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CHARACTERISTICS OF THE POROUS STRUCTURE OF CARBONIZED GLASS-REINFORCED PLASTICS

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The results of experimental investigations of the porous structure of four glass-reinforced plastics after the interaction of them with high-temperature flows have been presented. The dependences of the accessible porosity on the thermal-action time have been obtained. The values of the initial porosity of the glass-reinforced plastics have been determined. The values of the effective radii of micro- and macropores at different times of high-temperature heating of the glass-reinforced plastics have been calculated.

Introduction. Models of high-temperature heat and mass transfer in such popular thermal-protective materials as glass-reinforced plastics were developed fairly long ago [1, 2]; not only are these models widely employed in practice but they also find application as basis models for investigation of processes occurring in structurally inhomogeneous media with intense physicochemical transformations at high temperatures [3, 4]. The models of [1, 2] can be implemented given reliable information on the thermophysical, thermokinetic, and structural characteristics of glass-reinforced plastics under heating to high (500–1500 K) temperatures. But whereas the thermophysical and thermokinetic characteristics of glass-reinforced plastics have been established with a fairly high degree of reliability, information on the structural characteristics is virtually missing.

This work seeks to experimentally investigate the characteristics of the porous structure of typical glass-reinforced plastics after intense unilateral heating by a high-temperature gas flow. Polymer composite materials in the initial state have a considerable total (including accessible and inaccessible) porosity, attaining 5%. The reason has to do with both the properties of the materials employed and the technology of manufacture of polymer composites [5, 6]. In polymer composite materials, one recognizes porosity of three types: the porosity of a polymer matrix, that of a reinforcing material, and interphase porosity [6]. The porosity of resin, for example, is caused by the presence of water, impurities, solvents, and solidification products and by the technology of heat treatment [7–9]. The structure of a reinforcing filler possesses a developed microporosity. Intrareinforcement pores have a transverse dimension of $(35–70)\cdot 10^{-6}$ m. Interphase porosity arises from defects at the "polymer matrix–filler" boundary [7–9]. As the content of glass fiber increases, the density of the packing decreases but the specific interior surface and volume of the pores increase [8, 9].

However, the decisive role in the processes of heat and mass transfer of porous bodies is played by the open transport pores ensuring phase permeability of a material and not by the total porosity [1, 2].

The formation of the system of transport pores in polymer composite materials is mainly caused by the conditions of interaction of the material with a high-temperature gas flow [2].

Procedure of Experimental Investigations. For the experimental investigations we employed a setup (Fig. 1) whose basic elements were a gas generator and a rotating platform with three glass-reinforced-plastic specimens. The high-temperature gas flow produced by the gas generator was in parallel to the heated surface of a specimen. As a result, the glass-reinforced-plastic was heated to temperatures much higher than the temperature of the beginning of the decomposition of a binder. With propagation of the front of the beginning of destruction deep into the composite, a carbonized- material layer whose thickness was determined by the duration of high-temperature heating was formed. Once a coke layer with a thickness sufficient for experiments on the porosimeter had been formed, the heating of the specimen was discontinued. An air flow was supplied by a stainless-steel pipeline 1 of diameter $6.3\cdot 10^{-2}$ m to cool the specimen. The flow temperature was prescribed to be equal to 293 K; it was monitored by a thermocouple and

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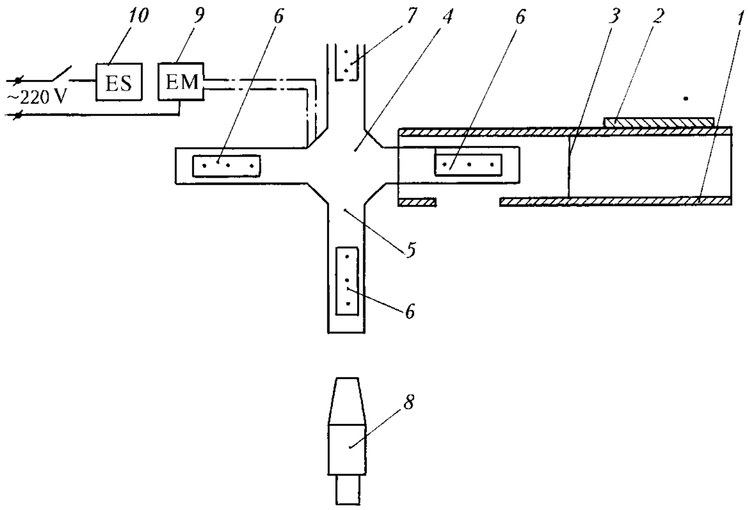


