kGy: 1 – 0, 2 – 50 3 – 500 4 – 2000; B – gamma irradiation of lamellar PTFE above the melting point, *D*, kGy: 1 – 0, 2 – 5, 3 – 10, 4 – 20, 5 – 100, 6 – 200, 7 – 400; C – gamma-irradiation of spherulite-like PTFE at room temperature, *D*, kGy: 1 – 0, 2 – 200, 3 – 1000, 4 – 2000.

From fig. 1 it's seen that the function *G(L)* essentially depends on the irradiation conditions. For lamellar PTFE at room temperature at low doses (less than 50 kGy), a sharp narrowing and shift of *G(L)* towards small values is observed, but then with further increase of the absorbed dose, function *G(L)* is significantly broadened (fig.1A). Irradiation of lamellar PTFE above the melting temperature leads to a monotonic narrowing and displacement of *G(L)* towards small values (fig. 1B). Irradiation of spherulite-like PTFE at room temperature leads to a monotonic broadening of the function *G(L)* and its shift towards larger values (fig. 1B).



A B

Fig. 2. Dependence of the average crystallite size <G(L)> on the absorbed dose.
A – gamma-irradiation of lamellar PTFE above the melting point, B - gamma-irradiation of PTFE at room temperature (1 – lamellar PTFE, 2 – spherulite-like PTFE).

The described patterns are well illustrated by the dependence of the average integral crystallite size *<G(L)>* on the absorbed dose (fig. 2). It is noteworthy that the *<G(L)>* crystallite size limit (about 20 nm) approximately corresponds to the transverse size of the fibrils (fig. 2A), as well as the significantly higher resistance to gamma irradiation of the spherulite-like structure compared to the lamellar structure (fig. 2B).

The authors are grateful to S.A.Ivanov for taking diffractograms of the studied samples.

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RADIATION-CHEMICAL SYNTHESIS AND PROPERTIES OF TETRAFLUOROETHYLENE TELOMERES OBTAINED IN CHLOROSILANES, AND THEIR USE FOR THE HYDROPHOBIZATION OF VARIOUS MATERIALS.

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Fluorinated organosilicon compounds are widely used to create hydrophobic and superhydrophobic coatings on various materials. Such coatings have unique characteristics: water resistance, resistance to biofouling and inorganic contaminants, corrosion resistance, self-cleaning, and anti-icing properties . Methods for preparing these compounds are based on functional reactions of organofluorine compounds with organosilicon compounds. One of the ways to obtain compounds of this type is the telomerization of fluoroolefins in silanes.

The kinetics of the process of radiation telomerization of TFE in dimethyldichlorosilane (DMDS) and trimethylchlorosilane (THMS) was studied by the method of kinetic calorimetry. TFE telomeres were obtained with the general formula A(TFE)nB, with active silane terminal groups A, B (Cl and $(CH_3)_2ClSi$ and $(CH_3)_3Si$). The average chain length of telomeres synthesized at various concentrations of TFE was calculated from the results of elemental analysis for chlorine content. The chain length of telomeres obtained in DMDS is ~ 35 and 70 TFE units, and in TMHS ≈ 20 and 30 TFE units at monomer concentrations of 0.2 and 1.0 mol / l, respectively [1].

The molecular structure of TFE telomers in chlorosilanes was studied by IR spectroscopy. Comparison of the spectra of the telomers, PTFE , and silanes shows that the most intense bands in the spectra of the telomers synthesized in both chlorosilanes, are at 1208 and 1152 cm^{-1} (ν_{C-F} of CF_2 groups). Along with these bands, the spectra exhibit several additional bands at 700–1300 and 3000 cm^{-1} due to the vibrations of the telomer end (silane) groups.

Solutions of TFE telomeres obtained in TXMS and DMDS can be used to hydrophobize various materials (glass fabrics, textiles, highly porous heat-shielding materials based on oxide fibers, etc.), since the presence of silane end groups in telomeres can provide good telomer adhesion to the substrate the liquid-phase state of the low-molecular-weight polymer TFE allows the use of traditional liquid-phase technologies (impregnation, pulverization).

Studies have been conducted on the use of such telomers for modifying aluminosilicate tissue. It is shown that when applying 3-4% telomeres on glass cloth and subsequent heat treatment at 150° C, it becomes hydrophobic. The wetting angles of the obtained samples are 105°-115°.

The urgent task of waterproofing highly porous heat-shielding materials based on quartz fibers, characterized by high hydrophilicity and used in extreme conditions (low temperatures, high humidity). TFE telomeres in TXMS were used to hydrophobize such materials (TZMK-10, TKV). Samples of hydrophobic TZMK-10 were obtained. Water absorption of samples decreases by 2 orders of magnitude; wetting angles exceed 1000 when the telomere content is ~ 5–6%.

The work was supported by the Basic Research Program of the Presidium of the Russian Academy of Sciences No. 55 “The Arctic is the scientific basis of new technologies of development, preservation and development” and the theme of the State Task No. 0089-2019-0008 using the USS «Gammatok-100» and the equipment of the Multi-User Analytical Center of IPCP RAS

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EFFECT OF GAMMA-IRRADIATION ON THE SURFACE PROPERTIES OF POLYTETRAFLUOROETHYLENE

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PTFE has high anti-adhesive properties and low surface energy (SE), which limits its compatibility with other materials. Increase SE PTFE is an urgent task when creating composites, adhesive of materials and many other practical applications. It is known that exposure to ionizing radiation leads to an increase in the surface energy of PTFE [1]. The mechanism of this increase in SE is not well understood.

The goal of the work was to study the laws of the effect of gamma irradiation on the surface properties of PTFE, depending on its supramolecular structure and irradiation conditions, as well as quantitative analysis of dispersion and polar intermolecular interactions in irradiated PTFE.

The object of the study was high molecular weight PTFE (MW ~ 5×10^6) of suspension polymerization of grade PN. Samples with different supramolecular structures were investigated: nonsintered powder of PTFE (F4PN), sintered PTFE (F4) and the pre-irradiated in the melt PTFE (F4RM). Surface energy and adhesion work were calculated using the values of wetting contact angles for water and tetradecane. Wetting angles were measured by the method of a lying drop on a KRUSS EasyDrop instrument with DSA1v1.92 software. The drop volume was 4 μl. In order to clarify the role of dispersion interactions in changing surface properties, the curves of isothermal decay of polarization and depolarization currents were studied, as well as quantitative calculations of the energy of dispersion interaction in the framework of the Lifshitz model. The samples were irradiated with ^{60}Co gamma-quanta (1.25 MeV) at room temperature in air. In tabl. 1 shows the relative changes in the components of the surface energy depending on the absorbed dose.

Table 1

Relative changes (%) of the dispersion and polar components of the surface energy of PTFE (η_s^{dis} and η_s^{pol}) and the work of adhesion for water $\eta(H_2 0)$ and tetradecane $\eta(C_{14}H_{30})$ depending on the absorbed dose.

Sample	η_s^{dis}	η_s^{pol}	$\eta(H_2 0)$	$\eta(C_{14}H_{30})$
F4PN-100	5.5	106	7.23	2.83
-200	5.5	253	12.5	2.83
-500	7.6	453	19.0	3.70
F4-100	3.19	260	11.9	3.70
-200	5.10	540	20.2	3.92
-500	8.20	1980	45.5	3.90
F4RM-100	2.43	197	13.1	0.64
-200	4.52	468	25.0	2.37
-500	6.20	1203	47.0	3.0

In the framework of the Lifshits theory, a quantitative analysis of the intermolecular interaction of the test liquid with the surface of irradiated PTFE was carried out for samples F4PN, F4 and F4RM. The calculations used data on changes in the dielectric increment and density depending on the absorbed dose. In tabl. 2 summarizes the calculated values of the relative changes in the Van-der-Waals adhesion work, taking into account the radiation-dielectric effect (RDE) (η_ε^{dis}) and density (η_ρ^{dis}) at various absorbed doses.

Table 2

Relative changes (%) of the Van-der-Waals (η^{dis}) component of the work of adhesion for water and tetradecane, calculated according to the Lifshitz theory

Sample	$\eta_\varepsilon^{dis}(H_2 0)$	$\eta_\varepsilon^{dis}(C_{14}H_{30})$	η_ρ^{dis}	$\eta_{\varepsilon,\rho}^{dis}(H_2 0)$	$\eta_{\varepsilon,\rho}^{dis}(C_{14}H_{30})$
F4PN-100	0	0	0	0	0
-200	0	0	0	0	0
-500	0.01	0.003	~0	0.01	0.003

F4-100	5.43	1.53	2.7	8.13	4.23
-200	5.65	1.60	3.0	8.65	4.60
-500	5.70	1.60	3.5	9.20	5.10
F4RM-100	5.50	1.60	0.3	5.80	1.90
-200	5.70	1.60	0.4	6.10	2.00
-500	5.77	1.60	0.6	6.37	2.20

From the comparison of the data presented in tabl. 1 and 2, it can be seen that there are differences between the experimental and calculated values of the changes in the relative work of adhesion for samples F4PN, F4 and F4PM. These differences can be explained by a significant difference in the concentration of ion pairs in irradiated PTFE [1]. According to the ion-pair mechanism, the RDE in irradiated PTFE is determined by the kinetic mobility of holes in the field of localized electrons [2]. In the case of the PTFE-water system, a part of the mobile holes near the surface of the PTFE, which left the sphere of the Coulomb interaction of electrons, will have an orienting effect on the water dipoles — the ion-dipole interaction [3]. The obtained results testify to the unified nature of changes in the dielectric characteristics, the work of adhesion and the polar component of SE during irradiation of PTFE. Based on the results obtained, an ion-dipole mechanism for increasing the polar component of the surface energy and the adhesion of PTFE under gamma irradiation was proposed. This mechanism is realized due to the formation of localized electrons and quasi-free holes in the volume of PTFE.

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INVESTIGATION OF THE PHYSICAL AND MECHANICAL CHARACTERISTICS OF A PLANED SHEET OF F-4M USED FOR LINING EQUIPMENT

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The production of technological equipment with the use of protection against aggressive environments sets the task of studying in detail the behavior of the material intended for lining the inner surface of apparatus under various exposure conditions and test temperatures. Among the most promising in terms of stability of aggressive media in a wide range of temperatures is polytetrafluoroethylene [1, 2, 3].

LLC "First Fluoroplastic Plant" for works related to the lining of equipment uses a sheet obtained by the method of gouging large-sized blanks from modified fluoroplast-4, supplied by HaloPolymer JSC.

The aim of the study is to obtain experimental dependences of the tensile strength (σ) and elongation (ε) at break, Young's modulus (E) and pore opening index (SVI) versus temperature (T) in the range from plus 22 to plus 250 °C.

The studies were carried out in the laboratory of technical control of PFZ LLC using a specialized machine for high-temperature tests of MPC 500 and using test methods [4-7].

To study behavioral trends, experimental data were displayed in the form of temperature dependence of the studied characteristics.

In fig. Figures 1 and 2 show the experimental dependences of the tensile strength and elongation at break of the F-4M sheet on temperature, respectively.

Data analysis in fig. 1 shows that the common point for the experimental points is a decrease in the value of the breaking stress with increasing temperature (T). At the same time, at the standard temperature for testing fluoroplastics plus 23 ± 2 °C, a difference in σ is observed, explained by the properties of the initial batches of fluoroplast-4M used for the manufacture of planed sheets.

With increasing temperature, a decrease in the scatter of experimental values for tensile strength is observed, and at temperatures above 150 °C the experimental values of σ practically coincide for different batches when the experimental error is taken into account, which is explained by the reaction of the material to external action and the formation of the structure along the stress axis.

