THERMAL CONDUCTIVITY OF CERTAIN ORIENTED POLYMERS

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An examination is made of results of an experimental study of the thermal conductivity of certain amorphous and crystalline polymers.

Oriented polymers possess anisotropy of their mechanical, optical, and thermal properties. If we designate the thermal conductivity in the direction of orientation as $\lambda_{||}$ and the same in the perpendicular direction as $\lambda_{\perp}$, then the ratio of the principal represents an estimate of the degree of anisotropy of thermal conductivity:

$$\eta_\lambda = \frac{\lambda_{||}}{\lambda_{\perp}}. \tag{1}$$

The degree of thermal conductivity anisotropy is often [1, 2] connected with the relative elongation. At the same time, it was shown in [3] that there is no relationship between the degree of orientation of polymethylmethacrylate as evaluated by the amount of birefringence and the degree of elongation. Well-oriented specimens with little elongation can be obtained, and so can poorly oriented polymers with a high degree of elongation. Here, elongation can be effected in both cases without viscous flow. Since thermal conductivity is a macroscopic parameter, it is most likely related to the integral spatial orientation of the macromolecular structure of the polymer. For thin materials, the temperature field on the surface corresponds to its volume distribution. Taking this into consideration, many investigators have used the method of a heated needle [1, 4, 5] to study the anisotropy of thermal properties of oriented polymer films. In the initial works [4], the temperature field about the needle was studied using a low-melting coating of paraffin or wax. This procecure yielded more graphic results compared to other temperature transducers, but gave only a qualitative picture of the temperature field. The patterns obtained were unsuited for quantitative study since the amorphous coating formed configurations with indistinct boundaries. The use of heat-sensitive paints to study temperature fields on heated surfaces improved significantly on the first technique. Fusion thermal indicators change color when a certain critical temperature is reached, and a clear isothermal boundary is obtained [5]. To study the degree of anisotropy of the thermal conductivity of oriented polymers, we used fusion thermal indicators with low critical temperatures: 309 and 317°K. All of the tests were conducted at room temperature. The heated needle was kept below 323°K. At least 10 fusion patterns were obtained for each polymer. The principal axes of the ellipse were measured with a microscope.

It was found from the solution of the thermal conductivity problem (two-dimensional case) for a thin anisotropic plate [6, 7] that the isotherms form a family of ellipses for which the following relation is valid

$$\frac{x^2}{\lambda_1} + \frac{y^2}{\lambda_2} = \text{const}, \tag{2}$$

where λ_1 and λ_2 are the principal thermal conductivities in the xy plane. A relation which follows from Eqs. (1) and (2) is used to calculate the degree of conductivity anisotropy (Fig. 1):

$$\eta_\lambda = \frac{a^2}{b^2}. \tag{3}$$

Thermal conductivity is a scalar parameter for an isotropic material, while it is a tensor for an anisotropic material, i.e., it depends on the direction of the heat flux. In such a case, it is interesting to know the conductivity at any angle to the major axis of anisotropy.

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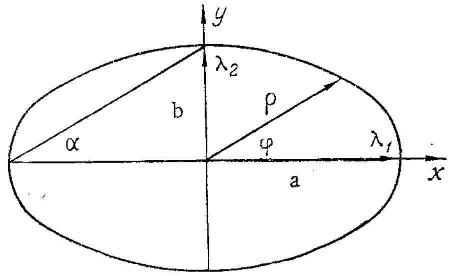

Fig. 1. Elliptical isotherm of oriented polymer.

