

## HEAT-INSULATING COMPOSITE BASED ON UNWOVEN MATERIALS AND ORGANOMINERAL BINDER

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*Composites based on unwoven cellulose-hydrate and carbon materials and an organomineral binder have been developed and investigated. Optimal compositions of the composites feature a higher fire resistance, a low density, and effective thermophysical characteristics. The composites are promising for use as heat-insulating materials with a rigid structure in different branches of the national economy and industry.*

**Keywords:** composite, heat insulation, fire resistance, oligomerepoxy, metallophosphate bond, unwoven material.

**Introduction.** Analysis of the domestic and foreign literature points to the fact that the most promising kinds of heat-insulating materials are composites with fibrous fillers characterized by low values of the heat conductivity coefficient and resistance to sharp temperature drops. They are able to relax temperature stresses and are easy to mount, and their production process has been organized [1]. The possibility of an arbitrary arrangement of fibers in the composites permits obtaining materials with various combinations and arrangements of pores, which provides favorable conditions for heat flows into the bulk of the material and their extinction in a limited volume [2]. As heat-insulating materials, of greatest interest are fibrous carbon-graphite materials (foam graphites, felt, cloth, cotton) having a high heat resistance, chemical inertness, radiation resistance, a low specific density, and a low heat conductivity coefficient [3]. Promising for civil and industrial engineering are rigid heat-insulating materials obtained by contact or volume "grouting" of fibrous structures with binders of various compositions, including those with an organic base [4, 3]. Among the disadvantages of such materials is their lower fire resistance. At the same time, under the conditions of more stringent requirements upon heat-insulating materials the problem of increasing their fire resistance is one of the main problems.

A decrease in the combustibility can be attained by using an inorganic matrix as a bond. However, such materials also have their disadvantages (low moisture resistance, brittleness, etc.). In this connection, the application of an organomineral binder for creating heat-insulating materials with improved service properties is a promising direction in the area of heat-shielding of articles and structures.

**Formulation of the Problem.** The aim of the investigations is to develop a heat-insulating composite on the basis of unwoven materials and an epoxy-mineral binder obtained by mixing metallophosphate bonds with epoxy oligomers and investigate the properties of the thus obtained material. Earlier it was shown by us that metallophosphate bonds are compatible with an organic matrix and can act as a hardener of the epoxy binder [6]. The application of epoxy oligomers in the organomineral binder makes it possible to increase the water resistance of the materials obtained and improve their strength characteristics. The use of phosphate bonds can increase the fire resistance of materials and exclude toxic amine hardeners of the epoxide binder [7].

In forming a heat-insulating material, to obtain an organomineral binder, we used epoxy oligomers: diglycidyl bisphenol ester A and epoxydiane ester ED-20, and for the mineral component we used the metallophosphate bond obtained by partial neutralization of orthophosphoric acid by metal oxides [8]. The fibrous base for the composites was formed from mercerized-cellulose and carbon unwoven materials which permitted obtaining composites with a low density and good heat-insulating properties. For the investigations, we chose mercerized-cellulose unwoven materials obtained by the needle-piercing technique providing looseness of packing and directional formation of interfibrous porosity. The thickness of the mercerized-cellulose unwoven material was 5.7–6.3 mm and that of the carbon unwoven

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material was 3.8–4.2 mm; the volume density was 120–180 kg/m<sup>2</sup> and 220–250 kg/m<sup>3</sup>, respectively. Huge amounts of fibrous waste of enterprises in Belarus serve as a reserve for manufacturing unwoven materials in the Republic. They can be used in the compositions of heat-insulating materials in the form of felts, mats, cut fibers, and other composition mixtures.

