Heat-resistant constructional materials based on thermoplastic polysulfones

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Abstract. The analysis of achievements in the field of creating composite materials filled with fibers based on high performance thermoplastics, as well as methods for producing prepregs based on activated unidirectional carbon fibers in form of layers and synthesized specifically for that purpose polyethersulfone based on 4,4'-dioxidiphenylsulfone and 4,4'-dichlodiphenylsulfone with an optimal molecular weight was conducted.

Aromatic polysulfones are constructional materials [1-3], that also are considered to be a common material for membranes technology [4, 5]. They are characterized by excellent thermal resistance, high mechanical and dielectric properties, one of the highest of modern polymers radiation resistance, chemical resistance, good creep resistance, low water absorption and melt shrinkage, the possibility of use in medicine and in contact with food [2].

The synthesis of these polymers is conducted by the nucleophilic substitution reaction by the interaction of disodium or dipotassium salts of bisphenols, or mixtures of bisphenols, with 4,4'-dichlorodiphenylsulfone in dipolar aprotic solvents [6-12]. Among them, the most famous industrial polysulfone (PSU) based on bisphenol A and 4,4'-dichlorodiphenylsulfone of the following structure:

polyethersulfone (PESU) based on 4,4'-dioxidiphenyl-sulfone and 4,4'-dichlorodiphenylsulfone of the following structure:
and polyphenylene sulfone (PPS) based on 4,4’-dioxidiphenyl and 4,4’-dichlorodiphenylsulfone of the following structure:

![Structure of polyphenylene sulfone](image)

Primary properties of these polymers are shown in Table 1 [13].

| Property                        | Polysulfone | Polyethersulfone | Polyphenylenesulfone |
|---------------------------------|-------------|------------------|----------------------|
| Glass transition temperature, °C | 187         | 225              | 220                  |
| Density, g/cm³                  | 1.23        | 1.5              | 1.29                 |
| HDT @ 1.8 MPa, °C               | 177         | 205              | 198                  |
| Tensile strength, MPa           | 75          | 85               | 74                   |
| Tensile modulus, MPa            | 2550        | 2650             | 2270                 |

Due to its excellent properties, PSU, PES and PPS belong to high performance polymers that are capable of continuous service under high temperature of 170-200 °C [2, 14-17]. However, their application temperature range and mechanical properties can be improved even further by developing composite materials reinforced with dispersed particles, continuous fibers or fabrics [18, 19].

This is relatively new field for polysulfones, hence it is required to apply and analyze experience gained from other polymers. Currently, usage of thermoplastics for matrices of composite materials evaluated to be about 25-35% of total matrices, the other 65-75% being thermosetting materials [19]. The majority of thermoplastic composites are polypropylene filled with short fiberglass, polyamides, polyethylene terephthalate, polybutylene terephthalate and polyphenylene oxide, the minority of thermoplastic composites are materials filled with aramid and carbon fibers. Fiber-filled polyphenylene sulfide, polyetherimides and polyetheretherketone are used for highly functional applications. They are presented on the market in the form of granules, sheets, rods, prepregs and ribbons [19].

The advantages of thermoplastics over thermosets as a matrix of a composite material are the absence of a long curing stage, less hazardous production, the possibility of waste recycling, unlimited shelf life of semi-finished products (prepregs), the possibility of welding under pressure, greater impact resistance, frost resistance and a number of other advantages, associated with a wide range of these materials. Disadvantages: high creep under load, problems associated with high viscosity of thermoplastics melts [19-22].

By filling thermoplastics with fibers following improvements can be achieved: an increase in head distortion temperature, modulus and strength, a decrease in the tendency to creep under constant load, anisotropy of properties, and decreased cost of the material [1-3, 19].

Generally, for composites filled with short fibers a gradual growth and then limitation of performance are observed with increase in fiber length (Fig. 1) [19]. An increase in the fiber content in a composite in different cases can either smoothly or rather sharply increase its performance (Fig. 2) [19].
Numerous studies [1-3, 18, 19, 23-27] have shown that the properties of the composite are largely dependent on the interfacial interaction between the fiber and the matrix, as well as on the absence of pores in the material. Only in the presence of strong adhesive or chemical bonds will the fiber-filled composite work as a unit, and the matrix will fully transfer the applied load to the reinforcing fiber.

For the formation of adhesive and chemical bonds, it is necessary for fiber to be in a very close contact with the matrix and, therefore, the matrix must impregnate the fiber surface to a sufficient degree. The strength of the interface adhesion is determined by the chemical nature and the number of polar groups on the surface of the fiber and in the polymer matrix. Since it is difficult and irrational to increase the polarity of the polymer via its chemical modification due to the deterioration of its properties (heat resistance decreases, dielectric properties deteriorate, water absorption increases, etc.), to achieve high interface adhesion surface of the reinforcing fibers is modified. For this purpose, a number of methods have been developed for activating the surface of glass, basalt, polyaramides and carbon fibers, including: applying active lubricants (sizings), thermal treatment, chemical treatment, radiation treatment, plasma treatment and combined methods [28-33]. Moreover, for different polymer matrixes different methods of activation of reinforcing fibers are selected, therefore, there is a
significant assortment of fiber fillers on the market and the development of new options taking into account price-quality parameters is ongoing [33].

