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Preparation and properties of heat-resistant composite materials based on polyimide foams

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In this study we have synthesized foaming polyimide binders based on ethyl ester of 3,3′,4,4′-diphenyl oxide tetracarboxylic acid dianhydride and diamines 4,4′-diaminodiphenyloxide and 4,4′-diaminodiphenylmethane in powder form. Polyimide foam composites based on the synthesized binders reinforced with polyimide fibers have been obtained. Thermal and mechanical properties of the polyimide foam composites have been investigated. The study has shown that, by varying the composition of the polyimide-binder diamine fragment, it is possible to obtain materials combining high thermal stability, heat resistance and mechanical properties with a low mass.

Keywords: polyimide binder, prepregs, foam composites, mechanical properties, heat resistance.

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Obtaining strong, lightweight, heat-resistant materials is a challenge in modern materials science, including such a field as development of new structural materials to be employed under extreme conditions. Among heat-resistant lightweight materials, polyimide foams are considered attractive. Due to their ultra-low weight, fire and thermal stability, excellent thermal and sound insulation abilities, radiation resistance and low dielectric constant, polyimide foams are indeed promising materials for high-tech industries such as aerospace, automotive and marine engineering, electronics and power production [1–4]. One of the methods commonly used for producing polyimide foams is thermal treatment of prepolymer powders [5,6]. This method has proven itself in producing lightweight and fire-resistant polyimides. However, mechanical characteristics of conventional polyimide foams are rather poor and cannot meet requirements for using them as structural materials. Mechanical properties of polyimides may be improved by increasing their density. However, low weight is a highly important characteristic in view of applying the material in the aerospace, transport and automotive industries, etc. In this regard, an important current issue is obtaining polyimides with higher mechanical properties and low density. One of the possible ways to achieve this is to create composite materials based on polyimide foams. Adding fillers may change the mechanical, thermal and thermophysical properties of polyimides [7–9]. Introduction of discrete glass [8], carbon [7,10] and organic fibers [11,12] may significantly improve the foam-composite mechanical properties and, in addition, affect the foaming process. Among all the reinforcing fibers, the most attractive ones in view of obtaining heat-resistant, lightweight and durable foam composites are organic fibers. However, there is very little information on the use of continuous reinforcing fibers in producing foam composites. Thus, in this study we have obtained and examined a foam composite based on polyimide foam and continuous organic polyimide fibers.

To obtain the foam composite, we synthesized powders of foaming compositions based on ethyl ester of 3,3′,4,4′-diphenyl-oxidetetracarboxylic acid (DPO) dianhydride with diamines 4,4′-diaminodiphenyl oxide (DADPE) and 4,4′-diamine-diphenylmethane (DADPM). The procedure for preparing prepolymers was similar to that of synthesis described in our previous publication [5].

To obtain the foam composite, a fibrous filler made of polyimide felt „Arimide" produced by LLC „Lirsot" (Russia) was used. The procedure for producing the polyimide-foam fiber composite (PIF FC) consisted of several operations. The obtained prepolymer powder was dried, ground and screened through a $200\,\mu$m sieve; thus, a fraction of $\leqslant 200\,\mu$m was formed. After that, the prepolymer powder was applied on the polyimide felt. Then the prepreg was fabricated by rolling the polyimide felt with prepolymer powder applied on it through thermostatically controlled calender rollers heated to $100-120\,^{\circ}$C (depending on the prepolymer composition). The rollers' rotation speed was 5 rpm for all the samples. In the process of calendering, the fibers were wetted with the molten prepolymer which spread over and penetrated into the filler interfiber space under capillary forces. In this way, the prepregs were obtained. The mass ratio between the prepolymer binder and polyimide fiber was 6 : 1. The obtained prepregs were cut into blanks 7×2.5 cm in size. The blanks were placed in eight layers of the required configuration in a metal mold which was then closed at the top and bottom. The mold with prepregs was placed in a press heated to $220\,^{\circ}$C and held there for 3 h. Schematic diagram of the foam composite production process is given in Fig. 1. THe structure obtained by heat treatment of the prepolymer with polyimide felt is porous because gaseous products (water and ethanol)