**Experimental.** The heat-insulating material was formed in the following way. An epoxy-mineral binder with chosen ratios of components was prepared. Dried unwoven fabrics were treated with the prepared binder and placed in layers, after which surplus binder was pressed out. The block formed was heat-treated in the temperature range of 100–200°C under a load of 0.02 kg/cm<sup>2</sup>, after which the gain in weight, i.e., the increase in the mass of the specimen upon "grouting" in percent, was determined. In mixing an inorganic bond with an epoxy oligomer, there occurs their physicochemical interaction with the participation of epoxy and hydroxyl groups of the epoxy oligomer and acid phosphor-acid groups of the metallophosphate bond with the formation of mono-, di-, and triesters of phosphoric acid. The process is initiated at room temperature and intensifies in the course of heating, which has been confirmed by the data of IR-spectroscopic studies in [6]. Simultaneously, due to the proceeding of the physical process of dewatering and swelling in heat treatment a composite with a higher porosity of the matrix and a combined cellular-capillary fibrous structure is formed.

The depth of epoxy oligomer transformation to a three-dimensional structure of the polymer was determined using the method of gel sol analysis via extraction of hardened specimens of composites by boiling acetone in the Soxhlet apparatus for 24 h. The volume density of the specimens was estimated by the ratio of their mass (weighing accuracy of 0.0001 g) to the volume (measurements of linear dimensions to an accuracy of 0.01 mm). The density of the composites was also determined by the method of hydrostatic weighing using the methods of [9]. Volume deformations of the composite were calculated by the change in the volume of the material upon its heat treatment compared to the initial composite. In the general case, these parameters are a function of the physical factor — the heat treatment conditions, as well as of the chemical factor — the content of the gas-forming product (water). The water absorption (in mass %) was determined by the mass increment of specimens upon their exposure in water for 24 h.

Fire resistance tests of composites were carried out in accordance with GOST 28157-89 "Plastics. Fire resistance determination methods," according to which the combustibility categories of plastics are arranged according to ascending fire resistances as follows: PG, PV-2, PV-1, PV-0. The thermophysical properties of hardened composites were determined in the 20–250°C temperature range in a monotonic regime on an IT-S-400 heat capacity meter and an IT-λ-400 heat conductivity meter. The thermal diffusivity of the materials was calculated by the formula  $\alpha = \lambda / (Cp)$  [10].

To estimate the thermochemical transformations in the composite, we used the method of differential thermal analysis (DTA) in combination with thermogravimetry (DTG and TG). Analysis was carried out with the use of an OD-103 MOM derivatograph (Hungary) in the 20–250°C temperature range in air at a rate of temperature rise of 2.5–5 deg/min. For a comparison standard, we used chemically pure aluminum oxide precalcinated at a temperature of 1400°C.

**Results and Discussion.** The investigations have shown that in the process of heat treatment of an organomineral binder in the temperature range of 130–200°C, concurrently with binder hardening reactions, processes of intensive removal of physically and chemically bound water, whose content in a metallophosphate bond can reach 76.35%, proceed. The curves of the differential-thermal analysis of the initial mineral bond show an intensive endothermal effect associated with its degradation. This effect has a maximum at 122°C and is accompanied by a maximum mass loss rate in this temperature range (Fig. 1, curve 2). The existence of this effect somewhat complicates the interpretation of the results of analysis of organomineral composites, since it overlaps with the exothermal effects that are due to the chemical interaction of metallophosphate bonds with epoxy oligomers and the formation of a three-dimensional structure of the polymer.

In the process of thermal treatment of the fibrous components used in the work, endoeffects are noted in the temperature ranges of 70–90°C and 140–180°C which are due to the water removal and are accompanied by a small mass loss. For carbon felt this loss is 3–4 mass %, and for mercerized-cellulose felt it is 7–8 mass % (Fig. 1, curves 3, 4). Moreover, for the mercerized-cellulose unwoven material upon heating to a temperature above 200°C, an endoeffect with a maximum at 230°C with a total mass loss of 14–15% (Fig. 1, curve 3) is observed. This effect is due to the intramolecular dehydration localized in amorphous regions of cellulose and leading to the removal of primary hy-

