

INFLUENCE OF FILLERS UPON THE THERMODYNAMIC
PROPERTIES OF GLASS-LIKE
POLYMETHYLMETHACRYLATE

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The article presents results relating to the influence of dispersed fillers upon the thermodynamic properties of glass-like polymethylmethacrylate.

The properties of polymers depend upon the presence of long, flexible macromolecules which form various supermolecular structures [1]. The flexibility of macrochains, the intermolecular interaction, and the ability to form ordered structures depend upon the chemical structure of the polymer [1, 2].

The heat transfer in polymer bodies depends presumably upon macromolecules which, due to the presence of chemical bonds parallel to the chains, are peculiar "thermal waveguides." Since the orientation of the macromolecule segments in space does not depend upon the position of neighboring sections, the individual sections of the waveguides, i. e., the so-called elementary waveguides, can have different orientations with respect to the direction of the heat flux (parallel, perpendicular, or at a certain angle relative to the heat flux).

The dimensions of the elementary waveguides cannot exceed the size of the segments and depend directly upon the flexibility of the macromolecules. A decrease in flexibility corresponds to an increase in the dimensions of the elementary waveguides.

In view of what has been said above, the heat transfer in polymers can be considered a consequence of two independent processes: a) exchange of energy between the atoms of the principal chain of macromolecules which are connected with chemical forces, and b) exchange of energy between the atoms or groups of atoms which do not form a part of the principal chain (lateral groups and branches of the same type of macromolecules), and energy exchange between neighboring macromolecules.

When a segment or its parts corresponding to elementary wave guides are oriented parallel to the direction of heat flux, the major part of the heat is transferred through the atoms of the principal chain. In the second limit case, in which the elementary waveguide and the heat flux are perpendicular, the corresponding portions of a segment are situated on a single isothermal surface, and the heat is transferred only via the intermolecular contacts. Thermal scattering occurs when intermediate orientations are assumed by the segments or parts thereof.

Lateral groups or end groups of macromolecules which are distributed at random in space contribute to the scattering of the thermal flux. The degree to which these groups participate in the general thermal conductivity depends upon the mobility of the groups and the interaction between the groups.

The heat transfer via the atoms of the principal chain is most effective. An increase in the size of the waveguides must therefore imply an increase in the thermal conductivity of the polymer.

Fillers are an effective means of modifying the structure and the properties of polymer materials. It is well known that introduction of a filler in a polymer can greatly influence the state of individual polymer

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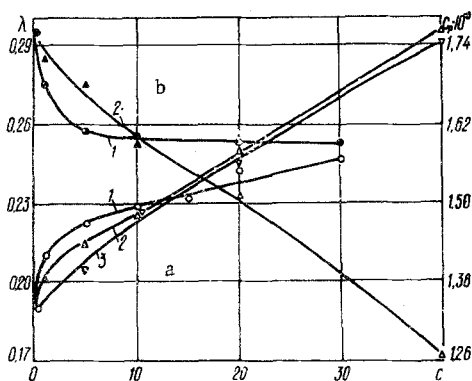


Fig. 1

Fig. 1. Dependence of the coefficient of heat conductivity λ , W/m · deg, (a) and dependence of the specific heat capacity c_p , J/kg · deg, (b) upon the concentration c of the filler, wt. % at 60°C, polymethylmethacrylate with: 1) kaolin; 2) quartz powder ($d < 50 \mu$); 3) quartz powder ($100 < d < 160 \mu$).

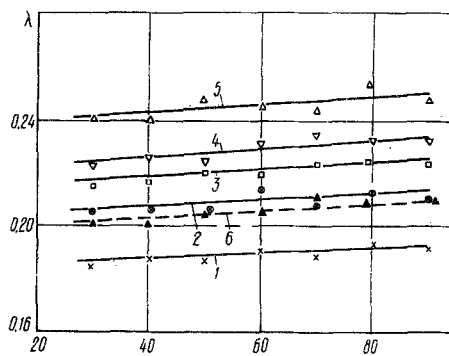


Fig. 2

Fig. 2. Dependence of the coefficient of heat conductivity λ , W/m · deg, upon the temperature t °C, of polymethylmethacrylate with various kaolin concentrations: 1) 0%; 2) 1%; 3) 5%; 4) 10%; 5) 30%; 6) 10% kaolin + GKZh-94.

