JOURNAL OF APPLIED POLYMER SCIENCE VOL. 19, PP. 49–68 (1975)

Induced Anisotropy of Thermal Conductivity of Polymer Solids under Large Strains

STEVENS T. J. PENG and ROBERT F. LANDEL, *Jet Propulsion Laboratory, California Institute of Technology, Pasadena, California 91103*

Synopsis

A simple analytical form of induced anisotropy of heat conductivity $k_{ij}(\lambda_1,\lambda_2,\lambda_3,T)$ of initially isotropic polymer solids results from employing the simplified theory of the three-chain model of the non-Gaussian network. The analytical form appears to be valid up to a stretch ratio of $\lambda = 2.65$, which is the limit of existing experimental data. The effect of induced anisotropy on the temperature distribution, due to the large deformations, is illustrated for a highly expanded spherical shell and a cylindrical tube under a steady-state heat flow using the derived analytical form of the strain-dependent heat conductivity.

INTRODUCTION

The induced anisotropic behavior of highly deformed polymer solids which were initially isotropic is caused by orienting the links of the polymer chain in the direction of stretch. The degree of anisotropy may depend on the monomer structure, but it depends mostly on the degree of deformation and thus orientation.

It is generally considered[1] that thermal energy is transmitted more readily along the polymer molecular chains than between molecules. Hence, it is reasonable to assume that there will be an induced anisotropy of heat conductivity for highly stretched polymer solids which will depend on the strain and the absolute temperature T; thus, the heat flux will be proportional to the temperature gradient $T,_j$. However, the constant of proportionality k_{ij}, i.e., the heat conductivity, may depend on the strain and temperature. Therefore, we assume that the law of heat conduction is given by

$$h^i = k^{ij}(\gamma_{kl},T)T,_j \tag{1}$$

where h^i is a contravariant component of heat flux vector $\vec{h}$ defined by unit area of deformed body and k^{ij} is the contravariant component of the tensorial induced anisotropic heat conductivity, both defined with respect to the imbedded curvilinear coordinate θ^i in the deformed state. The strain tensor γ_{ij} is defined[2] by

$$\gamma_{ij} = {}^1/_2(G_{ij} - g_{ij}) \tag{2}$$

where the tensor g_{ij} is a covariant metric of the imbedded curvilinear system θ^i of the undeformed body defined with respect to the material

Cartesian system X_i. Similarly, G_{ij} is the corresponding covariant metric of the imbedded curvilinear system θ^i of the deformed body defined with respect to the spatial Cartesian system Y_i. At the undeformed state, the form of the heat conductivity function degenerate to $k^{ij} = k_0 g^{ij}$, where k_0 is an isotropic Fourier heat conductivity.

In contrast to our basic assumption, it has been shown in the theory of nonlinear thermoelasticity that if one assumes the heat flux vector h_i to be a function both of the deformation gradient $\partial Y_k/\partial X_l$ and of the temperature gradient $T_{,k} \equiv \partial T/\partial Y_k$, i.e.,

$$h_i = h_i\left(\frac{\partial Y_k}{\partial X_l}, \frac{\partial T}{\partial Y_k}, T\right) \tag{3}$$

and also assumes the material to be initially isotropic, then by considering that the constitutive relation is invariant under superposed arbitrary rigid rotation of a spatial frame of reference, one obtains[2,3]

$$h_i = k_{ij}(I_1, I_2 \ldots I_7)T_{,j} \tag{4}$$

where

$$k_{ij} \equiv k_0\delta_{ij} + k_1 B_{ij} + k_2 B_{ik}B_{kj} \tag{5}$$

and k_0, k_1, and k_2 are polynomial functions of the seven joint invariants $(I_1, I_2, I_3 \ldots I_7)$ of $B_{kl} \equiv (\partial Y_k/\partial X_i)(\partial Y_l/\partial X_i)$ and $T_{,k}$; δ_{ij} is a Kronecker delta. In this expression, even though eq. (4) is quite similar in appearance to the form of Fourier heat law, because of having the temperature gradient $T_{,i}$ explicitly expressed, it should be noted that if the body is not deformed, i.e., $B_{kl} = \delta_{kl}$, eq. (4) becomes

$$h_i = k(I_4 \ldots I_7)T_{,i} \tag{6}$$

where $I_4 = I_5 = I_6 = I_7 = T_{,i}T_{,i}$. But this result contradicts the experimental observation that the heat flux is proportional to the temperature gradient, which requires that k should be independent of the temperature gradient $T_{,i}$. Thus, we assume eq. (1) directly for a highly deformed body.

In what follows we will show that, starting with eq. (1) and using the assumption of the simplified network theory of rubber-like elasticity of the three-chain model of Gaussian and non-Gaussian chains,[4] we obtain a simplified heat conduction equation. This equation described quite well the experimental data of the heat conductivity of poly(methyl methacrylate) (PMMA) and poly(vinyl chloride) (PVC) under large unaxial stretch, as obtained by Hellwege, Hennig, and Knappe.[5] Moreover, it provides a method which can be conveniently used to obtain an analytic form of the constitutive law of heat conductivity which is useful in the engineering analyses of boundary value problems. This is illustrated by showing the effects, due to the deformation on the temperature distribution under steady-state heat flow, in a highly expanded spherical shell and in a simultaneously extended and inflated cylindrical tube.

HEAT CONDUCTION LAW

We consider that an isotropic, homogeneous incompressible polymer solid before deformation will obey the classical Fourier heat law with an isotropic conductivity k_0 which, in general, depends on the absolute temperature, pressure, etc., but not on temperature gradients. When the solid is deformed, the heat conductivity is no longer isotropic and becomes anisotropic. We call this an induced anisotropic heat conductivity. We extend the Fourier heat law for this highly deformed body by assuming that the heat flux is proportional to the temperature gradient, but that the constant of proportionality k^{ij} (heat conductivity) may depend on the strain γ_{ij} and the temperature T. Thus, we assumed the heat conduction equation

$$h^i = k^{ij}(\gamma_{kl},T)T_{,j}. \tag{1}$$

Noting that k^{ij} is a tensorial function of the tensor variable γ_{kl}, one may write that

$$k^{ij} = \frac{\partial F(\gamma_{kl},T)}{\partial \gamma_{ij}} \tag{7}$$

where $F(\gamma_{kl},T)$ is a scalar function of the tensor variable γ_{kl}, i.e., the induced anisotropic heat conductivity can be derived from a certain scalar function of the tensor variable γ_{kl}. Since the polymer solid is initially isotropic and incompressible, the function $F(\gamma_{kl},T)$ can be expressed by two principal invariants of γ_{kl}, i.e., I_1 and I_2,[2] or by three principal stretch ratios λ_1, γ_2, and λ_3; i.e., $F = F(\lambda_1,\lambda_2,\lambda_3,T)$, where $I_1 = \lambda_1^2 + \lambda_2^2 + \lambda_3^2$ and $I_2 = \lambda_1^2\lambda_2^2 + \lambda_2^2\lambda_3^2 + \lambda_3^2\lambda_1^2$. (Note that λ_i here is a general stretch ratio and may be dependent on position in an inhomogeneous deformation, a point which will be utilized subsequently. For a homogeneous deformation, as in the deformation a cube, λ_i is the usual ratio of deformed to undeformed length and is independent of position in the body.)

