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Fluoropolymer films producing by extrusion method

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Abstract:*The article describes the features to obtain films from fluoropolymers by extrusion method.*

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High operating properties of thermoplastic fluoroplastics are best realized in film materials obtained by melt extrusion. Considering the protective properties of fluoropolymers, implemented in particular through the creation of various lacquered coatings, compositions or powders, it should be noted that the protection with the extrusion membrane has a number of advantages, which are: the best barrier properties because of their equal thickness, the absence of residual solvent or thermal degradation products, appeared in the final stage of forming a complete covering, and with help control properties. And in several cases only extrusion membrane can be used. For example in obtaining of a porous filter with desired geometry of pores and hydrophilicity, in production of ion-exchange membranes, in obtaining piezoelectric and fireactive elements.

The obvious advantages of fluoropolymer films are:
• Wide operating temperature range (from minus 200 to plus 250 °C),
• excellent chemical resistance;
• high barrier qualities;
• good dielectric and insulating properties;
• transparency in different wavelengths;
• anti-adhesive and anti-friction properties.

The thickness of the films ranges from 10 microns to several hundred microns, which is economically advantageous for many cases. These qualities of the membranes determine their successful use in antirust engineering, mechanical engineering, electronics, instrumentation, food industry, etc.

Due to the high aggressiveness of fluoropolymer melts with processing temperatures up to 380 °C, all parts of the extrusion facility which are in contact with the melt, are made of special, corrosion-resistant, heat-resistant steel brands such as *Hastelloy*. The optimum ratio between length and diameter of the Screw (L/D) for flouropolymers is 20-25. The increased viscosity of melts requires long compression zone and constant control pressure of the melt in the mold head. All of these requirements are satisfied by modern extrusion facility, which was launched into operation in 2010 at a pilot plant of FSUE RSC "Applied Chemistry".

In the production of fluoropolymer films in the world both companies which synthesize fluoropolymers and those who convert it are engaged. The main manufacturers and brands of extrusion membranes are given in the Table 1.

Table 1*. Brands of fluoropolymers films.*

Fluoropolymer (Russian analogue)	**Company**	**Brand of the film**	**Film Characteristics**
PVDF Poly(vinylidene fluoride) (fluoroplast-2 fluoroplast-2E fluoroplast-2M fluoroplast-2ME fluoroplast-62)	Arkema	PVDF Kynar Film	The highest strength at temperate temperatures, hardness, transparency and weather resistance, good chemical resistance, low cost.
	Saint-Gobain Performance Plastics	Norton PVDF	
	Nowofol Kunststoffprodukte GmbH & Co	Nowoflon PVDF	
	Westlake Plastics Company	Westlake PVDF Film	
	Polyflon Technology Limited	Flonfilm 700 PVDF	
ETFE Copolymer of ethylene and tetrafluoroethylene (fluoroplast-40 fluoroplast-40AM Haleon)	Du Pont	Tefzel DuPont	Radiation resistance, operating temperature range is -100 °C to + 200 °C, good transparency in the UV and visible range, good chemical resistance.
	Asahi Glass Company	Fluon Asahi Glass Company	
	Daikin	Neoflon ETFE Daikin	
PCTFE Polychlorotrifluoroethylene (fluoroplast-3 fluoroplast-3M)	3M	Kel-F	Excellent transparency and dielectric properties, operating temperature range is -195 °C to +150 °C, high chemical resistance, good selectivity at separation of gas mixtures.
	Daikin Industries	Neoflon PCTFE Film.	
	Honeywell	Honeywell Aclar Film	
FEP Copolymer of tetrafluoroethylene with hexafluoropropylene (fluoroplast-4MB fluoroplast-46)	Du Pont	Teflon FEP Film	Operating temperature range is -196 °C to +200°C, high electrical performance independent of temperature and frequency, excellent chemical resistance, high light transmission and permeability in the UV range.
	Nowofol Kunststoffprodukte GmbH & Co	Nowoflon FEP	
	Polyflon Technology Limited	Flonfilm 500 FEP	
	Saint-Gobain Performance Plastics	Norton FEP Fluoropolymer Film	
	Daikin	Neoflon FEP films	

PFA **Co-polymer of perftorpropyl-vinyl ether with tetrafluoroethylene** (fluoroplast-50)	Du Pont	Teflon PFA Film	Thermoplastic analog of PTFE, the widest operating temperature range for thermoplastic fluoropolymers is from minus 196°C to + 250°C, best electrical properties, excellent resistance to aggressive media at elevated temperatures.
	Dyneon GmbH	Dyneon PFA	
	Nowofol Kunststoffprodukte GmbH & Co	Nowoflon PFA	
	Saint-Gobain Performance Plastics	Norton PFA Film	

Producing fluoroplastic films is possible by using the flat forming head and by bag method with bulge. For the production of PVDF films by bag method the special polymer brands are designed (Kynar HMS), the main polymer chain of which has branches with long side chains. Due to this structure, the melt PVDF gets extra strength and resistance to sagging, which allows to obtain a bag with blow-up degree 4.4 with a membrane thickness of 5 mm.

Properties of extruded membranes are mainly determined by the properties of the original brands of fluoropolymers. However, such characteristics as tensile stress, relative elongation at tear, electric stability, thickness and appearance, as well as the piezoelectric properties, are highly dependent on technological modes of film formation.

