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Properties of polyimide foam composite obtained on the basis of polyamide acid salt and montmorillonite

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Polyimide foams were synthesized based on water-soluble polyamide acid salt from 3,3', 4,4'-benzophenonetetracarbonic dianhydride and 4,4'-diamidiphenylmethane with different contents of montmorillonite. The thermal and mechanical properties of the synthesized polyimide foam and composites based on it were studied. It was shown that introduction of 0,5% (wt.) montmorillonite can improve both the mechanical properties and heat resistance of polyimide foam.

Keywords: water-soluble polyamide acid salt, polyimide foam, montmorillonite, mechanical properties, heat resistance.

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One of the priority areas of Physical Materials Science is developing new polymer composites based on heat-resistant polymers. The leading position in the class of heat-resistant polymers is occupied by polyimides. At present, various materials based on polyimides are used. Polyimide foams (PIFs) are widely used in microelectronics to produce dielectrics with a very low dielectric constant, protective sensor coatings, stress buffers for compensating vibration loads, many of integrated circuit components; they are also employed as heat-insulating, sound-absorbing and vibration-damping materials in aviation and astronautics due to their high thermal stability and heat resistance, as well as fire resistance [1]. There exist several basic techniques for obtaining PIFs. The most common procedure is based on the chemical reaction of tetracarboxylic acid ester with diamines, whose result is formation of the relevant prepolymer [2]. An alternative to the above-mentioned method for PIF production may be the technique of forming a porous polyimide structure in the process of heat treatment of lyophilisates of water-soluble ammonium salts of polyamide acids (PAAs) [3]. Its peculiar feature is the possibility of obtaining isotropic foam materials of the required shape without using surfactants or other additives, because the porous structure gets formed due to the solution freezing with following water sublimation. However, adjustment of the foam material properties is in this case restricted to selecting concentration of the PAA salt solution and its freezing conditions. Also, one of the possible ways to steer the properties is introduction of various fillers [4]. Of particular interest in terms of improving the thermal and mechanical characteristics of polyimides are layered aluminosilicate nanoparticles [5]. Among widely used aluminosilicate nanoparticles there is montmorillonite characterized by availability and high degree of anisotropy. Thus, the goal of this study was to analyze the effect of aluminosilicate nanoparticles of montmorillonite on the thermal and mechanical properties of polyimide foam produced from water-soluble PAA salt.

As a filler, we used natural montmorillonite Cloisite Na+ (MMT) (produced by Southern Clay Products, Inc.), that is, natural aluminosilicate consisting of layers 1 nm thick; its general formula is $(Na,Ca)_{0.33}(Al,Mg)_2(Si_4O_{10})(OH)_2 \cdot nH_2O$. To obtain foam composites, there was prepared a 2 mass% solution of PAA salt based on 3,3',4,4'-benzophenonetetracarboxylic acid (BZP) dianhydride and 4,4'-diaminodiphenylmethane (DADPM). Detailed description of the synthesis procedure is given in [3]. To the obtained solution, 0.5, 1 or 3 mass% of MMT was added with stirring in ultrasonic bath for half an hour. Then the prepared aqueous dispersion was put into fluoroplastic molds, frozen to -25°C (with the cooling rate of 0.1°C/min) and lyophilized in vacuum [3]. As a result of freezing the PAA salt aqueous solution and mild water sublimation, a porous structure got formed. The obtained porous samples were put in a thermostat and heated at 250°C for an hour.

Thermal properties of composite PIFs were studied by thermographic analysis (TGA) performed at the TG 209 F1 setup (NETZSCH, Germany) and by differential scanning calorimetry (DSC) at the DSC 204 F1 Phoenix setup (NETZSCH, Germany) in the temperature range from 20 to 800°C at the heating rate of 10°C/min in the inert argon atmosphere. Mechanical properties of the composites were studied in the mode of compression with the 10% deformation according to GOST 23206−2017 using the Instron 5940 testing machine (USA) at 20°C; in testing, cubic samples with the edges of 10 ± 2 mm were used. For studying mechanical properties of foam materials, ten parallel samples were prepared.

