## LINEAR-EXPANSION COEFFICIENTS OF GLASS-FIBER-REINFORCED PLASTICS BASED ON POLYMETHYLSILOXANE RESIN, UP TO 1000°C

B. A. Kiselev, I. V. Sobolev, V. S. Shpet, V. V. Mayakov, and G. A. Ivanov UDC 539.4:678.067.5

The authors give the results of an investigation of the linear-expansion coefficients of glassfiber-reinforced plastics based on polymethylsiloxane resin and various types of filler when heated to 1000°C.

When plastics, including glass-fiber-reinforced plastics (GFRP), are heated, their linear-expansion coefficients vary, and this exerts a marked influence on the physicomechanical properties and durabilities of this class of materials under various mechanical and thermal loads. Interest therefore attaches to the temperature dependence of the linear-expansion coefficients  $[\alpha = f(t)]$  of GFRP from the viewpoint of an understanding of the action of both the GFRP itself with its heterogeneous structure and also its separate components.

Opinions differ as regards the explanation of the influence of  $\alpha = f(t)$  of GFRP on their durabilities and strength properties. Zherdev [1] emphasizes that the strength of a nonmetallic composite when heated falls mainly owing to the large difference between the linear expansion coefficients of the polymer matrix and the glass reinforcing filler [2-4].

However, Tarnopol'skii and Kintsis [5] and Bartenev and Motorina [6], starting with the model suggested by Outwater [7], state that the difference between the linear-expansion coefficients of the resin and reinforcement in GFRP leads on heating to compression of the polymer matrix and tension in the reinforcement, i.e., the polymer matrix and reinforcement work together in such a way that the strength of the nonmetallic composition is to some extent increased.

We must evidently suppose that both treatments can be correct for certain types of GFRP, but each operates in a definite temperature range.

In this article we give some results of an investigation of the functional dependence of the linear-expansion coefficients between 0 and 1000°C for polymethylsiloxane resin with augmented cross-linkage frequency and for GFRP based on it, reinforced with various types of silica fillers differing in the structure of the reinforcing fibers.

We investigated specimens of GFRP with felted, knitted, and layered structures, and also GFRP with a three-dimensionallycross-linked reinforcement structure. These types of structure are listed in Table 1 and shown in Fig. 1.

The strength properties of these materials are listed in Table 1. The indices of the physicomechanical properties were determined by standard methods. To elucidate the influence of the thermal expansion of the resin itself on  $\alpha = f$  (t) of the compositions and on their behavior, and to determine the mutual relation between  $\alpha = f$  (t) of the resin and the strength of the compositions at high temperatures, we made a number of dilatometric and strength tests on these nonmetallic compositions.

All-Union Scientific-Research Institute of Aviation Materials, Moscow. Translated from Mekhanika Polimerov, No. 3, pp. 531-535, May-June, 1974. Original article submitted February 22, 1973.

© 1975 Plenum Publishing Corporation, 227 West 17th Street, New York, N.Y. 10011. No part of this publication may be reproduced, stored in a retrieval system, or transmitted, in any form or by any means, electronic, mechanical, photocopying, microfilming, recording or otherwise, without written permission of the publisher. A copy of this article is available from the publisher for \$15.00.

Property index, kg/mm <sup>2</sup>	Comp. based on polymethylsiloxane resin and reinforcement								
	KT-11		MKT		TSP		STAN		KN-11
	0°	90°	0°	90°	0°	90°	0°	90°	0°
$\sigma f1$ $\sigma f1$ $\sigma - f1$ E Structure of re- inforcement	14,0 13,6 4,45 1465 Fig. 1 layer		11,1 11,0 3,45 830 Fig. 1 mult layer	i	9,1 9,1 2,65 1790 Fig. 1c linke laye	6,6 7,75 2,1 780 c,cross- ed in rs	7,3 6,45 2,85 505 Fig. 1 knit	1,9 6,2 	4,5 11,2 9,05 Fig. 1e, felted

TABLE 1. Physicomechanical Characteristics of Compositions Based on Polymethylsiloxane Resin

<u>Note</u>. Angles of determining strength properties: 0°, along warp; 90°, along weft of reinforcement.