Fig. 1. Basic diagram of the experimental setup.

maintained by a special heater 2. Grid 3 for laminarization of the air flow was installed in the midship section of the pipe. A rotating device 4, on which metal holders 5 with specimens 6 in three of them and with a heat-flux transducer 7 in the fourth were fixed, was employed for introduction of the specimens (heated by gas generator 8) into the pipe's cavity for cooling through the lateral cut and removal from the pipe after the experimental cycle. The rotating device was powered by electromagnet (EM) 9 that was switched on by a signal from an electric stopwatch (ES) 10 specifying the duration of the experiments. The shape of the stainless-steel holders allowed experiments with glass-reinforced-plastic specimens in the shape of 100 × 20 × 10 mm plates. Such a shape of the specimens, selected by analogy with [10], allowed elimination of some restrictions imposed on the results of experiments with specimens of another shape (for example, a cylinder with a spherical blunting or a hemisphere). The leading edge of the specimens was protected against the action of the high-temperature medium by a conical fairing. The trailing edge and lateral surfaces of a specimen were heat-insulated.

The order of the experiments was as follows. In the first step, we investigated the specimens in which measuring elements were installed. The rotating device allowed experiment with three specimens from a polymer composite material for constant parameters of the high-temperature gas flow. The value of the heat flux was determined by the transducers fixed in the fourth holder [11].

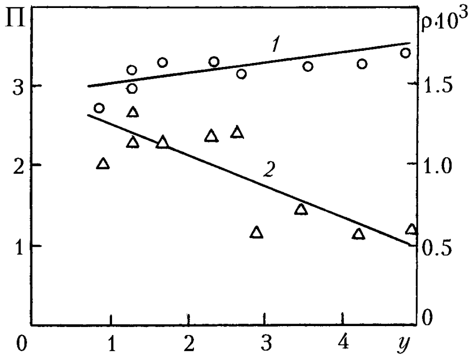
An important element of the setup was a unit for quenching of the specimens, which was employed to "stop" the process of thermal decomposition of the binder at a certain instant of time. For a prescribed period (4 to 10 sec) the specimens were exposed to the high-temperature gas flow and then rapidly cooled. After the cooling, we cut individual elements off the specimens and dried them in a heating cabinet. These elements were investigated on a mercury porosimeter [12].

The method of indentation of mercury allows investigation of the structure of porous bodies and information on the distribution of the total pore volume by the equivalent radii [12]. The volume of the pores of the specimen under study was calculated from the data obtained in measuring the resistance of the circuit in the experiments on a P-3M unit according to the following formula:

$$V = \frac{K\,(R - R_0)}{m} ,$$

whereas the radius of the pores was determined as [8]

$$r = \frac{2\sigma \cos\theta}{P} .$$



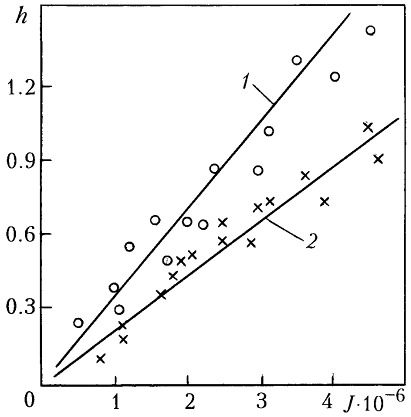


Fig. 2. Distributions of the density (1) and initial porosity (2) of material 1 over the coordinate *y*. ρ, kg/m^3; *y*, mm.