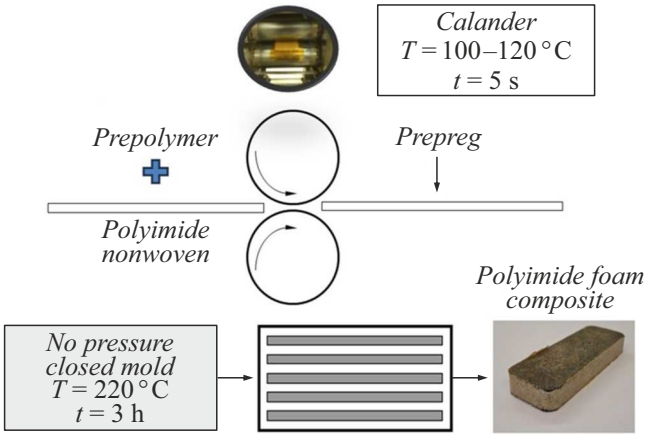

Figure 1. Scheme for obtaining a polyimide-foam composite based on prepolymers DPO–DADPE and DPO–DADPM.

are released in the prepolymer cyclization reaction (Fig. 2). Finally, PIF FC 70 mm long, 25 mm wide and 8 mm thick were formed (Fig. 1).

Thermal characteristics were studied by thermogravimetric analysis (TGA) using instrument TG 209 F1 (NETZSCH, Germany). The experiments were conducted in the temperature range of 20 to 800 °C at the heating rate of 10 °C/min in inert environment (argon). Temperature dependences of the storage (E') and loss (E'') moduli were determined by the dynamic mechanical analysis on setup DMA 242 C (NETZSCH, Germany) in the three-point bending mode. The measurements were performed at the frequency of 1 Hz, deformation amplitude of 0.1 %, and temperature growth rate of 5 °C/min.

To study the samples' mechanical characteristics under bending, testing machine Instron 5940 was used; samples $3 \times 10 \times 40$ mm in size were prepared; the inter-support distance was 32 mm, the crosspiece speed was 5 mm/min.

Density of PIF FC based on DPO–DADPM was 0.220 g/cm^3, that for DPO–DADPE was 0.250 g/cm^3. Since the mass ratio of the prepolymer binder to fiber remained constant (6 : 1), the difference may be explained by the difference in degrees of removing the volatiles (water and ethanol) in producing the composites, as well as by the difference in binder densities. The DPO–DADPE structure allowed obtaining the densest foam composites (see the Table).

The under-bending mechanical properties of foam composites based on binders DPO–DADPE and DPO–DADPM are presented in the Table.

The highest rigidity (260 MPa) and strength (12 MPa) are exhibited by the DPO–DADPE-based composite 0.25 g/cm^3 in density. The difference in strength and elastic modulus under bending from those for the DPO–DADPM-based composite is probably caused by the difference in the densities of obtained composites.

Onset temperatures of the thermal destruction of polyimides and polyimide-based composites in an inert environment were estimated via the TGA method by determining heat resistance index τ_5 (loss of 5 % of mass). Polyimide foams exhibit a high level of thermal stability (above 560 °C, see the Table). Comparing the composites based on polyimide foams DPO–DADPE and DPO–DADPM, we have revealed that the highest thermal stability with thermal stability index $\tau_5 = 586$ °C is inherent to the DPO–DADPE-based composites. In the case of the composite based on binder DPO–DADPM, the thermal degradation processes get activated already at lower temperature $\tau_5 = 560$ °C.

Dynamic mechanical characteristics of materials based on foam composite Arimide with polyimide foam binders DPO–DADPE and DPO–DADPM were determined in the temperature range of −50 to 320 °C (Fig. 3). The temperature dependence curve E'' demonstrates a maximum for the DPO–DaDPE-based foam composite at the temperature of ∼ 217 °C associated with the glass transition temperature. For the DPO–DaDPM-based polyimide foam composite, the glass transition temperature defined as the E'' maximum is somewhat higher and amounts to 233 °C. In addition, we have found out that elastic modulus E' for