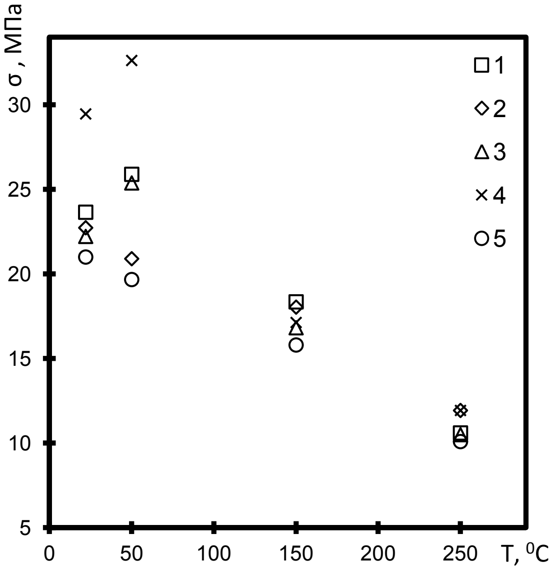


Fig. 1 Dependences of tensile strength on temperature for different batches of sheet Experiment: 1 ... 5 lots of sheet F-4M

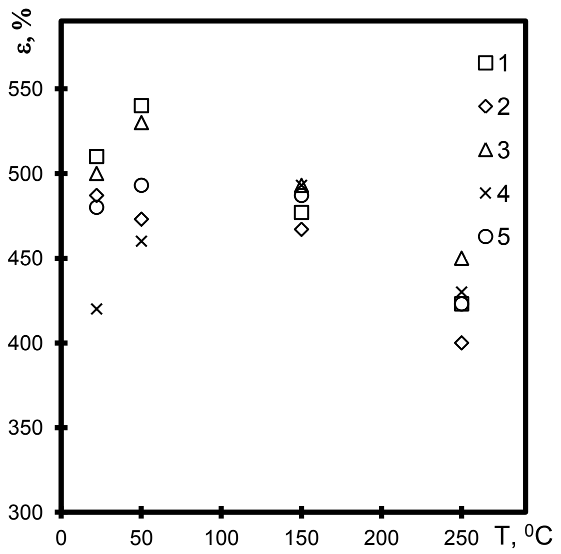


Fig. 2. Relative elongation versus test temperature for batches of material Experiment: 1 ... 5 lots of sheet F-4M

For the data presented in fig. 2, a nonlinear behavior of the deformation characteristic with increasing values of T is characteristic, which manifests itself in the peak of величины in the temperature range ~ 50 °C.

As an explanation of the discovered effect, we can assume that, with increasing temperature, it leads to macromolecule vibrations and some ordering of the material microstructure occurs, which manifests itself in the orientation of the long bonds of the molecule and, as a result, an increase in the relative elongation.

At a temperature higher than 50 °C, the magnitude of the amplitude of thermal vibrations is such [4, 5, 7] that it already plays the role of a softening element due to the weakening of the intermolecular bonds, and as a result, degradation of the величины value with increasing values σ of T should be observed that they demonstrate the experimental data in Fig. 2.

Young's modulus is essential in the study and description of the deformation behavior of the fluoroplastic in the region of linear proportionality between the acting tensile force and elongation of the sample. From the standpoint of describing the behavior of the material at different test temperatures, this characteristic has important practical and theoretical (applied to the design calculations) value.

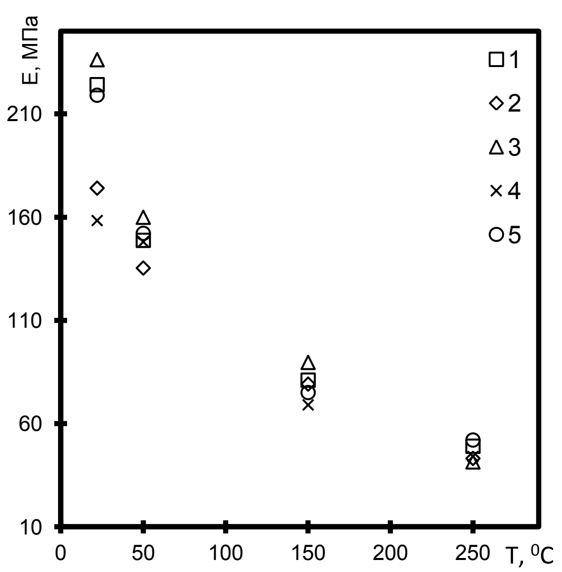


Fig. 3 Dependence of Young's modulus on test temperature for various batches of material. Experiment: 1 ... 5 lots of sheet F-4M

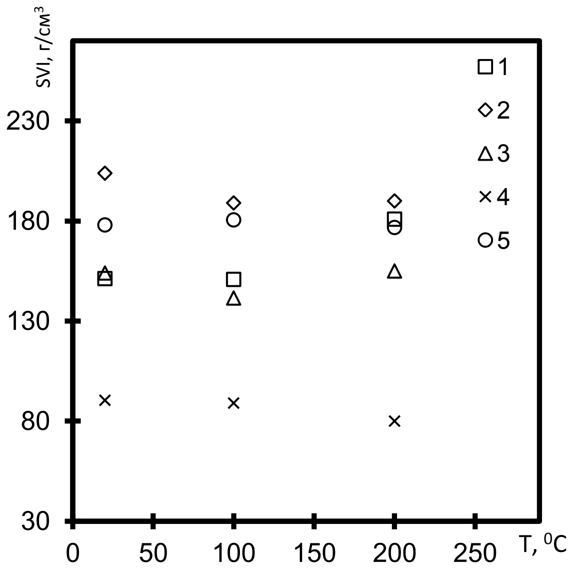


Fig. 4 The dependence of the pore opening index on the test temperature for various batches of material. Experiment: 1 ... 5 lots of sheet F-4M

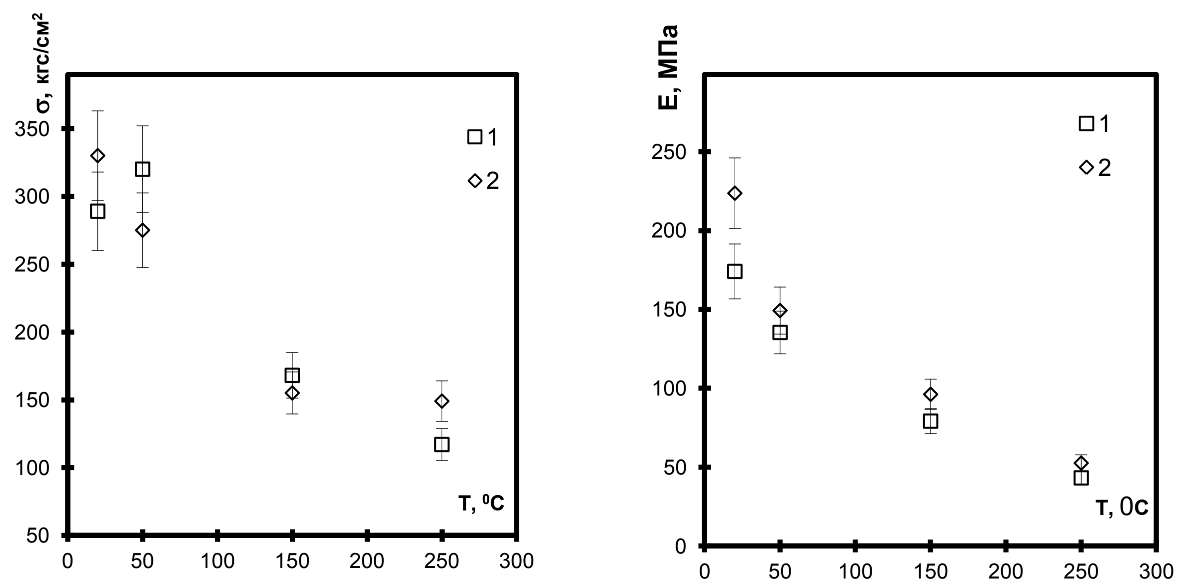
In fig. Figure 3 shows the experimental dependences of Young's modulus on test temperature for various batches of material.

For this graph, there is a decrease in the values of Young's modulus with increasing temperature. Moreover, for the test points at T = 22 °C there is a difference in the values of E for different batches of the polymer, and with an increase in temperature more than 100 °C this difference is comparable with the experimental error. The reason for the discovered phenomenon is the polymer structure formed during the sintering and cooling of the workpiece, carried out according to one technological process.

In fig. Figure 4 presents the SVI data for the beginning of a planed sheet, in the analysis of which, first of all, it is noteworthy that there is no general pattern in the behavior of the experimental points, and the obtained data do not indicate the presence of any dependence. Points (4) are distinguished as a difference from all experimental data, for which the values of the pore opening index are much smaller than for other batches; this difference is apparently explained by the properties of the initial polymer [4].

The anisotropy of the properties of the planed sheet was determined by comparing its characteristics at the beginning and end of gouging.

Comparative characteristics of a planed sheet are shown in Fig. 5.



a b

Fig. 5 Determination of the anisotropy of the physicomechanical properties of the sheet at different temperatures by the example of one batch.
a - tensile strength, b - Young's modulus. Experimental data: 1 – planing start 2 – end of planing

When considering the experimental points shown in Fig. 5a and fig. 5b draws attention to the close values f these characteristics in the material properties of the same preform when the test sample is located on its surface or in depth. It should be noted that the difference found is quite comparable with the experimental error, which includes not only random systematic error, but also includes the error associated with the structure of the material. Probably in this case. the error associated with the structure of the material in view of the characteristics of the properties of the modified PTFE-4 is predominant [1, 4, 5].

In conclusion, it should be noted that the obtained experimental temperature dependences of the physicomechanical characteristics of the F-4M planed sheet make it possible to predict the behavior of the fluoroplastic lining during equipment operation, to optimize the design of equipment protected by fluoropolymers and to ensure high quality of the delivered products .

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NEW DIRECTIONS FOR THE USE OF FLUOROPOLYMERS IN THE PROCESS OF MODIFYING SYNTHETIC FIBROUS MATERIALS

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The unique properties of fluoropolymers – low surface energy, extremely low friction coefficient, extremely high chemical inertness – make them effective modifiers for fibrous materials. Studies of the surface and bulk modification of fibrous materials are carried out in G.A. Krestov Institute of Solutions Chemistry of the Russian Academy of Sciences for a long time in order to improve the quality of fibrous materials and give them new properties. In particular, a number of effective directions for the modification of synthetic fibrous materials are implemented jointly with other institutes of the consortium “Fluoropolymer Materials and Nanotechnology” and are based on the use of fluoropolymers, fluorine-containing oligomers, as well as direct fluorination of fiber-forming polymers.

One of the developments in the field of modifying polypropylene filaments is a method for improving their consumer characteristics, based on the introduction of small amounts of ultra-dispersed polytetrafluoroethylene (PTFE) into the melt of a fiber-forming polymer at the stage of forming filaments [1]. When ultra-dispersed PTFE is input into polypropylene, the latter is persisted as a separate phase. It is distributed in the filaments relatively evenly. The nanoscale fraction of PTFE provides an increase in interfacial adhesion. Therefore modified polypropylene filaments possess an increased strength, high elasticity modulus and improved processability. Matted filaments can be obtained without use of titanium dioxide concentrate. For mass dyed filaments the filament breakage is greatly reduced. Fabrics made of modified polypropylene filaments have high modulus of elasticity and wear resistance, as well as increased hydrophobicity. Modified nonwoven polypropylene material is characterized by highly uniform density of the fabric. Modification provides higher strength down the length and across the width and enhanced resistance to deformation, improved spinning, and prolonged time of operation of the equipment without technological maintenance.

Another direction of modification of polypropylene filaments in the process of their formation is an easy and effective method of giving polypropylene yarns the same extremely high chemical resistance as fluoropolymers yarns have [2]. The method is based on the formation of an ultrathin, continuous and even coating of PTFE on a surface of each filament forming yarn. The adhesion of PTFE coating to polypropylene is provided by applying of a diluted suspension of high disperse PTFE on a surface of a semi-hardened polypropylene yarn at the oiling stage. Later, the yarn is subjected to orientational stretching. In the process of stretching the coating becomes uniform and oriented thanks to an ability of PTFE to pseudo-fluidity and a high coefficient of thermal expansion. The polypropylene yarn with a PTFE coating gets an extremely high resistance to the influence of nitric acid and sodium hydroxide. Its frictional coefficient is close to the frictional coefficient of PTFE and the strength is much higher than the strength of a common polypropylene yarn. The applied coating has a high resistance to an intensive abrasive action.

However, along with many advantages, PTFE-coated yarns have a number of disadvantages, in particular, they have a very high surface electrical resistance. To reduce the surface electrical resistance, magnetite nanoparticles, previously stabilized by a heat-resistant surface-active agent – sodium stearate – are input into the PTFE-based coating structure. We found that the introduction of stabilized magnetite nanoparticles into the coating structure allows us to reduce the surface electrical resistance of the polypropylene filament from 10^{15} Om to 10^{7} Om. In addition, these yarns acquire excellent barrier antibacterial properties against Gram-negative bacteria *Escherichia coli* and satisfactory – against Gram-positive bacteria *Staphylococcus aurous*.

An important direction of surface modification of the finished polyester fabrics is imparting them increased hydrophobic properties due to the formation on the surface of each individual yarn of an ultrathin coating with the properties of fluoropolymers. We achieved this goal by treating the fibrous material with the solutions of low molecular weight fraction of ultra-dispersed PTFE in supercritical carbon dioxide or with the solutions of tetrafluoroethylene telomers synthesized in acetone, butyl chloride and trimethylhorosilane [3]. We found that the treated fabric acquires a high hydrophobicity, a uniquely low water absorption and a high resistance to operational stress.

