TEMPERATURE-DEPENDENCE OF THE THERMAL CONDUCTIVITY OF POLYMERS

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A method is proposed for the generalization of test data pertaining to the thermal conductivity of polymers.

All the test data accumulated so far pertaining to the thermal conductivity of polymers reveal certain general trends. The generalization of test results for low-molecular substances is usually based on the principle of corresponding states (with the critical-point parameters as the reference scale), but a critical point is never reached in the case of high-molecular compounds and, therefore, this basis of evaluation is not applicable here. Using the triple point is also not feasible, for the same reason.

The search for a characteristic point suitable as a reference has led to the glass transition temperature. This choice is by no means ideal. There is another characteristic transition, brittleness, but that offers no particular advantages over glass transition. The temperature at which brittleness occurs depends, just as T_g, on the rate at which it is approached and it lies within some interval rather than at a definite point. On the other hand, the glass transition temperature offers some advantages. At that point all amorphous polymers have the same fraction of free volume [1] and, as will be shown here, approximately the same activation entropy. Furthermore, the glass transition temperature is uniquely related to the cohesion energy per unit length of molecular link [2]. The relation between these two quantities is shown in Fig. 1 as a curve, supplemented with new data. Evidently, the correlation between both quantities is close. All this gives the glass transition point a definite physical meaning and makes it an appropriate choice as a reference scale.

For the purpose of devising a generalized method of data evaluation, the entire temperature range is divided into two. This conforms strictly to the different modes of heat transmission: through a rigid structure at $T < T_g$ [3] and by slippage of parts or an entire macromolecule at $T > T_g$.

In view of this, the universal expressions must be different for both ranges. The subsequent discussion will be concerned with each range separately. Of course, both ranges meet at the T_g point.

Let us first consider the range $T < T_g$. In this range a substance is characterized by a fixed spatial configuration of the macromolecule and by a suppression of thermally induced flow [4].

It will be assumed that the heat transmission is described by equations of the kinetic theory of fluids [5]. As in the case of other transfer coefficients, we can write

$$\lambda = \lambda_0 \exp\left(-\frac{\Delta F}{RT}\right). \tag{1}$$

In the $T < T_g$ range ΔF is assumed to be a weak function of the temperature. This is confirmed in Fig. 2, where $\log\lambda$ has been plotted versus the reciprocal of the temperature and the line is straight for each case. In order to make the evaluation more convenient, we eliminate λ_0 from Eq. (1). In dimensionless form, the sought function becomes

$$\frac{\lambda}{\lambda_g} = \exp\left[-\frac{\Delta F}{RT_g}\left(\frac{T_g}{T} - 1\right)\right] \tag{2}$$

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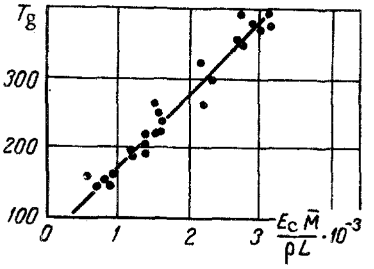

Fig. 1

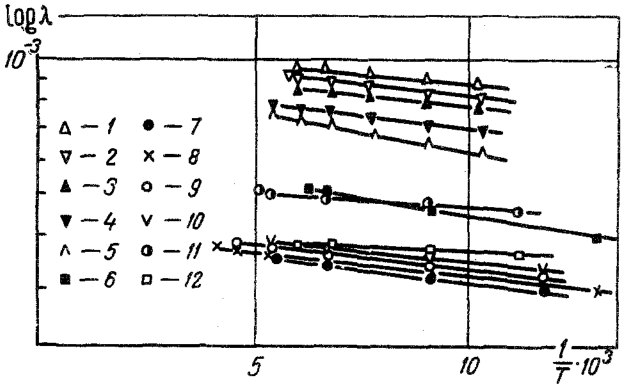

Fig. 2

Fig. 1. Glass transition temperature T_g (°K) as a function of the cohesion energy per unit length of molecular link.

