EFFECT OF HEAT-AGING ON THE THERMAL PROPERTIES OF GLASS-REINFORCED EPOXY PLASTIC

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Experimental studies of the thermophysical properties of epoxy-based glass-reinforced plastics have been conducted in the range of 10°-400°K. The appearance of secondary anisotropy in polymer has been observed after repeated cooling of the material.

At present the constructional glass-reinforced plastic is widely used as a material to make the components of cryogenic devices. As a rule, these devices are designed for long-term use, i.e., all the components are subjected to periodic heating and cooling in a wide range of temperatures. In view of this it is necessary to make a comprehensive study of the properties of materials in use over a wide range of temperatures.

The thermophysical properties (thermal conductivity, thermal diffusivity, and heat capacity) of glass-reinforced plastics based on epoxy binder ÉDT-10 have been experimentally studied by us in the temperature range of 10°-400°K.

The material under study is an epoxy resin (30%) reinforced with oriented glass fibers (70%).

The thermal properties of the materials under test were determined in a quasi-steady-state condition of heating the specimens in a setup according to the method described in [1, 2].

The specimens were prepared in the form of square plates and the thermal properties were studied in two directions with heat flow along and across the reinforcing fibers.

It is seen from the results given in Fig. 1 that the coefficient of thermal conductivity and specific heat capacity increase with rise in temperature and the coefficient of thermal diffusivity decreases in inverse proportion to temperature.

The coefficients of thermal conductivity and thermal diffusivity depend on the direction of heat flow and orientation of reinforcements, as they characterize the conductivity and thermal diffusion in one direction. The heat capacity practically does not depend on the direction of heat flow, as it characterizes a scalar volume, i.e., the energy accumulation. This is well exhibited in Fig. 1.

The solid reinforcements in the form of glass fibers exert a great influence on the properties of filling polymers. This effect is explained by the presence of a disjoining pressure and forces of molecular interactions between polymer molecules and adjacent phases. The specific structure of these layers imparts characteristic differences in their properties. In the longitudinal direction the molecules are joined by chemical bonds resulting in high values of strength and thermophysical characteristics. In the transverse direction they have forces of physical nature, which corresponds to much lower values of these factors. Under the action of these forces as a result of the orienting action of the reinforcing surface the polymer molecules can occur in a more or less ordered state.

Thus, the anistropy of properties of the glass-reinforced plastics takes place due to a different mechanism of heat transfer between the molecules of glass fillers and polymer binder and heat transfer in each of its components. This can be well demonstrated, if one makes use of electrothermal analogy, in which the intermolecular bonds are replaced by large or small thermal resistances. A polymer binder with glass reinforcement mainly has bonds of physical nature, which corresponds to a large thermal resistance. In addition, the main

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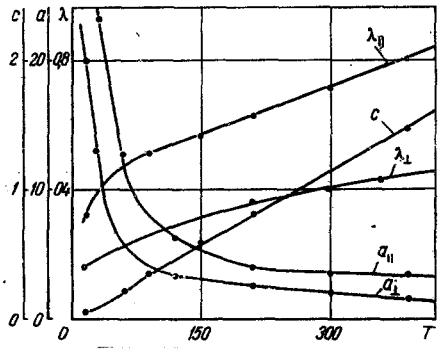

Fig. 1. Temperature dependence of thermal conductivity λ, W/m · deg thermal diffusivity a, 10^7 m^2/sec, and heat capacity c, 10^{-3} J/kg · deg of ÉDT-10 along (∥) and across (⊥) the fibers; T, °K.

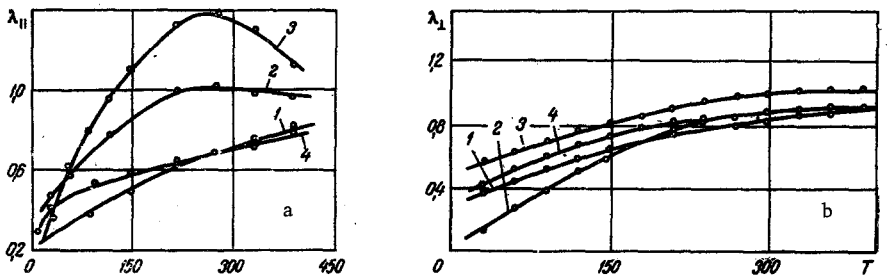

Fig. 2. Temperature dependences of the thermal conductivity of ÉDT-10 along the fibers (a) and across them (b) after single cooling (curve 1), 5-fold cooling (curve 2), 10-fold cooling (curve 3) and 60-fold cooling (curve 4). T, °K; λ, W/m · deg.