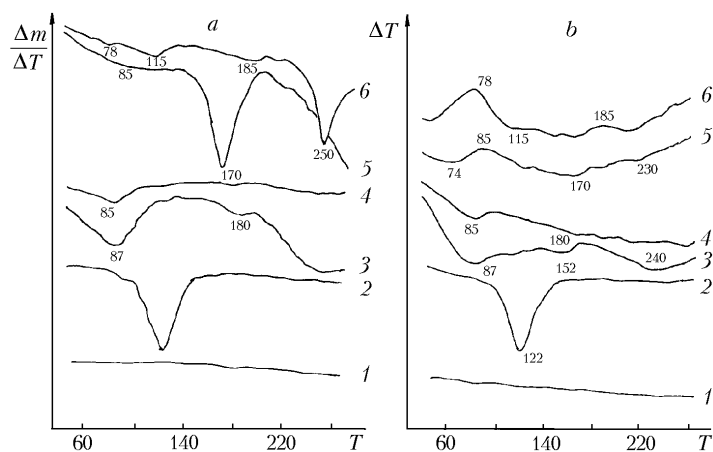


Fig. 1. DTG (a) and DTA (b) curves of the epoxy (1) and phosphate (2) binders, mercerized-cellulose (3), carbon (4) unweaved materials, and "grouting" products of the mercerized-cellulose (5) and carbon (6) unweaved materials with an organomineral binder containing 28 mass parts of ED-20.

TABLE 1. Properties of the Composites Based on the Epoxy-Mineral Binder and the Carbon Unwoven Material

Composition number	Content of epoxy oligomer, mass part	Yield of the gel-fraction, %	Gain in weight, mass %	Volume deformation, %	Density, g/cm <sup>3</sup>		Effective heat conductivity coefficient, W/(m·K)	Thermal diffusivity, 10 <sup>6</sup> , m <sup>2</sup> /sec	Water absorption, %	Fire-resistance
					volume	by the hydrostatic weighing method				
1	25	87.2	90	4.0	0.4	0.9	0.05	0.15	2.4	PV-1
2	36	82.3	100	2.3	0.43	0.91	0.05	0.21	3.5	PV-2
3	100	97.0	135	3.0	0.47	0.91	0.17	0.33	3.1	PG
4	150	96.0	140	2.5	0.37	0.92	0.16	0.45	13.2	PG

\*Tests were carried out on predried specimens.

droxyl groups of cellulose and decomposition of carboxyl-containing fragments with the formation of other volatile low-molecular compounds — carbon oxide and carbon dioxide [11].

"Grouting" of fibrous bases with an epoxy-mineral binder permits obtaining composites during whose heat treatment dehydration processes leading to a loosening of the structure of the material proceed. As a result of the adsorbed and bound water removal and partial thermal transformations of the cellulose unwoven material, the total mass loss in the composites reaches 25%. The data of the differential-thermal analysis also show that the heating of composites based on both mercerized-cellulose and carbon unwoven materials is accompanied by intensive exothermal effects observed in the 70–90°C temperature range, which do not show up for the initial components of the composite and are not their superposition. Small exothermal effects are also registered in the 120–190°C temperature range; they are most clearly defined in heating composites with the carbon unwoven material (Fig. 1b, curve 6). This is explained by the fact that the carbon unwoven material, unlike the mercerized-cellulose one, features a high absorptivity. The gain in weight upon impregnation, drying, and heat treatment of such composites can reach 130–150 mass % and, therefore, heat releases due to the chemical interaction between the mineral and organic components of the binder and the formation of the spatial-net structure of the polymer with a high yield of the gel fraction (Table 1) prevail over endothermal dehydration processes.

In composites with the mercerized-cellulose unwoven material, the fraction of the organomineral binder is small (the gain in weight is 10–15 mass %), and the main observed intensive thermal effects and maxima of the mass loss rates are due to the dehydration processes and the commencing thermdestructive transformations of the fibrous base. The effects associated with the binder hardening reactions are low-intensity compared to the dehydration effects and are, therefore, overlapped by them and do not show up on the curves of thermal analysis in the range of high

TABLE 2. Properties of the Composites Based on the Epoxy-Mineral Binder and the Mercerized-Cellulose Unwoven Material