We also carried out the directional change of the hydrophilic-hydrophobic properties of synthetic fibrous materials using the method of their direct gas fluorination. A treatment of polypropylene nonwoven fabric with F_2/N_2 mixture highly improved the barrier antibacterial properties relatively to test bacteria – Gram-positive *Staphylococcus aureus* (total reproduction suppression) and partially for Gram-negative *Escherichia coli*. A treatment with $F_2/N_2/O_2$ mixture totally suppressed *Candida albicans* microfungus reproduction [4]. Polypropylene nonwoven fabric tensile strength was slightly increased after fluorination. This is a consequence of increasing the compactness of the structure of the surface layer of the cloth after fluoridation.

The ability to impart an improved wettability to polyester fabric as a result of direct fluorination has been demonstrated. We found that the fluorination of polyester fibrous materials by gas mixtures containing 10% vol. fluorine, leads to a significant change in the surface energy of the polymer material [5]. Introduction to the fluorinating mixture 10% vol. oxygen causes the formation on the surface of the polyester material of an additional amount of oxygen-containing groups, which provide an increase in the surface energy of the fiber and its wettability. As a result of fluorination, the moisture absorption of the polyester fibrous material also significantly increases.

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RUBBER-TO-METAL ADHESION-ENHANCING MODIFIER FOR THE FLUOROELASTOMER-BASED RUBBER

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The goal of the study is to increase rubber-to-metal adhesion while retaining the rubber's most important properties. The rubber in question is hexafluoropropylene and vinylidene fluoride copolymers based.

Cobalt salts of weak acids are known to exhibit adhesion promotor properties and to enhance the rubber-to-metal adhesion [1, 2, 3].

To improve the rubber-to-metal adhesion we used a cobalt salt of 2-sulfobenzoic acid imide (CSSBAI). The CSSBAI was obtained as a precipitate upon draining aqueous solutions of cobalt chloride and sodium salt of 2-sulfobenzoic acid imide, then the precipitate was filtered off and dried up at room temperature.

The compositions of the tested rubber compounds are provided in Table 1.

Table 1

Rubber compound composition

Components	No additives	CSSBAI 0.5 pbw	CSSBAI 1.0 pbw	CSSBAI 1.5 pbw	CSSBAI 2.0 pbw
SKF-26	67.0	69.0	67.0	65.0	63.0
SKF-26 ONM	33.0	31.0	33.0	35.0	37.0
Baryte	30.0	35.0	30.0	25.0	20.0
Vulcaftor F (1,1-bis (4-hydroxyphenyl) – 2,2,3,3,4,4,5,5-octafluorop-entane)	2.0	1.5	2.0	2.5	3.0
Magnesium oxide	4.0	3.0	4.0	5.0	6.0
Calcium hydroxide	6.0	5.0	6.0	7.0	7.0

Triethylbenzylammonium chloride	0.3	0.2	0.3	0.4	0.5
Cobalt salt of 2-sulfobenzoic acid imide	–	0.5	1.0	1.5	2.0

The rubber stocks' viscosity was measured per GOST 10722-76. The stocks were vulcanized at 175°Celsius for 20 minutes. The tensile properties were measured per GOST 270-75. The rubber-to-metal adhesion strength was determined by means of the N(H)-method, using 9L15/27A cord as per GOST 14311-85.

The properties of the tested rubber compounds are provided in Table 2.

Table 2

Rubber compounds properties

Indic. name	No additives	CSSBAI 0.5 pbw	CSSBAI 1.0 pbw	CSSBAI 1.5 pbw	CSSBAI 2.0 pbw
Viscosity MB 1 +10 (120 ° C), Mooney units	123	113	136	113	115
Conditional stretching strength, MPa	8.3	8.5	8.6	7.9	9.0
Stretching strain at 50% elongation, MPa	1.7	1.6	1.5	2.2	2.4
Stretching strain at 100% elongation, MPa	2.6	2.2	2.1	3.6	4.3
Relative lengthening at breaking, %	340	370	340	310	290
Rubber-to-metal adhesion strength, N	37	47	48	52	59

The use of CSSBAI as a component of the rubber compound based on vinylidene fluoride and hexafluoropropylene copolymers improves the rubber-to-metal adhesion. The improved rubber-to-metal adhesion is explained by the action of the proposed modifier in the substitution reactions occurring on the metal's surface and the release of cobalt ions onto the interphase surface at vulcanization. Such ion release results in the formation of additional bonds between the rubber and the metal. The use of CSSBAI as a component of the rubber compounds based on general purpose natural and other kinds of rubbers also improved the rubber-to-metal adhesion.

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TRIBOLOGICAL PROPERTIES OF RADIATION-MODIFIED FLUOROCARBON EVALUATION

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Introduction. The reliability and life-time of the special purpose and ordinary vehicles largely depend on the phenomena of friction in the machines' parts and the wear thereof. The wear results in the units losing their air/leak tightness and components alignment and the loss of movements accuracy. There occur jams, shocks, vibrations leading to breakdowns. Friction causes power losses, units overheating, transmitted forces reduction, fuel/other materials consumption increase. Friction is beneficial for the operation of brakes, clutch and wheels traction. The phenomena of friction and wear are interrelated: friction leads to wear, while the wear of the parts' surfaces during operation leads to a change in friction. Polymers play special role in engineering. These materials are noted for their versatility in use, high chemical and thermal resistance, sufficiently high strength and good anti-friction properties. Major progress has been made in recent years in tribological engineering regarding the development and manufacture of composites. A large number of studies have been devoted to the issues of friction and wear of these materials, lubricated and not.

In relation to the aforesaid issues the objective of the given study is to increase the reliability of water-lubricated plain bearings through introduction of mesogenic surfactants. To achieve the stated objective we were supposed to cope with and solve the following tasks and problems:

1. To run model tribotechnical tests of neonol-class additives in a wide range of concentrations and friction modes;

2. To perform a series of tribological studies of aqueous nonionic surfactants solutions to explain the self-organization effects on friction.

Materials and methods. As the friction pair materials, we chose the most common material, i.e. steel 45 (M_1) and radiation-modified fluoroplast-4 (RMF-4)

(M_2) In the study we used the radiation-modified polytetrafluoroethylene [1] obtained at low radiation exposures close to the crystallite melting point.

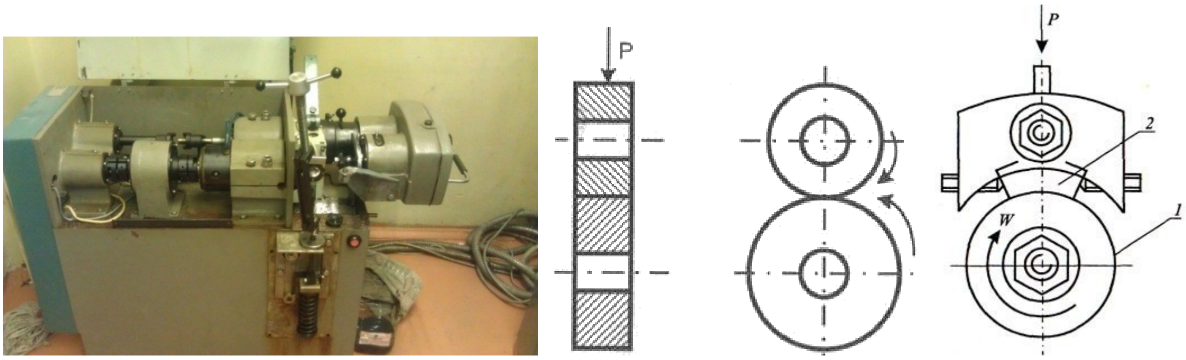
We used commercially available surfactants. It is feasible to run a three-stage wear test due to a great number of factors affecting friction and wear:

testing the materials for friction and wear in a laboratory (the SMTs-2 friction machine). Testing the materials' wear resistance depending on the friction modes;

testing the materials for the friction wear in various technological environments and at various friction modes;

materials bench-testing.

We used the SMTs-2 (by Tochpribor, Ivanovo, Russia) friction/wear bench to test the antifriction properties of polymers. The testing bench is of an open kinematic circuit type, where one of the samples is stationary. The sliding friction mode is in operation when the test specimen at a given load (*P*) slides upon a rotating disk and wears out. The disk-disk and disk-insert test is shown in Fig. 1. The friction occurred between a metal disk 50 mm in diameter and 12 mm in width and a polymer sample (Fig. 2). Allowable load measurement error is ± 5% of reading. The torque on the rotating disk's shaft was measured with a non-contact induction sensor. Electrical signals from the sensor's measuring coils are fed into the comparison electrical circuit and further on to the KSP-005 potentiometer, mounted in the control cabinet.



a *b* *c*

Fig. 1. The SMTs-2 friction bench: *a* – appearance; *b* – disk-disk friction test; *c* – disk-insert friction test

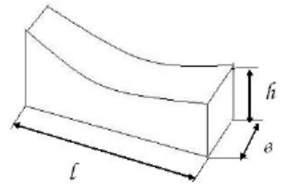
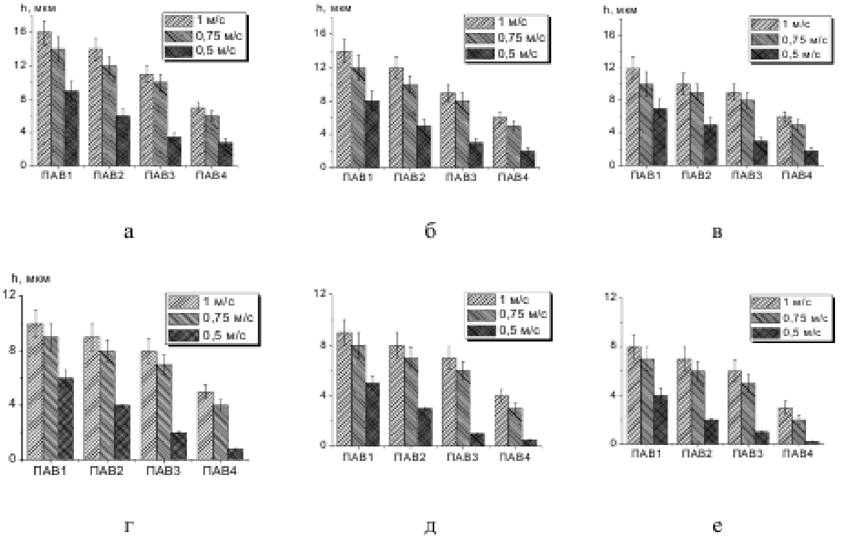


Fig. 2. Friction and wear test polymer sample, where *l* – length; *w* – width; *h* – height

Polymer samples size *d*=50 mm, *b*=10 mm. The samples' surface roughness is of grade 8 per GOST 2789-73. Disks of *d*=50 mm and thickness *15* mm, made of 45 steel (GOST 1050-60) HRC 50 were used as counterbodies. The disks' surface roughness was of grade 9 per GOST 2789-73. We chose the surface roughness grade to ensure the quickest running-in of the friction pair. The friction pair load is one of the main criteria in assessing the polymer materials wear resistance. **The study outcome and discussion** In a rather complex way the polymers' wear-resistance depends on the load, which determines the actual contact area, the deformation area, the average contact spot and the friction force. An increase in load at a constant sliding speed indirectly (through an increase in temperature) affects the wear resistance and fatigue properties of polymeric materials. The graphs shown in Fig. 3 demonstrate the behavior of polymers in the technological media at the constant temperature while under various loads.



а б в

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Fig. 3. Linear wear of water-lubricated friction pairs at: a - 5 wt. %, b – 10 wt. %, c – 15 wt. %, d – 20 wt. %, e – 30 wt. %, f – 40 wt. % aqueous solution of nonionic surfactants of the rotational velocity of the counterbody (υ_1=300 rpm, υ_2=500 rpm, υ_3=1000 rpm) at a constant normal load of 80 N

Analyzing the obtained dependences, we noted that the introduction of even a small amount of nonionic surfactant into the technological medium - water - greatly affects the wear resistance of the polymeric materials. The normal load on the tested samples reached 80 N. With the load rise, the wear increased slightly for M_2.

The friction processes of polymeric materials are complicated by the wear or abrasion, i.e. destruction of the surface layer under friction. At the polymer's deformation under friction, for each of the counterbody's surface unevenness, the polymer stretches and then contracts, undergoing multiple alternating loads. This leads to the accumulated damage in the polymer, resulting in the separation of particles from the friction surface.

