Evaluation of heat resistance of carbon fiber reinforced plastics based on organosilicon compounds

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Abstract. The paper presents composite materials based on elastomeric matrices in combination with phenol-formaldehyde resin, reinforced with carbon fiber fabric. Technology of obtaining composites is described. Polymer binder has been modified by introducing inorganic additives (SiC, ZrB₂, glass microspheres). Experimental data of thermogravimetric analysis of the obtained carbon plastics are presented. Comparative tensile strength tests of composite materials have been carried out before and after plasma treatment. Materials described in the paper are intended for use in high-temperature heat shielding.

1. Introduction

At present, there is an increased interest in improving the heat resistance and mechanical properties of airspace elements and structures, accordingly, increasing the requirements for materials used. One of the groups of such materials is heat-shielding polymer composites [1], that must withstand ever higher temperatures.

Polymer composite materials based on organosilicon elastomers are promising materials for use in highly heat-loaded operating conditions as heat-shielding materials. They have small weight and size characteristics, manufacturability, the ability to manufacture thin-walled products of complex shape.

The mechanism of thermal protection of polymeric materials is based on pyrolysis and ablation of materials, accompanied by the absorption of external heat flux [2].

Elastomeric materials based on rubbers (ethylene propylene diene, butadiene nitrile, organosilicon rubbers, etc.) are widely used for thermal protection [2-9]. They are used, for example, as the inner shells of rocket engines [10-12]. The most heat-resistant are organosilicon rubbers. At low and high temperatures, silicones retain their elasticity, unlike traditional diene-based rubbers.

Improving the thermophysical properties of heat-shielding polymeric materials is an urgent task in connection with an increase in operating temperatures.

Silicones have poor coking and sintering properties when undergoing pyrolysis. Various fillers were reported to improve physico-mechanical, thermophysical, and rheological properties [9]. Such fillers include dispersed (refractory particles: ZrB₂, SiO, SiC, ZrO₂; heat-resistant polymers [10, 12-18]), and fibrous fillers (glass, carbon, silica and other fibers and fabrics [2, 3, 19, 20]).

In this report, we consider composite materials based on a mixture of organosilicon polymer and phenol-formaldehyde resin. Modification of matrices with inorganic additives was carried out.
Thermophysical and mechanical properties of the obtained carbon fiber reinforced plastics (CFRP) are investigated.

2. Materials and methods

The investigated materials are multilayer composite materials based on a mixture of organosilicon elastomer with phenol-formaldehyde resin (PFR) with additives.

Polymer elastomeric matrix used in the present study was a mixture of "Yunisil-9728" silicone with "SF-015" phenol-formaldehyde resin in powder form.

Powders of silicon carbide (melting temperature ≈ 2730 ° C), zirconium diboride (melting temperature ≈ 3000 ° C) glass microspheres (melting temperature ≈ 1600 ° C) are used as modifying additives. SEM images of the powders are shown in Figure 1.

![SEM images of powders: glass microspheres (a), ZrB₂ (b), SiC (c) (magnification x1800).](image)

Figure 1. SEM images of powders: glass microspheres (a), ZrB₂ (b), SiC (c) (magnification x1800).

UWB-200-3K-TWILL2 / 2-100 carbon fabric (UMATEX, Russia) was used as a reinforcing component. Samples were made up of five layers of fabric.

The matrices were prepared as follows: component A of silicone was mixed with PFR in a 2:1 ratio (the choice of the optimal ratio is given in [18]) and inorganic additives. Then component B (hardener) was added to the mixture in a ratio of 1:10 mass parts of component A, as recommended by the manufacturer.

Composite materials were made by manual molding of a filler and a matrix: the prepared uncured matrix is evenly applied to the layers of carbon fabric, and then the samples are cured at 120 °C for 1.5 h in a drying oven in air.

The compositions of the experimental samples are shown in Table 1. The viscosity of the matrix was measured with Elcometer 2300 R viscometer and was 75 500 mPa s, which is technologically appropriate for manual molding.

Thermogravimetric analysis of CFRPs was carried out using a simultaneous thermal analyser STA 449 F1 Jupiter.

Scanning electron microscopy (SEM) images were taken on a Hitachi TM3000 microscope at 15 kV accelerating voltage.
Plasma treatment was carried out on an experimental plasmatron in a specially designed fixtures. Tensile tests were carried out on a Zwick / Roell Z250 machine.