Next, we postulate that the function $F(\lambda_1,\lambda_2,\lambda_3,T)$ is a symmetric, separable function of λ_1, λ_2 and λ_3, i.e.,

$$F(\lambda_1,\lambda_2,\lambda_3,T) = f(\lambda_1,T) + f(\lambda_2,T) + f(\lambda_3,T). \tag{8}$$

This postulate is based on the following assumptions:

1. The thermal energy can be transmitted more readily along the polymer molecular chains than between molecules.[1] In the undeformed state, this transmission will average out and a conductivity will be isotropic. In the deformed state, however, this will no longer be true but will depend on the average deformation, i.e., orientation, along a given direction. The general calculation of the orientation is not necessary, however; for Treloar has shown that the deformation of chain in a polymer network can be resolved into the deformations of three equivalent chains, one lying along each principal coordinate direction. This implies that the contribution to the conductivity can similarly be resolved into components along the principal

coordinate directions, and so we therefore assume the scalar function $F(\lambda_1,\lambda_2,\lambda_3,T)$ can be reduced to three independent sets.

2. The polymer solid is incompressible and initially isotropic. Since the material is initially isotropic, all material functions of the deformed body must be symmetrical with respect to the three principal stretch ratios λ_i. Incorporating this requirement with the assumption of three separate independent sets, we have the separable, symmetrical function of eq. (8).

The three principal values γ_α and three sets of principal directions $\vec{N}_{(\alpha)}$ ($\alpha = 1,2,3$) of the strain tensor γ_{ij} in a spatial coordinate system can be obtained from the following equations:

$$\gamma_{ij}N^i{}_{(\alpha)} = \gamma_{(\alpha)}N_j{}^{(\alpha)} \tag{9}$$

or

$$[G^{ik}\gamma_{ij} - \gamma_{(\alpha)}\delta_j{}^k]N^j{}_{(\alpha)} = 0 \tag{10}$$

where

$$G_{ij}N^i{}_{(\alpha)}N^j{}_{(\beta)} = \delta_{\alpha\beta}. \tag{11}$$

A nontrivial solution of eq. (10) exists if the coefficient determinant (the characteristic determinant) is equal to zero, i.e.,

$$|G^{ik}\gamma_{ij} - \gamma\delta_j{}^k| = 0. \tag{12}$$

Expansion of this determinant gives a cubic equation in γ, and the solution of the cubic equation gives three principal values $\gamma_{(\alpha)}$ ($\alpha = 1,2,3$) which can also be expressed with respect to the stretch ratio λ_α, i.e.,

$$\gamma_\alpha = {}^1/_2\,(1 - \lambda_\alpha{}^{-2}) \;(\alpha = 1,2,3) \tag{13}$$

where γ_α in eq. (13) are equivalent to the principal strains of the Almansi-Hamel strain tensor. Also, from eq. (10), eq. (11), and γ_α, we may obtain three sets of principal direction $\vec{N}_\alpha$ ($\alpha = 1,2,3$). Note that from eq. (9), one may obtain the following relation:

$$\gamma_\alpha = \gamma_{ij}\,N^i{}_{(\alpha)}\,N^j{}_{(\alpha)} \;(\alpha \text{ not summed}). \tag{14}$$

Thus, eq. (7) may be written as

$$k^{ij} = \sum_{\alpha=1}^{3} \frac{\partial F}{\partial \gamma_\alpha}\frac{\partial \gamma_\alpha}{\partial \gamma_{ij}}. \tag{15}$$

With eqs. (15), (14), (13), and (8), one obtains

$$k^{ij} = \sum_{\alpha=1}^{3} \lambda_\alpha{}^3 f'(\lambda_\alpha)\,N^i{}_{(\alpha)}\,N^j{}_{(\alpha)} \tag{16}$$

where

$$f'(\lambda_\alpha) \equiv \frac{df(\lambda_\alpha)}{d\lambda_\alpha}.$$

Thus, the heat conduction equation is given by

$$h^i = \left[\sum_{\alpha=1}^{3} \lambda_\alpha^3 f'(\lambda_\alpha)\, N^i_{(\alpha)}\, N^j_{(\alpha)} \right] T_{,j}. \tag{17}$$

For $\lambda_\alpha = 1$ ($\alpha = 1,2,3$), i.e., without deformation, eq. (16) becomes

$$k^{ij} = k_0 \sum_{\alpha=1}^{3} N^i_{(\alpha)}\, N^j_{(\alpha)} = k_0 G^{ij} = k_0 g^{ij} \tag{18}$$

where $k_0 \equiv f'(1)$ and $g^{ij} = G^{ij}$ in the undeformed state, and eq. (17) becomes

$$h^i = k_0 g^{ij} T_{,j} \tag{19}$$

which is the classical Fourier heat law of an isotropic solid.

EXPERIMENTAL DETERMINATION OF THE ANALYTICAL FORM OF THE INDUCED ANISOTROPY OF HEAT CONDUCTIVITY

For uniaxial deformation, we identify $\theta^i = Y_i$; thus, we have $G^{ij} = G_{ij} = \delta_{ij}$. The principal direction $\vec{N}^{(\alpha)}$ of simple extension in a spatial Cartesian coordinate system is given by

$$N_i^{(1)} = (1,0,0), \qquad N_i^{(2)} = (0,1,0), \qquad N_i^{(3)} = (0,0,1). \tag{20}$$

Substituting eq. (20) into eq. (16), one obtains

$$k_{11} = \lambda_1^3 f'(\lambda_1) \equiv k\|| \tag{21}$$

and

$$k_{22} = k_{33} = \lambda_2^3 f'(\lambda_2) \equiv k\perp \tag{22}$$

where λ_1 and $\vec{N}^{(1)}$ are parallel to the direction of stretch; λ_2 and $\vec{N}^{(2)}$ are perpendicular to the stretch. Since k_{11} is the heat conductivity parallel to the stretching direction, for convenience we denote $k\|| = k_{11}$. Since k_{22} is perpendicular to the direction of stretch, we denote $k\perp = k_{22}$.