chains and the entire polymer binding. A filler can have an orienting effect upon polymer chains and may modify the mobility of the chains [3, 4]. In systems containing a polymer capable of coating motions of structural elements, extended structures which are oriented by the surface of the filler developed. The flexibility of the macromolecules is then smaller than that of the initial polymer [5]. Apart from this, zones of reduced packing density of the polymer macromolecules can develop around the filler particles [6].

Accordingly, fillers must modify the heat transfer process and influence the thermodynamic characteristics of a polymer.

The incorporation of fillers complicates the heat transfer in polymers. As far as the classification of heterogeneous systems is concerned, polymers with fillers can be considered matrix systems in which solid particles are distributed in a continuous polymer matrix.

The heat conductivity of systems of this kind depends upon the heat conductivities of the polymer and the filler and upon the thermal contact resistance at the boundary between a polymer particle and a filler particle. The thermal conductivity of the medium is not necessarily identical with the thermal conductivity of the pure polymer, because the filler may induce substantial structural conversions in the polymer.

The influence of the thermal conductivity of individual components and of the thermal contact resistance upon the heat transfer in polymers with fillers is given by the form of the interaction of the components, the size of the filler particles, and the extent of filling.

In order to clarify these problems, we consider the concentration dependence and the temperature dependence of the coefficient of thermal conduction (λ), the coefficient of thermal diffusivity (a), and the coefficient of the specific heat capacity (c_p) of systems with fillers on the basis of L-3 polymethylmethacrylate and several other disperse fillers.

Polymethylmethacrylate is a typical representative of linear, amorphous polar polymers with strong intermolecular interaction facilitating the cooperating motion of structural elements [5].

The polymethylmethacrylate was purified by reprecipitation from a 4% solution in benzene by means of methanol, in order to remove admixtures of low molecular weight.

Prosyanyaya kaolin enriched by elutriation with nonisometric 1-4 μ particles, and two fractions of quartz powder ($d < 50 \mu$ and $100 < d < 160 \mu$) with almost spherical particles were used as filler materials.

These mineral fillers can form hydrogen bonds with polymethylmethacrylate, because -OH groups are present on the surface of the fillers [8].

This choice of fillers made it possible to determine the influence of the thermodynamic properties of the fillers, their degree of dispersion, and their interaction with the polymer upon the thermodynamic properties of the composition with the filler. Moreover, the mineral fillers reduced the cost of the polymer product and, at the same time, can improve the main physical and chemical properties of the polymer.

The components were combined by gradual addition of polymer to the filler, while a long-lasting mixing was executed at the same time in order to obtain uniform distribution. At a temperature exceeding the flow point by 15–20°C, samples were pressed from the mixture; the samples were thereafter slowly cooled under pressure application.

The polymethylmethacrylate samples with various filler concentrations had the following densities: pure polymethylmethacrylate 1195 kg/m³; polymethylmethacrylate + kaolin (1% 1200 kg/m³, 5% 1230 kg/m³, 10% 1262 kg/m³, 20% 1338 kg/m³, 30% 1390 kg/m³); polymethylmethacrylate + quartz powder, $d < 50 \mu$ (1% 1193 kg/m³, 5% 1206 kg/m³, 10% 1256 kg/m³, 40% 1567 kg/m³); polymethylmethacrylate + quartz powder, $100 < d < 160 \mu$ (5% 1206 kg/m³, 10% 1241 kg/m³, 20% 1286 kg/m³, 40% 1466 kg/m³). The density was determined at 25°C by hydrostatic weighing.

The coefficients λ and α were determined with an accuracy of 5–6% by the technique of dynamic α - and λ -calorimeters [9]. The quantity c_p was determined with an accuracy of 2.5% by thermal analysis according to [10].

An analysis of the resulting concentration and temperature dependences of λ , which are shown in Figs. 1 and 2, leads to the conclusion that within the interval of filler concentrations considered, the heat conductivity of systems with fillers depends mainly upon the polymer matrix the state of which is affected by the introduction of fillers.