Conclusions We have run the model tribotechnical tests of the radiation-modified fluorocarbon polymer. The tests have been done in a wide range of triboactive additives concentrations under varying friction modes; It has been demonstrated that an increase in the concentration of nonionic surfactants reduces the wear rate of polymeric materials, the mildest friction conditions occur in an aqueous solution of 20 wt. % phenoxol 9/10 ИМ (SAA_4). With the load increase, the wear rate rises, the friction coefficient decreases.

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PREPARATION OF POLYMERIC FIBROUS MATERIALS ELECTROSPINNING METHOD

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Among the limited number of modern ultrafine fiber technologies (e.g., phase separation, matrix synthesis, self-assembly of peptide-like molecules, etc.), electrospinning (ES) is considered to be one of the most promising methods [1]. The forming of polymer nanofibers under the conditions of electrodynamic interactions and viscoelastic deformations allows us to alter their various structural and morphological characteristics, create a high specific surface area, regulate their mechanical properties and porosity, and use a wide range of diffusion parameters. The use of natural polymers offers additional advantages in the development of fiber and matrix systems for environmental problems and biomedicine. These materials are biocompatible and biodegradable (under controlled conditions) without forming toxic products. In addition, for medical purposes, it is often required that the polymer fibers existing as individual filaments or forming a matrix should contain encapsulated biologically active compounds (for example, cell growth hormones or antibiotics) and provide targeted drug delivery for cell growth stimulation and prolonged therapy [2]. To create bioresorbable implants, cell engineering matrices, therapeutic systems for targeted drug delivery, and other biomedical articles, a limited range of polymers are used, among which it is necessary to note first of all polysaccharides, poly-α-oxyacids, and poly-β-oxyacids. The main alternative to the class of poly-α-oxyacids are poly-β-oxyacids (the synonym is poly-3-hydroxyalkanoates (PHAs)). These polymers exceed the synthetic polyesters conventionally used in implantation in their biomedical characteristics and have extremely wide prospects for use in various fields of medicine (preparation of dissolvable sutures, surgical constructionplates, osteoprosthetic devices, and implants with gradual replacement of biodegradable macromolecules by the connective tissue of the organism). The use of these polymers reduces the probability of toxic reactions in the organism due to the moderate rate of biodegradation for both short- and long-term implantation. At low diffusion and destruction rates, the duration of the targeted drug delivery by these polymers exceeds the similar characteristic for poly - α-hydroxyacids. Natural poly-3-hydroxybutyrate (PHB) has a very simple chemical structure and is the most widespread representative of the PHA family. That is why we studied the effects of the main parameters (viscosity and electric conductivity) of the polymer PHB solution on the possibility of obtaining ultrathin fibers with variable geometry.

The reagents used in this study included PHB with a molecular mass (MM) of 300, 450, and 850 kDa (BIOMER, Germany) in the form of a powder prepared by microbiological synthesis; chloroform (CF), formic acid (FA), and tetrabutylammonium iodide (TBAI) (all of “kh.ch.” (chemically pure) grade, Russia). Tetrabutylammonium iodide [CH3(CH2)3]4N was used in electroforming as an addition to increase the electric conductivity of the forming solution and thus to get rid of the morphological defects of fibers (socalled “bulbs”). Formic acid was added to adjust the viscosity and electric conductivity. Electrospinning of nonwoven fiber materials based on PHB was performed on a laboratory unit at a dynamic viscosity of solution of 9 P (0.9 Pa s), specific bulk conductivity of $\sim 10^{-3}$ (Ohm m)$^{-1}$, volumetric flow rate of the forming solution of (10–12) × 10^{-5} g/s, electric field voltage of 15 kV, interelectrode distance of 18 cm, and capillary diameter of 0.1 mm. The distribution of the fibers obtained from a PHB solution in CF/FA (0.9 : 0.1) in the presence of the TBAI electrolyte according to the diameter was studied by light and electron microscopy (MBI-6 optical microscope and Hitachi TM-1000 scanning electron microscope). The thermophysical and thermal characteristics (the temperatures of the start of the thermoand thermooxidative destruction) of PHB-based fibers were obtained using DSM-2 (Russia) and Perkin Elmer Pyris 6 DSC (United States) differential scanning calorimeters. The characteristics of a polymer solution largely determine the geometrical form and morphology of ultrafine PHB fibers obtained by ES. The transition from droplike to fibrillar structures depends on the important properties of the forming solution such as electric conductivity and viscosity. To obtain cylindrical fibers, low-molecular modifiers such as TBAI and FA, which increase the electric conductivity of the system, were added to the chloroform solution of PHB. In addition, the increase in the viscosity of solutions at higher concentrations and/or MM of the polymer also leads to improved homogeneity of fibers according to thickness and affects the diameter of ultrafine fibers and their distribution width according to the diameter (Fig. 1).

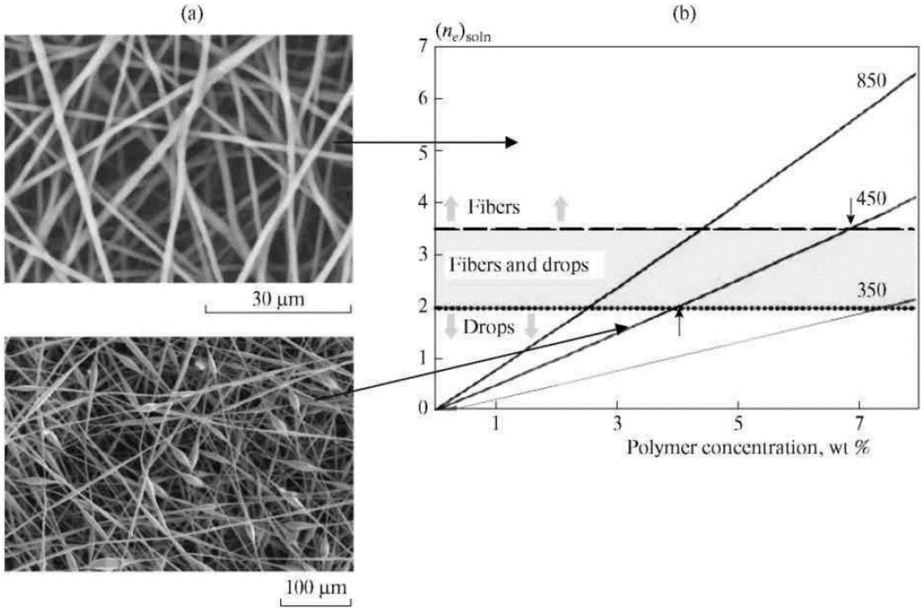

Figure 1. (a) Micrographs of the ultrafine PHB fibers and (b) schematic dependence of the effective number of interlocked nodes (ne)soln on the concentration of the model polymer. The small arrows show the transition region of the polymer concentrations (dark region). The figures indicate the molecular mass of the polymer in kDa. The large arrows show the correspondence between the fiber geometry and the region of the structures

Modification of the solutions with an ionogen electrolyte (TBAI) and hydrolytic agent (FA) decreases the initial MM of the polymer and leads to an increase in the viscosity of the system, which shows itself as a response to hydrolysis and was taken into account in the physicochemical measurements of the polymer solution at time intervals considerably exceeding the ES times (400 and 3/4 h, respectively). The obtained fibers have found use in biomedicine, in particular, in the design of locomotor elements.

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Acknowledgments

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FLUORINATED POLYSILOXANES BASED ON DIMER OF HEXAFLUOROPROPYLENE

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Polysiloxanes containing perfluorinated side groups are of great interest from the point of view of their unique properties. Perfluorinated polymers are well known to have low surface energy, which opens a lot of useful properties: low angle of wetting of surfaces coated with such polymers, high chemical inertness and heat resistance, inertness against many organic solvents. Nevertheless, modern approaches to production and use of polysiloxanes with perfluorinated substituents are not perfect, especially due to high cost of starting reagents and polymerization process cost.

The aim of this work was to develop new effective approaches to the preparation of polysiloxane polymers with perfluorinated substituents starting from commercially available reagents. One of such reagents is the hexafluoropropylene dimer (HFPd), a stable under standard conditions compound easily obtained from hexafluoropropylene and containing a double bond in its structure. HFP as an anion easily undergo the nucleophilic addition reaction, which opens up wide possibilities for further chemical transformations. In this paper, di- and trifunctional alkoxysilane derivatives 1 and 2 were obtained based on HFP (Figure 1).

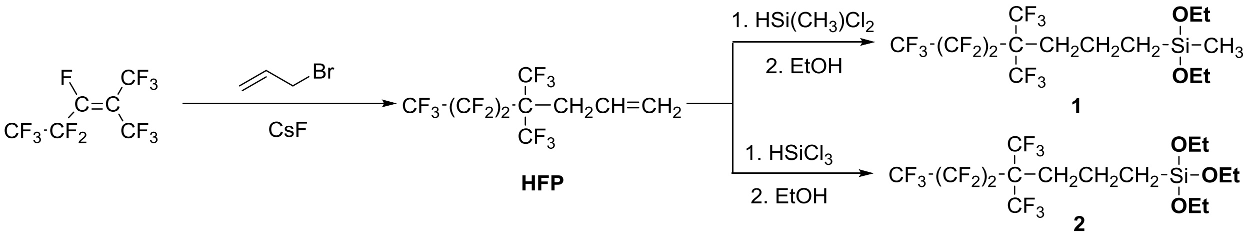

Figure 1. Synthesis of two- and thifunctional alkoxysilanes, containing branched perfluorohexyl substituent

Further, based on them, linear and branched polysiloxane polymers were synthesized by condensation under the active media conditions: in acetic or trifluoroacetic acid. It is shown, that the ratio of acid: monomer, reaction time, and the presence of various additives, can significantly change both the molecular weights of polymers and the ratio of linear and cyclic products. All of the products obtained were characterized by gel-permeation chromatography (GPC) using a mixture of dichloromethane and $CF_2Cl\text{-}CCl_2F$ as eluent. Molecular-weights characteristics were calculated using polystyrene standards.

In a similar way, a series of copolymers, contained different functional groups (-SH, $-N_3$, $-NH_2$, -COOH) were prepared by cooperative condensation alkoxysilanes, containing branched perfluorohexyl substituent and functional alkoxysilanes with different ratio (Figure 2). All the polymeric products were characterized by NMR, FTIR and GPC.

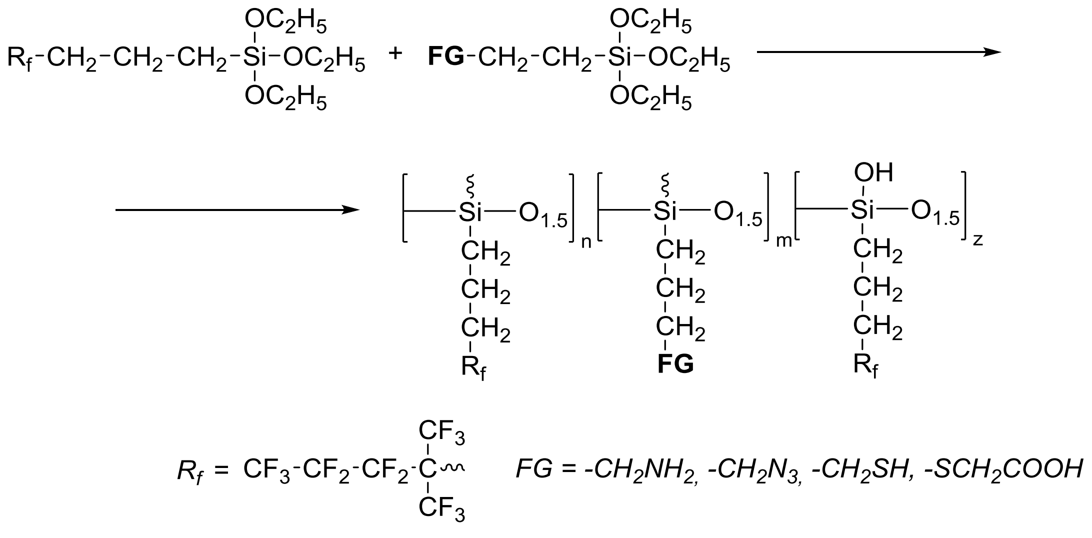

Figure 2. Synthesis of the copolymers of perfluorosiloxanes and alkoxysiloxanes with various functional groups

Some of the copolymers with functional groups were incorporated with epoxy resins in order to estimate their compatibility and the conditions of curing. In all cases with successful compatibility of the components, contact angle of surface-air interface was measured.

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ETHYLENE-TETRAFLUOROETHYLENE BASED FLUOROPOLYMERS: STRUCTURE AND PROPERTIES

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The paper presents the results of a study of DU POINT™TEFZEL®ETFE 750 (ETFE 750, granules) and FLUON®AGC ETFE TL-581 (ETFE TL-581, powder) co-polymers. Both products belong to the class of fluoropolymer which have found wide application due to their high corrosion resistance, durability over a wide range of temperatures, excellent chemical and electrical properties [1, 2].