The experimental results of Hellwege, Hennig, and Knappe,[5] who measured the anisotropy of thermal conductivity in uniaxially stretched polymer solids (see Fig. 1), show that for PMMA and PVC, the relative thermal conductivity along the uniaxially stretched direction depends almost linearly on the stretch ratio λ_1. (The heat conductivity of polystyrene in their paper is not considered here, since we suspect that because of the small effect of strain on heat conductivity, the experimental error may be relatively large.) Hence,

$$\frac{k\||}{k_0} = 1 + C(\lambda_1 - 1) \tag{23a}$$

or

$$k\|| = k_0[1 + C(\lambda_1 - 1)] = \lambda_1^3 f'(\lambda_1) \tag{23b}$$

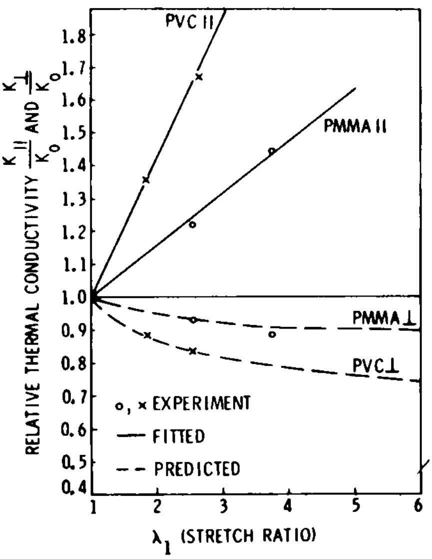

Fig. 1. Relative thermal conductivity of uniaxially stretched polymers (after Hellwege, Hennig, and Knappe[5]). || = Parallel to the direction of stretch; ⊥ = perpendicular to the direction of stretch.

where k_0 is the heat conductivity before deformation and C is the slope of the fitted lines. It has a value of 0.165 and 0.44 for PMMA and PVC, respectively. Note that k_0 and C may be dependent on temperature. From eqs. (23) and (21), we obtain, after integration,

$$f(\lambda_1) = k_0\left[-\frac{\lambda_1^{-2}}{2} + C\left(-\lambda_1^{-1} + \frac{\lambda_1^{-2}}{2}\right)\right]. \tag{24}$$

Then, from Eq. (8), we have

$$F(\lambda_1,\lambda_2,\lambda_3) = k_0 \sum_{\alpha=1}^{3}\left[-\frac{\lambda_\alpha^{-2}}{2} + C\left(-\lambda_\alpha^{-1} + \frac{\lambda_\alpha^{-2}}{2}\right)\right]. \tag{25}$$

Since the analytical expression of eq. (25) was obtained from the measurement of the heat conductivity parallel to the stretched direction alone, then, in order to test its validity or the applicability of postulate eq. (16), we may use eq. (25) to predict the heat conductivity perpendicular to the stretched directions, i.e., $k\perp$. To do so, we substitute eq. (25) into eq. (16) and obtain

$$k\perp \equiv k_{22} = k_0[1 + C(\lambda_2 - 1)]. \tag{26}$$

Since the material is incompressible, i.e., $\lambda_1\lambda_2^2 = 1$ under a uniaxial stretch, we have

$$k\perp = k_0\left[1 + C\left(\frac{1}{\sqrt{\lambda_1}} - 1\right)\right]. \tag{27}$$

Equation (27) is compared with the experimental data in Figure 1, and it can be seen that the theoretical curves predict the experimental data quite well (see lower part of Fig. 1).

TEMPERATURE DEPENDENCE OF INDUCED ANISOTROPIC HEAT CONDUCTIVITY DUE TO LARGE STRAIN

Figure 2 shows the thermal conductivity of stretched PVC as a function of temperature at different elongations. At zero stretch, the thermal conductivity is almost independent of temperature; however, for the stretched sample, it becomes dependent on temperature, and the dependence is almost linear with respect to the change of temperature. Thus, we write

$$C = a + bT \tag{28}$$

and so eqs. (23) and (27) become

$$k\| = k_0[1 + (a + bT)(\lambda_1 - 1)] \tag{29}$$

$$k\perp = k_0\left[1 + (a + bT)\left(\frac{1}{\sqrt{\lambda_1}} - 1\right)\right] \tag{30}$$

respectively, where k_0 = constant = 4×10^{-4} cal/°C-cm-sec. The values of the constants a and b are found from the topmost curve $k\|$ at $\lambda = 2.65$ to be 0.395 and 0.97×10^{-3}/°C, respectively. Now, using these values of a and b in eqs. (29) and (30), we calculate the remaining curves in Figure 2.

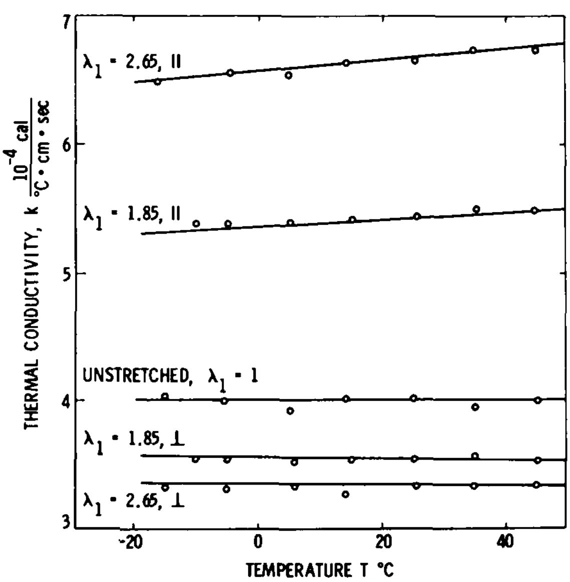

Fig. 2. Coupling effect of large strain and temperature on thermal conductivity (after Hellwege, Hennig, and Knappe[5]); (O) experimental data; (——) calculated.

It can be seen that the calculated curves predict quite well the experimental data in this temperature range, i.e., approximately −20°C to +50°C. Thus, the postulated form of the heat conductivity law not only describes the dependence on strain alone, but also that dependence coupled with temperature.

INDUCED ANISOTROPIC BEHAVIORS OF HEAT CONDUCTIVITY UNDER MULTIAXIAL DEFORMATION

The more stringent test of the validity of eq. (16) will come from predicting the heat conductivity in multiaxial deformations. With this in mind, we calculate the anisotropic behavior of the heat conductivity under strip biaxial (pure shear) deformation and equal biaxial deformation in accordance with eq. (25), which was obtained from the simple extension experiments.

For strip biaxial deformation, the heat conductivity perpendicular to stretch direction λ_1 is given by

$$(k\perp)_{SB} = k_0[1 + C(\lambda_3 - 1)] = k_0\left[1 + C\left(\frac{1}{\lambda_1} - 1\right)\right] \qquad (31)$$

where $\lambda_2 = 1$. For equal biaxial deformation, it is given by

$$(k\perp)_{EB} = k_0[1 + C(\lambda_3 - 1)] = k_0\left[1 + C\left(\frac{1}{\lambda_1^2} - 1\right)\right] \qquad (32)$$

where λ_1 is the stretched direction and λ_3 is the contracted direction perpendicular to λ_1.

