

## Viscoelastic properties of carbon plastics based on powdered polyimide binders

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Carbon fiber reinforced plastics based on thermoplastic partially crystalline fusible polyimide R-BAPB and oligoimide IDA (diacetyl imide) have been obtained. The thermal, thermomechanical and mechanical properties of carbon plastics based on polyimides have been studied. It has been shown that carbon plastics based on the used polyimide binders have increased crack resistance, which makes it possible to operate them at temperatures up to  $\sim 400^\circ\text{C}$

**Keywords:** carbon fiber reinforced plastic, polyimide binder, electrostatic spraying, interlaminar fracture toughness.

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Polymer fiber composite materials (FCMs) maintaining a high operating efficiency at both high (above  $+200^\circ\text{C}$ ) and low temperatures are in much demand at present. A combination of optimum thermal resistance, strength, rigidity, and fracture toughness parameters makes carbon plastics based on polyimide binders promising materials for the fabrication of structural components of high-speed transport vehicles and other similar purposes [1].

One known problem in the design of FCMs (including carbon plastics based on polyimide binders) consists in overcoming a natural discrepancy between a high thermal resistance and crack resistance. The majority of presently used polyimide polymer matrices for FCMs belong to the class of reactive binders [2,3]. While polyimides based on reactive binders feature a fine thermal resistance, they are brittle materials with modest crack resistance values (their crack resistance  $G_{1C}$  does not exceed  $500\text{ J/m}^2$ ). In contrast, thermoplastic matrices in FCMs provide high crack resistance levels, but the thermal resistance of composites is low [4]. In connection with the above, an urgent task is to search for chemical structures that make it possible to achieve a compromise option that reduces the sharpness of this contradiction.

ELUR P-0.08 carbon fibers in the form of a tape 200 mm wide with a linear density of 15 g/m were used as a reinforcing filler to obtain carbon plastics. The development of crystallizable polyimides may be an efficient approach to enhancing the thermal resistance, resistance to solvents, and mechanical characteristics of composites based on them. Thus, the following two polyimide binders developed at the Institute of Macromolecular Compounds of the Russian Academy of Sciences were used to produce a carbon plastic material: (1) partially crystalline fusible polyimide R-BAPB based on Russian resorcinol dianhydride P (1,3-bis(3,3',4,4'-dicarboxyphenoxy)benzene) and

tetranuclear diamine BAPB (4,4'-bis(4'-aminophenoxy)biphenyl) [5]; (2) fusible oligoimide IDA (diacetyl imide) based on 3,3',4,4'-diphenyl ether tetracarboxylic acid dianhydride and bis(4-acetamido)diphenyl ether.

The process of synthesis of thermoplastic partially crystalline polyimide R-BAPB was detailed in [5]. An IDA-type binder was produced in the interaction of the above-indicated initial components in melt at  $280\text{--}290^\circ\text{C}$  with the removal of 18% of volatile compounds [6]. In order to produce a carbon plastic, a powdered binder (polyimide R-BAPB or oligoimide IDA) was deposited by electrostatic spraying onto an ELUR P 0.08 carbon ribbon with subsequent calendaring at a temperature of  $210^\circ\text{C}$  (for IDA) or  $360^\circ\text{C}$  (for polyimide R-BAPB). The obtained polyimide prepregs were stacked in 36 layers and pressed at a temperature of  $360^\circ\text{C}$  under a pressure of 1 MPa for 1 h with subsequent cooling in a mold under pressure. The fiber content of carbon plastics based on R-BAPB and oligoimide IDA was 61 and 65 vol.%, respectively.

The interlaminar fracture toughness and bending strength of carbon plastic samples were examined using a 1958U-10-1 (Russia) tensile testing machine at  $20^\circ\text{C}$ . The interlaminar fracture toughness was determined in a „double cantilever beam“ test in accordance with ASTM D 5528-01. A detailed description of the examination method and the samples for interlaminar fracture and three-point bending tests of carbon plastics was given in [6].

Shear storage  $G'$  and loss  $G''$  moduli of carbon plastics were measured using an MCR-301 device produced by Anton Paar (Austria) in the mode of forced torsional vibrations at a frequency of 1 Hz, an amplitude of 0.1%, and a temperature varying from 20 to  $500^\circ\text{C}$  at a heating rate of  $5^\circ\text{C}/\text{min}$ . Thermal properties of samples were examined by differential scanning calorimetry (DSC) performed using a NETZSCH (Germany) DSC 204 F1 instrument. Tests were

Thermomechanical properties of carbon plastics based on polyimide binders

Polyimide binder	$G_{1C}$ , J/m <sup>2</sup>	$\sigma_b$ , MPa	$E'$ , GPa	$G'$ , GPa
R-BABP	1800 ± 100	1310 ± 50	83 ± 8	5.35
IDA	1080 ± 50	1260 ± 60	120 ± 10	5.30

Note.  $G_{1C}$  — interlaminar fracture toughness (crack resistance),  $\sigma_b$  — bending strength,  $E'$  — bending storage modulus,  $G'$  — shear storage modulus.

carried out within a temperature interval of 30–400°C at a heating rate of 10°C/min in inert atmosphere (argon).

