UNIVERSAL RELATION FOR THE THERMAL CONDUCTIVITY OF AMORPHOUS POLYMERS

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An invariant relation is derived for the thermal conductivity of amorphous polymers above the vitrification temperature.

Even though a huge quantity of experimental data has been accumulated on the thermal conductivity of polymer materials [1, 2, 4, 5], no attempt was made yet to generalize them in order to establish some universal relation.

It has been shown in those references, for instance, that variations in thermal conductivity can explain several structural phenomena occurring in polymers. In this article the author's aim was different, namely, to derive a universal relation for the thermal conductivity λ of polymers above the vitrification temperature T_V.

For this purpose, the thermal conductivity must be expressed as a function of a quantity whose variation is effected by the same structural properties of the substance as the variation of λ.

It is well known that the thermal conductivity of polymers depends on the forces of intramolecular and intermolecular interaction, on the thermal kinetics, on the flexibility of molecular chains, and on the rigidity of their individual links [3-5]. The parameter whose variation is governed by the same structural properties appears to be the free volume [6, 7]. It is logical that such a universal relation be established for substances in the ultraelastic state, although it may evidently be possible later to extend it to plastic polymers as well. The transition of polymers from the vitreous state to the ultraelastic state occurs at the vitrification temperature. This process is associated with significant changes within the substance. One very important fact is to be noted here. The same fraction of free volume, namely 0.025 ± 0.003, corresponds to different vitrification temperatures of many polymers [6]. A change in this fraction at a temperature above the vitrification point is effected according to the following relation:

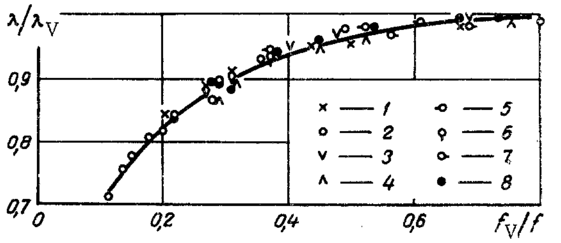

Fig. 1. Dimensionless thermal conductivity as a function of the free volume fraction: 1) for natural rubber [1]; 2) for silicone rubber [1]; 3) for polystyrene [2]; 4) for polymethylmethacrylate [2, 5]; 5) for polyvinyl chloride with 20% plasticizer [1]; 6) for ataxic polypropylene [4]; 7) for amorphous polyethylene [4]; 8) for polyvinyl chloride with 40% plasticizer [1].

$$f = f_V + \alpha (T - T_V). \tag{1}$$

Since the values of λ and f depend on the same structural properties, it is reasonable to assume that the sought function should be of the type

$$\lambda = \varphi (f). \tag{2}$$

The use of relation (2) for evaluating the test data would yield a set of curves for various materials. In order to construct a universal curve, it is necessary to represent it in terms of dimensionless coordinates. As the characteristic scale dimensions we choose those at the vitrification point. Then, if the preceding statements are correct, the entire set of curves for various materials should merge into a single curve, i.e., the relation

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$$\frac{\lambda}{\lambda_V} = \varphi_1\left(\frac{f_V}{f}\right) \tag{3}$$

should be invariant within the entire class of amorphous materials at temperatures $T > T_V$.

The temperature does not appear in Eq. (3) explicitly, but the fraction of free volume is a function of the temperature here.

The test data in [1, 2, 4, 5] were evaluated in terms of Eq. (3) for polymers with flexible chains (silicones, natural rubber) and for polymers with rigid chains (polyvinyl chloride, polystyrene, polymethylmethacrylate). The test points are shown in Fig. 1. It is evident here that all the test data for these particular polymers fit onto the same curve. Thus, an invariant relation has been obtained for these materials. The outstanding features of this result are obvious, since it becomes possible now, with the aid of the universal curve, to find λ at any temperature above T_V. For this purpose one needs to determine λ at one point only (e.g., at room temperature).

NOTATION

λ_V, λ	are the thermal conductivities of a substance at the vitrification temperature and above it, respectively;
f_V, f	are the fractions of the free volume at the vitrification temperature and above it, respectively;
T, T_V	are the temperature coordinate and vitrification temperatures, respectively;
α	is the thermal expansivity of a substance above T_V.

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