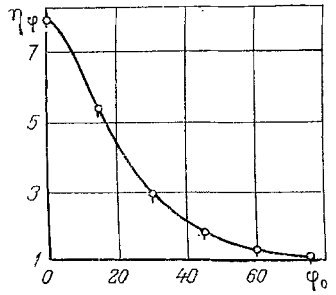

Fig. 2. Dependence of degree of thermal-conductivity anisotropy of oriented low-pressure polyethylene on the angle φ_0, deg.

i.e., to the x axis. The degree of thermal conductivity anisotropy in a direction at the angle φ can be represented in the form

$$\eta_\varphi = \frac{\lambda_\varphi}{\lambda_1} = \frac{\rho^2}{b^2},$$

where $\rho = \sqrt{x^2 + y^2}$. At the same time

$$\frac{\rho^2}{b^2} = \frac{a^2}{b^2}\left(\frac{1+\mathrm{tg}^2\,\varphi}{1+\dfrac{a^2}{b^2}\,\mathrm{tg}^2\,\varphi}\right) \quad \text{or} \quad \eta_\varphi = \eta_\lambda \frac{1+\mathrm{tg}^2\,\varphi}{1+\eta_\lambda\,\mathrm{tg}^2\,\varphi}. \tag{4}$$

If the principal thermal-conductivity tensors (λ_1 and λ_2) are known, then thermal conductivity λ_φ can be calculated from the formula

$$\lambda_\varphi = \frac{\lambda_1(1+\mathrm{tg}^2\,\varphi)}{1+\eta_\lambda\,\mathrm{tg}^2\,\varphi}. \tag{5}$$

Thus, knowing the thermal conductivities or one of the principal thermal conductivity coefficients and the degree of conductivity anisotropy, we can use Eqs. (4) and (5) to calculate thermal conductivity and the degree of anisotropy of the thermal conductivity of oriented polymers in any direction (Fig. 2).

We studied the thermal conductivities of several oriented polymers — low- and high-pressure polyethylene, polyvinyl chloride, polystyrene, polycapramide, and others in relation to the degree of elongation (stretching) and degree of orientation of the macromolecular structure (Fig. 3a). It can be seen from Fig. 3a that the conductivity anisotropy of oriented polymers depends not only on the degree of elongation, but on the nature of the polymer.

Using the heated-needle method with thermal indicators to study the anisotropy of the thermal conductivity of stretched polymers, the authors of [8] proposed that the total orientation of the macromolecular structure be evaluated from ellipsoidal fusion figures. A nonoriented polymer has isotropic properties and the orientation of its macromolecular structure is equal to zero. If the limiting orientation is taken as 100%, then the degree of orientation can be represented in the form $\eta = 1 - \tan\alpha$ (see Fig. 1), where α ranges from 0 to 45°. The quantity $\tan\alpha = b/a$ is determined in experiments. For an isotropic material, $\alpha = 45°$ ($b = a$) and $\eta = 0$. In the case of limiting orientation, $\alpha = 0$ and $\eta = 1$ or 100%. The design formula for the degree of orientation has the form

$$\eta = 1 - b/a. \tag{6}$$

The error of η, η_λ, and η_φ as determined by Eqs. (1), (4), and (6) is no more than 1%. The quantity η is an objective parameter which can most realistically characterize the degree of ordering of the structure of a polymer. Figure 3b shows the dependence of the degree of anisotropy of thermal conductivity on the parameter η. This curve is universal for all of the polymers investigated. By measuring η_λ, it is possible to find the degree of orientation of the macromolecular structure of any polymer. The phenomenon of thermal conductivity anisotropy in stretched polymers is explained by the effect of orientation of the macromolecular bonds in the stretching direction.

It has been made evident that heat transfer occurs in polymers primarily by means of covalent bonds along chains. Thus, the thermal conductivity will always be greater in the stretching direction than in the perpendicular direction. Molecular interaction is considerably weaker between chains than within the macromolecules themselves. Based on this, it may be suggested that the thermal resistance of an oriented macromolecular structure will be greater between chains, although it will change only slightly as a function of degree of orientation. This is confirmed by the results of studies of $\lambda_\parallel$ and $\lambda_\perp$ (Fig. 3b).

Two models — sequential and parallel — have been proposed to explain the effect of orientation [9]. In the first model, a nonoriented polymer is comprised of chaotically distributed units, each consisting of symmetrical elements the thermal conductivity of which is equal to the thermal conductivity of a completely oriented material. During stretching of the polymer, these elements are aligned one behind another, otherwise remaining unchanged. The thermal conductivity of a partially oriented polymer may be represented as the sum of the thermal resistances of the units with the passage of a uniform heat flow through them.