role in the binder is played by the van der Waals forces that also have great thermal resistance. But in the glass reinforcement the forces of chemical nature have the main importance and a small thermal resistance corresponds to these forces. Therefore, the heat flow propagating along the fibers encounters a smaller resistance than in the perpendicular direction. The more distinct the orientation of polymer molecules along the surface of glass fibers, the greater is the anisotropy. So the anisotropy of thermal conductivity and thermal diffusivity is more in ÉDT-10 than in AG-4S.

Thus, the thermal properties of glass-reinforced plastics significantly depend on the orientation of reinforcement.

It is particularly important to deal with the analysis of results of measurement of thermal properties, depending on heat-aging of the material. The material under test was subjected to repeated thermal impacts. Each thermal impact meant heating the specimen to 373°K and cooling it rapidly in liquid nitrogen. The thermophysical characteristics were determined after 1, 5, 10, and 60 thermal impacts. Thus, an artificial heat-aging of the material was caused. The thermophysical properties were determined along and across the fibers. The experimental results are presented in figures and tables. In Fig. 2a and b the temperature dependences of thermal conductivity of ÉDT-10 along and across the fibers after 1, 5, 10, and 60 cycles of cooling are presented as an example. Such an unusual behavior of thermal conductivity can be explained by the appearance of anisotropy in the properties of the polymer film.

As a result of the difference in the thermal-expansion coefficients of resin and glass fiber, stresses develop in thermal hardening, the magnitude of which depends also on the rate at which the thermal hardening is carried out. In this case the epoxy resin has the least value of stresses. The analysis of magnitude and nature of developing stresses indicates that they are primarily tangential and partly normal. The interface between resin and glass is especially favorable for concentration of stresses [4].

It is known that the structural residual stresses in a glass-reinforced plastic can have high values and can effect the properties of the material. It has been established in [3] that under various loads across a fiber the residual stresses lead to certain increase in the strength of a glass-reinforced plastic (based on binder ÉDT-10), which nevertheless remains below the initial strength of the polymer binder. The analysis of stress–strain state shows [3] that the higher the level of residual stresses, the faster is the breakdown of the polymer

TABLE 1. Thermophysical Properties of the Glass-Reinforced Epoxy Plastic (across the fibers), γ = 1820 kg/m^3