Since the deformation state of equal biaxial deformation is equivalent to simple compression for incompressible material, we note that $(k\|)$ simple compression = $(k\perp)$ equal biaxial. Using the C value obtained from Figure 1, the numerical values of $(k\perp)_{SB}$ and $(k\perp)_{EB}$ for PVC and PMMA are shown in Figures 3 and 4, respectively. It should be emphasized

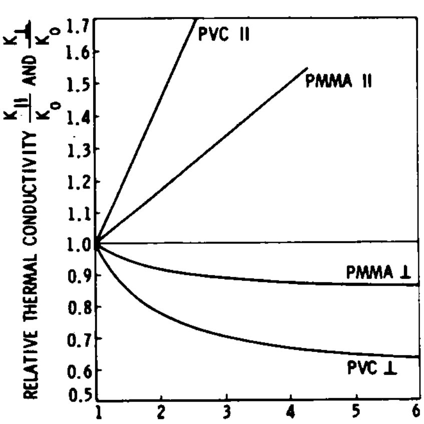

Fig. 3. Relative thermal conductivity of strip-biaxially stretched polymers.

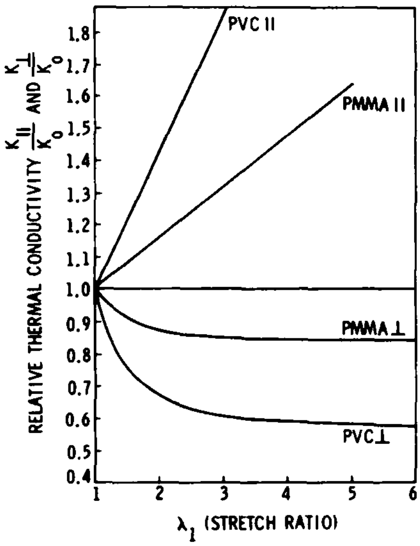

Fig. 4. Relative thermal conductivity of equal-biaxially stretched polymers.

that Figure 3 and 4 are not experimental curves but calculated ones. They are shown here partially to illustrate the dependence of k on λ in various deformation fields and partially in the hope of stimulating experimental work in this area.

TEMPERATURE DISTRIBUTION IN A HIGHLY INFLATED SPHERICAL SHELL AND CYLINDRICAL TUBE

Symmetrically Inflated Spherical Shell

It is of interest to observe the effect of the deformation-induced anisotropy of heat conductivity on the temperature distribution in a highly inflated spherical shell by using eq. (25) for the analytical expression for F and thus to compare the results with those without an induced anisotropy effect. Since the induced anisotropy effect is a function of deformation, the temperature distribution and heat flux will be markedly affected by deformation.

Consider a thick-walled spherical shell of an incompressible material which is expanded symmetrically with respect to its center. The undeformed state of internal radius r_1 and external radius r_2 are 1 and 5 units, i.e., $r_1 = 1$, $r_2 = 5$. The spherical shell undergoes symmetric expansion until the inner radius reaches a value of 5, i.e. $R_1 = 5$. Since the material is totally incompressible (i.e., mechanically and thermally incompressible), the outer radius $R_2 = 3\sqrt[3]{R_1^3 + r_2^3 - r_1^3} = 3\sqrt[3]{249}$, i.e.,

$$\text{Undeformed State} \begin{cases} r_1 = 1 \\ r_2 = 5 \end{cases} \qquad \text{Deformed State} \begin{cases} R_1 = 5 \\ R_2 = \sqrt[3]{249} \simeq 6.29 \end{cases} \tag{33}$$

In our proposed problem, we consider only the steady-state heat flow. We assume that the temperature varies radially, i.e., $T = T(R)$ and $h^i = h^i(R)$. The boundary conditions in the deformed state are given by $T = 100°C$ at $R = R_1$ (inner radius) and $T = 0°C$ at $R = R_2$ (outer radius).

The energy equation for the nonlinear thermoelastic theory is given[2,3] by

$$T \frac{D}{Dt}\left(\frac{\partial A}{\partial T}\right) = h^i{}_{;i} \tag{34}$$

where D/Dt denotes a material derivative with respect to time t, h^i is a contravariant component of heat flux, and ; denotes the covarient derivative with respect to a system of embedded curvilinear coordinates θ^i in the deformed state; A is a specific free energy which is a function of the strain invariants and absolute temperature. Equation (34) is a highly nonlinear partial differential equation. Since we consider only the steady-state heat flow, eq. (34) becomes

$$h^i{}_{;i} = 0 \tag{35a}$$

or

$$h^i{}_{,i} + \Gamma_{si}{}^i h^s = 0 \tag{35b}$$

where $\Gamma_{sj}{}^i$ is the second kind of Christoffel symbol.

For symmetrical expansion of a thick spherical shell, we take the imbedded curvilinear coordinate system θ^i in the strained body to be a system of spherical polar coordinates (R,θ,ϕ). Thus, the metric tensor is given by

$$G_{ik} = \begin{bmatrix} 1 & 0 & 0 \\ 0 & R^2 & 0 \\ 0 & 0 & R^2\sin^2\theta \end{bmatrix}, \qquad G^{ik} = \begin{bmatrix} 1 & 0 & 0 \\ 0 & \dfrac{1}{R^2} & 0 \\ 0 & 0 & \dfrac{1}{R^2\sin^2\theta} \end{bmatrix} \tag{36}$$

We assume that the displacement of the unstrained body possesses spherical symmetry, so that the point (R,θ,ϕ) was originally at the point (r,θ,ϕ). We note

$$Q(R) = r/R \tag{37}$$

for convenience in the algebra. Because we assume the material to be incompressible, we have

$$r^3 - R^3 = r_1^3 - R_1^3. \tag{38}$$

Thus,

$$Q(R) = \left(1 + \frac{r_1^3 - R_1^3}{R^3}\right)^{1/3}. \tag{39}$$

The metric tensor of the undeformed body is given by

$$g_{ik} = \begin{bmatrix} \dfrac{1}{Q^4} & 0 & 0 \\ 0 & R^2Q^2 & 0 \\ 0 & 0 & R^2Q^2\sin^2\theta \end{bmatrix}, \qquad g^{ik} = \begin{bmatrix} Q^4 & 0 & 0 \\ 0 & \dfrac{1}{R^2Q^2} & 0 \\ 0 & 0 & \dfrac{1}{R^2Q^2\sin^2\theta} \end{bmatrix} \tag{40}$$

Now we are going to employ eq. (12) to obtain the principle strain γ_α and the principal direction $\vec{N}_\alpha$. From eqs. (26) and (40), we obtain

$$\frac{1}{2}\begin{bmatrix} 1-\dfrac{1}{Q^4} & 0 & 0 \\ 0 & 1-Q^2 & 0 \\ 0 & 0 & 1-Q^2 \end{bmatrix} \tag{41}$$