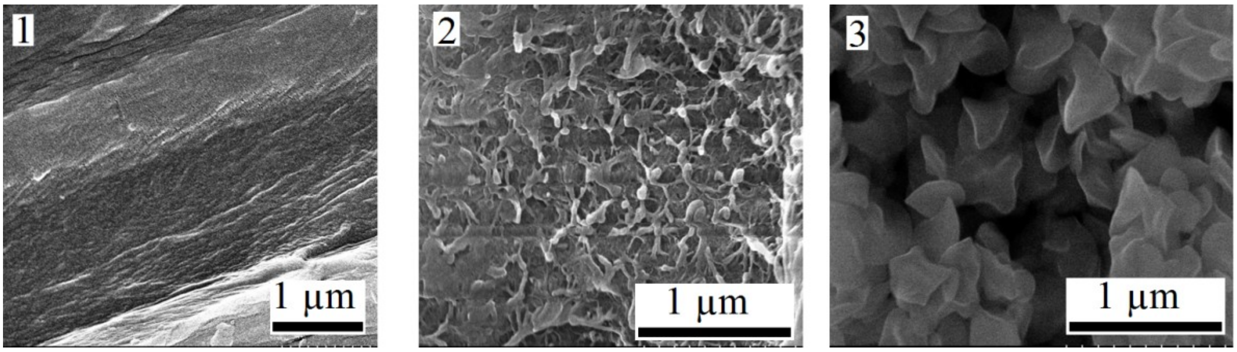

Figure 1. SEM image of ETFE 750 – 1, ETFE TL-581 – 2, sample after thermal treatment – 3.

Morphologically, the samples are not identical. Sample of ETFE 750 is formed as a monolithic mass, in which the layered formations with a thickness of ~ 25 nm, are viewed. In the sample of ETFE TL-581, the layers overlap each other noticeably and consist of agglomerates (~1 μm) and particles (~300 nm), which are interconnected by filaments of 25 nm wide and 1 – 5 μm long.

Table 1

EDS analysis of the samples

Sample	ETFE 750		ETFE TL-581		Sample after thermal treatment	
	C(ат.%)	F(ат.%)	C(ат.%)	F(ат.%)	C(ат.%)	F(ат.%)
	58.39	41.61	49.86	50.14	46.7	53.3

The results of the EDS analysis showed an excess content of carbon atoms not bound to fluorine in sample ETFE 750. The XPS and EDS analysis data showed a higher degree of fluorination in the sample of ETFE TL 581. In both samples, the ending of chains is performed by CF_2 groups, which are part of $-CF=CF_2$. In the structure of both samples, although in a small amount, there are groups of -CHF-, which, apparently, should be attributed to the defectiveness of the structure.

Table 2

XPS analysis of samples

Sample	F		C				
	E_b, eV	677.9	292.0	290.8	288.6	286.3	285.0
ETFE TL 581	at.%	53.3	2.8	20.3	2.8	16.4	4.4
ETFE 750	E_b, eV	688.4	292.5	291.5	288.8	286.8	285.0
	at.%	45.2	1.4	20.1	2.8	17.5	13.0
Thermal treatment sample	E_b, eV	688.0	292.1	291.0	288.7	286.5	285.0
	at.%	51.9	4.0	18.6	3.6	17.3	4.0
	group	CF_x	$-CF_2-\mathbf{C}F_2-$ $-CF=\mathbf{C}F_2$	$-CH_2-\mathbf{C}F_2-$	$-\mathbf{C}HF-\mathbf{C}HF-$	$-\mathbf{C}H_2-CF_2-$	$-\mathbf{C}H_2-CH_2$

The IR spectra of the discussed ETFE-based polymers are close, which corresponds to the similarity of their molecular structure. The bands characterizing stretching vibrations of C-H in CH_2 groups are shifted relative to the corresponding bands in the IR spectrum of polyethylene (more than 30 cm^{-1}). Such a noticeable shift of the bands is due to the influence of the presence of the CF_2 components in the chain. The structure of the fluoropolymer sections of the chain differs from that of PTFE. This is indicated by the shift in the position of the bands belonging to the CF_2 groups (more than 20 cm^{-1}) and the absence of a doublet at 639, 625 cm^{-1} which indicates the presence of the spiral twisting of the PTFE macromolecules. From the data of model quantum chemical calculations performed by us, the $C_{10}F_{22}$ molecule, modeling a fragment of the PTFE chain, is a spiral, the molecules of $(\text{-}CF_2\text{-}CF_2\text{-}CH_2\text{-}CH_2\text{-})_n$, which model the ETFE chain fragments, have a linear structure.

The sample of ETFE 750 is stable to a temperature of 393 °C and after 420 °C begins noticeably to lose mass and at 275 °C melts. ETFE TL-581 begins to lose mass at 365 °C and melt at 265 °C. When comparing TG and DSC samples, it is noticed that ETFE TL-581 both melts and begins to lose mass earlier than is the case for ETFE 750, but the process of mass loss is more active in ETFE 750.

When the process of mass loss of the samples was completed, the white like flour powders were collected on the specially supplied filter. The samples obtained are markedly different from the original products in morphology, structure and thermal properties. Neither layers nor filaments are observed in these samples (Fig.1(3)). The sample is an agglomerate of particles ranging in size from 300 to 500 nm. The powder obtained during heat treatment begins to lose mass at almost 100 °C. The melting process has a diffuse character with a weakly pronounced maximum.

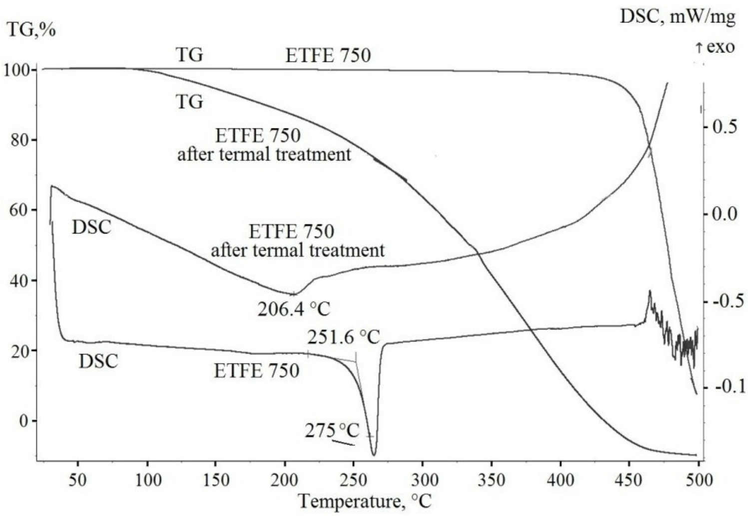

Figure 2. TG and DSC curves of ETFE 750 and ETFE 750 after thermal treatment

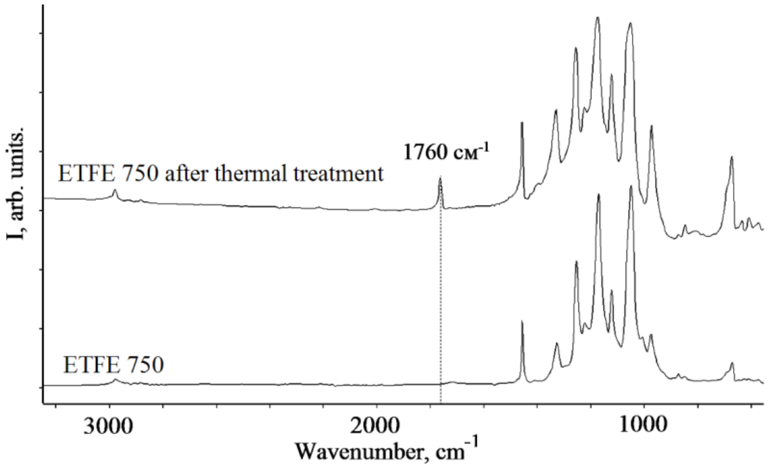

Figure 3. IR spectra of ETFE 750 and ETFE 750 after thermal treatment.

The analysis of the IR spectra revealed a number of facts. The spectra of the samples obtained are identical, which means that the same substance was obtained. The initial samples and samples after thermal treatment are based on ETFE. The most important result is the appearance of a noticeable band at 1760 cm^{-1}, which is absent in the IR spectra of the original samples. According to quantum chemical calculations and XPS data, this band corresponds to vibration of the -CF=CF$_2$ terminal groups. The noticeable intensity of this band in IR spectra indicates that shorter chains are present in the structure of the obtained powder than in the structures of the initial samples. This is consistent with the results of the XPS investigation: the number of terminal groups in the structure of the sample obtained after heat treatment is almost two times higher than in initial one.

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MELT SPINNING AND STUDYING THE PROPERTIES OF POLYPROPYLENE YARNS WITH FLUOROPLASTIC COATING DOPED WITH MAGNETITE

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Polypropylene yarns are widely used for the manufacture of disposable materials for medical purposes. Fibrous materials intended for use in medical institutions must be able to suppress the development of pathogenic microorganisms and protect the patient and the physician from contact with the source of infection. Silver nanoparticles are widely used to impart biocidal properties to materials from natural fibers that have a large number of functional groups.

Polypropylene fiber has the appearance of a nearly perfect cylinder, devoid of pores, having a chemically inert smooth surface. It is very difficult to firmly fix a metal particle on the surface of such a fiber. In the works performed at the Institute of Solution Chemistry RAS [1, 2] it was shown that polypropylene filaments modified with iron-containing nanoparticles stabilized with polyolefins suppress the development of pathogenic microorganisms. The described method of modification of the filaments is based on the introduction of the polymer concentrate of iron-containing nanoparticles based on polyolefins into the polypropylene melt during the molding of the filaments. Nanoparticles are distributed in the total volume of the fiber and firmly held in it when implementing this method.

We set the task to firmly fix the nanoparticles on the surface of the filament. A fundamentally new method of producing polypropylene threads with fluoroplastic coating was proposed at the Institute of Solution Chemistry of the Russian Academy of Sciences. Yarns have a surface of polytetrafluoroethylene and have the properties of fluoroplastic such as high chemical resistance and hydrophobicity, low friction coefficient [3]. The novelty of the development is protected by two patents of the Russian Federation for invention [4, 5]. We have proposed the use of a fluoroplastic coating for fixing magnetite nanoparticles and imparting antimicrobial properties to the threads. Nanoparticles on the surface of the fiber give a good antimicrobial effect. The negative effect of aggregated nanoparticles on the strength of the filaments is absent.

In this paper, studies aimed at obtaining and studying the properties of polypropylene filaments with a fluoroplastic coating doped with magnetite nanoparticles have been carried out.

The composition for the modification of the threads we received in several stages. First, we synthesized magnetite in the presence of sodium stearate to reduce the aggregation of nanoparticles. The composition was treated with ultrasound, then added suspension of fluoroplastic SF-4D and other components.

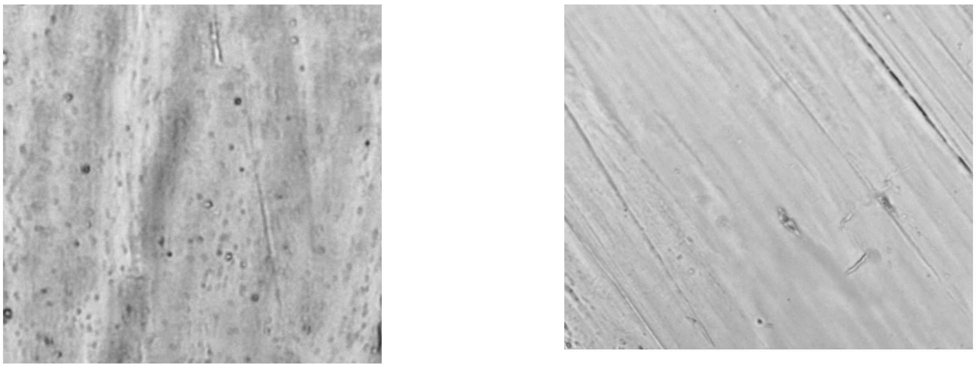
We carried out the formation of filaments on the laboratory bench SFPV-1. In the process of molding, we applied a composition for modification of filaments with known quantities of polytetrafluoroethylene and magnetite. After forming, the threads were subjected to orientation stretching and thermal stabilization using the OCB-1 test bench. We obtained polypropylene filaments with a coating formed on the surface of each filament on the basis of a fluoroplastic 4D suspension containing magnetite. Physical and mechanical characteristics modified filaments are given in table. 1 and 2.