Fig. 3. Thickness of the carbonized ("charged") layer *h* vs. heat pulse *J*: 1) material 3; 2) material 2. *h*, mm; *J*, J/m^2.

TABLE 1. Characteristics of the Studied Materials

No. of material	Type of reinforcing filler	Binder	Weight content of the binder	Density, kg/m^3
1	VPR-10M knitting-sewing material	IFÉD	28–37	1740
2	The same	ÉKhD-U	28–37	1720
3	TS 8/3-VM-78 glass cloth	IFÉD	25–31	1850
4	The same	ÉKhD-U	25–31	1770

It was taken into account that the pores of the carbonized layer in the specimens were covered with pyrolytic soot; therefore, in the calculations, we selected a wetting angle of 142^o (as that of carbon).

Results of the Experiments and Their Discussion. Special investigations of the specimen's microstructure have shown that no phenomena of mechanical removal of material [10] were observed under the indicated experimental conditions. The process of formation of the porous structure of the specimens was accompanied by blowing of the gaseous products of decomposition of the binder into the wall region of the external gas flow via the pores.

The investigations have been carried out with four glass-reinforced plastics differing in composition (Table 1). We performed experiments on determination of the initial porosity of uncarbonized glass-reinforced plastics according to the procedures described above.

Figure 2 give the initial-porosity distributions over the thickness of the specimens for material 1 (see Table 1). It is seen that the porosity changes, even if only slightly. This effect is most probably caused by the technology of manufacture of wound glass-reinforced plastics [5, 6]. In the vicinity of the free surface, the porosity of polymer composites manufactured by the method of winding is somewhat higher than that in the vicinity of the surface of contact with the mandrel.

In analysis of the experimental results, we were able to determine two further important characteristics of the material: thickness of the carbonized layer *h* and apparent density ρ_a.

Figure 3 gives the thickness of the carbonized layer *h* for glass-reinforced plastics 2 and 3 (see Table 1) as a function of the heat pulse *J,* which is determined as

$$J = \int_0^t q(t)\,dt\,.$$

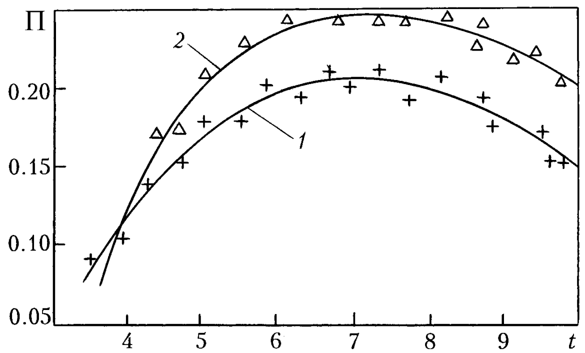


Fig. 4. Secondary accessible porosity vs. thermal-action time: 1) material 1; 2) material 2. Π, %; *t*, sec.

TABLE 2. Effective Radii of Micro- and Macropores as Functions of the Thermal-Action Time

Heating time, sec	Micropores	Macropores
	r, 10^{-7} m	
>5.5	0.20	6
>8.0	0.35	9
<10	0.17	7

The character of the dependences obtained, despite the certain scattering of experimental points, shows that the quantity *h* is in direct proportion to the heat pulse in the range of variation of the parameters, which has been singled out in the experiments. The results obtained are in satisfactory agreement with the theory of thermal protection [1, 2]. Also, it is necessary to note that the difference in the thicknesses of the carbonized layer of two different glass-reinforced plastics, which has been established in the experiments, is no larger than 40% for the maximum experimental thermal loads. On the one hand, such a scale of variation of *h* values for confidence intervals of determination of this characteristics of ±15% cannot be recognized as large; on the other hand, we cannot but note it. Probably, the variations of the thermophysical and thermokinetic characteristics of the glass-reinforced plastics studied, which are caused by the dissimilar compositions of the composites, influence the intensity of the processes of heat transfer and destruction of these materials. But this influence is smoothed out to a certain extent by an objective instability of some parameters of the polymer composites.

