Investigation of the processes of modification of polyimide systems required to create reinforced composite materials by 3d printing

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Abstract. To obtain polyimide films the processes of modification of polyamic acid were investigated. The rheological and deformation-strength properties of the modified polyimide materials were determined. The modified polyimide systems with adjustable properties were developed.

1. Introduction
For the development of the aerospace industry, it is necessary to create fundamentally new composite materials. Currently, much attention is paid to the manufacture of products by 3D-printing, however, the main disadvantage of this kind of products is the low range of operating temperatures. To create heat-resistant high-strength products by 3D-printing with continuous fiber, it was proposed to use heat-resistant polyimide and polyetherimide matrices as polymeric binders.

Carbon fiber in the manufacturing process is treated with a finishing agent of various chemical structures to prevent them from puffing, protect against abrasion, transportation and, most importantly, to create an active layer that provides the strength of the adhesion interaction between the fiber and the polymer matrix.

The right choice of finishing agent and method of its application plays an important role in creating high-quality carbon plastics. This is explained by the following reasons:

• The adhesion of polymers to carbon fiber and the wetting ability of the fiber is low due to the absence of polar groups on its surface, compared to, for example, glass fiber.

• The surface of the fiber has pores of various sizes oriented along the stretch.

Large pores with a diameter of 100-300 Å the molding of a composite material are filled with a binder and the adhesive strength of the binder with the fiber increases. Small pores with a diameter of several tens of angstroms can fill only low molecular weight components of the binder.

There are several ways to increase the adhesion strength of carbon fiber with a polymer matrix, the effectiveness of which is assessed by increasing the strength of the composite material during shear:

• removal of the finishing agent film from the surface of carbon fibers after the end of textile processing and its replacement with an effective finishing agent for this type of polymer matrix;
etching the surface of carbon fibers with oxidizing agents;

tenmetallization of carbon fibers;

growing on the surface of fibers of crystal whiskers with high shear resistance.

In some cases, several processing methods are applied.

2. Result and discussion

During the project, an alternative method of pre-impregnation of reinforcing fiber was developed. The preparation of reinforced carbon fiber was carried out by a two-step method. At the first stage, carbon fiber was impregnated by solutions of monomers, oligomers and copolymers with isocyanate groups of various concentrations. At the second stage, fiber was impregnated with solutions of thermosetting plastic and thermoplastic polyimides of various chemical structures followed by drying.

A number of organic polymers and copolymers based on 3,3',4,4'-diphenyloxide tetracarboxylic acid, 3,3',4,4'-benzophenone tetracarboxylic acid and 2,2-bis (3,4-dicarboxyphenyl) — hexafluoropropane anhydride were synthesized and presented in the figure 1:

![Figure 1. Structural formulas of dianhydrides.](image)

The developed polymer blends made it possible to avoid fiber stratification, increased its technological properties, and also increased adhesion with the polymer matrix during subsequent impregnation. A series of polyimide matrices was synthesized for use as impregnating compositions containing various modifying additives to improve the technological properties and performance characteristics. The promise of a wide modification of polyimide systems was considered in [1].

To improve the compatibility of the components, reduce the viscosity of the system and also to improve the fiber impregnation the organosilicon compound — polysiloxane–polyyoxyalkylene block copolymer (ISC) as well as the effective surface active agent polymethylsiloxane (PMS) [2] were used as modifiers.

To change the surface tension of the films, monomeric cyclocarbonate (CC) was used. To increase the values of deformation-strength parameters, polyvinylformal ethyl (Viniflex) was used. Epoxy-Urethane was used to increase the adhesion of the polyimide matrix to carbon fiber.

Polyamide films based on polyamic acid (PAA) and selected modifiers were manufactured using a multi-step imidization method. The rheological properties of the obtained PAA with various modifiers were investigated. The Brookfield DV2T viscometer was used, the study was carried out by measuring the resistance of a viscous system to expiration at a given shear rate. The presented figures are shown a significant decrease in the viscosity of PAA + 2% viniflex + ISC compositions. A marked decrease in viscosity, especially at 25°C, is observed for PAA + 2% PC + 0.5% ISC and PAA + 3% aldehyde rubber + 0.5% ISC compositions. The data obtained testifies to the improvement of the technological properties of these compositions and the possible decrease in the temperature of their further processing.