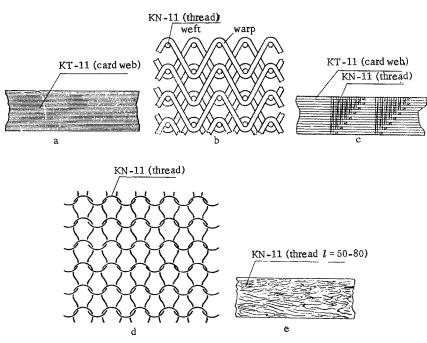


Fig. 1. Appearances of structures of GFRP based on silica fibers. a) KT-11; b) MKT; c) TSP; d) STAN; e) KN-11.

In these tests we studied the linear-expansion coefficient of various nonmetallic compositions when heated at 10 deg/min or 50 deg/min to 1000°C in inert gas or in air. We determined the influence of the type of reinforcement and of anisotropy of the properties of the GFRP on their thermal expansion and shrinkage. The temperature dependences of  $\alpha = f(t)$  of the materials were measured in a dilatometer ("LINZAIS" system) on specimens  $6 \times 6 \times 40$  or  $5 \times 5 \times 40$  mm in size.

To understand the functional dependence of the linear-expansion coefficient on temperature, we must first know how the resin itself behaves on heating.

Figure 2 shows the temperature dependence of the linear-expansion coefficient of polymethylsiloxane resin. We see that up to  $350^{\circ}$ C the resin undergoes rapid expansion, but on reaching  $350^{\circ}$ C the expansion decreases, reaching negative values at T=600-700°C. As remarked above in our reference to [2-4], the linear-expansion coefficient of the resins is an order of magnitude higher than the linear-expansion coefficients of the reinforcement and the GFRP themselves. This difference in the linear-expansion coefficients is reflected in the behavior of GFRP on heating.

The different arrangements of the silica threads in the polymer matrix largely determine the behavior of the GFRP on heating. Figure 3 plots the temperature dependences of the linear-expansion coefficients for the composites based on polymethylsiloxane resin. Comparing the graphs in Fig. 3, we see that the more mobile the reinforcement structure, the more closely does the behavior of the composite on heating correspond to the behavior of the resin itself.

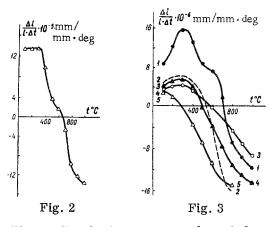


Fig. 2. Graph of  $\alpha$  vs t for polymethylsiloxane resin.

Fig. 3. Graphs of  $\alpha$  vs t for compositions based on KN-11 fiber. 1) Fibrous composite; 2) knitted filler STAN; 3) MKT fabric; 4) TSP fabric; 5) KT-11 fabric.

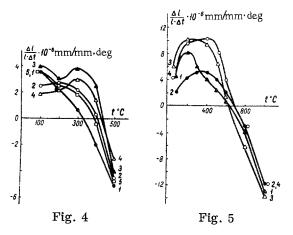


Fig. 4. Graphs of  $\alpha$  vs t for composite based on KT-11 fabric. 1) Along warp; 2) at 30°; 3) at 45°; 4) at 60°; 5) along weft.

Fig. 5. Graphs of  $\alpha$  vs t for composites based on MKT fabric (1, 2) and TSP fabric (3, 4). 1), 3) Along warp; 2), 4) along weft.

From our preliminary results from a comparison of  $\alpha = f(t)$  for the composite and the change in strength of the same composite on heating, we can find the correlation between these indices. A similar relation can be followed if we compare the anisotropy of  $\alpha = f(t)$  of the GFRP (Figs. 4 and 5). From the graphs in Fig. 4 we see that the composite behaves most like the resin in those directions in which the mechanical properties of GFRP based on KT-11 are weakest from the viewpoint of the anistropy, namely, in the directions at 30, 45, and 60° to the warp. But the behavior of composites based on MKT and TSP fabrics corresponds to the strength indices of these composites (see Table 1) in the direction of the warp and weft and reflects the conclusions drawn from the graphs in Figs. 3 and 5. In addition, the behavior of composites based on MKT fabric along the warp and weft (Fig. 5) is an additional confirmation of the conclusions of Tarnopol'skii et al. [8] who deduced the linearity of the reinforcing fibers increases the strength and reduces the deformability of the composites.