Glass and basalt fibers contain active silanol groups on their surface that react with silane lubricants containing amine, glycidyl, methacrylic, vinyl and other groups (γ-aminopropyltriethoxysilane, γ-glycidoxypropyltrimethoxy silane, γ-methacrylpropyltriethoxysilane and others). The presence of organic fragments with polar and chemically active groups provides good adhesion and, in some cases, chemical bonding with many polymer matrices (epoxy and polyester resins, polypropylene, polyethylene terephthalate, polyurethanes, polyetherimides) [2, 19, 34, 35].

The surface of the carbon fiber is inert and does not contain polar groups, has graphite flakes loosely bonded to the bulk of the fiber; therefore, such fibers are poorly wetted by resins or melts of thermoplastics and form weak adhesive bonds with the matrix, mainly due to mechanical engagement along microcracks and shells [36]. Carbon fibers are activated in various ways: calcined in air at 500 °C [32, 33, 37], oxidized with chemical oxidizing agents, treated with plasma in air, all of which results in formation on the surface of fibers hydroxyl, carboxyl, ketone, ether bonds. Additionally, vacuum deposition of metals (copper, aluminum, stainless steel) is carried out on such fibers [38]. The main industrial activation methods is impregnating of polyacrylonitrile carbon fiber obtained after pyrolysis with aqueous solutions or emulsions of organic low molecular weight lubricants with polar groups [2, 34].

Activated carbon fibers can significantly improve the interfacial interaction between the fibers and the polymer matrix, which leads to a significant increase in the mechanical properties of reinforced composites of modified carbon fibers in comparison with composites containing untreated fibers: on average, Young's modulus, tensile strength and shear strength are increased by 25-45%. A decrease in the mobility of macromolecules of the interfacial layer leads to an increase in the glass transition temperature of the polymer matrix by 3-5 degrees. Composites with good adhesive strength and low porosity have increased impact resistance, which is associated with improved energy transfer to the fiber filler and its dissipation in the material [19].

Considering all the above, the aim of our work was to develop methods of manufacturing prepregs based on activated unidirectional fibers in the form of ribbons and the synthesized by us polyethersulfone based on 4,4'-dioxidiphenyl-sulfone and 4,4' -dichlodiphenylsulfone with a given molecular weight. The choice of the direction of work was due to the fact that one of the problems in the manufacture of carbon composites with low porosity by hot pressing of pads from prepregs is the high viscosity of the polymer melt, which leads to poor impregnation of individual filaments in the carbon fiber. Therefore, the choice of the optimal molecular weight of polyethersulfone, which provides good performance of the matrix at a relatively low melt viscosity, was of scientific and practical interest.

The synthesis of polyethersulfone labeled PES-12 was carried out using N-methylpyrrolidone as solvent in an inert atmosphere at a temperature of 160-170 °C according to the following reaction equation:

\[
\text{nHO-} + \text{nCl}\text{-Cl} + \text{nK}_2\text{CO}_3 \xrightarrow{T_{\text{reox}}} \text{nKCl} + \text{nCO}_2 + \text{nH}_2\text{O}
\]

The method of synthesis of 100 g of polyethersulfone.

In a three-necked 500 ml flask equipped with an overhead mechanical stirrer, argon inlet, Dean-Stark trap, reflux condenser and bubble counter, 53.87 g of 4,4'-dioxiphenyl-sulfone, 35.70 g of potassium carbonate, 320 g of N-methylpyrrolidone and 60 g of toluene were loaded. The Dean-Stark trap was filled with 50 ml of toluene and then flask was heated using a silicone bath equipped with a magnetic stirrer and a thermocouple.

At a bath temperature of 160 °C, an azeotropic toluene-water mixture is distilled off for 10 hours and a suspension of 4,4'-dioxiphenylsulfone dipotassium salt in a mixture of N-methylpyrrolidone and
toluene is obtained. After the water is distilled off, it is removed from the Dean-Stark trap and the toluene is completely distilled off from the flask for 2 hours. The result is a solution of the dipotassium salt of 4,4'-dioxiphenylsulfone in N-methylpyrrolidone. Then, 61.82 g of 4,4'-dichlorodiphenyl sulfone is introduced into the flask, the bath temperature is increased to 170 °C and the polyethersulfone formation reaction is carried out for 20 hours.

Upon completion of the reaction, 100 g of N-methylpyrrolidone are introduced into the flask and the polymer is precipitated in 2.5 l of distilled water with vigorous stirring of the precipitant. The precipitated powdery precipitate is filtered off and washed from solvent and potassium chloride until a negative sample for chlorine ions (using an aqueous solution of silver nitrate) is achieved. After the cessation of the appearance of turbidity (silver chloride crystals) in the water at room temperature, the polyethersulfone is filtered off and dried at 120 °C for 3 hours. The polymer yield is 96-98% of theoretical.