Composition number	Content of epoxy oligomer, mass part	Yield of the gel-fraction, %	Gain in weight, mass %	Volume deformation, %	Density, g/cm <sup>3</sup>		Effective heat conductivity coefficient, W/(m·K)	Effective specific heat capacity, kJ/(kg·K)	Thermal diffusivity, 10 <sup>6</sup> , m <sup>2</sup> /sec	Water absorption, %	Fire-resistance
					volume	by the hydrostatic weighing method					
<i>Phosphate binder contains 75% of water</i>											
1	—	—	20.0	20.5	0.37	0.88	0.12	1.3	0.08	60	PV-0
2	6	82	12.0	23.0	0.29	0.74	0.07	1.2	0.1	25	PV-0
3	18	83	10.0	27.0	0.29	0.90	0.10	0.95	0.09	20	PV-1
4	28	85	9.0	30.0	0.35	0.91	0.13	0.9	0.1	12	PV-2
5	100	80.1	13.0	20.0	0.38	0.86	0.07	0.95	0.1	3.9	PG
<i>Phosphate binder contains 50% of water</i>											
1	—	—	15.0	20	0.42	0.88	0.29	0.9	0.11	50	PV-0
2	18	89.2	8.5	22	0.4	0.92	0.08	1.2	0.12	12	PV-1
3	25	92.3	9.0	20	0.3	0.88	0.07	1.1	0.11	10	PV-2
4	44	97.5	10.0	24	0.38	0.99	0.08	1.0	0.13	6	PG
5	140	90.0	15.0	26	0.43	1.07	0.11	1.2	0.14	5.8	PG

\*Tests were carried out on predried specimens.

temperatures. Under these conditions products of the commenced thermodestruction of the mercerized-cellulose unwoven material pass into the gaseous phase, which promotes an intensive increase in the volume of the composite: volume deformations equal 20–30% (Table 2). Unlike the composites described above, in the composites based on the carbon material the increase in the volume caused by the heat treatment is insignificant (2.3–4.0%, Table 1).

The dehydration processes proceeding in the thermal treatment of the organomineral composite, promoting the formation of a developed porous structure of the matrix, promote the binder hardening process. Variation of the intensity of the process of porous structure formation is attained by changing directionally the heat treatment conditions, the rate of rise, and the final temperature of treatment. The porosity, along with the other characteristics of the composite, depend also on the water content in the phosphate binder. For instance, Table 2 gives the properties of composites with a different degree of dilution with water. The application, as hardeners of epoxy resins, of mineral bonds containing a large quantity of water, has its own advantages and disadvantages. Thinning with water provides a higher porosity (the volume density of the materials is 0.26–0.38 g/cm<sup>3</sup>), increases the mobility of the bond and its workability, decreases the thickness of interfibrous interlayers upon "grouting" of unwoven materials, and reduces the binder consumption. At the same time, such treatment leads to a layering and worsening of the organomineral mixture compatibility, a decrease in the strength of the composites and their embrittlement, an increase in their water absorption to 20–25%, and a decrease in the degree of hardening of the epoxy component. Therefore, the treatment temperature of the composites has to be increased to 180–200°C. However, even these measures cannot provide a degree of hardening of composites higher than 85%. Moreover, inspite of the increase in the porosity of composites, there is no significant decrease in the effective heat conductivity coefficients. Probably, the process of complete removal of moisture from the materials obtained presents certain difficulties. With the use of more concentrated solutions of binders the maximum degree of hardening (96–98%) is observed already at a treatment temperature of 160°C (Table 3), which leads to good service properties of the materials.

The mineral bonds used in the present work are solutions of acid phosphates, which, when stored for a long time, may pass into two-phase dispersion characterized by a low water-resistance. The initial binders form upon hardening coagulation structures characterized by the ability to fail and sorb moisture in storage (water absorption up to 50–60%). When resin is added, the hardening process proceeds, the binder pH changes, and the system goes to a stable state. As the quantity of oligomers in the binder is increased to 100 mass parts, the yield of the gel fraction upon composite hardening increases, but a further increase in the content of the epoxy oligomer leads to some decrease in the degree of hardening. From this point of view optimal are compositions containing 18–100 mass parts of the epoxy oligomer. On the face of it, these data disagree with the results of [8] according to which the recommended ratios between the epoxy and phosphate components can be varied over a wider range. However, it is necessary to take into account that in the composites investigated in the present work a fibrous base is present and because of the possible