Table 1

Physical and mechanical characteristics modified threads

The components of the composition for the modification of polypropylene threads				Specific strength, SN / tex	Relative extension, %
Magnetite,%	Suspension of fluoroplast SF-4D, %	Sodium stearate, %	Lubricator, %		
-	-	-		51,13±2,31	39,95±1,91
0,4	3	0,5	-	60,6±2,67	43,4±2,36
0,5	9	1		50,7±2,03	40,4±1,39
0,7	7,5	-		65,1±3,92	38±3,22
1	10	-	10	53,5± 2,03	52,4±1,29
1,5	7,5	1,4	10	62.6±2.06	41±2.96
3	9,6	7	25	55.4±0.9	31.6±2.7
7,5	6	1		59,9±2,52	50,1±2,53

Table 1 contains the physical and mechanical characteristics of the filaments, which were modified by a composition that was not treated with ultrasound. The threads had high specific strength, but very high tensile elongation. During orientation stretching of these filaments, a high breakage was observed, due to the presence of magnetite aggregates and an uneven application of the composition to the surface of the filaments. The composition used to produce yarns was applied to a polypropylene film, which was stretched 5 times on the OSV-1 stand at 120 ° C. Micrographs of the film surface were obtained (Fig. 1), in which magnetite aggregates up to several microns in size are clearly visible.



a b

Figure 1. Micrograph of a film with a fluoroplastic coating containing magnetite 1%:
a) without ultrasonic treatment, b) with ultrasonic treatment. Increase 400 times.

Table 2

Physical and mechanical characteristics of polypropylene filaments with fluoroplastic coating containing magnetite

The components of the composition for the modification of polypropylene threads				Specific strength, SN / tex	Relative extension, %
magnetite, %	Suspension of fluoroplast SF-4D, %	Sodium stearate, %	Lubricator, %		
-	-	-		51,13±2,31	39,95±1,91
0,5	7,5	-	-	51,13±1,91	40,05±1,94
0,7	7,5	-		52,7±1,96	35±1,73
1,0	7,5	1	-	57,7±1,96	32±1,73

1,5	7,5	1,4	10	76.9±3.99	32.5±1.97
1,5	12	2	10	69,9±0,96	40,3±1,38
3	9,6	7	25	69±3.04	26.9±1.71

The composition for modification for the destruction of the aggregated magnetite particles was subjected to ultrasonic treatment in a low-frequency ultrasonic disperser of the type UZDN-2T in a temperature-controlled vessel at a frequency f = 22. The exposure time was 2 minutes. Preliminary treatment of the composition for the modification of the threads with ultrasound can significantly improve the course of the orientation process and reduce the breakage of the threads (table 2, fig.1b).

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COMPOSITE MATERIALS BASED ON CATION-EXCHANGE MEMBRANES AND ZIRCONIA WITH A SULFURED SURFACE

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In modern industry, homogeneous perfluorinated cation-exchange membranes, for example, Nafion or MF-4SK, are widely used to create fuel cells, sensor devices and gas separation [1]. Doping of membranes with inorganic particles (introduction of the latter into the system of pores and membrane channels) in some cases allows increasing the selectivity of ionic transport and the conductivity of the materials obtained [2, 3]. The introduction of zirconia with a surface modified with acidic, for example, sulfo groups, due to the formation of an electrical double layer near the surface of the dopant leads to a pronounced transport properties of hybrid membranes [4].

A homogeneous perfluorinated sulfonic acid membrane MF-4SK and a heterogeneous membrane manufactured by Mega (Czech Republic) type membrane foil (MPC) were used as base membranes. Zirconia with a surface modified with sulfonic acid groups was synthesized by an in situ method in a system of pores and membrane channels.

Modifications material such as membrane foil with zirconia leads to a decrease in the effective capacity and conductivity of the membrane (Table 1). The reason for this is that zirconia is partially bound to the sulphoric groups of the membranes with the formation of salt bridges. In addition, the moisture content of the modified membranes is reduced due to the displacement of a part of water by dopant particles. When zirconia is modified by acid groups, these effects are leveled by the fact that the surface of the dopant becomes more acidic. However, the ion-exchange capacity and moisture content of the membranes are somewhat less than for the original foil. It is interesting to note that the modification method used leads to a partial dissolution of the dopant when sulfonic acid groups are introduced onto its surface.

The ionic conductivity of membranes doped with zirconium oxide decreases sharply. At the same time, the conductivity increases when the surface of zirconium oxide is sulfonated (Table 1). The sample MFC-ZrO_2-SO_3H (1M) has the highest conductivity. This emphasizes the possibility of the participation of the surface of a dopant containing acid groups in the transfer processes.

Table 1

Dopant containing (ω ZrO_2), moisture content (ω H_2O), ion-exchange capacity (IC) conductivity (σ) at 30°, conductivity activation energy (Ea) samples of composite membranes of the series "membrane foil"

	ω (ZrO_2), %	IC, mmol/g	ω (H_2O), %	σ, S/sm	Ea σ, kJ/mol
MFC	-	1,26	44	0,0081	17,8±0,4
MFC -ZrO_2	20,5	0,22	29	0,0020	25,1±0,6
MFC -ZrO_2-SO_3H (0.2M)	14	0,89	28	0,0030	32±2,3
MFC -ZrO_2-SO_3H (1M)	1,1	1,19	43	0,0316	5,9±0,26

In the case of composite membranes based on MF-4SK, the content of dopant is significantly lower compared to membranes based on membrane foil and does not exceed 2%, which is consistent with a smaller intra-pore volume in homogeneous membranes. Exchange capacity grows for all modified samples (Table 2). At the same time, the moisture content of the membranes is practically unchanged for almost all modified samples

Table 2

Dopant containing (ωZrO_2), moisture content (ω H_2O), ion-exchange capacity (IC) conductivity (σ) at 30°, samples of composite membranes of the series MF-4SC

	ω(ZrO_2), %	IC, mmol/g	ω (H_2O), %	σ, S/sm
MF-4SC	-	0,53	17	0,024

MF-4SC -ZrO_2	5	0,59	16	0,027
MF-4SC -ZrO_2-SO_3H (0.2M)	1,7	0,64	16	0,026
MF-4SC -ZrO_2-SO_3H (1M)	0,5	0,71	18	0,032

At low temperatures and 100% humidity (in water) conductivity of membrane MF-4SC -ZrO_2 and MF-4SC -ZrO_2-SO_3H (0.2M) slightly higher than for the original MF-4SC, while at high the difference between samples is negligible. The highest conductivity values are demonstrated by samples with an oxide, surface-modified sulfuric acid of higher concentration. When reducing the relative humidity to 95%, only samples with zirconium oxide modified with acid groups demonstrate increased proton conductivity. In this case, close values of the activation energy of conductivity may additionally indicate that the proton transfer proceeds with the participation of the sulfate groups of the modified zirconium oxide.

Also for the obtained samples we measured diffusion permeability and diffusion coefficients. Modified membranes show higher ion-exchange parameters than unmodified ones, which suggests that the use of this modification method is promising.

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USE OF PREPERATA FORUM FOR HYDROPHOBIC PROCESSING OF POLYESTER TEXTILE MATERIALS IN SUPERCRITICAL CARBON DIOXIDE

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The most effective surface modifiers used for making the surface unwettable are fluorinated hydrocarbons having low surface energy (18.5–26 mJ / m^2) [1]. In hydrophobization of textile materials, these substances are traditionally used in the form of suspensions or emulsions. Surface modification of fibrous materials causes changes in their structure and surface energy, which is a direct manifestation of intermolecular interactions. It should be noted that the surface free energy is determined by surface forces, which rapidly decrease with the depth. Therefore, to make the surface hydrophobic, it is sufficient to apply an ultrathin layer of an appropriate material onto a high-energy surface.

Today polyester fibers play an important role in industry. The majority of them are produced from poly(ethylene terephthalate) (PET). These fibers are widely used owing to their cheapness, feasibility of dressing, and sufficient strength and wear resistance, but are insufficiently hydrophobic.

To obtain a hydrophobic material, additional modification aimed to decrease its surface energy by deposition of a stable low-energy coating is necessary. The hydrophobizing agents used in textile industry cannot ensure formation of a high-quality hydrophobic coating on the PET surface, because they are difficultly soluble in the traditionally used aqueous medium. Among the known materials, polytetrafluoroethylene (PTFE) has the lowest surface energy. However, it is practically insoluble in all the known solvents, its processing is difficult, and its adhesion is poor [1]. The negative properties of PTFE are due, to some extent, to the high molecular weight of the polymer. Therefore, coatings are usually deposited from emulsions and suspensions of specially synthesized fluorinated substances of lower molecular weights. However, with this deposition procedure, the coatings are contaminated with trace amounts of emulsifiers. To attain the required effect, multiple layers of a fluorinated substance are deposited in succession onto a support. The problem of depositing ultrathin polymeric coatings can be solved by using supercritical carbon dioxide (SC CO_2) as a solvent for fluorinated hydrophobizing agents. This solvent is characterized by high solubility of nonpolar substances in it and by absolute wettability of the material being modified. Owing to unique dissolving properties, high diffusion mobility, and easy complete removal from the material after the end of the process, SC CO_2 shows promise for wide use in diverse branches of chemical technology. The supercritical state of carbon dioxide is attained at relatively low parameters (P_c = 7.39 MPa,

T_c = 31.6 °C), which, in combination with ready availability and relative chemical inertness, makes SC CO_2 favorable as a medium for performing a number of processes of textile chemistry [2].

By treatment of the polyester textile material with Forum agent in SC CO_2, we obtained on the polyester fabric a stable ultrahydrophobic coating characterized by the contact angle of 137° ± 3°. It should be noted that the contact angle of the polyester fabric attained with one of the most effective hydrophobizers, Nuva TTH fluorinated agent (Clariant Company), is 133° ± 3°. Examination by IR MATIR spectroscopy and X-ray diffraction analysis confirmed the formation of the coating on the surface of the treated films and fabrics and furnished information on its qualitative composition and structure. The IR absorption spectra of the polyester fabric treated with a solution of the prepolymer in SC CO_2 are shown in Fig. 1. The x-ray diffractograms of the untreated PET fabric and fabric treated with SC CO2 and treated with a solution of Forum in SC CO_2 are shown in [3].

To make the material stably hydrophobic, oleophobic, and superhydrophobic, the surface energy should be decreased to 40, 20, and 10 mJ / m^2, respectively. The surface energy was determined by the method of two liquids [1]. To this end, we used a poly(ethylene terephthalate) film treated under the conditions similar to those of the fabric treatment. We measured experimentally the contact angles of the film with two liquids having different values of the dispersion and polar terms of the surface tension, namely, with water (surface tension 72.8 mJ / m^2) and α-bromonaphthalene (surface tension 44.6 mJ m^2). Surface energy of the treated material, which appeared to be 29 ± 5 mJ / m^2 (for the untreated PET film, 50 ± 5 mJ / m^2) [4].

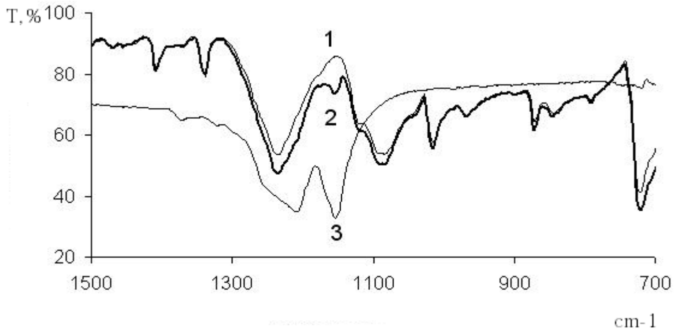

Figure 1. IR MATIR absorption spectra. (T) Transmittance and (ν) wavenumber. (1) Initial fabric, (2) fabric treated with Forum agent in SC CO_2 at a pressure of 20 MPa and 90 °C, and (3) Forum agent

From the results of elemental and rapid gravimetric analysis, we determined the gravimetric content of the main property-determining elements. The results are given in Table 1. They show that, in treatment of the polyester fabric with a solution of Forum agent in SC CO_2, the amount of the hydrophobizing agent deposited onto the fabric is considerably smaller than in treatment with a dispersion of Nuva TTH agent. Similar data confirming low fluorine content on the surface of the sample treated with a solution of Forum agent in SC CO_2 and with a dispersion of Nuva TTH agent were obtained by energy-dispersive analysis.