Composites based on polymethylsiloxane resin are very resistant to thermooxidative degradation and have practically equal thermal expansion and shrinkage whether heated in air or in an inert medium. The

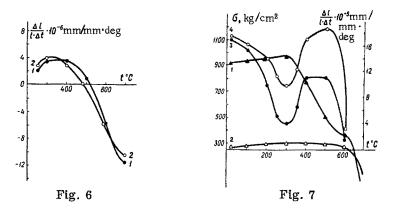


Fig. 6. Graphs of  $\alpha$  vs t for composites based on polymethylsiloxane resin. 1) In inert medium (helium); 2) in air.

Fig. 7. Graphs of  $\alpha$  vs t for resin (1) and composites based on MKT fabric (2), and graphs of strength under static flexure vs temperature for MKT in warp (3) and weft (4) directions.

graphs in Fig. 6 fit in well with the results of a number of thermophysical and strength tests on the thermooxidative degradation resistances of composites based on polymethylsiloxane resin [2, 3, 9].

The anisotropy of the thermal expansion of plastics, illustrated in Figs. 4 and 5, leads to a complex state of stress in the material at high temperatures, and this may be one cause of premature loss of strength in structures subjected to rapid heating. Note that composites reinforced by mobile structures (KN-11, STAN, MKT) suffer from cracking during heating to a lesser extent, indicating the possibility of redistribution of the stresses and hence of the thermal expansion and shrinkage phenomena in this type of structure.

It is interesting to compare the temperature dependence of the strength with  $\alpha = f$  (t) for composites based on polymethylsiloxane resin and multilayer MKT silica fabric. As we see from the combined graphs, which are plotted in Fig. 7, the maxima for  $\alpha = f(t)$  for the GFRP and the resin itself coincide with the minimum flexural strength for the GFRP; the subsequent rise and stabilization of the strength of the composite coincide with a region close in absolute values of  $\alpha = f$  (t) to the resin itself and the composite as a whole. We can explain this effect by means of the model suggested by Outwater [7]. Thus, taking into consideration the maximum difference in the thermal expansion of the resin and plastic at temperatures up to 350°C, we can suppose that the compsite at the given moment cannot act as a single whole. In this case the fall in strength, in our opinion, is due to the separate action of the resin and reinforcement, which largely corresponds to the hypotheses given by Zherdev and Korolev [1], and is also related to a certain rupture of the adhesive bonds between the resin and reinforcement due to the different thermal expansions of the resin and reinforcement. On further rise of temperature there is some increase and partial stabilization of the strength; this is apparently due to the appearance of frictional forces between the resin and reinforcement, because a zone of intensive shrinkage of the resin sets in and we get combined action of the polymer matrix and the reinforcement filler, i.e., this supports the hypothesis in [4, 5]. The subsequent fall in strength at 500°C is due to the onset of active degradation of the polymethylsiloxane resin [9] and the fall in strength of the actual silica filler. According to our preliminary results, there is a similar relation for certain other types of organosilicon resins in conjunction with the same types of reinforcement fillers.

## LITERATURE CITED

- 1. Yu. V. Zherdev and P. Ya. Korolev, Plast. Massy, No. 1 (1965).
- 2. B. A. Kiselev, Glass-Fiber-Reinforced Plastics [in Russian], Gosizdat (1961).
- 3. B. A. Kiselev et al., Plast. Massy, No. 2 (1967).
- 4. G. D. Andreevskaya, High-Strength Glass-Fiber-Reinforced Plastics [in Russian], Nauka, (1966).
- 5. Yu. M. Tarnopol'skii and T. Ya. Kintsis, Mekhan. Polimerov, No. 1, 100 (1965).
- 6. G. M. Bartenev and L. I. Motorina, Mekhan. Polimerov, No. 1, 89 (1965).
- 7. J. O. Outwater, Trans. ASME, Paper N 056-A-201 (1956).
- 8. Yu. M. Tarnopol'skii, G. G. Portnov, et al., "The influence of stretching and curling of the reinforcing fibers on the strength and deformability of glass-fiber-reinforced plastics," IMP Akad. Nauk LatvSSR, ONTI (1968).
- 9. K. A. Andrianov, Heat-Resistant Organosilicon Dielectrics [in Russian] (1964).