Fig. 2. Curves of log λ versus the reciprocal of the temperature, for: 1) high-pressure polyethylene irradiated with 0 MR; 2) 100 MR; 3) 300 MR; 4) 600 MR; 5) 1000 MR; 6) silicon rubber and polyvinyl chloride irradiated with 10 MR; 7) 20 MR; 8) 40 MR; 9) Vulcalan; 10) natural rubber; 11) 0 MR; 12) 100 MR.

or

$$\frac{\lambda}{\lambda_g} = f\left(\frac{T_g}{T}\right). \tag{2a}$$

The results of evaluation in terms of Eq. (2a) are shown in Fig. 3. As is evident here, the test data from [6-16] for about 30 amorphous polymers are described by a single curve with a spread not beyond the limits of experimental inaccuracy.

Expression (2) is helpful for further studies concerning the characteristics of the glass transition point. Considering that

$$\Delta F = \Delta U - T\Delta S$$

and assuming that $\Delta U = \text{const}$ at $T < T_g$ (ΔS is rigidly fixed [17]), one can determine the value of ΔU_g at T_g. The activation entropy at T_g must be numerically equal to $\Delta U_g/T_g$. Then ΔU_g is found from the slope of the $\log\lambda = \varphi(1/T)$ lines.

Calculated values of $\Delta U_g/T_g$ are given in Table 1. It appears here that $\Delta U_g/T_g$ is approximately the same for all amorphous polymers, except rubbers, and equal to 0.25 ± 0.05. As has been said earlier, they all have the same fraction of free volume equal to 0.025 ± 0.003 at the glass transition temperature [1].

At temperature $T > T_g$ there occurs spatial slippage in a macromolecule, with more of thermally induced motion as a result and with a greater role of entropy effects, so that Eqs. (2) and (2a) are unsuitable now for generalization without the temperature-dependence and the entropy-dependence of ΔF taken into account.

According to [17], at $T > T_g$ the activation energy is an exponential function of the temperature. In the expression for ΔF, however, there appears not only ΔU but also ΔS. In order to determine the form of the ΔF function, therefore, one must know how ΔU as well as ΔS vary. For ΔU one could use the expression proposed in [17], but even then ΔS will remain unknown. The qualitative trend of the thermal conductivity λ in the $T > T_g$ range can be analyzed on the basis of Eq. (2). Indeed, as long as ΔU and ΔS remain constant, T/T_g will be the argument of the sought dimensionless parameter. Only after the temperature has risen above T_g, will λ be determined not so much by the change in temperature as by the changes in ΔU and ΔS. Considering that with rising temperature these quantities may vary at different rates, we can analyze the λ(T) relation by examining the exponent in (2).

Let us rewrite Eq. (2) as follows:

$$\frac{\lambda}{\lambda_g} = \exp\left[-\frac{\Delta U_g}{RT_g}\left(\frac{\Delta U}{\Delta U_g} \cdot \frac{T_g}{T} - 1\right)\right] \exp\left[\frac{\Delta S_g}{R}\left(\frac{\Delta S}{\Delta S_g} - 1\right)\right] \tag{3}$$