Thus, substituting eq. (41) into eq. (12), we obtain

$$\gamma_1 \equiv \gamma_{(R)} = \frac{1}{2}\left(1-\frac{1}{Q^4}\right), \qquad \gamma_2 \equiv \gamma_{(\alpha)} = \frac{1}{2}(1-Q^2),$$

$$\gamma_3 \equiv \gamma = \frac{1}{2}(1-Q^2) \tag{42}$$

since

$$\gamma_\alpha = {}^1/_2\,(1-\lambda_\alpha^{-2}). \tag{13}$$

Thus, in terms of the (general) extension ratios, we have

$$\lambda_{(R)} \equiv \lambda_1 = Q^2 = \left(1+\frac{r_1^3-R_1^3}{R^3}\right)^{2/3}$$

$$\lambda_2 \equiv \lambda_{(\theta)} = \lambda_3 \equiv \lambda_{(\phi)} = \frac{1}{Q} = \left(1+\frac{r_1^3-R_1^3}{R^3}\right)^{-1/3}. \tag{43}$$

The corresponding principal directions in the spatial coordinate system can be obtained by using eqs. (10), (11), (40), and (41). That is,

$$\left.\begin{aligned} N_{(1)}{}^i &\equiv N_{(R)}{}^i = (1,0,0) \\ N_{(2)}{}^i &\equiv N_{(\theta)}{}^i = \left(0,\frac{1}{RQ},0\right) \\ N_{(3)}{}^i &\equiv N_{(\phi)}{}^i = \left(0,0,\frac{1}{RQ\sin\theta}\right) \end{aligned}\right\}. \tag{44}$$

Since we assume $T = T(R)$, $T_{,2} \equiv \dfrac{\partial T}{\partial \theta} = 0$ and $T_{,3} \equiv \dfrac{\partial T}{\partial \theta} = 0.$ Hence, with eqs. (17) and (44), one obtains

$$h^1 = \lambda_{(R)}{}^3 f'(\lambda_{(R)})\frac{dT}{dR}, \qquad h^2 = h^3 = 0. \tag{45}$$

Substituting eq. (24) or eq. (25) into eq. (45), one obtains

$$h^1 = k_0[1 + C(\lambda_{(R)} - 1)]\frac{dT}{dR} \tag{46}$$

or, substituting for $\lambda_{(R)}$ according to eq. (43),

$$h^1 = k_0\left\{1 + C\left[\left(1+\frac{r_1^3-R_1^3}{R^3}\right)^{2/3} - 1\right]\right\}\frac{dT}{dR}. \tag{47}$$

Here, for simplicity, we assume k_0 and C are independent of temperature.

Now consider eq. (35b). The nonzero components of $\Gamma_{ij}{}^{i}$ are

$$\Gamma_{22}{}^{1} = -R, \qquad \Gamma_{33}{}^{1} = -R\sin^2\theta, \qquad \Gamma_{33}{}^{2} = -\sin\theta\cos\theta,$$
$$\Gamma_{12}{}^{2} = \Gamma_{13}{}^{3} = \frac{1}{R}, \qquad \Gamma_{23}{}^{3} = \frac{\cos\theta}{\sin\theta} \tag{48}$$

and, since $h^2 = h^3 = 0$, eq. (35) becomes

$$\frac{dh^1}{dR} + \frac{2}{R}h^1 = 0. \tag{49}$$

In the spherical coordinate, it is easy to show that $h^1 = h_1$, i.e., contravariant components and covariant components of $\vec{h}^1$ are the same.

Substituting eq. (47) into eq. (49), one obtains

$$\frac{d}{dR}\left[\left\{1 + C\left[\left(1 + \frac{a}{R^3}\right)^{2/3} - 1\right]\right\}\frac{dT}{dR}\right] + \frac{2}{R}\left\{1 + C\left[\left(1 + \frac{a}{R^3}\right)^{2/3} - 1\right]\frac{dT}{dR}\right\} = 0 \tag{50}$$

where $a \equiv r_1{}^3 - R_1{}^3 = 1 - 125 = -124$. The solution of eq. (50) is given by

$$T = K_1\int_{R_2=\sqrt[3]{249}}^{R}\frac{dx}{x^2\{1 + C\,[(1 - 124/x^3)^{2/3} - 1]\}} + K_2 \tag{51}$$

where K_1 and K_2 are integration constants which can be determined by boundary conditions.

The boundary conditions are

$$T = 100°\text{C at } R = R_1 = 5 \text{ (inner radius)} \tag{52a}$$

$$T = 0°\text{C at } R = R_2 = \sqrt[3]{249} \text{ (outer radius)}. \tag{52b}$$

From the boundary condition (52b), we have $K_2 = 0$. Thus, eq. (51) becomes

$$T = K_1\int_{R_2=\sqrt[3]{249}}^{R}\frac{dx}{x^2\{1 + C\,[(1 - 124/x^3)^{2/3} - 1]\}}. \tag{53}$$

Now we would like to investigate the effect of the material constant C on the temperature distribution. We consider three values of C, i.e., $C = 0$ (i.e., no anisotropic effect), $C = 0.5$, and $C = 1.0$. Since the integral eq. (53) is not integrable by analytical means, we employ a numerical method to obtain the results which are shown in Figure 5.· The anisotropic effect on temperature distribution is markedly shown. The dashed line indicates the temperature distributions to be expected for a simple slab which is equivalent to spherical shell with an infinite radius of curvature. The difference between this line and the solid one labeled $C = 0$ shows the usual effect of specimen geometry when there is no anisotropy effect; with increasing C,

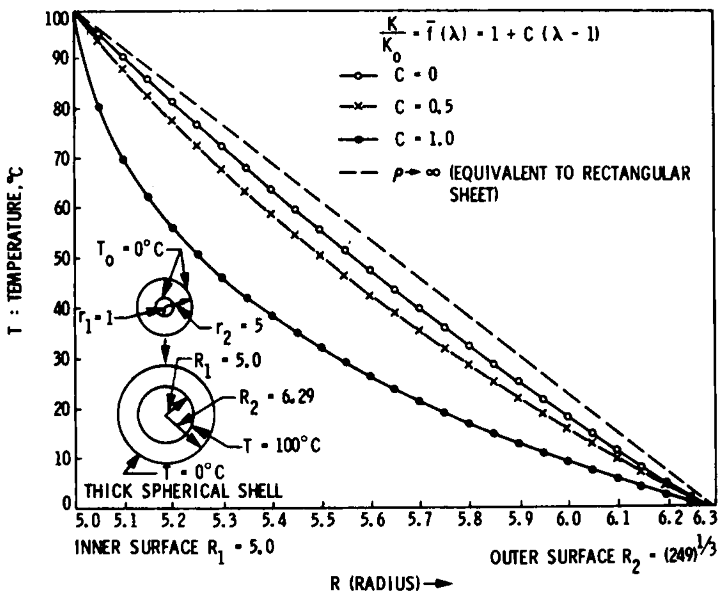

Fig. 5. Temperature distribution in a highly expanded spherical shell.

the discrepancy becomes progressively larger until, for $C = 1$, it approaches 30°.