The test results of the rheological properties of the obtained compositions are presented in Table 1.
Table 1. Values of the rheological characteristics of compositions based on PAA and modifiers at a shear rate of 0.25 1/s

| Composition                      | Viscosity, Pas | Torque effect, % | Shear stress temperature, °C |
|---------------------------------|---------------|-----------------|------------------------------|
|                                 | temperature, °C | temperature, °C | temperature, °C              |
| PI                              | 25            | 50              | 80                           |
| PAA + 0.5% ISC                  | 0.127         | 0.036           | 0.011                        |
| PAA + 2% CC + 0.5% ISC          | 0.075         | 0.038           | 0.012                        |
| PAA + 2% Viniflex               | 0.113         | 0.059           | 0.021                        |
| PAA + 2% Viniflex + ISC         | 0.040         | 0.023           | 0.017                        |
| PAA + 3% Epoxy-Urethane         | 0.124         | 0.109           | 0.020                        |
| PAA + 3% Epoxy-Urethane + 0.5% ISC | 0.082   | 0.033           | 0.015                        |

The data presented are shown that a significant decrease in viscosity is observed in the compositions: PAA + 2% Viniflex + ISC, PAA + 2% PC + 0.5% ISC and PAA + 3% Epoxy-Urethane + 0.5% ISC. The data obtained testifies to the improvement of the technological properties of these compositions and the possible decrease in the temperature of their further processing.

The specific free surface energy, the dispersion and polar component of the surface tension of the obtained films were determined by Owens-Wendt-Rabel-Kaelble’s method. To find the polar and dispersive components of the surface tension of the developed films, the wetting angles of ethylene glycol and water on the surfaces of these films were determined [3].

Table 2. Surface tension γLV, its dispersion γdLV and polar γpLV components (mJ/m²) of the films obtained

| Composition                      | Dispersion component of surface tension, mJ/m² | Polar component of surface tension, mJ/m² | Surface tension, mJ/m² | The proportion of the dispersion component | The proportion of the polar component |
|---------------------------------|-----------------------------------------------|-------------------------------------------|------------------------|--------------------------------------------|--------------------------------------|
| PI                              | 2.24                                         | 1.56                                      | 3.80                   | 59%                                        | 41%                                  |
| PI + ISC                        | 1.85                                         | 2.04                                      | 3.88                   | 48%                                        | 52%                                  |
| PI + CC + ISC                   | 1.53                                         | 2.09                                      | 3.62                   | 42%                                        | 58%                                  |
| PI + WACKER 060L                | 1.91                                         | 1.69                                      | 3.61                   | 53%                                        | 47%                                  |
| PI + PMS-500                    | 2.06                                         | 1.64                                      | 3.70                   | 56%                                        | 44%                                  |
| PI + Viniflex                   | 1.82                                         | 2.12                                      | 3.94                   | 46%                                        | 54%                                  |
| PI + Viniflex + ISC             | 2.38                                         | 1.60                                      | 3.97                   | 60%                                        | 40%                                  |
| PI + 3% Epoxy-Urethane          | 1.98                                         | 2.20                                      | 4.18                   | 47%                                        | 53%                                  |

The data presented in Table 2 are shown that the addition of modifiers increases the value of the polar component of the surface tension. This is especially noticeable with addition of PI + PC + ISC (the polar component increases from 41% for unmodified polymer to 58%). Accordingly, to increase the contact between the fiber and the binder, it is reasonable to use the composition PI + PC + ISC.
Physical and mechanical tests of the polyimide films obtained were carried out, the results of which are presented in Table 3.

**Table 3. Values of tensile strength and breaking elongation of PI films**

| Composition                  | Tensile strength, MPa | Tensile elongation, % |
|------------------------------|-----------------------|-----------------------|
| PI                           | 63,8                  | 4,6                   |
| PI + 2% Viniflex             | 88,9                  | 8,1                   |
| PI + 2% CC + 0,5% ISC        | 54,0                  | 6,8                   |
| PI + Epoxy-Urethane          | 46,2                  | 10,3                  |
| PI +2% Viniflex + ISC        | 86,5                  | 11,0                  |

The data obtained are shown that the addition of Viniflex increases the tensile strength by about 1.3 times. In addition, an increase in the deformation properties was achieved by adding Epoxyurethane to the system.

**3. Conclusion**

Thus, as a result of research, a decrease in the viscosity of modified compositions of PAA + 2% Viniflex + ISC, PAA + 2% PC + 0.5% ISC and PAA + 3% Epoxy-Urethane + 0.5% ISC was found. The data obtained indicate an improvement in the technological properties of these compositions and a possible decrease in the temperature of their processing.

The introduction of the ISC modifier markedly increases the value of the polar component of the surface tension was found. To increase the contact between the fiber and the binder, it is advisable to use the composition of the composition of the PI + PC + ISC.

It was also found that the use of Viniflex modifiers leads to an increase in the tensile strength of the films, which makes it possible to obtain polyimide films with improved deformation and strength properties.

Thus, depending on the requirements of the consumer to the technological and operational properties of polyimide films, using modifiers it is possible to obtain polyimide systems with tunable properties, which will make it possible to create polyimide multilayer composite materials and structures from them.

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