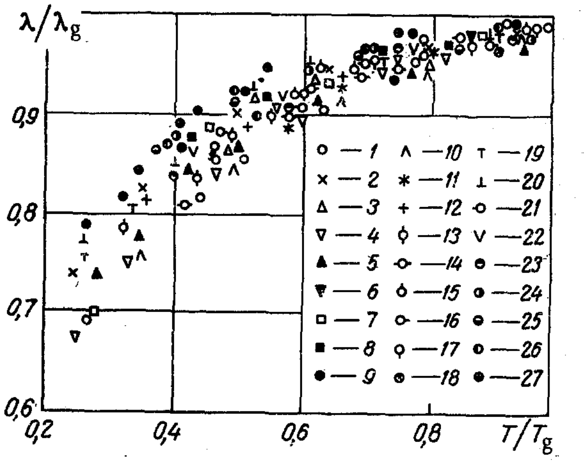

Fig. 3

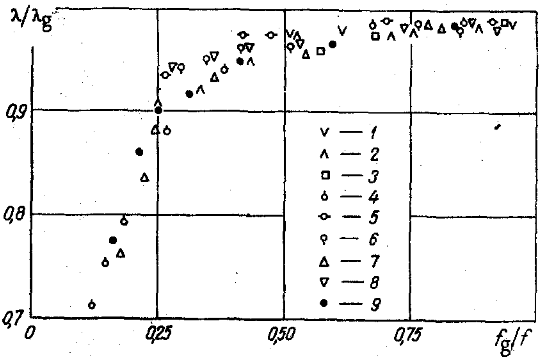

Fig. 4

Fig. 3. Relation $\lambda/\lambda_g = f(T/T_g)$ for: 1) polychlorotrifluoroethylene; 2) polymethylmethacrylate; 3) Vulcalan; 4) natural rubber; 5) polyvinyl chloride with plasticizer 0%; 6) 10%; 7) 20%; 8) 40%; 9) polyethylene terephthalate; 10) silicon rubber; 11) high-pressure polyethylene irradiated with 0 MR; 12) 100 MR; 13) 300 MR; 14) 600 MR; 15) 1000 MR; 16) polymethylmethacrylate copolymer with acrylonitrile 1%; 17) 2%; 18) 3.5%; 19) polymethylmethacrylate linked to triallyl cyanate 1 and 5%; 20) 7%; 21) 10%; 22) nylon 6 pN; 23) 6 pw; 24) 6.6 pw; 25) 6.1 pN; 26) 6.1 pw; 27) 6.6 pN.

Fig. 4. Relation $\lambda/\lambda_g = \varphi(f_g/f)$ for: 1) polyvinyl chloride with plasticizer 10%; 2) 20%; 3) 40%; 4) natural rubber; 5) polymethylmethacrylate; 6) polystyrene; 7) atactic polypropylene; 8) polyethylene; 9) silicon rubber.

then differentiate the right-hand and the left-hand side with respect to T:

$$\frac{d\left(\frac{\lambda}{\lambda_g}\right)}{dT} = \frac{\lambda}{\lambda_g}\cdot\frac{d}{dT}\left[-\frac{\Delta U_g}{RT_g}\left(\frac{\Delta U}{\Delta U_g}\cdot\frac{T_g}{T}-1\right)+\frac{\Delta S_g}{R}\left(\frac{\Delta S}{\Delta S_g}-1\right)\right]$$

or

$$\frac{d\ln\left(\frac{\lambda}{\lambda_g}\right)}{dT} = \frac{d}{dT}\left[-\frac{\Delta U_g}{RT_g}\left(\frac{\Delta U}{\Delta U_g}\cdot\frac{T_g}{T}-1\right)+\frac{\Delta S_g}{R}\left(\frac{\Delta S}{\Delta S_g}-1\right)\right]. \tag{3a}$$

A closer examination will show that the temperature characteristic of the thermal conductivity depends, in the case of amorphous polymers above T_g, on the sign of the right-hand side in Eq. (3a). This sign, in turn, depends on the absolute values of the slopes of the first and the second term. Under these circumstances, there are possible three different variants of the λ(T) relation above T_g:

a) the right-hand side of Eq. (3a) is equal to zero

$$\frac{d}{dT}\left|-\frac{\Delta U_g}{RT_g}\left(\frac{\Delta U}{\Delta U_g}\cdot\frac{T_g}{T}-1\right)\right| = \frac{d}{dT}\left|\frac{\Delta S_g}{R}\left(\frac{\Delta S}{\Delta S_g}-1\right)\right|$$

so that $\frac{d\ln\left(\frac{\lambda}{\lambda_g}\right)}{dT} = 0$ and λ = const;

b) the right-hand side of Eq. (3a) is positive

$$\frac{d}{dT}\left|-\frac{\Delta U_g}{RT_g}\left(\frac{\Delta U}{\Delta U_g}\cdot\frac{T_g}{T}-1\right)\right| < \frac{d}{dT}\left|\frac{\Delta S_g}{R}\left(\frac{\Delta S}{\Delta S_g}-1\right)\right|,$$

then $\frac{d\ln\left(\frac{\lambda}{\lambda_g}\right)}{dT} > 0$ and λ increases;