T°, K	5-fold cooling		10-fold cooling		60-fold cooling		100-fold cooling		
	$a \cdot 10^7$, m^2/sec	$c \cdot 10^{-3}$, J/kg·deg	$a \cdot 10^7$, m^2/sec	$c \cdot 10^{-3}$, J/kg·deg	$a \cdot 10^7$, m^2/sec	$c \cdot 10^{-3}$, J/kg·deg	λ, W/m·deg	$a \cdot 10^7$, m^2/sec	$c \cdot 10^{-3}$, J/kg·deg
10	6,40	0,0343	—	—	53,9	0,0185	0,173	—	0,016
20	4,80	0,0664	25,0	0,0582	33,6	0,0327	0,188	—	0,040
30	4,20	0,0994	17,5	0,0868	11,2	0,1065	0,204	19,4	0,080
40	3,87	0,1348	13,9	0,1135	8,0	0,1601	0,218	13,2	0,120
50	3,65	0,1713	11,0	0,1495	6,9	0,1976	0,231	8,6	0,160
60	3,50	0,2083	9,0	0,1895	6,0	0,2401	0,244	6,9	0,200
70	3,37	0,2475	7,6	0,2320	5,3	0,2874	0,256	6,0	0,240
80	3,25	0,2885	6,6	0,2750	4,77	0,3354	0,269	5,4	0,280
90	3,20	0,3240	5,9	0,3180	4,40	0,3799	0,282	4,9	0,320
100	3,15	0,3660	5,4	0,3580	4,10	0,4238	0,293	4,4	0,360
110	3,10	0,4040	5,0	0,3970	3,90	0,4610	0,301	4,2	0,400
120	3,05	0,4480	4,6	0,4440	3,70	0,5023	0,310	4,0	0,432
130	3,00	0,4910	4,4	0,4760	3,50	0,5467	0,319	3,9	0,472
140	2,95	0,5280	4,2	0,5110	3,35	0,5859	0,329	3,7	0,512
150	2,90	0,5690	4,0	0,5550	3,20	0,6289	0,336	3,5	0,560
160	2,80	0,6210	3,8	0,5920	3,10	0,6634	0,342	3,3	0,600
170	2,75	0,6620	3,7	0,6210	2,98	0,7029	0,347	3,2	0,656
180	2,70	0,7010	3,6	0,6620	2,90	0,7356	0,351	3,1	0,704
190	2,65	0,7400	3,5	0,6860	2,80	0,7736	0,354	3,0	0,752
200	2,60	0,7790	3,4	0,7200	2,70	0,8125	0,356	2,9	0,801
210	2,50	0,8320	3,25	0,7660	2,60	0,8543	0,357	2,8	0,856
220	2,43	0,8790	3,15	0,8050	2,50	0,9017	0,359	2,7	0,896
230	2,37	0,9170	3,00	0,854	2,45	0,9291	0,401	2,6	0,944
240	2,30	0,9650	2,90	0,893	2,35	0,9780	0,403	2,55	1,010
250	2,20	1,0220	2,80	0,934	2,27	1,0197	0,404	2,50	1,040
260	2,15	1,0650	2,70	0,975	2,18	1,0694	0,405	2,35	1,104
270	2,05	1,1300	2,50	1,040	2,09	1,1207	0,406	2,30	1,152
290	1,85	1,3050	2,40	1,120	1,90	1,2472	0,407	2,05	1,210
310	1,67	1,4300	2,25	1,205	1,72	1,3905	0,408	1,90	1,408
330	1,60	1,5350	2,10	1,300	1,55	1,5537	0,409	1,75	1,582
350	1,50	1,620	2,00	1,375	1,39	1,7444	0,410	1,70	1,751
370	1,42	1,720	1,89	1,462	1,20	2,0297	0,410	1,65	1,920
400	1,33	1,845	1,71	1,601	0,985	2,631	0,412	1,55	2,201

matrix, when a unidirected glass-reinforced plastic is under tension. Under such circumstances the breakdown of the polymer matrix takes place much before the breakdown of the glass-reinforced plastic.

The strength of a glass-reinforced plastic decreases as a result of cracking of the binder.

In studying the strength characteristics of material ÉDT-10 [3] it was shown that in loading the glass-reinforced plastic across the fibers the residual stresses lead to increase in strength. Depending on the type of loading, the strength increases by 20-40% of the initial strength of the epoxy binder.

In stretching the glass-reinforced plastic along the fibers a premature cracking of the binder is observed (before the glass-reinforced plastic is broken). The higher the level of residual stresses, the earlier is the cracking.

In compressing along the fibers there is joint deformation of the reinforcing elements and binder right up to the breakdown of the glass-reinforced plastic, irrespective of the magnitude of residual stresses.

A similar picture is observed in studying the thermophysical properties. It follows from what has been stated above that by virtue of the great difference in the linear-expansion coefficients and forces of interaction of the polymer with the reinforcement the internal stresses are so large that they cause structural changes in the polymer and give rise to anisotropy in properties.

From Fig. 2. it is evident that the thermal conductivity of glass-reinforced plastic ÉDT-10 increases with rise in the number of thermal impacts and it reaches a maximum (along the fibers) after 10-fold cooling (in material AG-4S this maximum appears after 5-fold cooling). This is related to the fact that the epoxy resin possesses low porosity and primarily has closed pores. Besides, at the time of hardening stresses of lower magnitude develop in it.

