Aromatic polysulfone to create polymer materials with high resistance to frost

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Abstract. The creation of materials that ensure high reliability and environmental safety of Arctic structures under extremely harsh operating conditions is an urgent scientific and technical task. This article deals with the creation of domestic aromatic polysulphones to create on their basis polymer construction materials with high frost resistance, resistance to environmental factors. Method for the synthesis of aromatic polysulfones of high-temperature condensation in solution is both simple (from the perspective of technological implementation) and affordable method of producing structural polymers in quantities necessary for practical application in the creation of polymer composite materials on their basis for usage in devices planned for operation in Arctic conditions. Physico-mechanical, dielectric, thermal properties of the synthesized aromatic polysulfone and its fire resistance at the level of characteristics of well-known foreign brands. The synthesized material is not deformed to a temperature of minus 60 °C, and the impact of negative temperatures over time does not reduce its physical and mechanical characteristics.

1. Introduction

When creating materials for technical devices and structures, the conditions in which they will be used and applied are crucial. The development and implementation of modern, reliable structural materials, including those adapted to the Arctic and other aggressive environments, is one of the priorities of the development of materials science [1-3]. The main operating conditions that determine the performance of polymeric material (PM) and polymer structural materials (PCM) based on them are the ambient temperature, its humidity, the presence of external chemically aggressive effects and operating conditions (types of loading, cyclicity, possible critical transitions, etc.). This is due to the fact that parts and materials of construction must ensure reliable operation of products in the Arctic under the influence of the following climatic factors: the amplitude of temperature changes-about 100 °C (average daily-30 °C); increased corrosion-erosion wear under conditions of high salinity ice, exposure to solar radiation in the polar day, etc.

The problem of choice of PM and PCM on its basis appears as when you create new types of products, and the replacement of traditional materials as well as those already used for polymers with improved operational and technical characteristics, or more available for purchase. This problem can be faced by various specialists, including those for whom PM processing technology is not the main
specialty. The initial task requiring a solution is to select the base polymer based on the study of the initial data on the complex of the most important for a particular type of product performance (mechanical, electrical, chemical, etc.) characteristics [4].

One of the solutions to these problems is to study the possibility of using aromatic polysulfone as a matrix polymer. This is due to the fact that the main physical and mechanical characteristics of the polysulfone are stable at high and low temperatures (up to temperatures 10-15 °C higher than the glass transition temperature \( T_{gtt} \) at minus 100 °C), under the influence of aggressive agents and radiation of different nature, which opens up the possibility of competition of this series of polymers with metal in areas where other thermoplastics can not be used [5, 6].

2. Purpose of research
The purpose of the study is to show the prospect the manufacture of polymer composite materials on the basis of the aromatic polysulfones for products proposed for use in Arctic conditions.

Polysulfone (PSU) is an amorphous thermoplastics, which is a part of highly structural polymeric materials. Plastic is characterized by stability of shape and strength parameters in the temperature range from -100°C to +160°C.

Properties of PSU:
- great strength, stiffness and hardness;
- high creep resistance (higher than in the case of PE and PET);
- high static viscosity at sub-zero temperatures reaching -70°C, PSF becomes brittle only at temperatures of the order of -100°C;
- high dimensional stability and low water absorption;
- stability of physical and chemical properties in a wide temperature range and a small coefficient of linear thermal elongation;
- resistance to cracking as a result of deformation stresses, especially in contact with polar and aromatic compounds;
- high dielectric properties;
- chemical resistance to gasoline, oils, fats, alcohol, dilute acids and alkalis;
- resistance to hydrolysis and multiple sterilization by water vapor does not cause decrease of transparency and durability of plastics;
- resistance to high-energy radiation (eg, \( \gamma \)), x-rays, microwave, infrared radiation (2.5 to 40 microns), combined with their high permeability. The exception is infrared, which is largely damped;
- high fire resistance;
- moderately hazardous material toxicity when burning.

The main drawback on an industrial scale in Russia is not produced. The need for domestic industry in PSF is covered by imports, which in the conditions of constantly tightening sanctions policy has a negative impact on the timing of production of products necessary for work in the Arctic.

Currently, within the framework of the agreement No. 14.577.21.0241 of September 26, 2017 "Development of a new high-performance technology for obtaining heat-resistant dielectric superconstructive polymers of long service life" (unique identifier of works (project) RFMEFI57717X0241), funded by the Ministry of education and science of the Russian Federation, a domestic laboratory technology for obtaining PSU by high-temperature polycondensation in solution has been developed.

The structure of the synthesized PSU is shown in fig. 1.

![Figure 1. The structure of the synthesized PSU](image-url)
The obtained PSU of the General formula C$_{27}$H$_{22}$O$_4$S is characterized by the following elemental composition: C – 73.28, H – 5.01, O – 14.46, S – 7.25. Molecular weight-40-50 thousand degree of polycondensation (n) – 70-120. Softening temperature-180 OC. The characteristic viscosity in chloroform is 0.55 dl/g.

During the research tests, physical and chemical, dielectric, thermal properties, as well as fire resistance and toxicity during combustion were evaluated. The results of the research are presented in table. 1, compared to PSU trademark ULTRASON® S6010 BASF [7].

Analysis of the results presented in the table.1, shows that the physical and mechanical properties of PSU synthesized by the new technology are not inferior to foreign analog. Dielectric properties of the experimental polysulfone sample correspond to the parameters related to their dielectric materials. The thermal properties of the experimental sample polysulfone will allow their operation in areas of high temperatures – up to +160 OC. Fire resistance of the experimental polysulfone sample is estimated as high.

