

High performance carbon–carbon composites obtained by two-step process from phthalonitrile matrix composites

Vladislav V. Aleshkevich, Boris A. Bulgakov, Yakov V. Lipatov, Aleksandr V. Babkin and Alexey V. Kepman

Materials and methods. Carbon fabric 22502 from JSC INCMaT 2×2 twill wave from 3k UMT42S from UMATEX fiber was used for CFRP preparation. Auxiliary materials for vacuum infusion were purchased from Airtech, USA. Phthalonitrile resin PNT and phthalonitrile prepreg were obtained from Itecma, Russia. Properties of used CFRPs are presented below (Table S1).

Table S1 Properties of used CFRPs

	PNT (PN-1)	PHENIX (PN-2)
Interlaminar shear strength, MPa	35.9	35.1
Compression strength, MPa	535	512
Compression modulus, GPa	67.6	60.0
Density, g cm ⁻³	1.5876	1.5934

Thermoset preparation. Pure thermoset was obtained by the following procedure: phthalonitrile resin PNT was melted and degassed in a 100ml flask at 130°C while stirring. The melted resin was poured into mold and cured at 180°C with a subsequent post-curing at 375°C.

CFRP preparation. CFRP with phthalonitrile matrix was fabricated by two different methods. The first sample set (PN-1) was prepared with a vacuum infusion method, using and a low-melting phthalonitrile composition PNT. The second sample set (PN-2) was prepared with an autoclave molding, using a phthalonitrile prepreg.

Infusion process. A stainless-steel plate with dimensions $500 \times 700 \times 4 \text{ mm}^3$ coated with release agent (except for the edges) was used to produce CFRP by the vacuum infusion process. The general procedure is shown in Figure S1. Sealing tape was secured along the perimeter. Silicone rubber tubes for resin feed and evacuating channels were installed on the opposite edges of the plate. At the side of the feed channel, 10 layers of 200 g m^{-2} carbon fabric were placed and covered with peel ply and distribution medium. Further, vacuum film was attached to the sealing tape and the vacuum bag was placed in the oven, connected to the vacuum pump, and heated to $120 \text{ }^\circ\text{C}$. Upon reaching 1 mmHg inside the vacuum bag, the degassed and preheated resin was infused via the feed channel. After 10–15 min, the resin exited the vacuum bag into the vacuum channel, which indicated the end of impregnation. After the completion of the infusion process, the temperature was raised to $180 \text{ }^\circ\text{C}$ at the rate of $2 \text{ }^\circ\text{C}/\text{min}$ and held for 8 h. During this time, the glass transition temperature of the specimen increased above $190 \text{ }^\circ\text{C}$. A relatively low precuring temperature and hence long curing time was associated with the thermal stability of the auxiliary materials. After that, the package was disassembled and the precured sample was postcured. The panel was heated from $180 \text{ }^\circ\text{C}$ to $375 \text{ }^\circ\text{C}$ with a heating rate of $10 \text{ }^\circ\text{C}/\text{h}$ and was held at this temperature for 8 h. The obtained CFRP contained 38 mass% of the matrix.