Figure 4 gives the secondary porosity of the two of the materials studied as a function of the thermal-action time.

For all the materials in question we have established the following regularity: the secondary porosity increases for 6–8 sec of heating but then its value decreases. It should be noted that the results on determination of the secondary porosity are in satisfactory agreement with experimental data on determination of the gas-permeability coefficient [13].

The experimental procedure [12] of determination of the secondary porosity enables us to obtain the distribution of the entire pore volume by the effective radii (it is assumed that the pores represent cylinders). Table 2 gives results of determination of the effective radii of micro- and macropores of material 2 versus the thermal-action time.

It is assumed at present that the mechanism of formation of secondary porosity for polymer composite materials substantially influences both the dynamics of mass removal of the gaseous products of decomposition of a polymer binder and the thermomechanical destruction of the polymer composite material. The hypothesis for deposition of pyrolytic carbon on the macropore walls of charring thermal-protective materials was put forward for the first time quite a long time ago [14]. This hypothesis was subsequently confirmed in [15] and was repeatedly discussed in analyzing the results of investigation of high-temperature heat and mass transfer in carbonizing thermal-protective materials [16, 17]. The results of the present work (Figs. 3 and 4) also confirm the possibility that the process of deposition of pyrocarbon can be realized on the pore walls of the coke of thermal-protective materials. However, it should be noted that the scale of the effect discussed is small, on the whole. The reduction in porosity amounts to no more that

25% of the maximum value attained for each of the four materials studied. When the porosity is 0.15 to 0.20, realization of the effect of "clogging" of the macropores [14–16] seems unlikely.

Furthermore, the experimental results show that the maximum reduction in porosity amounts to about 18% for a number of composites (Fig. 4). If we take into account that the initial porosity in glass-reinforced plastics changes 1.5–2 times over the thickness (see Fig. 2) and the variations in the thermophysical and physicomechanical characteristics of typical polymer composites amount to ±(15–20)% according to the data of [18], we can assume that it is also unlikely that the scale of the effect identified in the conducted experiments in changing over to other materials or heating regimes will increase.

It should be taken into account that in none of the experiments have we recorded a totally inaccessible (upon completion of the process of thermal decomposition) porosity and a porosity close to the initial one (of the uncarbonized material). Consequently, the experimental data obtained cannot be employed to prove the existence of the "clogging" effect considered as the actual process for glass-reinforced plastics as early as over 35 years ago [14].

CONCLUSIONS

The formation of accessible secondary porosity in the group of glass-reinforced plastics under the action of a high-temperature gas flow has been investigated experimentally. The experimental data obtained on the porosity of typical glass-reinforced plastics upon completion of the process of thermal decomposition of the binder and on the effective radii of micro- and macropores offer information characterizing the properties of the materials studied. It can also be used as an additional basis for the development of models of heat and mass transfer in glass-reinforced plastics under high-temperature heating by external flows [1, 2]. Data on the effective radii of micro- and macropores represent an important result of the experimental investigations performed. The results obtained create objective prerequisities for modeling of the structure of the carbonized layers of typical modern glass-reinforced plastics and for calculation with the models of [1, 2] of such an important characteristic of the "charred layers" as permeability. The characteristics obtained by the method of mercury porosimetry have very small errors, on the whole, and are an objective base for further development of the theory of heat and mass transfer in glass-reinforced plastics at high temperatures.

NOTATION

K, dilatometer constant, kg·m^3/Ω; R, resistance of the circuit at a given equilibrium pressure, Ω; R_0, resistance of the circuit at initial pressure, Ω; m, weight of the specimen, kg; r, pore radius, m; σ, coefficient of surface tension of mercury, N/m; θ, wetting angle; P, reduced pressure, Pa; V, pore volume, m^3; h, coke-layer thickness, m; J, heat pulse, J/m^2; Π, porosity, %; y, coordinate, m; ρ, effective density, kg/m^3; t, time, sec; $q(t)$, heat flux to the specimen's surface, W/m^2. Subscripts: 0, initial; app, apparent.

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