Development of imid-containing appretes for carbon fibers and carbon fabrics

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Annotation. The results of research on synthesis and approbation of new imide-containing high-molecular and oligomeric compounds as appretiruyuschih compositions for carbon fibers under thermoplastic polyetherimide matrix (“Ultem-1000”) are presented. It is shown that both polymeric and oligomeric compositions can be used for carbon fiber appreting, but the greatest effect is manifested when using oligomeric apprets.

1. Introduction
Reinforced plastics based on glass, polymer, carbon and ceramic fibers are widely used in special areas of modern technology. Without their application, it is now impossible to imagine rocket or aviation, they are increasingly used in other areas of the national economy-engineering, shipbuilding, construction, etc. [1-2]. Such widespread polymer composites are due to its high strength, combined with low density, good moisture and chemical resistance, corrosion resistance, resistance to cracking. In recent years, actively developing research in the development, production and application of composite materials based on super-strong (5000-7000 MPa) carbon fibers with high elongation limits(1.5-2.0%) [3-5].

Of particular interest is the work on the use of binders based on structural thermoplastic materials with increased heat resistance, namely-polymide materials that allow the operation of products made of them at temperatures above + 250°C (depending on the duration of operation and the environment), at cryogenic temperatures, the impact of penetrating radiation doses of 104 Mrad and more, high mechanical loads and a combination of the above conditions [6-11]. Of no less interest as a binder are superconstructions thermoplastics, e.g. polyether sulfones and polyetherimides [12-19].

The low shear strength of composite materials is a limiting factor in the use of carbon fiber on a thermoplastic polymer matrix. It is known that on the surface of carbon fibers there are small micro-scales containing an increased amount of crystalline graphite, as well as inclusions and microcracks. This structure of the surface of carbon fibers leads to low adhesion of the binder to their surface [4,20, 21]. Thus, it is obvious that the creation of high-quality composite carbon plastics is impossible without a purposeful synthesis of not only heat-resistant polymer matrices, but also materials that ensure their adhesion to carbon fiber, known as textile and operational appretes.

Appretiruyuschie coating increases the adhesive and cohesive properties of the interface between the phases of the carbon fiber-polymer matrix. Composite materials with well-chosen appendages well perceive and transmit loads, have a high resistance to cracking of the material at the interface at high loads.
It should be noted that in the literature there are rarely specific data on the compositions of the appreting compositions and the conditions of their application, since these data are often the subject of know-how.

This paper presents the results of research on the development and testing of new imide-containing high-molecular and low-molecular compounds as appretingusih compositions for carbon fibers under thermoplastic polyimide or polyethyrimide matrix.

As macromolecular coupling agents were synthesized copolyimide (SPI) with the General formula:

\[
\begin{align*}
\text{C} & \text{C} \quad \text{C} \\
\text{C} & \text{N} \quad \text{O} \\
\text{O} & \text{O} \quad \text{C} \\
\text{H}_3 & \text{N} \\
\end{align*}
\]

To assess the effect on the appreting properties of the chemical composition and molecular weight (MM) of copolymers, the ratio of "x:y" links based on benzophenonetetracarboxylic (BPDA) and pyromellitic (PMDA) acids varied in the range of 70:30% by weight. (SPI-1 and SPI-2, MM), 60: 40% by weight. (SPI-3), 50: 50% by weight. (SPI-4 and SPI-5) and 40: 60% by weight. (SPI-6). These copolymers have solubility in dipolar aprotic solvents (dimethylformamide, dimethylacetamide, N-methylpyrrolidone, dimethylsulfoxide) and can be applied to carbon fiber in the form of solutions of different concentrations.

In addition, low molecular weight copolymers based on BPDA of the following structure (SPI-7) were synthesized to compare the appreting properties:

\[
\begin{align*}
\text{O} & \text{C} \\
\text{N} & \text{C} \\
\text{O} & \text{C} \\
\text{O} & \text{O} \\
\text{C} & \text{C} \\
\text{C} & \text{N} \\
\text{O} & \text{O} \\
\text{C} & \text{H}_3 \\
\end{align*}
\]

and based on PMDA (SPI-8):

\[
\begin{align*}
\text{O} & \text{C} \\
\text{N} & \text{C} \\
\text{O} & \text{C} \\
\text{O} & \text{O} \\
\text{C} & \text{C} \\
\text{C} & \text{N} \\
\text{O} & \text{O} \\
\text{C} & \text{H}_3 \\
\end{align*}
\]

The BADA-based oligomeric appret SPI-9 with terminal anhydride groups and x=3 was a compound of the following structure:

\[
\begin{align*}
\text{O} & \text{C} \\
\text{C} & \text{O} \\
\text{N} & \text{C} \\
\text{O} & \text{O} \\
\text{C} & \text{C} \\
\text{C} & \text{N} \\
\text{O} & \text{O} \\
\text{C} & \text{H}_3 \\
\end{align*}
\]

SPI-10 oligomer based on PMDA with terminal anhydride groups and x=3 had the following structure:
The synthesized compounds were characterized by the methods of elemental analysis, IR spectroscopy, thermogravimetry, the viscosity values of their 0.5% solutions in N-methylpyrrolidone at 25°C.