Simultaneous Extension and Inflation of a Cylindrical Tube

Consider a thick cylindrical tube which in the unstrained state has a length L_0 and has internal and external radii $r_1 = 2$ and $r_2 = 6$ units, respectively. The tube is strained by a uniform simple extension with extension ratio $\lambda = 2$ and by symmetric expansion with respect to the cylindrical axis until the inner radius reaches a value of 6, i.e., $R_1 = 6$. Since the material is incompressible, we have

$$L_0(\pi r_2^2 - \pi r_1^2) = \lambda L_0(\pi R_2^2 - \pi R_1^2). \tag{54}$$

Thus, we have

$$R_2 = \sqrt{(r_2^2 - r_1^2)/\lambda + R_1^2} = \sqrt{(6^2 - 2^2)/2 + 6^2} = \sqrt{52} \simeq 7.2111$$

i.e.,

$$\left.\begin{array}{l}\text{Undeformed State}\\ \text{Length} = L_0\end{array}\right\} \begin{array}{l} r_1 = 2 \\ r_2 = 6\end{array} \qquad \left.\begin{array}{l}\text{Deformed State}\\ \text{Length} = 2L_0\end{array}\right\} \begin{array}{l} R_1 = 6 \\ R_2 \simeq \sqrt{52} = 7.211\end{array}$$

In this illustrative problem, we consider only the steady-state heat flow. We again assume that the temperature varies only along the radius of the tube, i.e., $T = T(R)$. The boundary conditions in the deformed state are given by $T = 100°C$ at $R = R_1$ (inner radius) and $T = 0°C$ at $R = R_2$ (outer radius).

The imbedded curvilinear coordinate system θ^i in the strained state of the cylinder is taken to be a system of cylindrical polar coordinates (R,θ,Z). Then the point (R,θ,Z) was initially at the point $(r,\theta,Z/\lambda)$, where r is a function of R only. The metric tensor of the strained body is given by

$$G_{ik} = \begin{bmatrix} 1 & 0 & 0 \\ 0 & R^2 & 0 \\ 0 & 0 & 1 \end{bmatrix}, \qquad G^{ik} = \begin{bmatrix} 1 & 0 & 0 \\ 0 & \dfrac{1}{R^2} & 0 \\ 0 & 0 & 1 \end{bmatrix} \tag{55}$$

and the metric tensor of the unstrained body is given by

$$g_{ij} = \begin{bmatrix} r_R^2 & 0 & 0 \\ 0 & r^2 & 0 \\ 0 & 0 & \dfrac{1}{\lambda^2} \end{bmatrix}, \qquad g^{ij} = \begin{bmatrix} \dfrac{1}{r_R^2} & 0 & 0 \\ 0 & \dfrac{1}{r^2} & 0 \\ 0 & 0 & \lambda^2 \end{bmatrix} \tag{56}$$

where $r_R \equiv dr(R)/dR$. The mixed strain tensor is given by

$$G^{ik}\gamma_{kj} = \frac{1}{2}\begin{bmatrix} 1 - r_R^2 & 0 & 0 \\ 0 & 1 - \dfrac{r^2}{R^2} & 0 \\ 0 & 0 & 1 - \dfrac{1}{\lambda^2} \end{bmatrix} \tag{57}$$

Following procedures similar to those used in a previous problem, we obtain three principal strains:

$$\gamma_1 \equiv \gamma_{(R)} = \frac{1}{2}(1 - r_R^2), \qquad \gamma_2 \equiv \gamma_{(\theta)} = \frac{1}{2}\left(1 - \frac{r^2}{R^2}\right),$$

$$\gamma_3 \equiv \gamma_{(Z)} = \frac{1}{2}\left(1 - \frac{1}{\lambda^2}\right). \tag{58}$$

From eq. (13), we have three stretch ratios:

$$\lambda_{(R)} = \frac{1}{r_R}, \qquad \lambda_{(\theta)} = \frac{R}{r}, \qquad \lambda_{(Z)} = \lambda. \tag{59}$$

Since the material is incompressible, we have the following relation:

$$\lambda_{(R)}\lambda_{(\theta)}\lambda_{(Z)} = \frac{R\lambda}{r_R r} = 1 \tag{60}$$

or

$$r\frac{dr}{dR} = R\lambda. \tag{61}$$

The solution is given by

$$r^2 = \lambda R^2 + (r_1^2 - \lambda R_1^2) = \lambda R^2 + a \tag{62}$$

where $a \equiv r_1^2 - \lambda R_1^2 = 2^2 - 2\times 6^2 = -68$. The corresponding principal directions $\vec{N}_{(\alpha)}$ in the spatial coordinate system are given by

$$\left.\begin{aligned} N_{(R)}{}^i &\equiv N_{(1)}{}^i = (1,0,0) \\ N_{(\theta)}{}^i &\equiv N_{(2)}{}^i = (1, 1/R, 0) \\ N_{(Z)}{}^i &\equiv N_{(3)}{}^i = (0,0,1) \end{aligned}\right\} \tag{63}$$

Since $T = T(R)$, $T_{,1} = dT(R)/dR$, $T_{,2} = \partial T/\partial\theta = 0$, and $T_{,3} = \partial T/\partial Z = 0$. Hence, with eqs. (17) and (63), we obtain

$$h^1 = \lambda_{(R)}{}^3 f'(\lambda_{(R)}) \frac{dT}{dR}, \qquad h^2 = h^3 = 0. \tag{64}$$

Substituting eq. (24) or eq. (25) into eq. (64), and with eq. (62) one obtains

$$h^1 = k_0[1 + C(\lambda_{(R)} - 1)] \frac{dT}{dR}. \tag{65}$$

Now we consider eq. (35). Since the non zero components of $\Gamma_{sj}{}^i$ of cylindrical coordinates are given by

$$\Gamma_{22}{}^1 = -R, \qquad \Gamma_{12}{}^2 = \Gamma_{21}{}^2 = \frac{1}{R} \tag{66}$$

and since $h^2 = h^3 = 0$, eq. (35) becomes

$$\frac{dh^1}{dR} + \frac{1}{R} h^1 = 0. \tag{67}$$

Substituting eq. (65) into eq. (67), we obtain

$$\frac{d}{dR}\left[\left\{1 + C\left[\frac{(\lambda R^2 + a)^{1/2}}{\lambda R} - 1\right]\right\}\frac{dT}{dR}\right] + \frac{1}{R}\left\{1 + C\left[\frac{(\lambda R^2 + a)^{1/2}}{\lambda R} - 1\right]\right\}\frac{dT}{dR} = 0 \tag{68}$$

using

$$\lambda_{(R)} = \frac{1}{r_R} = \frac{r}{R\lambda} = \frac{(\lambda R^2 + a)^{1/2}}{R\lambda} \tag{69}$$

which is obtained from eqs. (59), (61), and (62).

