EFFECT OF REPEATED COOLING ON THE THERMOPHYSICAL PROPERTIES OF CONSTRUCTIONAL GLASS PLASTICS IN THE TEMPERATURE RANGE 10-400°K

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The thermal conductivity, thermal diffusivity, and specific heat of the constructional glass plastic AG-4S are measured at 10-400°K after single, five-fold, and ten-fold cooling. Reasons for changes taking place in the thermal properties of the materials are discussed. The thermal properties are analyzed along and across the filaments of the filler.

Constructional glass plastics are used extremely widely in modern cryogenic technology; however, the thermal properties of these materials have been insufficiently studied at low temperatures [1].

We studied the thermophysical properties of constructional glass plastics in the temperature range 10-400°K. The complex determination of thermal conductivity, thermal diffusivity, and specific heat in thermally-insulating materials over a wide temperature range was indicated in full detail in [2, 3].

The basis of the method lay in solving the problem of the temperature-field distribution in an unlimited solid of regular geometrical shape for boundary conditions of the second kind in the steady-heating mode.

Samples of the test material were prepared in the form of two types of plates in which the filler filaments lay either parallel or perpendicular to the plane of the plate. On using a plane heater this enabled us to measure the thermophysical properties along and across the filling filaments of the material.

The equations for analyzing the experiments then take the form

$$\lambda = \frac{q\delta}{4\Delta T}, \qquad a = \frac{\delta^2}{2\Delta T} \cdot \frac{dT}{d\tau}, \qquad c = \frac{Q}{m} \bigg/ \frac{dT}{d\tau}.$$

One of the most widely used construction polymers is the glass plastic AG-4S (Table 1). Handbook data [1] only provide the specific heat and thermal conductivity at room temperatures. The material in question is intended for making parts of a structural, and electrotechnical nature by direct extrusion or die casting and also by winding, with subsequent heat treatment.

TABLE 1. Properties of the Material AG-4S [1]

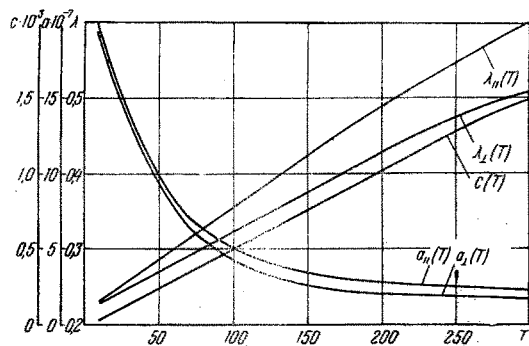| Components	Weight content	Form of material supplied
Binder, modified phenol-formaldehyde resin of the resol type	30±2	Strip or cloth made from oriented primary or twisted glass fibers impregnated with binder
Filler, alkali-free aluminoborosilicate glass cloth	70±2	

Fig.1. Temperature (T, °K) dependence of the coefficients λ (W/m·deg), a (m²/sec), and c (J/ kg·deg) of AG-4S along (‖) and across (⊥) the filaments after a single cooling.
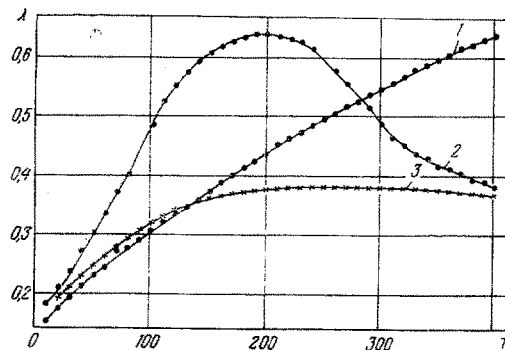
Fig.2. Temperature dependence of the thermal conductivity of AG-4S along the filaments after a single cooling (1) and after five (2) and ten (3) times cooling.

Figure 1 illustrates the temperature dependence of the thermal conductivity, thermal diffusivity, and specific heat along and across the fiber of AG-4S after a single cooling, i.e., the samples were first cooled to liquid-helium temperature, then continuously heated to 400°K under adiabatic conditions; by recording the readings of the corresponding instruments we were able to determine the coefficients λ, a, and c over the whole temperature range 10-400°K.

We see from Fig.1 that the thermal conductivity and thermal diffusivity of the material increase monotonically, without any deviation, suggesting that the material preserves its original structure and has no zones of phase transformation (e.g., zones of vitrification such as occur in certain polymers).

However, a study of the thermal properties of the glass plastic after repeated cooling gives a completely different picture. The results of an analysis of the coefficients λ, a, and c along and across the fiber of AG-4S material after five and ten times cooling are presented in Table 2.

A single cooling involved cooling the sample of test material in liquid nitrogen and then heating in a muffle furnace to 380°K.

By way of example Fig.2 gives a set of curves representing the temperature dependence of the thermal conductivity of AG-4S (thermal flux along the filaments) after one, five, and ten coolings.

We see from Fig.2 that after repeated cooling the thermal conductivity of the material changes considerably, and even its character alters. Whereas after a single cooling the thermal conductivity increased monotonically, after a five-fold cooling it increases up to a temperature of the order of 200°K and then falls; on further increasing the multiplicity of the cooling to ten times the thermal conductivity falls in absolute value but the general character of its temperature dependence is a rising one.

As a result of the repeated effects of low temperatures the glass plastic evidently changes its thermal (and hence also mechanical) properties.