It is interesting to compare the thermal conductivity of glass-reinforced epoxy plastic along and across the fibers. It is seen from the figure that the thermal conductivity across the fibers does not have a pronounced maximum as the thermal conductivity along the fiber has. This is evidently related to the fact that glass rein-

TABLE 2. Thermophysical Properties of the Glass-Reinforced Epoxy Plastic (along the fibers)

T,° K	5-fold cooling		10-fold cooling		60-fold cooling		100-fold cooling		
	$a \cdot 10^7$ m²/sec	$c \cdot 10^{-3}$ J/kg·deg	$a \cdot 10^7$ m²/sec	$c \cdot 10^{-3}$ J/kg·deg	$a \cdot 10^7$ m²/sec	$c \cdot 10^{-3}$ J/kg·deg	λ, W/m·deg	$a \cdot 10^7$ m²/sec	$c \cdot 10^{-3}$ J/kg·deg
10	40,8	0,0494	41,0	0,0240	110,2	0,0105	0,200	—	0,016
20	31,6	0,0716	32,0	0,0624	50,0	0,0256	0,224	—	0,040
30	24,3	0,1033	17,5	0,1130	12,8	0,1095	0,248	19,9	0,08
40	17,8	0,1533	15,5	0,1565	9,0	0,1688	0,271	14,4	0,12
50	13,5	0,2180	14,3	0,2020	7,2	0,2265	0,292	10,05	0,16
60	11,6	0,2710	13,4	0,2460	6,2	0,2829	0,312	8,6	0,20
70	10,4	0,3340	12,7	0,2900	5,75	0,3240	0,336	7,71	0,24
80	9,4	0,3750	12,3	0,3280	5,55	0,3584	0,358	7,03	0,28
90	8,8	0,4210	11,9	0,3690	5,40	0,3902	0,376	6,40	0,32
100	8,5	0,4570	11,6	0,4050	5,20	0,4268	0,401	5,60	0,36
110	8,0	0,5080	11,3	0,4400	5,00	0,4663	0,417	5,30	0,40
120	7,6	0,5570	11,0	0,4740	4,80	0,5080	0,435	4,60	0,43
130	7,4	0,5940	10,8	0,5110	4,65	0,5474	0,456	4,50	0,47
140	7,3	0,6240	10,6	0,5440	4,45	0,5960	0,472	4,00	0,51
150	7,1	0,6620	10,4	0,5760	4,35	0,6331	0,488	3,90	0,56
160	6,9	0,7040	10,3	0,6050	4,20	0,6812	0,512	3,70	0,60
170	6,7	0,7460	10,2	0,6320	4,10	0,7239	0,521	3,60	0,66
180	6,5	0,7910	10,1	0,6600	4,00	0,7634	0,536	3,50	0,70
190	6,3	0,8260	9,9	0,6920	3,85	0,8140	0,544	3,40	0,75
200	6,0	0,8880	9,7	0,7220	3,75	0,8556	0,556	3,30	0,80
220	5,5	0,9850	9,2	0,7850	3,55	0,9445	0,576	3,10	0,89
240	5,1	0,9989	8,8	0,8350	3,30	1,0566	0,592	3,00	1,01
260	4,7	1,1610	8,3	0,8870	3,10	1,1644	0,608	2,90	1,10
270	4,5	1,2120	8,1	0,9050	3,00	1,2282	0,616	2,80	1,15
290	4,1	1,3360	7,7	0,9360	2,80	1,3579	0,624	2,70	1,21
310	3,8	1,4260	7,2	0,9800	2,55	1,5351	0,640	2,50	1,408
350	3,3	1,6350	6,4	1,0380	2,05	2,0060	0,668	2,10	1,751
400	2,95	1,8150	5,9	1,0460	1,55	2,5280	0,696	1,70	2,201

forced plastic ÉDT-10 has clear orientation of glass fibers and the branching in the structure of the polymer binder is small. The polymer molecules are also oriented along the surface of glass fibers. With rise in temperature the thermal fluctuations of the polymer molecules increase in the transverse direction, which leads to monotonic rise of thermal conductivity across the fibers. When the number of cooling cycles is increased and when the crystallinity is raised, the thermal conductivity across the fibers also increases in its absolute value and reaches a maximum after 10 cycles, but the total change of the coefficient remains monotonic. With further increase in the number of cycles the thermal conductivity decreases due to cracking and stratification.

When the number of cycles is increased, the anisotropy of properties first increases and then decreases, when the number of cycles becomes large. This is related to the additional orientation of molecules of the binder along the surface of the reinforcements, when the number of cycles is small. The more oriented the occurrence of macromolecules of the binder along the reinforcement surface and the less branched their structure is, the greater is the anisotropy. Further heat-aging leads to the disintegration of the material and transition to an isotropic state.

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