At the same time, the frost resistance of aromatic polysulphons was evaluated. In work [8] it is shown that the most informative methods establishing frost resistance of polymeric materials, including PCM, especially when assessing compliance with the requirements established in the RTD for the product, are standardized test methods developed in 1960-80, repeatedly updated and giving a stable reproducibility of the results [9 - 11].

At the laboratory base of MSTU. Bauman was studied to determine the frost resistance of the synthesized samples of aromatic polysulphons in comparison with the samples of ULTRASON® S6010, by determining the temperature of brittleness at impact [9]. The brittleness temperature is the temperature at which a 50% probability of failure of specimens is achieved when tested using this method. Brittleness temperature is designated as t50. Preparation of samples for testing, testing, processing of results was carried out in strict accordance with the requirements of GOST16782-92 (ISO 974-80). As a medium, a mixture of methanol with solid CO2, which has inertness to the materials under study, was used. As the minimum temperature was chosen temperature min $-60$ OC. No tests were performed at lower temperatures. The test results are shown in table. 2. comparison with the characteristics for ULTRASON® S6010.

Table 1. Results of testing of experimental samples of aromatic polysulfone in

| Characteristic                      | Dimension | Information on ULTRASON® S6010 | The synthesized PSU |
|------------------------------------|-----------|--------------------------------|---------------------|
| Density                            | g/cm$^3$  | 1.23                           | 1.25                |
| Water absorption in 24 hours       | % mass    | 0.3                            | 0.3                 |
| Maximum operating temperature      | °C        | 150-177                        | 160                 |
| Tensile modulus of elasticity      | megapascal| 2550                           | 2634                |
| Charpy impact strength on notched specimens | kJ/m$^2$ | 7.0                            | 6.7                 |
| Ball indentation hardness          | megapascal| 100                            | 132                 |
| Specific volumetric electrical resistance | Om*cm    | $1 \times 10^{15}$           | $6 \times 10^{15}$ |
| Category of Flammability           | relative unit | V0                            | Г1 (V0)            |
| Dielectric property:               | relative unit | 3.2                           | 3.18                |
| $\varepsilon$                      | relative unit | 0.0035                        | 0.0034             |
| Thermal properties:                |           |                                |                     |
| specific heat;                     | J/(g*°C)  | -                              | 3.26                |
| thermal conductivity;              | Vt/mK     | -                              | 0.21                |
Characteristic | Dimension | Information on ULTRASON® S6010 | The synthesized PSU
---|---|---|---
diffusivity | m²/s | 0,53*10⁻⁴ | 1,3*10⁻⁷
Fire-resistance:
flame spread index; | relative unit | - | material slowly spreading the flame over the surface
ignition temperature; | °C | - | 305
autoignition temperature; | °C | - | 551
oxygen index | relative unit | - | 31

Table 2. The results of the evaluation-brittle transition temperature (tₜ₀) aromatic polysulfone and polysulfone brand ULTRASON® S6010 for ГОСТ16782-92 (ISO 974-80).

| Experimental samples of aromatic polysulfone | ULTRASON® S6010 |
|---|---|
| Tᵢₐₜ, °C | tₜ₀ | Tᵢₐₜ, °C | tₜ₀ |
| -60 | No defects | -60 | No defects |
| -55 | No defects | -55 | No defects |
| -50 | No defects | -50 | No defects |
| -45 | No defects | -45 | No defects |
| -40 | No defects | -40 | No defects |
| -35 | No defects | -35 | No defects |
| -30 | No defects | -30 | No defects |

Analysis of the results presented in table 2 shows that both the synthesized experimental sample and the comparison sample (ULTRASON S6010) have a stable frost resistance up to minus 60 °C.

To assess the effect of negative temperatures on a number of physical and mechanical characteristics of the obtained material, the experimental samples were kept for 48 hours at a temperature of minus 50 °C, after which they were extracted from the cryostat, conditioned for 3 hours at a temperature of plus 23 °C and subjected to tests. The test results are presented in table 3.

Table 3. Results of testing of experimental samples of aromatic polysulfone after thermostating for 48 hours at minus 50 °C

| Characteristic | Dimension | The synthesized PSU |
|---|---|---|
| Maximum operating temperature | °C | 160 | 160 |
| Tensile modulus of elasticity | megapascal | 2634 | 2630 |
| Charpy impact strength on notched specimens | kJ/m² | 6,7 | 6,8 |
| Ball indentation hardness | megapascal | 132 | 135 |

Analysis of the results presented in the table. 3, shows the impact of negative temperatures does not affect the physical and mechanical characteristics of the material.

Experience in the development and creation of PCM based on polysulphones of foreign brands for the needs of the domestic industry can be the basis for the development of a fully domestic material that provides products with high performance properties and the required frost resistance for operation in the Arctic. Moreover, the introduction of reinforcing materials (fibers, dispersed solids, etc.) into
the polymer matrix based on the synthesized aromatic polysulfone will allow to obtain materials with a high synergistic effect of the polymer and filler properties.

3. Conclusion
Method for the synthesis of aromatic polysulfones of high-temperature condensation in solution is both simple (from the perspective of technological implementation) and affordable method of producing structural polymers in quantities necessary for practical application in the creation of polymer composite materials on their basis for usage in devices planned for operation in Arctic conditions.

Physico-mechanical, dielectric, thermal properties of the synthesized aromatic polysulfone and its fire resistance at the level of characteristics of well-known foreign brands. The synthesized material is not deformed to a temperature of minus 60 °C, and the impact of negative temperatures over time does not reduce its physical and mechanical characteristics.

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