Table 1

Content of hydrophobizing agent and elemental composition of polyester suit fabric treated with a solution of Forum agent in SC CO_2 and with Nuva TTH agent

Treatment parameters	Agent content, g /m^2	Content, %		
		F	C	H
Forum, 20 MPa, 90°C	0,85±0,01	<0,2±0,002	62±0,05	4,03±0,01
Dispersion of Nuva TTH	1,88±0,01	<0,5±0,002	61,9±0,05	4,02±0,01

agent,30 g / l				

The use of the built-in JED-2300 X-ray spectrum analyzer in the energy-dispersive analysis allows recording of a wide range of elements, i.e., a study of the composition of materials. The X-ray radiation consists of narrow emission lines, which are characteristic of elements present in the sample. In the resultant energydispersive spectrum, the characteristic X-ray peaks correspond to the observed peaks. Identification of these peaks furnishes information on the elements present in the sample. In our case, we detected carbon, fluorine, oxygen, and nitrogen.

Quantitative data on the sample composition were obtained by comparing the peak intensities, using mathematical processing commonly termed the matrix correction method (ZAF or PhiRhoZ). Quantitative composition estimation for the modifi ed samples allows a conclusion that the fluoropolymer coating localized on the surface is highly uniform and very thin. According to the results of energy-dispersive analysis, the fluorine content on the sample treated in SC CO_2 is 1,8 times lower.

Detailed information on the structure of the coating formed in the course of modification of the textile material was obtained by atomic force microscopy.

After the hydrophobization of the polyester fabric in SC CO_2, the water absorption by the fabric was 3.7%, and after the treatment with Nuva TTH agent, 12%. For the initial fabric, this parameter was as high as 38%.

Table 2

Resistance of the hydrophobic effect to service actions

Agent	Θ in, deg	Θ, deg		
		after wearing	after launderings	after dry cleanings
Solution of Forum agent in SC CO2, 20 MPa, 90°C	137 ± 3	131 ± 3	136 ± 3	135 ± 3
Dispersion of Nuva TTH agent, 30 g l–1	132 ± 4	117 ± 4	108 ± 5	126 ± 5

The polyester textile material modified with ultradispersed polytetrafluoroethylene using supercritical carbon dioxide as solvent surpasses in the hydrophobicity the fabric treated with Nuva TTH agent. The coating is ultrathin, continuous, and flawless and exhibits good adhesion properties.

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INFLUENCE OF THE MODIFIED ZEOLITE ON PROPERTIES OF COMPOSITES ON THE BASIS OF POLYTETRAFLUOROETHYLENE

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Polytetrafluoroethylene (PTFE) is a basic polymer of fluoropolymers class, it has a number of surprising properties: high chemical resistance, high hydro and lyophobic property, high climatic resistance, non-aging, non toxic [1]. But along with advantages of PTFE, it has disadvantages, such as cold flow, low wear resistance and ability to be deformed even at small loadings. One way to eliminate the disadvantages is development of the polymeric composites (PC) with the introduction of the modified fillers [2].

In this work, the effect of natural zeolite modified by fluoropolymers ultradispersed polytetrafluoroethylene UPTFE and F-4MB brand on the properties of polytetrafluoroethylene based composites is investigated.

Object of a research are PTFE (the PN brand, GOST 10007-80) and composites on its basis. Natural zeolites are chosen as a filler, these are the silica-alumina minerals having high adsorptive activity and molecular and screen properties. As polymeric modifiers of a filler the brand UPTFE ultradispersed polytetrafluoroethylene the Forum (TU 2229-004-02698192-2002) and fluoroplastic of the F-4MB brand (TU 301-05-73-90) served.

The technology of joint mechanoactivation [3] of zeolites with UPTFE and F-4MB in a planetary mill of "Pulverizette 5" of “Fritch” is developed for increase in compatibility with hydrophobic PTFE. The modified zeolites received thus used as PTFE fillers in number of 1-5 pts.wt.%.

Also the PC tribotechnical properties on the basis of PTFE and the modified UPTFE of zeolite are given in table 1 deformation and strength.

Table 1

Deformation and strength, tribological properties of composites based on PTFE and modified UPTFE zeolite

№	Composition	Ratio zeolite: UPTFE	Content of zeolite, %	σ, MPa	ε,%	E, MPa	I, mg/h	T,°C
1	PTFE	-	-	19	310	469	92,7	39,4
2	PTFE+1 pts.wt.% (zeolite:UPTFE)	1:1	0,5	19	247	494	10,0	37,5
3		2:1	0,67	20	280	498	4,4	37,1
4	PTFE+2 pts.wt.% (zeolite:UPTFE)	1:1	1	22	311	503	5,2	36,5
5		2:1	1,33	23	374	546	0,6	38,4
6		1:2	0,67	19	281	503	8,8	37,2
7	PTFE+2 pts.wt.% zeolite	-	2	22	350	400	2,2	-
8	PTFE+5 pts.wt.% (zeolite:UPTFE)	1:1	2,5	19	245	578	0,9	37,1
9		2:1	3,33	20	251	617	0,1	42,0
10	PTFE+5 pts.wt.% zeolite	-	5	20	330	-	0,6	-

The use of the modified UPTFE of zeolite as a filler of PTFE leads to complex improvement of properties of composites: tensile strength and elongation at rupture increase by 20% compared to the initial polymer. The wear resistance increases by 3-6 times, in comparison with the composites containing only the activated zeolite and by 900 times in comparison with the initial polymer.

The results of the influence of joint activation of components on the deformation and strength and tribological characteristics of composites based on PTFE and modified zeolite F-4MB are shown in Table 2. Introduction of 1-2 wt.% modified zeolite F-4MB leads to an increase in tensile strength and elongation at rupture of materials by 20-40% compared with the initial polymer. Compared with PC, obtained without joint activation, and PC containing only activated zeolite, these composites have increased strength, which indicates an increase in the adhesive interaction of the polymer and filler. Increase in filler content up to the 5pts.wt.% leads to insignificant decrease elongation at rupture. Tensile strength of PC remains at the level of the initial polymer, and the elastic modulus raises by 1.5 times. The wear resistance of these composites containing 5% of the modified zeolite increases by 150 times in comparison with initial polymer.

Table 2

Deformation and strength, tribotechnical properties of composites based of PTFE and the modified F-4MB of zeolite

№	Composition	Ratio zeolite: F-4MB	Content of zeolite, %	σ, MPa	ε,%	E, MPa	I, mg/h	T,°C
1	PTFE	-	-	19	310	469	92,7	39,4
2	PTFE+1 pts.wt.% (zeolite:F-4MB)	1:1	0,5	29	357	688	31,1	27,1
3		2:1	0,67	29	359	708	5,7	38,6
5	PTFE+2 pts.wt.% (zeolite:F-4MB)	1:1	1	27	335	726	6,4	27,8
6		2:1	1,33	25	265	708	5,4	39,9
8	PTFE+2 pts.wt.% zeolite	-	2	22	350	400	2,2	-
9	PTFE+5 pts.wt.% (zeolite:F-4MB)	1:1	2,5	26	307	738	0,77	39,1
10		2:1	3,33	22	326	665	0,62	40,9
11	PTFE +2 pts.wt.% zeolite +3 pts.wt.% F-4MB	-	2	20	292	652	1,23	40,2
12	PTFE +2 pts.wt.% zeolite +2 pts.wt.% F-4MB	-	2	21	428	762	1,10	36,4

On the basis of the obtained data it is possible to draw a conclusion on prospects of application of joint activation for zeolite modification. Use of UPTFE and F-4MB of zeolite modified by fluoropolymers leads to significant increase in deformation and strength and tribotechnical characteristics of PTFE that is important when using such composites not only as tribotechnical elements of frictional units, but also in designs of the mobile consolidations.

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EFFECT OF THE PRODUCTION TECHNOLOGIES OF POLYMER COMPOSITES BASED ON PTFE AND CARBON FIBERS ON THE PHYSICAL-MECHANICAL AND TRIBOLOGICAL PROPERTIES

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Abstract: The given article presents physical-mechanical and tribological studies of polymer composites based on polytetrafluoroethylene and carbon fibers of UVIS-AK-P brand obtained by various technologies.

It is known that there are two main problems in the development of any polymer composites, especially based on PTFE, which is characterized by inertness and high melt viscosity. The solution of these problems will determine the final properties of the materials being created:

1) ensuring the uniform distribution of the filler over the matrix volume;

2) ensuring high adhesion of fillers with a polymer matrix [1].

Uneven distribution of the filler in the polymer matrix causes the formation of agglomerates. This can lead to premature deformation during strength tests, as a result of which unreliable or non-convergent results are derived [2].

To improve the quality of mixing the filler with the polymer matrix, a technique was used to obtain the filler concentrate in the polymer with subsequent dilution of the concentrate with the polymer to the required content of the filler.

To intensify the interaction process of the polymer-filler system, two methods of mechanical activation were used in the present work: 1) obtaining the filler concentrate in the polymer in a planetary mill at a drum rotation speed of 400 rpm for 2 minutes; 2) passing the powder mixture between two rotating rollers when the distance between the rollers is less than 1 mm.

The prospects of using carbon fibers of UVIS-AK-P brand produced by UVIKOM as a PTFE filler are shown in [3, 4]. In these studies, PTFE + 1, 3, and

5 wt.% UVIS-AK-P formulations were investigated. A composite with 5 wt.% CF content obtained using the technology of joint mechanical activation demonstrated the best results. The wear resistance of the composite was increased 2024 times compared with the original PTFE. To continue the investigation of the effect of PCM production technologies on the operational properties, PTFE + 7 and 10 wt.% UVIS-AK-P formulations are inspected in this article.

The results of the study of the stress-strain and tribotechnical properties of PTFE and composites based on it are presented in Table 1.

Table 1

Dependence of the physical-mechanical and tribological properties on UVIS-AK-P concentration and the production technology of PCM

Composition	Production technology of PCM	σ_t, MPa	ε_b, %	E, MPa	Compression strength		I, mg/h	f
					10%	25%		
PTFE	-	20	304	469	14	23	161,90	0,22
PTFE+5wt.% UVIS-AK-P	1	20	354	514	20	33	0,08	0,25
PTFE+7wt.% UVIS-AK-P	1	12	113	378	14	25	4,35	0,12
PTFE+10wt.% UVIS-AK-P	1	8	34	273	12	22	1,36	0,11
PTFE+7wt.% UVIS-AK-P	2	13	113	582	17	29	3,80	0,11
PTFE+10wt.% UVIS-AK-P	2	12	55	531	14	26	0,33	0,16

Note: 1 – obtaining the filler concentrate in the polymer in a planetary mill at a rotation speed of drums of 400 rpm for 2 minutes; 2 - passing the powder mixture between two rotating rollers when the distance between the rollers is less than 1 mm.

σ_t *- tensile strength;* ε_b *is the relative elongation at break; E is the modulus of elasticity at break; I - mass wear rate, mg/h; f is the friction coefficient.*

According to the table, the stress-strain and tribological properties decrease with the increase of the carbon fiber content in the polymer. This can be explained by the formation of a loose porous PCM structure resulting in a deterioration of the connection between the fibers and their combined action under load. The technological method of mechanical activation by way of roll milling of PCM powder mixture was used to solve this problem. In [1] it is demonstrated that this method leads to an increase in the strength characteristics of highly filled composites based on PTFE. As it can be seen from the table, this technological method leads to an increase in the modulus of elasticity, compressive strength and durability of PCM as compared with composites obtained using the technology of joint mechanical activation of components.

Thus, various technological approaches have been developed based on the methods of joint mechanical-chemical activation of components and mill rolling of the polymer mixture contributing to improved operation characteristics. In the future, it is planned to continue the study of the effect of PCM properties depending on the method of their production.

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DEVELOPMENT OF SELF-LUBRICATING POLYMER COMPOSITES BASED ON PTFE AND NATURAL ZEOLITES

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The use of self-lubricating materials in friction units is becoming increasingly important in mechanical engineering. The introduction of friction bearings and other triboelements of sliding joints, functioning without additional lubrication, leads to an increase in the serviceability of machine maintenance. From this perspective, a promising direction of creating self-lubricating materials is the impregnation of porous materials with liquid lubricants.

Powder metallurgy is used to make porous parts of friction units sintered from powders, which are impregnated with liquid lubricant before use in friction units [1]. Details made from such materials are used in friction couples with insufficient lubrication or when other lubrication systems are unacceptable. Such oil-saturated porous details have good strength and antifriction properties and are widely used in various friction units.

Recently, a promising direction is the development of oil-filled polymer composites [2]. Antifriction self-lubricating bioresistant composite materials of “Maslianit” brand manufactured by the Joint-Stock Company “Orion Bureau for Design and Technology” are widely known [3].