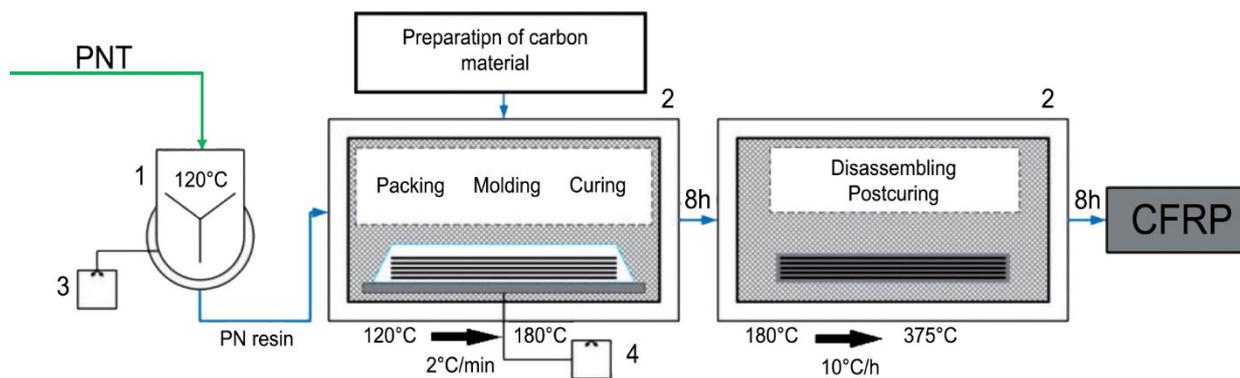


Figure S1 CFRP manufacture with vacuum infusion method: 1 – mixer, 2 – oven, 3,4 – vacuum pumps

Autoclave molding. A stainless-steel plate with dimensions $500 \times 700 \times 4 \text{ mm}^3$ coated with release agent (except for the edges) was used to produce CFRP by autoclave molding. In the center of a steel plate 10 layers of phthalonitrile prepreg were stacked on top of each other. A separating film and a breather were placed on the top of a prepreg pile. A vacuum bag with a valve was assembled around the steel plate. A vacuum bag was placed in the autoclave and connected to the vacuum pump. The pressure in the autoclave was set at 10 bar. Upon reaching 1 mmHg inside the vacuum bag, the temperature in the autoclave was raised to 180 °C at the rate of 2°C/min and held for 8 h. After that, the package was disassembled and the precured sample was postcured. The panel was heated from 180 °C to 375°C with a heating rate of 10 °C/h and was held at this temperature for 8 h. The obtained CFRP contained 39 mass% of the matrix.

CFRP carbonization. The carbonization process was conducted in a high temperature oven under nitrogen atmosphere. Nitrogen was supplied to the furnace using polyamide pipes going from cryogenic storage Dewar's tank filled with liquid N_2 . The samples were put into the fine powder coke to avoid probable oxidation. The heating was carried out according to the following mode: RT → 450 °C, 1 °C/min, 450 °C → 800 °C, 0.12 °C/min, 800 °C → 1000 °C, 0.5 °C min, dwell at 1000 °C, 1h.

Second impregnation. A stainless-steel plate with dimensions $500 \times 700 \times 4 \text{ mm}^3$ coated with release agent (except for the edges) was used to impregnate the C/C composite. The general procedure is

shown in Figure S1. Sealing tape was secured along the perimeter. Silicone rubber tubes for resin feed and evacuating channels were installed on the opposite edges of the plate. At the side of the feed channel, C/C composite was placed and covered with peel ply and distribution medium. Further, vacuum film was attached to the sealing tape and the vacuum bag was placed in the oven, connected to the vacuum pump, and heated to 120 °C. Upon reaching 1 mmHg inside the vacuum bag, the degassed and preheated resin was infused via the feed channel. After 10–15 min, the resin exited the vacuum bag into the vacuum channel, which indicated the end of impregnation. After the completion of the infusion process, the temperature was raised to 180 °C at the rate of 2 °C/min and held for 8 h. After that, the package was disassembled and the precured sample was postcured. The panel was heated from 180 °C to 375 °C with a heating rate of 10 °C/h and was held at this temperature for 8 h. The obtained composite gained 9.6% mass compared to original C/C composite.

Sample characterization. The mass change was measured by comparing masses of samples before and after carbonization process. The linear shrinkage was measured by comparing the samples thickness in normal direction to the reinforcement plane. The density was measured by hydrostatic weighing in water at 23 °C. The ILSS was measured by GOST 32659.

Porosity was obtained by Mercury intrusion porosimetry method on an automatic mercury porosimeter AutoPore V 9605. All samples were degassed at a temperature of 150 °C to a pressure of 20 torr, with a dwell at these conditions for 5 minutes. Intrusion was performed at room temperature. Isotherms were recorded as the dependences of the logarithm of differential intrusion on pressure. The data was further processed in the software package into the dependence of intrusion on the diameter of inlet pores.

Compression strength was measured by GOST 56812. COF was measured by GOST 11629, where both the sample and counterface were made of obtained C/C composite.