CALORIMETRIC STUDY OF THE MOLECULAR MOBILITY IN A FILLED PLASTICIZED EPOXIDE RESIN

V. P. Dushchenko and Yu. N. Krasnobokii

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Results are presented on the observed dependence of the thermophysical parameters C_p, λ, and a on temperature, filler content, and plasticizer concentration for ÉD-5 epoxide resin.

Filled polymers are now widely used, especially epoxide resins. There are many papers [1, 2] on the physicochemical and mechanical properties of such resins, most of which are experiments on particular compositions. To decide how to forecast optimal properties for filled materials for use under various thermal conditions, one needs to use concentration temperature relationships for thermophysical properties in order to elucidate the interactions between the polymer matrix and the filler.

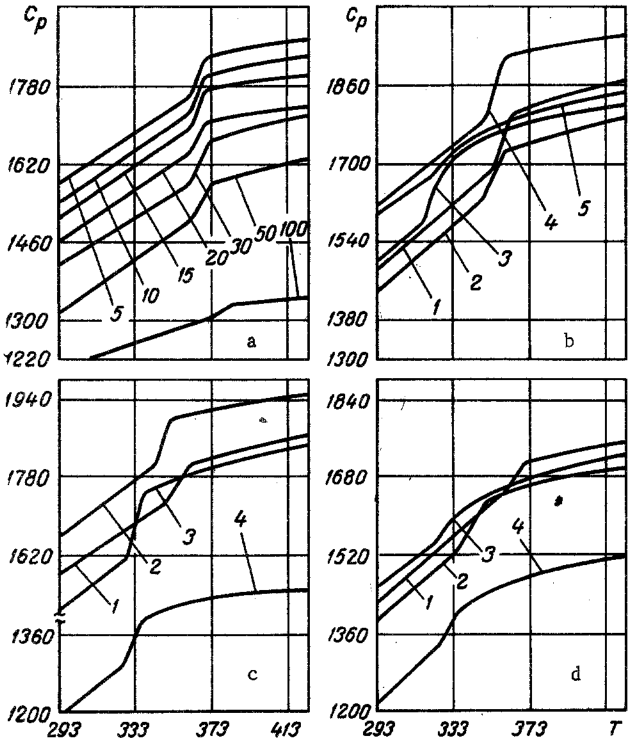

Fig.1. Temperature dependence of the specific heat C_p (J/kg·deg) of compositions – based on ÉD-5 (all proportions as parts by weight). a: 1) ÉD-5 + QS (numbers on curves are QS as weight parts of resin); b: 1) ÉD-5 alone, 2) ÉD-5 + 1 DBP, 3) ÉD-5 + 15 DBP, 4) ÉD-5 + 5 NUB-1; 5) ÉD-5 + 30 NUB-1; c: 1) ÉD-5 + 20 QS + 5 DBP, 2) ÉD-5 + 20 QS + 10 DBP, 3) ÉD-5 + 20 QS + 15 DBP, 4) ÉD-5 + 100 QS + 15 DBP; d: 1) ÉD-5 + 20 QS + 10 NUB-1, 2) ÉD-5 + 20 QS + 20 NVB-1, 3) ÉD-5 + 20 QS + 30 NVB-1, 4) ÉD-5 + 20 QS + 30 NVB-1.

We have examined the effects of a filler (quartz sand, QS) and two plasticizers (dibutylphthalate, BBP, and thiokol, NVB-1) as regards the thermophysical properties (C_p, λ, a) for ÉD-5 filled epoxide resin.

To determine $\lambda(T)$ and $a(T)$ we used the methods of [3], while for $C_p(T)$ we used the methods of [4]; the coefficient of variation in the results did not exceed 5%.

The carefully washed quartz sand was heat-treated and etched in hydrochloric acid to remove organic materials, and then was washed in distilled water until the reaction for chloride was negative. It was reduced to absolute dryness before incorporation into the resin, and the particles had d ≤ 50 μ. The resin and the two plasticizers were used as made by chemical manufacturers in the USSR and had characteristics in accordance with the State Standards and technical instructions. The hardener in every case was polyethylene polyamine (10 parts by weight of the resin).

Figure 1 shows* $C_p(T)$ for ED-5 resin filled with QS and plasticized with various amounts of the plasticizers and other such combinations.

Figure 1a shows that $C_p(T)$ increases with T in every case; C_p decreases as the proportion of

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*The curves of Figs. 1 and 2 are averages from 3-6 measurements.

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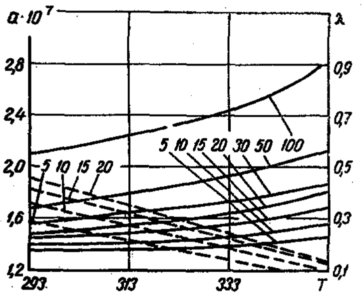

Fig.2

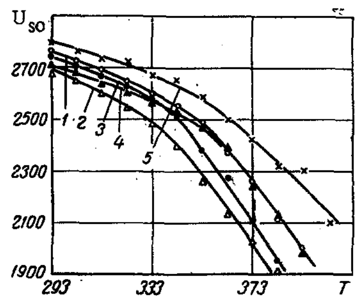

Fig.3

Fig.2. Temperature dependences of λ, W/m·deg (solid lines) and a, m^2/sec (broken lines) for ÉD-5 filled with QS. The numbers on the curves are the amounts of QS in parts by weight of the resin.

