Improvement in Thermal Stability of Glass Fiber-reinforced Polyimide Honeycombs

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Abstract. Results of researches of influence of 1,7-di(oxymethyl) - m-carborane on thermal stability polyimide binding the SP-97K brands are given in article. It is shown that introduction of bis-oxymethyls-carboranes allows to receive more heat-resistant high-coked compositions. The assumption is made that increase in thermal stability happens due to interaction of carborane fragments to oxygen of air and formation of compounds of B₂O₃ boron oxide.

Intensive development of aerospace engineering and creation of new product samples involve tightening of technical requirements imposed on the basic properties and operating conditions of polymer composite materials. High speeds of the present-day aerospace flight vehicles give rise to aerodynamic heating of the vehicle structures to very high temperatures, and not all of the existing polymer materials ensure the retention of adequate strength under these conditions.

In laminated composite structures, a honeycomb is used to reduce weight along with the improvement in performance capability. The honeycomb making an integral part of sandwich structures is used as sound-proofing and heat insulation in aerospace vehicles, watercraft and other transport facilities.

JSC ORPE “Technologiya” named after A.G.Romashin” have developed and currently produce a wide range of glass fiber-reinforced honeycombs of different purpose. Well-known domestic thermostable glass fiber-reinforced polyimide honeycombs of the SSP-7 type are on a par with HRH-327 honeycombs of Hexcel (USA), and still they afford an operating temperature of no more than 300 °C [1]. For higher operating temperatures of sandwich structures, no honeycombs are available.

Honeycomb thermal stability is basically governed by matrix properties. Among the resins attractive for making thermostable glass fiber-reinforced honeycombs, Type SP-97K polyimide resin has shown good performance.

Polymer thermal stability improvement can be made possible by the development of new resins meeting the new requirements (however, it is a very long and cost-intensive process) or by modification of well-known polymers with additives that alter their properties in accordance with the field of application.

The research showed that introduction of carborane-containing compounds into polymer improves the composition thermal stability [2-4]. The present work [5] revealed the effect of ortho-carborane on...
SP-97K polyimide resin thermal stability. Carborane meta-isomers are known to be more thermally stable than ortho-isomers.

The purpose of this work was the research of 1,7-di(oxyethyl)-m-carborane effect on SP-97K polyimide resin thermal stability.

The study was carried out on SP-97K + D-m-18 compositions cured at various temperatures, particularly, to linear polyimide condition at 170 °C (composition 1) and to cross-linked structure at 300 °C (composition 2).

The research of compositions weight loss in the course of aerodynamic heating was conducted using thermo-gravimetric analysis (TGA) (see Fig. 1, 2). 10 % weight loss temperature was selected as thermal stability value.

Figure 1. 10 % weight loss temperature of SP-97K + D-m-18 composition as a function of D-m-18 concentration

Figure 2. Residual weight value of SP-97K + D-m-18 composition as a function of D-m-18 concentration at 700 °C
According to the data of aerodynamic thermo-gravimetric analysis carried out at heating in the air, active displacement of 10 % weight loss temperature up to higher temperatures is observed in composition 1, the availability of D-m-18 5 % weight leads to decrease in thermal stability growth rate, while it slightly alters with increase in D-m-18 concentration. Such displacement is not observed in composition 2. It should be noted that all compositions are observed to have the rise in carbon residual which almost completely ceases when D-m-18 concentration is more than 5 % weight. Therefore, 5% weight concentration of D-m-18 was selected as the optimal one.

When introducing D-m-18 into SP-97K resin it is necessary to take into account the availability of MFSN-A silicone additive in the resin. Using thermo-gravimetric analysis, the interaction between D-m-18 and MFSN-A was studied by determining the weight losses of the test compositions samples in the course of aerodynamic heating within the temperature range of 20-700 °C. The samples were the solutions of clear and modified MFSN-A with different content of D-m-18 (1 - 10% weight). Then, the compositions were cured at final curing temperature of 170 °C in step-by-step time-temperature mode.