The solution of eq. (68) is given by

$$T = \lambda^2 k_1 \int_{R_2=\sqrt{52}}^{R} \frac{dx}{\{1 + C\,[(\lambda x^2 + a)^{1/2}/\lambda x - 1]\}\,x} + K_2 \tag{70}$$

where $\lambda = 2$, $a = -68$. The thermal boundary conditions are

$$T = 100°\text{C at } R = R_1 = 6 \text{ (inner radius)} \tag{71a}$$

$$T = 0°\text{C at } R = R_2 = \sqrt{52} \text{ (outer radius)}. \tag{71b}$$

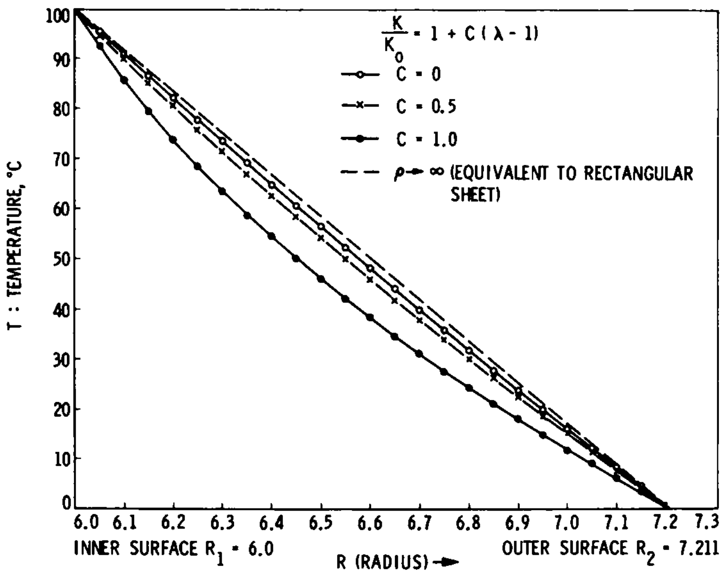

Fig. 6. Temperature distribution in a highly expanded and stretched long cylindrical tube.

From (71b), we have $K_2 = 0$. Thus, eq. (70) becomes

$$T = \lambda^2 K_1 \int_{R_1 = \sqrt{52}}^{R} \frac{dx}{\{1 + C\ [(\lambda x^2 + a)^{1/2}/\lambda x - 1]\}\ x}. \tag{72}$$

The temperature distribution in the expanded, stretched cylindrical shell is shown in Figure 6 for three values of C, i.e., $C = 0$, $C = 0.5$, and $C = 1.0$. The results are similar to those of Figure 5.

More general cases can be treated in the above manner too, e.g., those in which the temperature depends on the R,Z coordinates, $T = T(R,Z)$. The solution is more involved, therefore we will only set up such a problem as an illustration of our approach and for comparison with the ordinary heat conduction problem.

Consider the case that $T = T(R,Z)$, or $\partial T/\partial R \neq 0$, $\partial T/\partial Z \neq 0$ but $\partial T/\partial \theta = 0$. Then, from eqs. (17) and (63), we obtain

$$\begin{aligned} h^1 &= h_{(R)} = k_0[1 + C(\lambda_{(R)} - 1)]\,\frac{\partial T}{\partial R} \\ h^2 &= h_{(\theta)} = 0 \\ h^3 &= h_{(Z)} = k_0[1 + C(\lambda_{(Z)} - 1)]\,\frac{\partial T}{\partial Z} \end{aligned} \tag{73}$$

where $\lambda_{(R)} = [(\lambda R^2 + a)^{1/2}]/R\lambda$ as given by eq. (69), and $\lambda_{(Z)} = \lambda = 2$. With eqs. (35) and (66), one obtains

$$h^1{}_{,1} + h^3{}_{,3} + \frac{1}{R}\,h^1 = 0. \tag{74}$$

Substituting eq. (73) into eq. (74), one obtains

$$\frac{\partial}{\partial R}\left\{[1 + C(\lambda_{(R)} - 1]\frac{\partial T}{\partial R}\right\} + [1 + C(\lambda_{(Z)} - 1)]\frac{\partial^2 T}{\partial Z^2} + \frac{1}{R}[1 + C(\lambda_{(R)} - 1)]\frac{\partial T}{\partial R} = 0. \quad (75)$$

Using the method of separation of variables, one assumes

$$T(R,Z) = X(R)Y(Z). \quad (76)$$

Substituting eq. (76) into eq. (75), one obtains

$$\frac{1}{X}\left[\frac{d}{dR}\left\{[1 + C(\lambda_{(R)} - 1)]\frac{dX}{dR}\right\} + \frac{1}{R}[1 + C(\lambda_{(R)} - 1)]\frac{dX}{dR}\right] = -\frac{1}{Y}[1 + C(\lambda_{(Z)} - 1)]\frac{d^2Y}{dZ^2}. \quad (77)$$

Since the left side of eq. (77) is a function of R alone, while the right-hand side is a function of Z alone, it follows necessarily that both sides must be equal to a constant η, i.e.,

$$\frac{d}{dR}\left\{[1 + C(\lambda_{(R)} - 1)]\frac{dX}{dR}\right\} + \frac{1}{R}[1 + C(\lambda_{(R)} - 1)]\frac{dX}{dR} = -\eta X(R) \quad (78)$$

$$[1 + C(\lambda_{(Z)} - 1)]\frac{d^2Y}{dZ^2} = +\eta Y(Z). \quad (79)$$

Note that, when $C = 0$, eq. (78) becomes a Bessel's equation of zero order.

SUMMARY

By employing the postulates that the thermal energy could be transmitted more readily along the polymer molecular chains than between molecules and that the non-Gaussian chain network may be represented by three-chain model, one greatly simplifies the method needed to characterize the induced anisotropic heat conductivity of polymeric materials. If the induced anisotropic heat conductivity is expressed in terms of invariants $I_1, \ldots, I_7$, then the equations offered to characterize it are complex and difficult to use. One needs not only multiaxial deformation experiments, but also close control of many variables. Obviously, the latter is a difficult, if not insurmountable, task in the eyes of the experimentalist. Our theory gives a very efficient and simple way to circumvent these difficulties.

The last two sections offer the numerical calculations of relative heat conductivities and temperature distributions. The theory is shown to be readily extendable to multiaxial deformation fields. It is shown that the results of the equal biaxial and strip biaxial deformations might be used to give a stringent test to the theory. The calculations of temperature distri-