**Table 1. Compositions of experimental samples.**

| Designation                  | Carbon fiber, number of layers | The matrix                      | Additive                   | Matrix content, wt. % |
|-----------------------------|-------------------------------|---------------------------------|----------------------------|-----------------------|
| Silicone + PFR (2:1)         | 5                             | "Yunisil-9728"                  | -                          | 75                    |
| Silicone + PFR (2:1) + 2 % SiC| 5                             | "Yunisil-9728"                  | SiC, 2 wt. %               | 74                    |
| Silicone + PFR (2:1) + 2 % ZrB$_2$| 5                          | "Yunisil-9728"                  | ZrB$_2$, 2 wt. %          | 73                    |
| Silicone + PFR (2:1) + 3 % SiC + 3 % ZrB$_2$ + 4 % SiO-spheres | 5                          | "Yunisil-9728"                  | SiC, 3 wt. %, ZrB$_2$, 3 wt. %; SiO-spheres, 4 wt. % | 76 |
| Silicone + PFR (2:1) + 5 % SiC | 5                            | "Yunisil-9728"                  | SiC, wt. 5%                | 77                    |
| Silicone + PFR (2:1) + 5 % ZrB$_2$ | 5                            | "Yunisil-9728"                  | ZrB$_2$, wt. 5%           | 75                    |

3. Results and discussion

In order to assess the influence of the introduced modifiers on the thermophysical properties of composite materials, thermogravimetric analysis of CFRPs was carried out at up to 1000 °C at a rate of 10 °C / min in air. The test results of experimental samples are shown in table 2.

**Table 2. Thermogravimetric analysis study results.**

| Designation                  | Atmosphere | Temperature of the beginning of thermal transformations | Temperature of the end of thermal transformations | Residual mass |
|-----------------------------|------------|--------------------------------------------------------|--------------------------------------------------|---------------|
| Silicone + PFR (2:1)         | Air        | 422.9 °C                                               | 546.0 °C                                          | 25.53 %       |
| Silicone + PFR (2:1) + 2 % SiC| Air        | 424.7 °C                                               | 563.3 °C                                          | 17.99 %       |
| Silicone + PFR (2:1) + 2 % ZrB$_2$ | Air        | 434.8 °C                                               | 573.2 °C                                          | 18.94 %       |
| Silicone + PFR (2:1) + 3 % SiC + 3 % ZrB$_2$ + 4 % SiO-spheres | Air        | 433.6 °C                                               | 551.1 °C                                          | 30.09 %       |

Under stationary heating, materials have a fairly high thermal stability of ≈ 422 °C - 434 °C, thermal transformations are completed in the range of ≈ 546 °C - 573 °C. The upper boundaries of the intervals are provided by the introduction of 2 wt. % ZrB$_2$. The effect of the introduced modifying additives on the residual mass differs significantly, the most effective being complex modification (residual mass – 30.09%).
Estimation of operating conditions close to real material work requirements was carried out in a series of experiments utilizing a plasmotron. CFRPs were machined into samples for tensile strength testing, then plasma treated at $T \approx 1400 \, ^\circ C$ for 60 s (Figure 2). Samples (Figure 3) were tensile tested before and after exposure (see table 3).

**Figure 2.** Plasma exposure process.

**Figure 3.** Images of samples before (a) and after plasma exposure (b).

Comparative analysis of strength shows that after exposure to high-temperature plasma, the strength of the samples decreases by about 50% and averages at approximately 45 MPa. It should be noted that test results show significant error from sample to sample. This phenomenon may be explained by the difficulties in focusing plasma flow exactly on the critical part of the sample.

**Table 3.** Results of tensile strength testing.

| Designation                                         | Tensile strength before influence, MPa | Tensile strength after influence, MPa |
|----------------------------------------------------|----------------------------------------|--------------------------------------|
| Silicone + PFR (2:1)                                | 95.6                                   | 63.5                                 |
| Silicone + PFR (2:1) + 5 % SiC                      | 106.6                                  | 43.1                                 |
| Silicone + PFR (2:1) + 5 % ZrB$_2$                  | 96.6                                   | 35.5                                 |
| Silicone + PFR (2:1) + 3 % SiC + 3 % ZrB$_2$ + 4 % SiO- spheres | 85.4                                   | 36.9                                 |
Pure organosilicon rubbers form a weakly bound amorphous ceramic residue during pyrolysis. Under conditions of high-temperature oxidative action, matrix based on a composition of silicone and phenolic resin promotes the formation of silicon carbides, and the dispersed additives may serve as centers of crystallization of ceramic phases. This combination of components is reflected in the acceleration of sintering and the formation of a monolithic protective surface layer.

4. Conclusions

CFRPs based on a mixture of silicone and phenol-formaldehyde resin reported in the present paper exhibit thermal stability up to 422 °C. The introduction of such modifiers as silicon carbide, zirconium diboride, glass microspheres leads to an increase in the resistance of materials to thermal loads. The greatest effect is demonstrated by the introduction of 2 wt. % ZrB₂ (the stability of the composite up to 434 °C). The residual mass of the samples due to the introduction of a complex of additives (3% SiC, 2% ZrB₂, 4% glass microspheres) into the organosilicon binder increases by 5 wt. %.

A strong protective surface layer is formed on the samples in the area of exposure to a short-term plasma flow (1400 °C, 60 s). Comparative mechanical tests have shown a 50 % reduction in strength after high-temperature exposure to a plasma stream.

5. References

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