The second model assumes a uniform temperature gradient, leading to a summation of thermal conductivities. The final relation connecting λ_0, $\lambda_\perp$, and $\lambda_\parallel$ on the basis of these models [9] is

$$\frac{3}{\lambda_0} = \frac{2}{\lambda_\perp} + \frac{1}{\lambda_\parallel}, \tag{7}$$

where λ_0 is the thermal conductivity of the isotropic polymer. Empirical data for several amorphous polymers agrees satisfactorily with Eq. (7).

Yet one more model, based on kinetic-molecular theory, has been proposed [10] to explain the effect of orientation on heat transfer in polymers. According to this model, segments of chains in a polymer interact with segments of their nearest neighbors with a certain frequency. Due to the difference in intrachain and interchain forces, the frequency of interac-

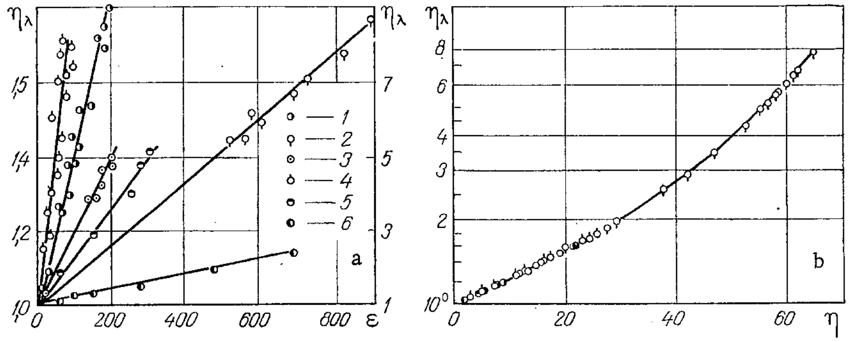

Fig. 3. Dependence of degree of anisotropy of thermal conductivity of oriented polymers on degree of elongation (a) and the parameter η (b): 1) low-density polyethylene; 2) high-density polyethylene; 3) polycapramide; 4) polyvinyl chloride; 5) polystyrene; 6) impact-proof polystyrene. ε; η, %.

tion for neighbors on the same chain is different from the frequency for neighbors on different chains. It is proposed that the energy transferred in each interaction is proportional to the difference in energies between the interacting segments. The thermal conductivity of the polymer is described by the relation

$$\lambda_0 = \lambda_1 \sqrt[3]{\eta_\lambda}. \qquad (8)$$

Although Eqs. (7) and (8) are quite different in form, the results obtained from calculations with each using available empirical data on anisotropy of the thermal conductivity of amorphous and polycrystalline polymers falls within the error limits [11]. This indicates that the above models can be used to explain heat transfer in oriented polymers.

For certain stretching regimes, the orientation of the macromolecular structure for crystalline polymers is considerably greater than for amorphous polymers, and the degree of thermal conductivity anisotropy reaches values significantly greater than 10. This means that crystalline polymers, especially low-pressure polyethylene, have a thermal conductivity which is an order higher in the direction of orientation than in the perpendicular direction. This curious effect leads to the conclusion that the macromolecule itself is highly anisotropic, thermally speaking, and the thermal conductivity along its covalent bonds is comparable to the thermal conductivity of semiconductors and alloys.

NOTATION

λ_0, $\lambda_\parallel$, $\lambda_\perp$, thermal conductivity of an isotropic material in the direction of orientation and directions perpendicular to the orientation, respectively; $\lambda_1 = \lambda_\parallel$, $\lambda_2 = \lambda_\perp$; η_λ, degree of anisotropy of thermal conductivity; a, b, principal semiaxes of an ellipse; ρ, radius vector; η_φ, degree of anisotropy of thermal conductivity at an angle φ to the heat flow; η,%, parameter of orientation of the macromolecular structure.

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