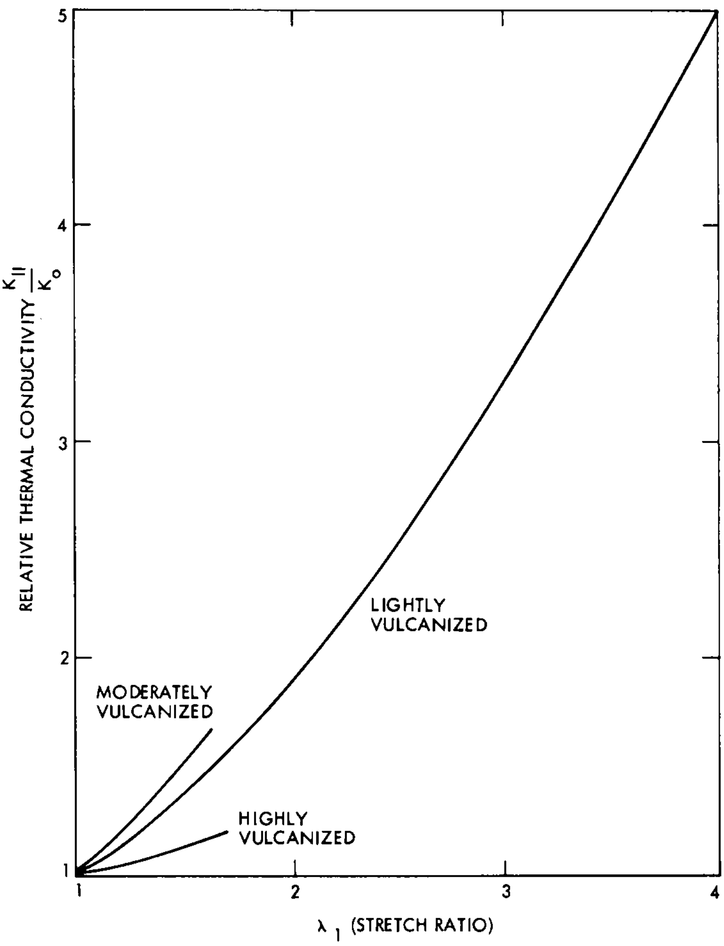

Fig. 7. Relative thermal conductivity of uniaxially stretched vulcanized rubber (after Tautz[6]).

bution in highly expanded spherical shells and cylindrical tubes are used to illustrate the effect of the induced anisotropy on the temperature distribution. For a more complex case of temperature varying along two coordinates, a sample problem is formulated to indicate the procedure that one might follow.

As demonstrated here, in analysis of heat transfer in these materials, the induced anisotropy heat conductivity law plays a significant role. It is generally expected that the effects of orientation on heat conductivity of a melt are to be similar to the effects on a solid, amorphous polymer. Hence, our theory may be used to calculate the required heat transfer for such chemical processes, i.e., extrusion and blow molding of polymer melts which are under both shearing and stretching and are significantly oriented.

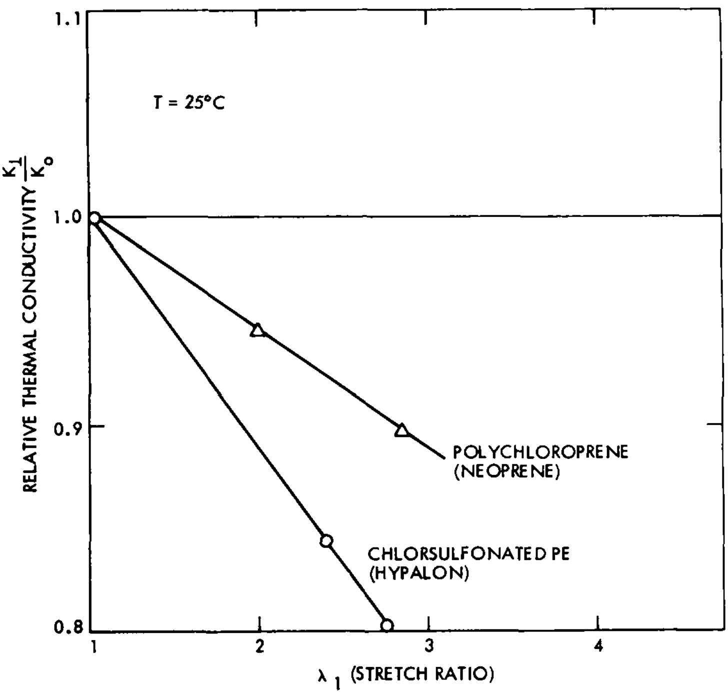

Fig. 8. Relative thermal conductivity of uniaxially stretched Neoprene and Hypalon (after Hennig and Knappe[7]).

Appendix

Note that the analytic form of eq. (25) is not the only one we should consider. One may obtain a different expression for different kinds of elastomers. The essence of this paper is that the heat conduction law of elastomeric materials can be expressed by eq. (17) through the postulation of (8), i.e.,

$$h^i = \left[\sum_{\alpha=1}^{3} \lambda_\alpha^3 f'(\lambda_\alpha) N_{(\alpha)}{}^i N_{(\alpha)}{}^j\right] T_{,j} \tag{17}$$

where the analytic expression of $f(\lambda)$ will depend on the specific material which we characterize. For example, from the data of Tautz[6] on the induced anisotropic heat conductivity of vulcanized rubber parallel to the stretched direction, we find that the analytic expression of $k\|$ *for lightly vulcanized rubber* (Fig. 7) can be expressed by the following equation:

$$k\| = \lambda_1^3 f'(\lambda_1) = k_0[1 + 0.9(\lambda_1 - 1)^{13.9}]. \tag{80}$$

Thus, after integrating eq. (80), and substituting it into eq. (8), we obtain

$$F(\lambda_1,\lambda_2,\lambda_3) = k_0 \left\{\sum_{\alpha=1}^{3} \left[-\frac{1}{2}\lambda_\alpha^{-2} + 0.9 \int \frac{(\lambda_\alpha - 1)^{1.39}}{\lambda_\alpha^3}\, d\lambda_\alpha\right]\right\}. \tag{81}$$

From eqs. (81) and (16), we have

$$k\perp = \lambda_2^3 f'(\lambda_2) = k_0[1 + 0.9(\lambda_2 - 1)^{1.39}] = k_0[1 + 0.9(1/\sqrt{\lambda_1} - 1)^{1.39}]. \tag{82}$$

Here we note again that the direction of λ_2 is perpendicular to the stretching direction λ_1.

In another example, we consider the data of Hennig and Knappe[7] on Neoprene and Hypalon. We find from Figure 8 that

$$k\perp = \lambda_2^3 f'(\lambda_2) = k_0[1 - C(\lambda_1 - 1)] \tag{83}$$

or

$$f'(\lambda_2) = \frac{k_0}{\lambda_2^3}[1 - C(1/\lambda_2^2 - 1)] \tag{84}$$

where C is the slope of the straight lines. Thus, after integrating eq. (84) and substituting into eq. (8), we have

$$F(\lambda_1,\lambda_2,\lambda_3) = k_0\left[\sum_{\alpha=1}^{3}\left[-\frac{1}{2}\lambda_\alpha^{-2} - C\left(-\frac{1}{4}\lambda_\alpha^{-4} + \frac{1}{2}\lambda_\alpha^{-2}\right)\right]\right]. \tag{85}$$

The heat conductivity parallel to the stretch direction then is given by

$$k\| = k_0[1 - C(1/\lambda_1^2 - 1)]. \tag{86}$$

* This paper represents one phase of research carried out by the Jet Propulsion Laboratory, California Institute to Technology, Pasadena, California, sponsored by the National Aeronautics and Space Administration under Contract No. NAS7-100.

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Received January 16, 1974
Revised June 21, 1974