During the synthesis, sampling was performed to assess the molecular weight of the polymer and its glass transition temperature. The structure of the synthesized polymer was confirmed by IR spectroscopy and elemental analysis.

The molecular weight of the polymer was evaluated by determining the reduced viscosity of the sample solutions in N-methylpyrrolidone and according to gel permeation chromatography.

Method for determining the reduced viscosity of polyethersulfone solutions.

A portion of PES-12 in an amount of 0.125 g was dissolved in 25 ml of N-methylpyrrolidone, the resulting solution was filtered through a polyamide filter cloth and poured into an Ostwald glass viscometer with a capillary diameter of 0.56 mm, placed in a temperature-controlled vessel with water at 25 °C. The flow time of the solution was determined from the upper to the lower mark of the viscometer and the value of the reduced viscosity of the solution was calculated by the formula [39]:

\[ \eta_{\text{red}} = \frac{\tau_{\text{sol}} - \tau_{\text{solv}}}{\tau_{\text{solv}}} \cdot C \]  

where:
\( \eta_{\text{red}} \) – reduced viscosity of polymer, dl/g;
\( \tau_{\text{sol}} \) – average flow time of polymer solution, sec;
\( \tau_{\text{solv}} \) – average flow time of solvent, sec;
C – concentration of polymer solution, g/dl.

Glass transition temperatures for polymer samples taken during synthesis were determined using differential scanning calorimetry (DSC) using the NETZH DSC 204 F1 Phoenix instrument. The heating rate in an inert gas atmosphere was 10 degrees/minute, the polymer sample in the form of a compressed tablet weighed 10-13 mg, the glass transition temperature was recorded during the secondary heating of the sample.

Figure 3 shows the dependence of the glass transition temperature of polyethersulfone on the time of polymer synthesis. It can be seen that after 16 hours of synthesis, almost the maximum glass transition temperature of this polymer is achieved. Further continuation of the reaction will lead to an increase in the molecular weight of the polymer (Figure 4), and hence to an increase in the viscosity of the melt, which is not desirable when impregnating carbon fabrics with a melt of polyethersulfone.
From Figures 3 and 4, it can be concluded that the optimal ratio of glass transition temperature and reduced viscosity of polyethersulfone is achieved in 15-16 hours of reaction, which corresponds to a value of reduced viscosity equal to 0.5 dl/g. Considering the obtained results, in the future, PES-12 with a reduced viscosity of 0.50-0.55 dl/g was used for the manufacture of prepregs. According to gel permeation chromatography («Waters» company instrument, N-methylpyrrolidone eluent, polystyrene standards) this corresponds to the number average molecular weight $\text{Mn} = 49700$, the weight average molecular weight $\text{Mw} = 96000$, and the molecular weight distribution $\text{Mw} / \text{Mn} = 1.93$.

As unidirectional carbon tape LU-P/0,1-A manufactured by «Argon» company (GOST 28006-88) was used, the width of the tape 255 mm, the thickness of the monolayer 0.1-0.12 mm, the number of filaments in the warp threads 3K (or 3000 pieces), and the tape “FIBARM TAPE-230/300” manufactured by «Holding Company Composite» (specification 1916-005-61664530-2011), the tape width is 300 mm, the thickness of the monolayer is 0.23 mm, the number of filaments in the warp yarn is 12K.

Two methods were used to make prepregs based on the above unidirectional tapes and synthesized polyethersulfone. Method 1 consisted of impregnating carbon tapes with solutions of thermoplastic in
dimethylformamide in two steps: first, for better impregnation of the polymer solution between carbon fiber filaments, impregnation with a low-viscosity 5% solution, followed by drying in a heating cabinet at 120 °C for 12 hours was carried out, and then, to apply an additional amount of thermoplastic, another impregnation of carbon fabric with a 20% polymer solution with drying in a heating cabinet on an even substrate at 120 °C for 18 hours was carried out. The ratio of carbon fiber/polymer was 60:40 by weight.

Method 2 consisted of impregnating carbon fabric with a 5% polymer solution in dimethylformamide and sprinkling wetted sticky fiber with polyethersulfone powder, followed by drying the semi-finished product in a heating cabinet on an even glass substrate at 120 °C for 12 hours. The ratio of carbon fiber / polymer was 60:40 by weight.

Samples of unidirectional composite plates with a thickness of 4 mm were made from the obtained prepregs of 330x330 mm by hot pressing. Pressing was carried out according to the step-by-step mode of temperature gain up to 340°C and pressure up to 9 MPa. The resulting plates were used for cutting elementary samples to study the mechanical and temperature characteristics of composites. Initial studies using an electron microscope showed that the obtained carbon composites have a dense, homogeneous structure, which allows us to hope to obtain high performance when testing samples. Research is ongoing.

Conclusions
It was shown that to obtain prepregs based on activated carbon fibers and thermoplastic polyethersulfone with high degree of impregnation it is crucial to use polymer of optimal molecular weight, ensuring good mechanical properties of polymer matrix and manageable viscosity of its melt.

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