The results of the research on the development of antifriction composites based on polytetrafluoroethylene (PTFE) obtained using mineral motor oil of M-8B brand are presented in the given paper. Several technologies for producing oil-filled composites are introduced depending on the method of loading liquid motor oil into the volume of the polymer composite. Activated natural zeolites were used as solid-phase structurally-active fillers and as additives that intensify the process of oil absorption as well.

The first technology for manufacturing oil-filled polymer composite materials (PCM) is to impregnate the preformed porous polymer blanks with liquid motor oil for 24 hours at different temperatures followed by further thermal treatment. Polymer composites obtained by this technology are characterized by 160–1000 times increase in wear resistance depending on the specific load of friction and by the values of the friction coefficient, which are at the level of the initial PTFE. The reason for the increased wear resistance is that the oxidation products of motor oil, play the role of wear inhibitors [4].

The next method of introducing a liquid lubricant into the composite lies in the use of activated natural zeolites pre-impregnated with a mineral motor oil of M-8B brand. Further, the oil-saturated zeolite is used as a filler for PTFE. Testing samples were obtained by standard cold-pressing technology. The oil content in composites filled with 2 and 5 wt.% zeolite was 0.6 and 1.4 wt.%, respectively. When filling PTFE with zeolite pre-impregnated with motor oil M-8B, 63-600 times decrease in the mass wear rate depending on the specific friction load was observed.The friction coefficient reduced 2 times, while the relative elongation at break and the ultimate tensile strength were maintained at the level of the initial PTFE.

These two methods lead to an increase in the wear resistance and a decrease in the friction coefficient.However, liquid lubricants undergo profound changes duringthermal processing in oil-modified composites. Therefore, it is difficult to refer them to oil-filled composites.

From this perspective, materials based on PTFE with an open-porous structure have been developed with the ability to absorb oils after the thermal treatment stage. Activated natural zeolites are used as fillers as well. Ammonium chloride served as a pore-forming agent. The oil content in the composites was 1-2.5 wt.% When using a blowing agent and introducing natural zeolites into PTFE in an amount of 5 wt. %, a decrease in the mass wear rate up to 90 times, friction coefficient up to 2 times is observed. The temperature in the contact zone reduces 2 times in comparison with the initial PTFE. Modification of PTFE with zeolite alone leads to a decrease in the rate of mass wear up to 75 times with an increase in the friction coefficient in comparison with the initial polymer. An increase in the wear resistance and a decrease in the friction coefficient is due to the fact that during the friction wear, the oil contained in the pores of the composite is squeezed out of the volume of the polymer materialwith the formation of lubricating layers on the friction surfaces in the sort of “plastics sweat”, which leads to 1.5-2 times decrease in the friction coefficient. With the exhaustion of the liquid-phase components in the friction zone, their delivery processes are resumed. However, the service life of the developed composites is limited since the amount of absorbed motor oil is small.

Thus, it has been established that the most wear-resistant are the oil-modified composites obtained by impregnation of porous blanks with motor oil followed by thermal treatment. The increase in the wear resistance of these composites confirms the fact that the products of complete and incomplete combustion of motor oil during the heat treatment of PCM at 375°C are essential to the formation processes of the triboresistant structure both in volume and in the surface layer of the composite.

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PERFLUORINATED SULFOCATIONIC MEMBRANES NEPEM-117 IN LI^+ FORM, CONTAINING POLAR APROTIC SOLVENTS: SOLVATION AND IONIC CONDUCTIVITY

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Lithium-ion batteries (LIBs) are widely used as power or energy sources for portable devices due to their high energy density. Along with novel electrode materials for LIBs, development of novel electrolytes that should provide ionic transport is also crucial. One of the most promising types of electrolytes is plasticized polymer electrolytes based on cation-exchange membranes and polar aprotic solvents. The most important characteristic of the electrolyte is ionic conductivity, which is responsible for the fast ionic transport between the electrodes during battery operation. In this work, the solvation and ionic conductivity of perfluorinated NEPEM-117 (Thinkre membrane materials, China) membranes with the sulfonic groups in a Li^+ form were investigated. The following solvents and mixtures, containing the equal volume of solvents, were chosen as plasticizers: ethylene carbonate – propylene carbonate (EC–PC), ethylene carbonate – dimethylacetamide (EC–DMA), ethylene carbonate – propylene carbonate –dimethylacetamide – tetrahydrofuran (EC–PC–DMA–THF), ethylene carbonate – propylene carbonate –dimethylacetamide (EC–PC–DMA), dimethylformamide (DMF), dimethylsulfoxide (DMSO) and dimethylacetamide (DMA). One part of the polymers in Li-form was immersed in a large excess of solvents, the other part was placed in a calculated amount of solvents for limited swelling n DMA. Ionic conductivity of the obtained samples was investigated by impedance spectroscopy at temperature range −20…+50 °C under argon atmosphere on symmetric cells carbon/membrane/carbon.

It was shown that ionic conductivity increases and activation energy decreases with increasing of the solvation degree of polymers (fig. 1).

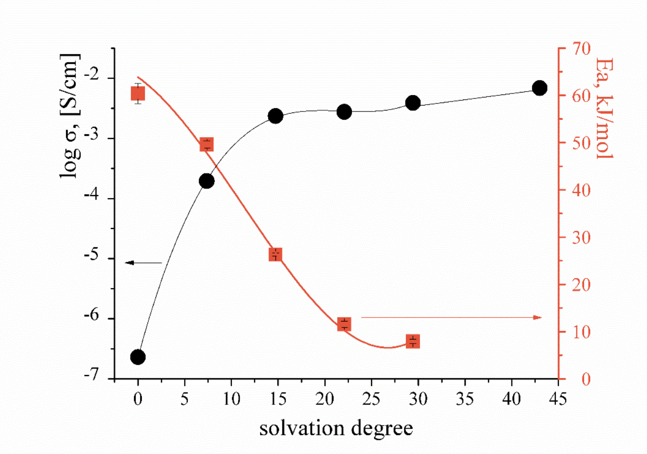

Figure 1. Dependence of ionic conductivity (25 °C) and activation energy on solvation degree for membranes containing DMA.

Constancy of the phase composition in a wide temperature range is one of the important characteristics of electrolytes, ensuring the safety of battery use. Linear dependences of ionic conductivity on temperature are observed for membranes containing individual DMF and mixtures of EC-PC-DMA and EC-PC-DMA-THF (fig. 2), that means constancy of phase composition in observed temperature range. Membranes containing this solvents are characterized by the highest ionic conductivities at negative temperature.

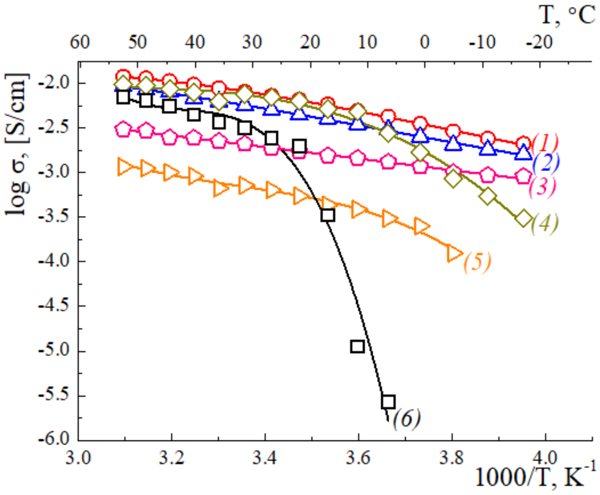

Figure 2. temperature dependence of ionic conductivity of membranes containing EC-PC-DMA (1), DMF (2), EC-PC-DMA-THF (3), EC-DMA (4), EC-PC (5) and DMSO (6)

It was shown that in the general membranes containing solvents with a higher dielectric constant are characterized by the highest conductivity at comparable degrees of solvation.

Maximal values of ionic conductivity at room and negative temperatures were obtained for membranes containing mixture of EC-PC-DMA (8.1 and 2.1 mS/cm at +25 °C and -20 °C, respectively).

Obtained values of ionic conductivity of polymer electrolytes based on NEPEM membranes are comparable with values for common used liquid electrolytes.

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SURFACE PROPERTIES OF GAMMA-IRRADIATED PTFE

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PTFE has high anti-adhesive properties and low surface energy (SE), which limits its compatibility with other materials. Increase SE PTFE is an urgent task when creating composites, adhesive of materials and many other practical applications. It is known that exposure to ionizing radiation leads to an increase in the surface energy of PTFE [1]. The mechanism of this increase in SE is not well understood.

The goal of the work was to study the laws of the effect of gamma irradiation on the surface properties of PTFE, depending on its supramolecular structure and irradiation conditions, as well as quantitative analysis of dispersion and polar intermolecular interactions in irradiated PTFE.

The object of the study was high molecular weight PTFE (MW ~ 5×10^6) of suspension polymerization of grade PN. Samples with different supramolecular structures were investigated: nonsintered powder of PTFE (F4PN), sintered PTFE (F4) and the pre-irradiated in the melt PTFE (F4RM). Surface energy and adhesion work were calculated using the values of wetting contact angles for water and tetradecane. Wetting angles were measured by the method of a lying drop on a KRUSS EasyDrop instrument with DSA1v1.92 software. The drop volume was 4 µl. In order to clarify the role of dispersion interactions in changing surface properties, the curves of isothermal decay of polarization and depolarization currents were studied, as well as quantitative calculations of the energy of dispersion interaction in the framework of the Lifshitz model. The samples were irradiated with ^{60}Co gamma-quanta (1.25 MeV) at room temperature in air. In tabl. 1 shows the relative changes in the components of the surface energy depending on the absorbed dose.

Table 1

Relative changes (%) of the dispersion and polar components of the surface energy of PTFE (η_s^{dis} and η_s^{pol}) and the work of adhesion for water $\eta(H_2 0)$ and tetradecane $\eta(C_{14}H_{30})$ depending on the absorbed dose.

Sample	η_s^{dis}	η_s^{pol}	$\eta(H_2 0)$	$\eta(C_{14}H_{30})$
F4PN-100	5.5	106	7.23	2.83
-200	5.5	253	12.5	2.83
-500	7.6	453	19.0	3.70
F4-100	3.19	260	11.9	3.70
-200	5.10	540	20.2	3.92
-500	8.20	1980	45.5	3.90
F4RM-100	2.43	197	13.1	0.64
-200	4.52	468	25.0	2.37
-500	6.20	1203	47.0	3.0

In the framework of the Lifshits theory, a quantitative analysis of the intermolecular interaction of the test liquid with the surface of irradiated PTFE was carried out for samples F4PN, F4 and F4RM. The calculations used data on changes in the dielectric increment and density depending on the absorbed dose. In tabl. 2 summarizes the calculated values of the relative changes in the Van-der-Waals adhesion work, taking into account the radiation-dielectric effect (RDE) (η_ε^{dis}) and density (η_ρ^{dis}) at various absorbed doses.

Table 2

Relative changes (%) of the Van-der-Waals (η^{dis}) component of the work of adhesion for water and tetradecane, calculated according to the Lifshitz theory.

Sample	$\eta_\varepsilon^{dis}(H_2 0)$	$\eta_\varepsilon^{dis}(C_{14}H_{30})$	η_ρ^{dis}	$\eta_{\varepsilon,\rho}^{dis}(H_2 0)$	$\eta_{\varepsilon,\rho}^{dis}(C_{14}H_{30})$
F4PN-100	0	0	0	0	0
-200	0	0	0	0	0
-500	0.01	0.003	~0	0.01	0.003

F4-100	5.43	1.53	2.7	8.13	4.23
-200	5.65	1.60	3.0	8.65	4.60
-500	5.70	1.60	3.5	9.20	5.10
F4RM-100	5.50	1.60	0.3	5.80	1.90
-200	5.70	1.60	0.4	6.10	2.00
-500	5.77	1.60	0.6	6.37	2.20

From the comparison of the data presented in tabl. 1 and 2, it can be seen that there are differences between the experimental and calculated values of the changes in the relative work of adhesion for samples F4PN, F4 and F4PM. These differences can be explained by a significant difference in the concentration of ion pairs in irradiated PTFE [1]. According to the ion-pair mechanism, the RDE in irradiated PTFE is determined by the kinetic mobility of holes in the field of localized electrons [2]. In the case of the PTFE-water system, a part of the mobile holes near the surface of the PTFE, which left the sphere of the Coulomb interaction of electrons, will have an orienting effect on the water dipoles — the ion-dipole interaction [3]. The obtained results testify to the unified nature of changes in the dielectric characteristics, the work of adhesion and the polar component of SE during irradiation of PTFE. Based on the results obtained, an ion-dipole mechanism for increasing the polar component of the surface energy and the adhesion of PTFE under gamma irradiation was proposed. This mechanism is realized due to the formation of localized electrons and quasi-free holes in the volume of PTFE.

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