TABLE 1. Calculated Values of Activation Energy and Entropy

Substance	Activation energy, cal/mole	Glass transition temperature, T_g, °K	$\Delta U_g/T_g$, cal/mole · °K
Polymethylmethacrylate + triallyl cyanate			
0%	86,0	351	0,244
1%	105	373	0,282
2%	117	405	0 289
3,5%	129	443	0,293
High-pressure polyethylene with MR (megaroentgens)			
0	39,0	193	0,202
100	53,0	193	0,254
300	47	203	0,232
600	57,4	223	0,257
1000	65,0	256	0,254
Methylmethacrylate + acrylonitrile			
0%	78,5	357	0,22
1 and 5%	84	369	0,278
7%	88,8	375	0,237
10%	97,2	376	0,259
Polymethylmethacrylate	73.3	363	0,202
Polychlorotrifluoroethylene	71	348	0,204
Polyethylene terephthalate	76,7	380	0,202
Polychlorotrifluoroethylene	90	355	0,253
Polymethylmethacrylate	715	353	0,191
Polyethylene terephthalate	102,5	353	0,290
Polymethylmethacrylate	86,5	373	0,236
Polyvinyl chloride	75,5	370	0,21
Polyvinyl chloride + 10% plasticizer	57,3	313	0,188
Polyvinyl chloride + 20% plasticizer	55	273	0,203
Polyvinyl chloride + 40% plasticizer	50,8	223	0,201
Silicon rubber	64	188	0,34
Vulcalan	35,2	336	0,152
Natural rubber	24.2	203	0,12

c) the right-hand side of Eq. (3a) is negative,

$$\frac{d}{dT}\left|-\frac{\Delta Ug}{RT_g}\left(\frac{\Delta U}{\Delta U_g}\cdot\frac{Tg}{T}-1\right)\right|>\frac{d}{dT}\left|\frac{\Delta Sg}{R}\left(\frac{\Delta S}{\Delta S_g}-1\right)\right|,$$

then $\dfrac{d\ln\left(\dfrac{\lambda}{\lambda_g}\right)}{dT} < 0$ and λ decreases.

The last case is characteristic of amorphous polymers. This represents the overall trends in the variation of thermal conductivity. As for devising a universal method of data evaluation, the use of Eq. (2) and accounting for the temperature-dependence of ΔF is difficult. For this reason, our universal relation for the $T > T_g$ temperature range has been based on the theory of free volume by analogy to viscosity [19].

The test data in [6-15] were evaluated in terms of

$$\frac{\lambda}{\lambda_g}=\varphi\left(\frac{fg}{f}\right). \tag{4}$$

The results of this evaluation are shown in Fig. 4. As for the vitreous state, we obtained an invariant thermal conductivity relation for the superelastic state too. It is to be noted that the deviation of test data from the average curve does not exceed the limits of experimental inaccuracy.

New data for copolymers and cross-linked polymers as well as earlier data for amorphous polymers, irradiated polyethylene, atactic polypropylene, and polyamides (of different crystallization levels) were evaluated in terms of Eqs. (2a) and (4).

NOTATION

E_c is the cohesion energy;
$\overline{M}$ is the mean molecular weight;
ρ is the density;
L is the length of link in polymer molecule;
T is the instantaneous temperature;
T_g is the glass transition temperature;

λ_g, λ, λ_0	are the thermal conductivity at T_g, T, and $T \to \infty$, respectively;
ΔF, ΔF_g	are the free activation energy at T and T_g, respectively;
ΔU, ΔU_g	are the activation energy at T and T_g, respectively;
ΔS, ΔS_g	are the activation entropy at T and T_g, respectively;
f, f_g	are the fraction of free volume at T and T_g, respectively.

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