TABLE 3. Influence of the Temperature and the Duration of Treatment on the Binder Transformation Depth in the Composite Based on the Epoxy-Mineral Binder and the Mercerized-Cellulose Unwoven Material

Sample number	Final treatment temperature, °C	Treatment time, h	Yield of the gel-fraction, %
1	140	1	66.3
2	140	2	75.6
3	140	3	75.8
4	160	1	84.4
5	160	2	96.6
6	160	3	97.5
7	180	1	93.2
8	180	2	93.8
9	180	3	94.1
10	200	1	97.5
11	200	2	95.8
12	200	3	96.9

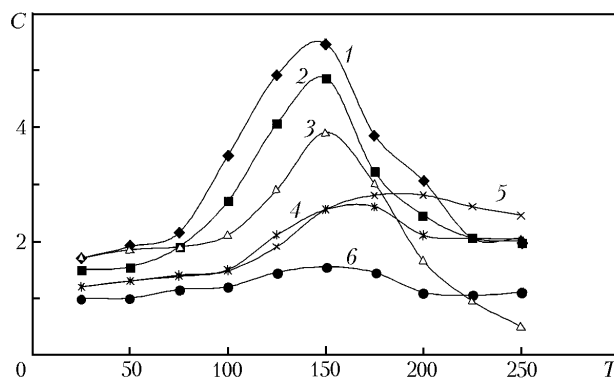


Fig. 2. Temperature dependences of the effective specific heat capacity of the initial mercerized-cellulose (1) and carbon (2) unwoven materials and of the mercerized-cellulose unwoven material treated with a phosphate binder (3, 6) and an organomineral binder containing 28 (4) and 18 (5) mass parts of ED-20 [3] primary heating upon air-storage of specimens, 6) secondary heating].

selective sorption by it of individual components of the binder the initial ratio between the epoxy and mineral components may be violated, as a result of which composites with a high content of the oligomer (up to 150 mass parts) can be characterized by a lower degree of hardening.

Figure 2 presents the temperature dependences of the effective specific heat capacity  $C$  of the fibrous bases and their compositions with an organomineral binder determined in the temperature range from 20 to 250°C. It is seen that the effective specific heat capacity of the unwoven materials is fairly high and depends linearly on the temperature. The temperature curves have maxima at a temperature of 150°C determined by the specificity of unwoven structures, their high surface energy, porosity, and moisture capacity. The decrease in the effective specific heat capacity as a result of the "grouting" of the fibrous base with the binder seems natural, since in this process the porosity decreases and the density of the materials increases (Tables 1, 2). At the same time it should be noted that there are considerable differences in the character and shape of the temperature curves for composites obtained with the use of the mineral bond alone. Upon heating of the composites obtained with a high concentration of the inorganic component, which were stored under conditions with a higher humidity, the value of the effective specific heat capacity is fairly high, and the shape of the curve of the temperature dependence of the heat capacity of the composite is analogous to the initial unwoven material (Fig. 2, curve 3). Further measurements of  $C$  in the same temperature range show a marked decrease in the value of the effective specific heat capacity. The curve of the temperature dependence is slightly bent with barely marked and blurred maxima at temperatures of 100 and 150°C corresponding to the dehydration region (Fig. 2, curve 6). The data obtained confirm the above inference that composite materials are unstable when only the mineral bond is used and capable of sorbing moisture in storage.

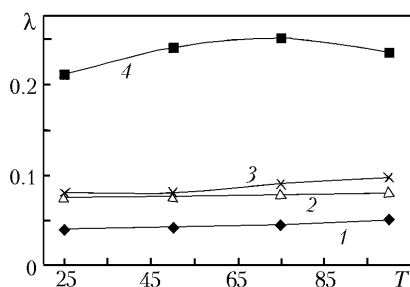


Fig. 3. Temperature dependences of the effective heat conductivity coefficient of the initial mercerized-cellulose unwoven material (1) and of that treated with phosphate (4) and an organomineral binder containing 18 (2) and 28 (3) mass parts of ED-20. Testing on predried specimens.