It follows from Fig. 1 that incorporation of kaolin up to 5% by weight leads to a sharp increase in λ . The specific heat decreases sharply (Fig. 1).

We made special experiments to determine in this concentration interval the increase in the velocity of ultrasound, the increase in the vitrification temperature, and the microhardness of the material.

The results prove that the interaction between the polymer and the filler via hydrogen bonds reduces sharply the flexibility of the macromolecules, which can modify the lengths of the elementary waveguides. Moreover, changes in the polymer are possible on the supermolecular level, when a solid surface acts upon systems of this kind [5].

It seems that these changes in the polymer are responsible for the increase in λ at small filler concentrations. In this case, almost the entire heat is transferred via the polymer matrix. The heat conductivity of the filler can be ignored because the amount of filler present is very small. Zones with reduced packing density, which developed from the strong binding of the polymethylmethacrylate to the kaolin around filler particles, reduce the thermal contact of the components and, hence, reduce the contribution of the filler to the total heat conductivity.

The relative increase in λ is reduced when the filler concentration becomes greater than 5%, because the volume of the polymer matrix within the total volume of the system decreases. Though the value of λ for the filler is an order of magnitude greater than λ for the polymer, the filler contributes but insignificantly to the heat transfer, because the thermal resistance at the points of contact is high. Moreover, the large number of loose zones scatters the thermal flux.

We must bear in mind that the bonds which develop between the polymer and the filler particles are obviously peculiar thermal bridges which improve the heat conductivity at the point of contact. The bridges cause an increase in λ when the filler concentrations exceed 10%.

Loosening the microstructure of the polymer in the layers near the surface has also an influence upon the concentration dependence of c_p .

Quartz powder has a greater particle size and a smaller interaction with polymethylmethacrylate than kaolin. Incorporation of the quartz powder into polymethylmethacrylate changes, to some extent, the concentration dependence of λ . In addition, the ratio of the contributions of the components and the thermal contact resistance to the total heat conductivity changes.

Since the interaction and the total surface of the filler are small, the polymer undergoes less extensive structural conversions in systems containing quartz powder. This conclusion is confirmed by the fact

that the increase in the vitrification temperature of these systems is two times smaller than in the corresponding compositions containing kaolin. Accordingly, the conductivity of the polymer matrix decreases. The importance of the heat conductivity of the filler increases relative to that of systems containing kaolin. This behavior is explained by the reduced contact resistance, which is directly related to changes in the extent of the interaction between the components of the system.

In view of what has been said above, the thermodynamic properties of systems containing small concentrations of quartz powder used as a filler change to a lesser extent, or, at high filler concentrations, change to a greater extent than those of the corresponding compositions with kaolin (Fig. 1).

The role which the interaction between the polymer and the filler surface plays for the thermodynamic properties is further corroborated by research on the thermodynamic properties of polymethylmethacrylate filled with kaolin the particle surface of which had been treated with the hydrophobizing silicone liquid GKZh-94. The organic radicals partially shield the -OH groups of the filler surface, which reduces the interaction energy of the components along the interface [11]. Accordingly, it was observed that modification of kaolin by GKZh-94 liquid results in higher c_p values and a much smaller ultrasound velocity than in corresponding systems with natural kaolin, the filler concentrations being equal. This means that the binding of the polymer by the filler is reduced and that all above factors capable of increasing λ in the particular range of filler concentrations have become less important. As a result, the λ values are reduced.

At increasing temperatures, the λ values of the polymer and of the compositions with fillers increase proportionally to c_p (Fig. 2), which agrees with Debye's phonon theory of heat conduction. When heated, c_p increases to a greater extent than the velocity of sound. The density of the polymer and the free path length of the phonons remain almost constant.

The changes in the coefficient of thermal diffusivity are directly related to the changes in λ , c_p , and the density of the compositions.

NOTATION

- λ is the coefficient of heat conductivity;
 a is the coefficient of thermal diffusivity;
 c_p is the specific heat;
 d is the particle size.

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