Comparative studies of formation modes of fluoroplastic films from ethylene-tetrafluoroethylene (ETFE) - brand ET6235 by Dyneon and new brand Haleon (F-40) by JSC Halogen were conducted in the RSC "Applied Chemistry". As a result new modes were found which allowed to obtain high-quality samples of the transparencies for both brands, with thicknesses of 100 and 200 microns, not containing various inclusions and surface defects. Despite the fact that in literature you can find the info about the difficulties of the processing of domestic brands such as F-40, it is still possible to obtain high-quality membrane with modern equipment for polymers synthesized by fundamentally different technologies.

The main characteristics of domestic films, developed in the parent organization on flouropolymers - JSC "Plastpolymer" are **presented in Table 2**. Special properties of each kind of membrane and the price determine the preferential use in a particular assignment.

Films from PVDF (F-2M) are used in electronics for the production of printed circuit boards, condenser membrane, winding cables, for piezoelectric and pyroelectric (F-2ME) in sensor switches, microphones, sensors, etc. Filled F-2M film is good lining material in construction. In foreign countries films based on PVDF are widely used as a weather-resistant, vandal-proof covers of advertising and informational booths. In medicine and pharmaceutics - the films is used in packaging instruments for external protection of the package, in production of porous microfilters. In the chemical and nuclear industries films F-2M is used in the manufacture of porous track filters to filter particles from aggressive media traces. Thin special films F-2M are best for production of super power-consuming capacitors.

Films from PCTFE (F-3M). These films are used for making foiled films and flexible cables, for covering code cards, printed circuit boards, for high temperature sensors protection. F-3M films is used in lining of chemical equipment and as a sealing material. In foreign countries films of F-3M type are used as bags for storing gases due to exceptional humidity-resistant properties (in 10 times higher than that observed for other membranes) and have the shape of packaging for food storage and medicines.

Films from FEP (F-4MB) .These films are widely used as resistant to aggressive media materials for protection of chemical plants, pipelines, oil production equipment and facilities. Also they are used as dielectric heat-resistant materials in electrical engineering (ribbon cables, slot insulation in transformers), for printed circuit boards, high-temperature sensors. Metallized films F-4MB are used in temperature control systems of external surfaces of different devices. In medicine, the films F-4MB are used for the production of membranes, disposable containers which are necessary in low-temperature preservation of the blood and bone marrow. In aircraft engineering the films F-4MB is used for the manufacture of fuel tanks which do not undergo hard bending deformation during operation; as an anti-adhesion layer for separation while autoclave formation of products made of composite materials with single and double curvature, as lining for parts of the reinforced epoxy resins for the sections of tail and wings of an airplane and for a fuselage and engine parts, and at installation of fluorescent light ceiling in planes. In space technology - as transparent, lightresistant coatings of solar cells.

Films from ETFE (F-40). Films made of F-40 are used in Russia for manufacturing insulating gaskets and electrical wires. Metallized with aluminum and silver, films F-40 is used in parabolic mirror solar collectors. Films elements of roofing are also made. In foreign countries ETFE films are increasingly used in the construction of sports facilities roofs.

Films from PFA (F-50). The films are used for adhesion and corrosion protection, for containers lining. As an anti-adhesion layer for separation in vacuum autoclave molding. For insulation of electrical wiring in airplanes. Films are used in printed circuit boards, and in high temperature sensors.

Methods for obtaining hydrophilic films that are suitable for micro filtration in industrial processes, the microbes and blood elements in medicine, etc. are also described in today's patent and technical literature.

A perspective direction in the processing of fluoropolymers is to obtain membranes based on sulfonated copolymers of tetrafluoroethylene, so-called ionomers. These compounds are known as trademark Nafion, manufactured by DuPont and domestic development is copolymer F-4SF. This compounds have the following chemical structure (Fig. 1)

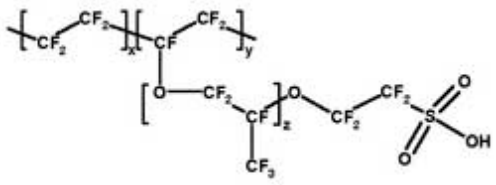

Fig.1. Copolymer F-4SF structure

The main direction of ionomers application is in fuel cells as proton exchange membranes (PEM). Nature of proton exchange properties of ionomers is determined by their morphology. Recently, the water channel model was extended, which is characterized by self-organization of sulfonic acid functional groups in the hydrophilic channels with a diameter about 2.5 nm. This size of the channel or pore allows to transport protons, while the hydrophobic frame with crystallites provides good mechanical strength.

Till now the PEM is mainly produced by JSC "Plastpolymer" by casting. On an experimental extrusion machine in RSC "Applied Chemistry" different modes of extrusion obtaining of membranes based on F-4SF with thickness of 100 to 500 microns were tested. The resulting samples showed satisfactory results on the strength characteristics. Now the experimental batch is in operation to complete the study, including the ionic conductivity.

Extrusion method has a number of technological advantages over casting, including improved performance and the possibility of multiple recycling of material. The correlation of the processing conditions of F-4SF and properties of the films is an essential condition of production of high-quality ion-exchange membranes based on them. To the study of these correlations the authors will apply in the following articles.

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