It is reasonable to assume that the filling polymer (existing in the form of a thin film between the glass fibers) ruptures. It was indeed indicated in [4] that the stresses arising in resins of various compositions during their hardening on glass films were very considerable.

On increasing the rate of hardening of the resin, the stresses in the film increase, reaching 60-70 kgf/cm² for phenol-formaldehyde resin after 1.5 h at 160°C, 5-7 kgf/cm² for epoxy resin, and 100 kgf/cm² for organosilicon resin at 200°C [4]. On subsequent cooling of the hardened resin film, the stresses increase very sharply as a result of the difference in the thermal-expansion coefficients of the glass and resin. The total stresses reach 300-320 and 140-150 kgf/cm² for phenol-formaldehyde and epoxy resins respectively. This high stress intensity of the resin films is evidently one of the chief reasons for the reduction in the strength of the glass plastics for which they form the base.

The main reason for the stresses which arise in the resin film in the course of cooling is the difference between the expansion coefficients of the glass and resin. This difference is so great that an increase in the thermal expansion coefficient of the glass film by a factor of 2 ($42.7 \cdot 10^{-5}$ to 90.10^{-5} deg^{-1})

TABLE 2. Thermophysical Properties of AG-4S Material after Repeated Cooling

T, °K	5-fold cooling			10-fold cooling		
	λ, W/m·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
Along the filaments						
10	0,182	21,3	0,050	0,194	28,5	0,041
30	0,236	14,75	0,093	0,213	13,6	0,094
50	0,302	12,15	0,145	0,248	5,60	0,267
70	0,370	10,40	0,207	0,280	4,60	0,368
90	0,428	9,15	0,272	0,309	4,20	0,441
110	0,523	8,15	0,373	0,331	3,95	0,502
130	0,572	7,30	0,457	0,350	3,75	0,560
150	0,604	6,50	0,544	0,362	3,43	0,635
170	0,629	5,70	0,642	0,370	3,10	0,718
190	0,641	5,00	0,746	0,376	2,80	0,807
210	0,638	4,30	0,865	0,379	2,50	0,910
230	0,627	3,70	0,986	0,381	2,20	1,041
250	0,594	3,20	1,080	0,383	1,90	1,212
270	0,559	2,72	1,196	0,383	1,70	1,352
290	0,518	2,30	1,313	0,382	1,55	1,480
310	0,469	1,90	1,436	0,381	1,40	1,635
350	0,420	1,00	2,443	0,376	1,05	2,15
400	0,384	0,800	2,792	0,369	0,55	3,92
Across the filaments						
10	0,227	28,3	0,047	0,170	25,4	0,039
30	0,288	12,0	0,140	0,204	17,9	0,066
50	0,348	9,45	0,214	0,232	8,30	0,172
70	0,407	8,40	0,282	0,256	6,05	0,246
90	0,464	7,76	0,348	0,280	4,88	0,334
110	0,516	7,20	0,417	0,303	4,30	0,410
130	0,566	6,65	0.495	0,323	3,95	0,476
150	0,613	6,15	0,580	0,344	3,55	0,564
170	0,660	5,70	0,674	0,360	3,30	0,635
190	0,705	5,20	0,789	0,376	3,00	0,729
210	0,740	5,00	0,842	0,383	2,80	0,806
230	0,760	4,30	1,028	0,397	2,60	0,888
250	0,768	3,80	1,176	0,404	2,40	0,979
270	0,768	3,63	1,334	0,409	2,20	1,081
290	0,735	2,90	1,474	0,413	2,13	1,128
310	0,687	2,50	1,599	0,414	2,00	1,206
400	0,499	0,90	3,225	0,422	1,50	1,637

is not appreciably reflected in the magnitude of the stresses in the resin, since the difference in the thermal expansion coefficients of the resin and the glass film changes by only 0.6% in such cases [4]. In addition to this, the composition of the surface and the surface energy of the glass extend their influence to the interphase layer.

It is thus reasonable to assume that glass plastics such as AG-4S retain their properties after a single cooling (since as yet the elastic components of the internal stresses in the resin film have not been exhausted and the structure of the resin remains intact). After five coolings the internal stress of the resin film increases, and under the influence of the surface energy of the glass the interphase layer may change its structure (curve 2 after five times cooling in Fig. 2); the proportion of crystalline component of the resin increases, or the material may develop an oriented disposition of the chains of polymer molecules, which produces an increase in the thermal conductivity up to 200°K, while above this temperature the thermal conductivity of the material diminishes. Evidently after 200° the internal stresses exceed the strength of the filler film, microcracks appear, and the film breaks up into layers. With increasing temperature the porosity of the film increases, and this causes a corresponding reduction in thermal conductivity. This conclusion is also supported by the λ(T) curve after ten-fold cooling (Fig. 2). In view of the fact that the binder becomes porous and acquires a layered structure, the polymer does not now experience severe internal stresses; its thermal conductivity is considerably lower than the original value and changes very little with rising temperature. Clearly, further repeated cooling is unlikely to produce many more changes in the properties of the material.

NOTATION

λ, thermal conductivity, W/m·deg; a, thermal diffusivity, m²/sec; c, specific heat, J/kg·deg; q, specific thermal flux, W/m²; δ, plate thickness, m; ΔT, temperature drop °K; τ, time, sec; m, mass, kg; Q, thermal flux, W; T, temperature, °K.

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