Fig.3. Temperature dependence of the speed of sound u_{so}, m/sec for ÉD-5 containing the following parts by weight: 1) ÉD-5 alone; 2) ÉD-5 + 10 DBP; 3) ÉD-5 + 10 NVB-1; 4) ÉD-5 + 10 QS; 5) ÉD-5 + 100 QS.

filler increases, and at the vitrification point T_v we get a discontinuity in the specific heat ΔC_p, whose magnitude decreases as the proportion of QS increases. Here T_v was determined as the mean temperature in the range where the specific heat discontinuity occurs [5], and this tended to shift towards higher temperatures as the proportion of filler increased. We have observed [6] similar changes in properties for other filled amorphous polymers.

It is clear that the solid particles influence particularly the cross-linking processes, i.e., the density and uniformity of the spatial linking in the polymer; the rise in T_v and fall in C_p may be related either to the increased density in the bond network or to binding of some part of the macromolecules to the surface of the filler.

Sorption [7] and gas diffusion [8] show that the molecule packing density in the filled case is less than in unfilled specimens, which is due [9] to reduction in the configuration entropy of the polymer as a result of the restrictions imposed by the solid surface. A study can be made [10] of the sorption of water vapor by filled and unfilled epoxide resins. The thermodynamic functions of such systems indicate that there are regions of local ordering in the polymer near the surface of the filler; these ordered regions and mode of production of them have been examined [11], and electron micrographs on epoxide coatings show [11] that the resin around the particles produces ordered structures of globular type, whose dimensions are dependent on the amount of filler in the system. We can take it therefore as demonstrated that the polymer interacts at the filler at the supermolecular level, which agrees with the generally accepted view on the interaction of polymers with fillers [9].

The specific heat is determined by all forms of molecular mobility for all macromolecules, so the fall in C_p at high filler contents is due to the increased number of supermolecular formations related to the solid surface and to loss in macromolecular mobility. This is as regards C_p; the rise in T_v is due to slower relaxation in the filled systems as a result of restricted mobility of the macromolecules near the interfaces [9]. This is confirmed by the opposite behavior of the $C_p(T)$ curves for systems in which the molecular interaction has been weakened by plasticizer (Fig.1b), which reduces the molecular interaction in the epoxide resin and tends to mobilize the structural elements, which in general increases C_p and reduces T_v [9, 12]. Figures 1c and d show $C_p(T)$ as representing competition between the plasticizer and the filler as regards the macromolecular mobility; a small proportion of filler (20 parts by weight) was used with various amounts of plasticizer, and the effects were much as for the pure unfilled polymer, and only large amounts of filler produced a substantial reduction in C_p (curves 4 in Figs.1c and d), i.e., the properties of the filled plasticized materials for small proportions of filler are determined in the main by the amount of plasticizer. There is no appreciable increase in T_v for DBP contents above 15-20 parts by weight, or NVB-1 above 30; this again confirms that the vitrification temperature is dependent not on the thermodynamic flexibility of the chains but on the kinetic flexibility, which is dependent on the molecular interactions and is governed by the concentrations of polar functional groups and the strengths of the bonds between them. In our case, high plasticizer concentrations very greatly weaken the three-dimensional network of bonds in the resin and so weaken the molecular interaction, the result being that increase in filler concentration does not raise T_v. There are some differences in the disposition of the $C_p(T)$ curves for the plasticized system (Fig. 1b) on account of the different types of plastification produced by BBP and NVB-1; the first is an external plasticizer for epoxide resins, while the second is a structural one [2, 12].

Figure 2 shows the observed λ(T) and a(T) for ÉD-5 + QS. We have previously [13] reported the temperature dependence of λ and a for unfilled ÉD-5, which was linear over the range 293-353°K. We also found slowly rising curves for λ(T) when QS was added, but the curves were not quite straight. Debye gives

$$\lambda = 1/3\ \rho C_p\ u_{so} \bar{l}.$$

The λ(T) curves are influenced by ρ(T), $C_p(T)$, $u_{so}(T)$, $\bar{l}(T)$ ($\bar{l}$ and ρ decrease as T rises for amorphous polymers). We measured u_{so} as a function of T by a pulse method [14] at 0.98 MHz (Fig. 3), and the temperature coefficient was negative for all compositions. Also, u_{so} falls in the highly elastic region, which indicates change in the elastic properties. Then only C_p in (1) increases with T (Fig. 1), while all the other quantities decrease, which explains the small positive derivative for λ(T).

Also, λ increases with the QS content, though the effect is small at low contents, because in that case the heat transfer occurs solely via the polymer matrix, while supermolecular structures at the particle surfaces increase the size of the defects and facilitate scattering of the heat flux, which reduces the effect of the filler on the heat transfer. QS contents above 50 parts by weight cause a considerable rise in λ on account of heat conduction by the filler.

The trends in a(T) follow from the relationship $a = \lambda/C_p$ and are determined by the temperature dependence of the quantities in this formula; increase in the concentration of QS results in an increase in a (broken lines in Fig. 2).

Plasticizers increase λ and a for the filled system; this is ascribed to reduction in the contact resistance at the interfaces, and also to reduction in the dispersal of the heat flux by the structural elements in the polymer, which are surrounded by plasticizer.

These results show that one has to allow for the properties in the solid particles in examining such thermophysical properties for filled polymers.

NOTATION

C_p	is the specific heat capacity at constant pressure;
λ	is the thermal conductivity;
a	is the thermal diffusivity;
ΔC_p	is the specific heat discontinuity;
T_v	is the vitrification point;
ρ	is the density;
u_{so}	is the velocity of sound;
l	is the phonon mean free path;
f	is the frequency.

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