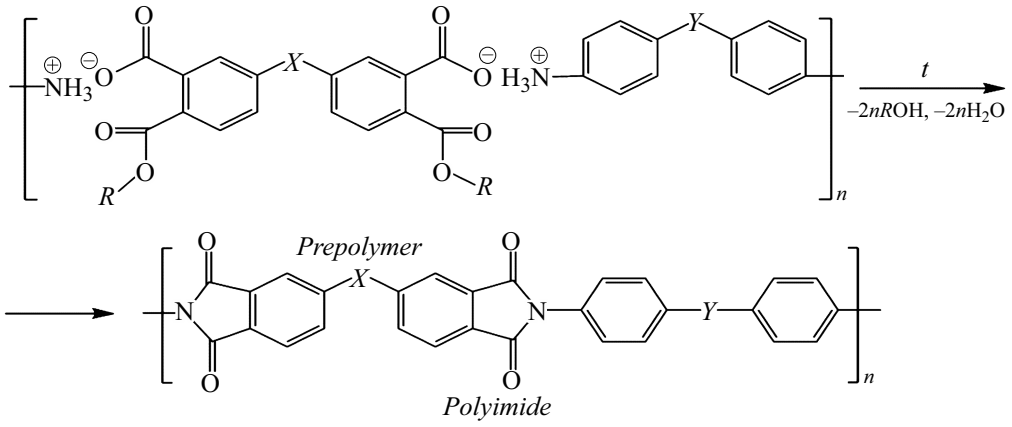

Figure 2. Schematic diagram of the imidization reaction of prepolymers DPO–DADPM at $X = -O-$, $Y = CH_2$ and DPO–DADPE at $X = -O-$, $Y = -O-$.

Mechanical and thermal properties of foam composites based on binders of different chemical structures

Composite structure	Fracture strain σ, MPa	Elastic modulus E, MPa	Fracture stress ε, %	Density ρ, g/cm^3	Heat resistance τ_5, °C
DPO–DADPM	10.34	149.7	10.6	0.220	560
DPO–DADPE	12.55	260.3	7.0	0.250	586

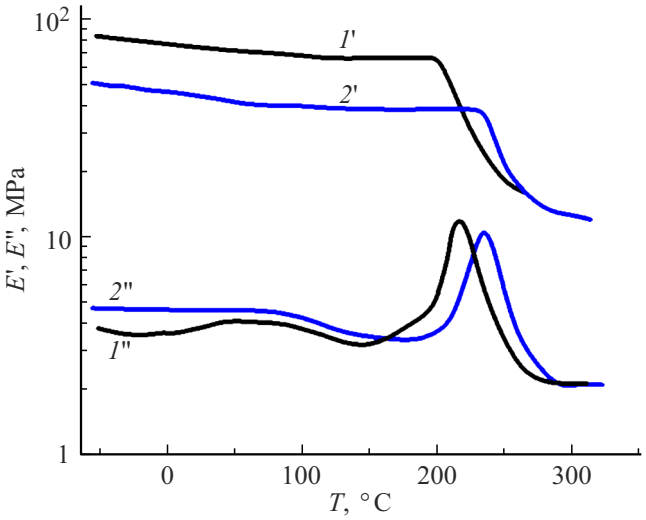

Figure 3. Temperature dependences of the bending elastic E' ($1'$, $2'$) and loss E'' ($1''$, $2''$) moduli for foam composites based on polyimide felt and polyimide. $1'$, $1''$ — DPO–DADPE; $2'$, $2''$— DPO–DADADPM.

the DPO–DADPE-based composite sample is higher than that of the DPO–DADPM-based one, which is associated with the higher density of the DPO–DADPE polyimide foam composite (see the Table).

Thus, in this study lightweight foam composites ($\rho = 0.22–0.25$ g/cm^3) based on polyimide binders DPO–DADPE and DPO–DADPM with continuous polyimide fibers were obtained for the first time. The obtained polyimide foam composites exhibit high heat resistance (233 °C) and mass loss onset temperature (586 °C). The maximum composite bending strength (12 MPa) at the density of 0.25 g/cm^3 is achievable when DPO–DADPE is used as a binder.

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Conflict of interests

The authors declare that they have no conflict of interests.

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