The effectiveness of the appreting action of the synthesized compounds was evaluated by SEM-photos of the surface and cut-off samples of the manufactured prepregs. Micrographs were obtained using a scanning electron microscope "Hitachi SU 1510" (Japan) at magnification of 200, 500, 1000 and 2000 times. As a model binder was selected industrial polyethyrimide brand " Ultem-1000 " (firm "SABIC").

2. Receiving samples

For the experiment, we used 1.5 K carbon fiber (made in Taiwan), appretirovannoe under epoxy resin. Samples of prepregs for the study of coupling efficiency of the synthesized products were made according to the scheme consisting of two stages: 1) cleaning carbon from a source of size and dressing of new compounds and 2) impregnating the treated fibers with a solution of polyetherimide "Ultem-1000".

In the first step, the original carbon fiber was successively passed through a bath of chloroform to remove the factory "textile" appret, and then through a bath with a solution of the new appret in dimethylacetamide. The impregnated thread was passed through a step-heating furnace (first stage +250°C, second +300°C) for 90 seconds for each heating stage. At this stage, it was important to select a suitable concentration of appret in the solvent. The result was evaluated visually: dry appretirovannaya thread with a suitable concentration of appret was soft, bent into a loop without creases and retained solidity (not fluffed) when stretched through the impregnation plant at the second stage of processing. At excessive concentration of an appret the thread appeared too rigid and was wrung at bending; at insufficient concentration of a polymer or oligomer in an appretating solution the thread was torn or stratified at attempt of its broach through impregnating installation. After determining the optimal concentration of the appretating solution, a prototype of the appreted fiber was developed, which was then directed to impregnation with a matrix polymer solution.

The second stage is to obtain a fiber prepreg. The pre-appretirovannoe fiber was successively stretched through two baths filled with 20% solution "Ultem-1000" in chloroform. Between the first and second impregnation bath, the thread was pressed using Teflon rollers to achieve uniform impregnation of the filaments throughout the fiber volume. The geometry of the impregnated fiber was formed by means of a die, then the fiber was stretched through a step-heated furnace (the first stage +350°C, the second +430°C) for 45 seconds for each stage. The hot fiber was wound on a receiving coil with a diameter of 12 cm and removed after complete cooling.

3. Discussion of results

The characteristics of the synthesized compounds are given in tables 1 and 2.

Table 1. Reduced viscosity of synthesized compounds

| Шифр полимера | \( \eta_{пр.} \), д/л/г | Шифр полимера | \( \eta_{пр.} \), д/л/г | Шифр полимера | \( \eta_{пр.} \), д/л/г |
|--------------|----------------|--------------|----------------|--------------|----------------|
| SPI -1       | 0,24           | SPI -5       | 0,47           | SPI -8       | 0,14           |
| SPI -2       | 0,38           | SPI -6       | 0,41           | SPI -9       | 0,10           |
Table 2. Results of thermogravimetric analysis of thermoplastic polyimides

| Шифр полимера | The temperature loss 5% weight of the sample, °C | The temperature loss 10% weight of the sample, °C |
|---------------|---------------------------------|---------------------------------|
| SPI-1         | 416 in argon 442 in the air     | 513 in argon 522 in the air     |
| SPI-2         | 484 in argon 460 in the air     | 540 in argon 490 in the air     |
| SPI-3         | 435 in argon 454 in the air     | 530 in argon 488 in the air     |
| SPI-5         | 486 in argon 460 in the air     | 537 in argon 486 in the air     |
| SPI-6         | 480 in argon 452 in the air     | 526 in argon 452 in the air     |
| SPI-7         | 452 in argon 438 in the air     | 506 in argon 511 in the air     |
| SPI-8         | 458 in argon 440 in the air     | 508 in argon 515 in the air     |
| SPI-9         | 465 in argon 454 in the air     | 521 in argon 526 in the air     |
| SPI-10        | 460 in argon 448 in the air     | 511 in argon 508 in the air     |

Using a scanning electron microscope, the density of the composite material in the cross sections of the samples destroyed during bending was determined. Analysis of the obtained data allows to conclude that the effectiveness of the coupling action is highly dependent on the molecular weight of the synthesized copolyimides. So, when using a macromolecular size of SPI-3 in the cross section of the fiber observed spalls, voids, gaps between the fiber and the matrix, the looseness of the structure of the surface shell fibers (figure 1), in the case of oligomeric size SPI-10 (figure 2) in the section of the fault gouges are practically absent, the fracture surface is smooth, without voids, the contact between the matrix and fibers is complete.

Thus, oligomeric compounds with reduced viscosity of 0.5% solutions in N-methylpyrrolidone from 0.10 to 0.16 DL/g were more effective devices. These oligomers were used to appretirovaniya carbon fibers and tissues before applying melts of thermoplastic polyethyrimide brand "Ultem-1000" and high-molecular copolyimides SPI-3 and SPI-5. The resulting thermoplastic carbon composites are currently being tested.

![Figure 1. SEM - photo of the section of the prepreg obtained using high molecular weight appret SPI-3.](image-url)
Figure 2. SEM - photo of the section of the prepreg obtained using low molecular weight appret SPI-10.

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