Table 1. Thermal properties of polyimide foam composites

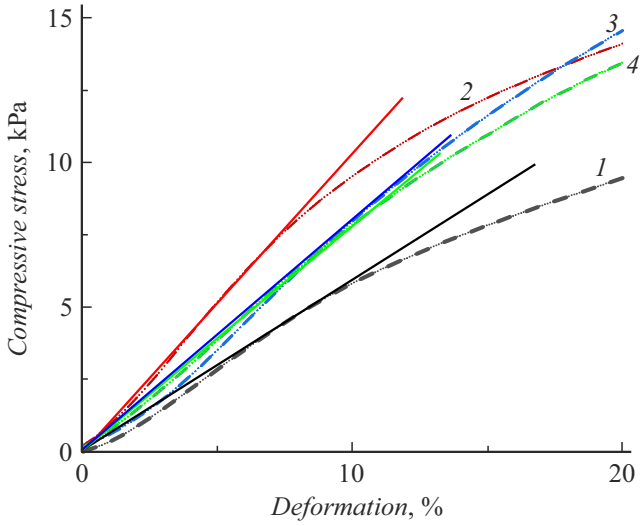
Polyimide foam	T_g, °C	τ_5, °C
BZP–DADPM	271	531
BZP–DADPM with 0.5 mass% of MMT	277	537
BZP–DADPM with 1 mass% of MMT	278	535
BZP–DADPM with 3 mass% of MMT	273	540

The results of TGA and DSC of the synthesized samples presented in Table 1 show that all the obtained PIFs exhibit high heat resistance and thermal stability, while introduction of MMT leads to an increase in temperature τ_5 (at which 5% of the sample mass gets lost) and temperature of the relaxation transition from the glassy state to highly elastic state (glass-transition temperature T_g characterizing the polyimide foam heat resistance). The thermal stability index of the sample with 0.5 mass% of MMT is slightly higher than that of the sample with 1 mass% of MMT. This may be explained by the MMT and polymer particles surface interaction in the case of a low filler concentration and efficient dispersing.

The mechanical test results for the obtained samples are presented in the Figure and Table 2.

The deformation curves (see the Figure) have characteristic elastic regions (indicated by tangent lines) up to 10% deformation, after which the slopes change. Introduction of MMT improves the PIF mechanical characteristics (Table 2). The maximum increase in strength and elastic modulus relative to the same characteristics of unmodified PIF is observed when 0.5 mass% of MMT is introduced (stress increases from 5.8 to 9.0 kPa, the elastic modulus rises from 60 to 90 kPa) (see the Figure and Table 2). The increase in strength and modulus is probably associated with that the montmorillonite particles reinforce the obtained polyimide foam structure. Apparently, in preparing the nanocomposite, polymer molecules penetrate at the stage of dispersion into the space between the layers of MMT particles, due to which their exfoliation takes place. Due to their high specific surface area, exfoliated MMT particles exhibit strong interaction with the polymer matrix and, hence, reinforce the obtained foamed material even at the concentration of 0.5 mass% [6]. Further increase in the MMT content to 1 and 3 mass% leads to a slight reduction in the compression characteristics. This is probably caused by aggregation of MMT particles in the polyimide matrix, which promotes a reduction of the reinforcing effect due to formation in the polymer bulk of stress concentrators in the form of microscale defects rather than nanoscale ones.

Thus, in this work foam composites based on the BZP–DADPM polyimide matrix and MMT were obtained. All the obtained samples possess high thermal stability. The paper demonstrates that an increase in the filler content results in an increase in the PIF heat resistance and in the point of the PIF thermal decomposition commencement. In addition, introducing MMT even in the amount as small as



Typical deformation curves of synthesized PIF samples (BZP–DADPM) with different MMT contents. *1* — sample free of MMT, *2* — sample with 0.5 mass% of MMT, *3* — sample with 1 mass% of MMT, *4* — sample with 3 mass% of MMT.

Table 2. Mechanical properties of synthesized PIFs with different MMT contents

MMT content, mass%	Stress at the 10% deformation, kPa	Elastic modulus, kPa
0	5.8 ± 0.6	60 ± 20
0.5	9.0 ± 0.9	90 ± 10
1	8.0 ± 0.7	70 ± 10
3	7.6 ± 0.8	70 ± 10

0.5 mass% increases the PIF strength and compression modulus by more than 1.5 times as compared with unmodified polyimide matrix.

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Conflict of interest

The authors declare that they have no conflict of interests.

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