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Synthesis and application of ω-bromo-perfluoroalkylvinyl ethers

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Report V. Study of physical and mechanical properties of copolymers of fluoroolefins with ω-bromoperfluoroalkylvinyl ethers.

1. Introduction

In report IV (1) the routes to modify fluoroplasts by copolymerization of tetrafluoroethylene (T and vinilydene fluoride (VDF) with bromo-perfluoroalkylvinyl ethers (BrAVE) of the general forr of $Br(CF_2)nOCF=CF_2$ where n=2 (BrAVE-2) and n=4 (BrAVE-4) have been described. introduction of fluoroalkylvinyl ethers to copolymerization with olefins is known to imp processibility of the copolymers, increases their resistance to low temperatures and their sta in aggressive chemical media.
They are used as the second and third copolymers (2-4)

In particular, a fluoroelastomer based on triple TFE copolymer, perfluoromethylvinyl ether substituted perfluoroalkylvinyl ether of the general formula of $CF_2=CFOR_fX$ is known.
Bromine-containing molecules allow to synthesize new types of fluoroplasts possessing hydrop conductivity, improved solubility and better processibility. Thus, for example, the introductio bromotrifluoroethylene to the composition of polytetrafluoroethylene increases amphoterisn the copolymer and reduces its melting temperature (5).
Bromine-containing monomers, for example 1-bromo-2,2-difluoroethylene, have found v application in processes of copolymerization with TFE, VDF, hexafluoropropylene and o fluoroolefins to produce fluoroelastomers and general rubber goods based on rubbers (6-9). In case bromine atoms are convenient active centers to form space-network structures (10-
There are known many polymer compositions of radical solidification based on bromated iodinated fluoroelastomers (17-21).
It was planned to produce new fluoroplasts and fluoroelastomers with a set of performa characteristics peculiar to copolymers based both on perfluoroalkylvinyl ethers and on brom containing fluoromonomers using BrAVE monomers as modifiers of fluoropolymers in reaction copolymerization with fluoroolefins.
In the present paper we state the results of the determination of general physical and mecha characteristics of copolymers of BrAVE with the most widespread fluoromonomers, TFE and V and their resistance in different aggressive chemical media.

2.Test procedure

Physical and mechanical characteristics of materials were determined on the basis of the res of tensile tests carried out on a test machine of 2055 P-05 type of "TochPribor" (c. Ivan Russia) made.
Test samples were two-sided scoops manufactured by blanking from films with a special knife. machine is equipped with a hermetic autoclave of a special design with controllable elect heating to provide testing the samples in different aggressive chemical media.
Based on the tensile test results the following physical and mechanical characteristics v calculated:

- ***breaking stress, MPa***

$$\sigma p = \frac{Pp}{Fo}, \text{ MPa}$$

where *Pp* is the load at the sample destruction, N
Fo is the starting surface of the sample cross-section, cm;

- ***modulus of elasticity, MPa***

$$Ep = \frac{(P_2 - P_1) * l_o}{(\Delta l_2 - \Delta l_1) * Fo}, \text{ MPa}$$

where P_1, P_2 are the loads chosen at the initial linear part of the tensile diagram, N;
Δl_2 - are the sample elongation at the loads of P_1, P_2 respectively, cm;
lo- is the length of the sample test part, cm;

- ***percent elongation***

$$Ep = \frac{\Delta l_p}{l_o} 100,\%$$

where Δl_p is the sample elongation at rupture, cm;

- ***percentage change of the breaking stress***

$$\pm \sigma_p = \frac{\sigma_{p1} - \sigma_{p0}}{\sigma_{p0}} * 100,\%;$$

where σ_{p1} is the breaking stress in a medium, MPa;
σ_{p2} is the breaking stress in air, MPa;

- ***percentage of the modulus of elasticity***

$$\pm \Delta E = \frac{E_{p1} - E_{p0}}{E_{p0}} * 100,\%;$$

where E_{p1} is the modulus of elasticity in a medium, MPa;
E_{po} is the modulus of elasticity in air, MPa

- ***change of percent elongation***

$$\pm \varepsilon_p = \frac{\varepsilon_{p1} - \varepsilon_{p0}}{\varepsilon_{p0}} * 100,\%;$$

where ε_{p1} is the percent elongation in a medium, %;
ε_{po} is the percent elongation in air,%.
To determine chemical resistance of the copolymers, samples were subjected to aging for 7 d in 20% solutions of sulfuric acid and caustic soda at a temperature of 90°C and then their phy and mechanical properties were determined at tensile at 20°C.

2. Study of physical and mechanical characteristics of copolymers of TFE.

The fluoroplast of F-10 type widely used for making flexible pipelines, gasket materials etc.

used as the comparison standard.
The comparison of modificating affect of BrAVE monomer and other fluoromonomers such fluorosulfuryl-perfluoroalkylvinyl ether (FS-141), perfluoroallylvinyl ether , perfluoroallylalkyl diether was of an undoubted interest also. Some results of the conducted experiments are g in Table1.
The study has shown that the strength characteristics and modulus of elasticity consider increase after treatment in alkali for almost all types of copolymers of TFE tested. Some reduc in the modulus of elasticity of copolymers with FS-141 was observed in tests in sulfuric against a background of some increase in the strength parameters. Deformation characteristic the all copolymers of FS-141 tested (with different content of comonomer) are reduce aggressive media and to a greater degree in aging in alkali.
As regards to BrAVE monomers, all their physical and mechanical parameters increase both in and in alkali media and the modulus of elasticity and breaking stress increase to the grea extent.
It is seen from Table 1 that effectiveness of BrAVE monomers goes down with the chain le growth. The increase in the strength characteristics of copolymers based on BrAVE after t aging both in acid and in alkali is explained by additional cross-linking of the copolymer which ta place at the contact of the bromine-containing copolymer with an aggressive medium.