It follows from the analysis of DSC curves that the glass transition temperature of carbon plastics (CPs) based on R-BABP and oligoimide IDA is 203°C and –272°C, respectively. Both CPs had endothermic peaks, which correspond to crystallite melting, at 320°C (R-BABP) and 403°C (oligoimide IDA; see Fig. 1). The degree of crystallinity of the carbon plastic material based on R-BABP was determined using the enthalpy of melting, which is 90 J/g [5] for entirely crystalline R-BABP. According to the DSC data, the degree of crystallinity of the carbon plastic material based on R-BABP is ~36%.

The results of examination of temperature dependences of shear storage and loss moduli of the obtained CPs are presented in Fig. 2. The temperature of the shear loss modulus maximum is 230°C and 254°C for carbon plastics based on R-BABP and oligoimide IDA, respectively. The shear storage modulus of the CP based on R-BABP decreases somewhat at these temperatures. However, owing to the presence of the crystalline R-BABP phase, the storage modulus remains fairly high through to a temperature of ~337°C. The crystalline phase in the CP based on R-BABP starts melting at temperatures above 340°C, and the storage modulus decreases sharply as a result (Fig. 2). The thermomechanical curve for the CP based on oligoimide IDA demonstrates that its storage modulus decreases beyond the maximum of the loss modulus (to ~0.2 GPa). However, the

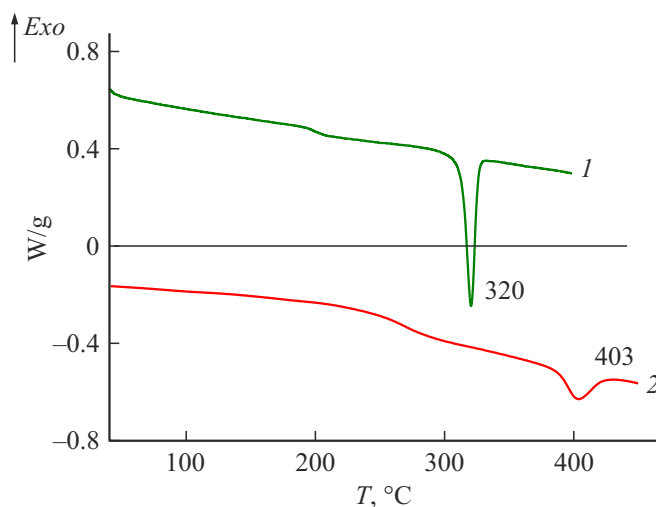


Figure 1. DSC curves of carbon plastics based on R-BABP (1) and oligoimide IDA (2).

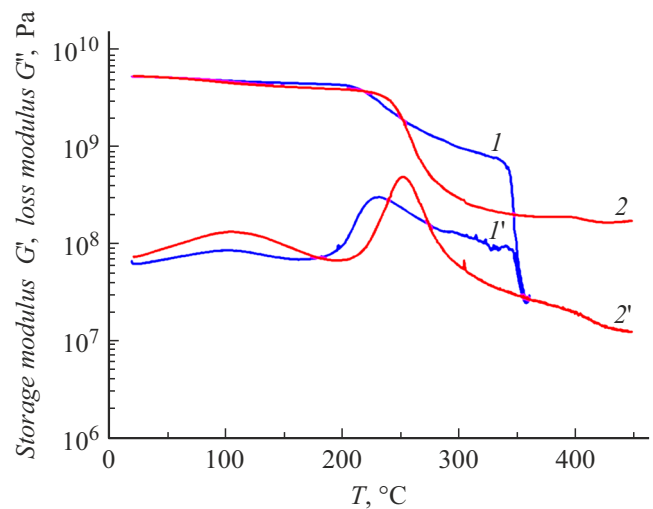


Figure 2. Dependences of shear storage  $G'$  (1, 2) and loss  $G''$  ( $1'$ ,  $2'$ ) moduli of carbon plastics based on R-BABP (1,  $1'$ ) and oligoimide IDA (2,  $2'$ ).

shear storage modulus remains fairly high at temperatures above 254°C and undergoes almost no changes through to 400°C. This may be attributed to the presence of the crystalline phase, which melts at temperatures above 403°C, in polyimide produced from oligoimide IDA. Thus, the maximum operating temperatures of CPs based on R-BABP and oligoimide IDA are 320–330°C and ~400°C, respectively.

Carbon plastics based on the partially crystalline R-BABP binder have the highest values of interlaminar fracture toughness (~1800 J/m<sup>2</sup>; see the table). The corresponding values for the CP based on oligoimide IDA are somewhat lower: ~1100 J/m<sup>2</sup>.

Thus, carbon plastics based on thermally resistant polyimide binders were produced. Their viscoelastic properties (shear storage and loss moduli and interlaminar fracture toughness at 20°C) were examined. CPs formed based on the synthesized polyimides feature high levels of both interlaminar fracture toughness (up to 1800 J/m<sup>2</sup>) and thermal resistance (up to ~400°C).

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### Conflict of interest

The authors declare that they have no conflict of interest.

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