![Figure 3](image1.png)

**Figure 3.** 10 % weight loss temperature of MFSN-A + D-m-18 composition as a function of D-m-18 concentration

![Figure 4](image2.png)

**Figure 4.** Residual weight of MFSN-A + D-m-18 composition as a function of D-m-18 concentration at 700 °C
The results of thermo-gravimetric analysis (see Fig. 3, 4) demonstrate that the availability of D-m-18 in MFSN-A structure improves its thermal stability. The analysis of carbon residual and weight loss dynamics reveals the similarity of thermal resistance improvement behavior of SP-97K-based compositions. As may be supposed, D-m-18 does not react with silicone compound, forming interpenetrating three-dimensional structures with it.

Structural-group changes in the modified polyimide resin cured at the temperature of 300 °C were studied using infrared spectrometry. IR spectra of pure SP-97K and SP-97K+D-m-18 composition (5 wt%) are presented in figures 5 and 6. In the IR-spectrum of SP-97K resin modified with D-m-18 there is an absorption band at 2600 sm⁻¹ conforming to B-H stretching vibrations of a carborane nucleus. The comparative curve analysis shows no changes in the imide cycle band intensity of 1780 sm⁻¹ and 1850 sm⁻¹. This suggests that the modifying agent has no effect on the curing process of the initial polyimide resin.

Based on the research it was assumed that thermal stability improvement of the resin was caused by interaction between carborane fragments and atmospheric oxygen preventing decomposition of an organic part of the composition.

The phase composition of modified compounds was studied using X-ray phase analysis. The samples are SP-97K+D-m-18 (5 wt%) composition powders cured in a step-by-step mode with the final curing temperature of 300 °C. The samples were heat treated at 500 °C during 15 minutes.
X-ray phase analysis of the samples shows presence of an amorphous material on X-ray patterns, which indicates that the main component of the material is an amorphous phase. In such a case, diffraction peaks of boron oxide (B$_2$O$_3$) crystalline phases are detected on some X-ray patterns (figure 7).

![Figure 7. X-ray pattern of SP-97K + D-m-18 composition (5 wt%)](image)

**Conclusions**

1. Thermo-gravimetric analysis demonstrates that introduction of D-m-18 into SP-97K composition increases its thermal stability. The optimal concentration of D-m-18 in the resin is 5 wt%.

2. The study of structural-group changes using IR- spectrometry in the investigated composition under curing shows that the resin components do not react with D-m-18, but form interpenetrating three-dimensional structures.

3. The study of the phase composition of cured compounds shows that compounds of boron oxide B2O3 are formed at the temperature of 500 ºC.

4. The proposed method of polyimide resin modification makes it possible to produce glass-fiber-reinforced honeycombs able to work at the temperature up to 500 ºC.

**References**

[1] Volkov V S, Korneychuk A N, Denisova E V, Kulagina I V and Shul G S, 2014 New Thermostable Glass Fiber-Reinforced Honeycombs *Russia. J. Aviation Industry* 3 52-6

[2] Petrova A P, Lukina N F and Kotova E V 2013 Carborane-Containing Siloxane Adhesives *Russia. Adhesives. Sealants. Techniques* 7 2-4

[3] Davydova I F, Kavun N S and Shvetsov E P 2012 High-Thermostable Carborane-Containing Glass Fiber Plastics *Russia. All materials. Encyclopedic Reference Book* 9 18-24

[4] Petrova A P and Laptev A B 2017 Thermal Stability of Carborane-Containing Phenol-Formaldehyde Oligomer Adhesive Systems *Russia. Adhesives. Sealants. Techniques* 7 2-6

[5] Petrova A P 2007 Polyurethane Glues on the Basis of Carborane-Containing Connections *Russia. Adhesives. Sealants. Techniques* 1 2-6

[6] Korneychuk A N, Lebedev A K, Volkov V S, Miychenko I P, Shul G S and Bukharov S V 2016 *Ways to Improve Thermal Stability of Polyimide Honeycombs* (France: University of Montpellier)