Upon the introduction into the mineral binder of epoxy oligomers entering into the reaction of interaction with the metallophosphate bond, a more rigid spatial-net structure of the polymer is formed, the water absorption of the fabricated composites markedly decreases, and the strength increases. From Fig. 2 it is seen that upon heating of such composites to the vitrification temperature the specific heat capacity changes linearly (Fig. 2, curve 4), which is in good agreement with the literature data for amorphous polymers [12, 13]. Upon devitrification of the system (above 100°C) the heat capacity sharply increases as a consequence of the increase in fluidity of the polymer chain formed and its individual links [14]. In so doing, the temperature dependence of  $C$  in the 175–225°C temperature range corresponds to the flexible rod model [15]. The observed jump and sharp increase in the effective heat capacity can be due to both the continuing processes of structure formation in the organomineral matrix and the destructive transformations of the unwoven material.

Figure 3 presents the results of the investigation of the temperature dependence of effective heat conductivity coefficients of the mercerized-cellulose unwoven material and its compositions with a mineral and an epoxy mineral binders. For the fabrics proper, a linear increase in the heat conductivity from 0.04 to 0.05 W/(m·K) upon heating from 25 to 100°C is observed (Fig. 3, curve 1). Treatment of the fabrics with binding matrices leading to the filling of the porous fibrous base changes their ability to transfer heat. This shows up most vividly in composites with a water-based mineral binder (Fig. 3, curve 4): the heat conductivity of the composite sharply increases to values above 0.2 W/(m·K) and upon heating it has an extreme character. The addition of up to 50 mass parts of the organic component into the mineral bond and the subsequent treatment and hardening lower the effective heat conductivity coefficient to values from 0.07 to 0.08 W/(m·K) (Fig. 3, curves 2, 3). A further increase in the organic component for the chosen systems is inexpedient, since practically all basic indices of the properties of the obtained composition differ from one another insignificantly, and the effective heat conductivity coefficient begins to grow again and thus the heat-insulating properties worsen (Table 1). We have also revealed the influence of the heat treatment temperature in forming composites from unwoven materials and an epoxy-mineral binder on the value of the effective heat conductivity coefficient: as the heating temperature is increased from 140 to 180°C, the coefficient decreases by 17–24% on average, which is due to the increase in the degree of hardening of the composites and the formation of a more rigidly bound structure of the polymer matrix (Table 3).

The fire-resistance of the developed compositions of the composites has been determined. As is seen from Tables 1 and 2, composites obtained by treating unwoven fabrics with a metallophosphate binder exhibit the maximum resistance. They have the combustibility category PV-0. The introduction into the mineral binder of up to 20 mass % of the organic component leads to some decrease in the fire-resistance of the composites. However, this characteristic for the above compositions is also high (combustibility category PV-1). A further increase in the content of the epoxy oligomer in the binding matrix leads to a decrease in the fire-resistance, shifting the combustibility category of composites to PV-2 and PG.

**Conclusions.** The investigations made and the analysis of the experimental data obtained have made it possible to optimize the compositions and the conditions for the formation of composites based on an organomineral binder and unwoven (mercerized-cellulose- and carbon-based) materials. Composites exhibiting a complex of improved properties: higher fire-resistance, low water absorption, low density, and effective heat-insulating properties have been de-

veloped. The composites are intended for use as heat-insulating materials and can be employed in various branches of the national economy and industry.

## NOTATION

$C$ , effective specific heat conductivity, kJ/(kg·K);  $T$ , treatment temperature, °;  $\alpha$ , thermal diffusivity, m<sup>2</sup>/sec;  $\lambda$ , effective heat conductivity coefficient, W/(m·K);  $\Delta m$ , mass loss, %;  $\Delta T$ , temperature difference, deg;  $\rho$ , density, g/cm<sup>3</sup>.

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