

Dependence of the Thermal Conductivity on Mechanical Stress in Polymers

J. S. FOX* and M. IMBER, *Polytechnic Institute of Brooklyn,
Brooklyn, New York*

Synopsis

An examination of the theory of thermal conductivity of amorphous dielectrics as applied to polymeric materials indicates that it is reasonable to expect that the conductivity is stress dependent. An experimental investigation was undertaken to determine the validity of this hypothesis for a number of plastics at temperatures below their respective glass transition points. Poly(methyl methacrylate), nylon, and Delrin were chosen as representative of a wide range of percentage crystallinity and were tested at compressive stresses up to 140 kg./cm.² and temperatures between 4 and 38°C. The results indicate that the conductivity may increase as much as 20% and that the dependence on stress is a function of temperature and the type of polymer examined.

Introduction

A number of investigators have noted that the thermal conductivity of a polymer can be modified through mechanical deformation. The data of Tautz¹ demonstrated the existence of such behavior for a number of types of rubber. In natural rubber the percentage increase in conductivity in the direction of stretch was found to be approximately equal to the per cent deformation for strains up to about 300%, while a comparatively minor dependence was found in highly vulcanized rubbers. Tautz suggested that the observed behavior was a result of a decrease in structural disorder and which produced an increase in the scattering length for the elastic waves constituting the thermal transport. Eiermann and Hellwege² also observed this type of phenomenon in tests performed on PMMA, PVC, and other polymers. The materials were heated to temperatures above their glass points and then plastically stretched. They were then returned to the glassy state before undergoing thermal testing. The conductivity was found to be anisotropic: augmented in the direction of deformation and diminished in the lateral direction. If it is assumed that the material possesses a greater capability for transmitting thermal energy along polymer chains than between adjacent chain segments, this result can be attributed to orientation of the polymer chains in the direction of stretch. Hellwege and co-workers,³ presenting similar data, proposed a model utilizing inter-

* Present address: Department of Mechanical Engineering, University of Hawaii, Honolulu, Hawaii 96822.

chain and intrachain conductivity. This approach resulted in a successful correlation between the anisotropic thermal conductivity and the anisotropic linear coefficient of thermal expansion.

Hanson and Ho⁴ have suggested that the strain dependence of the conductivity can be explained without recourse to considerations of orientation and derived an expression for the thermal energy transmission rate per unit cross section. This equation, demonstrated to yield excellent agreement with data on natural rubber, exhibits the proper behavior through a simple increase in the distance which thermal energy is transmitted in each collision process. It is assumed that the other parameters affecting the transport rate are unaffected by elongation. However, it can be argued that the collision frequency is also modified because of the nonlinear nature of the bonding forces. Also, it does not appear reasonable to assume that a macroscopic deformation is transmitted to the microscopic level as an affine transformation of coordinates. Indeed, the theory of rubber elasticity would instead suggest a higher probability of elongated chain configuration without any significant change in intrachain distances. The derivation also ignores the fact that the number of segments and hence thermal emitters per unit cross-section increases under elongation. The result of this effect would be to make the per cent increase in thermal conductivity proportional to the axial strain for an incompressible medium, thus providing a rationale for the data of Tautz.¹

In all of the cases discussed above, the mechanical strains were comparable to or larger than the percent changes in thermal conductivity they produced. The polymers all underwent their conductivity transformations at temperatures above glass transition. However, examination of a number of models of thermal conduction, as applied to amorphous material, suggests that the thermal conductivity of a glassy polymer should also be dependent on its state of mechanical stress. The mechanisms for such a dependency are, in general, connected with small reversible deformations rather than the large deformations and associated orientation previously discussed.

In the thermal transport models of Kincaid and Eyring⁵ and of Sakiadas and Coates,⁶ the thermal conductivity is inversely proportional to the distance across the free volume between adjacent hard-shell spherical molecules. Deformation of the material in question may be expected to change this distance and consequently produce a variation in the thermal conductivity. This effect could be large compared to the strain if the free volume is small compared to the total volume. The theory of Kittel,⁷ devised to explain a sharp increase in thermal conductivity of glass with decreasing temperature, also appears to be relevant. Previously, as in the models of Bridgman⁸ and Jeffreys,⁹ it was assumed that the scattering distance for thermal transport was of the order of the molecular spacing or distance of short-range order for amorphous materials. However, Kittel advanced the hypothesis that at sufficiently low temperatures the molecular oscillations correspond to wavelengths which are large compared to the

distance of short-range order, and that local disorder will consequently cause less scattering. If this same model is now applied to a material held at constant temperature, but undergoing deformation, a similar result is indicated. A change of the average separation between oscillating molecules or atoms will produce a change in the vibrational frequency spectrum because the binding forces are nonlinear. Application of Kittel's model indicates that a stress causing a shift in the thermal spectrum to higher frequencies would result in increased scattering, while lower frequencies would have the opposite effect. It should also be expected that a critical temperature exists for which the sensitivity of the conductivity to mechanical strain would be a maximum. This would correspond to the temperature for which the thermal oscillation frequency of highest probability density yields a wavelength equal to the distance of short-range order.

Examination of the above models for thermal transport suggests another manner in which elastic strain may modify the thermal conductivity. The application of a stress produces strains on a microscopic level which change the profile of the potential associated with holes or vacancies. A hole acts as a reflector of all particles with energies insufficient to surmount the potential barrier surrounding it. Therefore, holes act as scatterers in the transport of thermal energy. If the strain is such as to diminish the height of the potential barrier, this mode of scattering and its associated contribution to thermal resistance will decrease. Such changes in potential barriers may also encourage crystallinity where such a tendency is already present, thereby increasing the average local order and further enhancing thermal conduction.

Experimental

The objective of the experiments was to investigate the possibility of interaction between applied stress and thermal conductivity in polymeric materials at temperatures below the glass point. Hence, the apparatus was designed so as to yield a high sensitivity to conductivity changes, although not necessarily providing precise data on the absolute value of the conductivity itself. Further, no attempt was made to identify the polymers used in this exploratory study beyond their generic names. The technique used for determining the conductivity was basically a one-dimensional symmetrical heat flow method in which the heat flux and temperature gradient were measured. A hydraulic mechanism was provided to produce a constant compressive stress during testing.

Samples to be tested were prepared by machining rods of commercial polymer to yield disks measuring approximately 2.5 cm. in diameter and 0.65 cm. thick. The faces were polished to provide a flat and smooth contact surface. Aluminized Mylar was cemented to the periphery of each sample in order to obtain a surface with a low thermal radiation emissivity. Two matched samples were placed on opposite faces of a cylindrical heater assembly, forming a sandwich arrangement which was subsequently placed between the anvil and ram of the loading assembly.

In all cases, the contacting surfaces were coated with a film of vacuum pump oil to minimize interface resistance. A series of tests was carried out with samples of different thicknesses and for varying numbers of interfaces to verify that, in fact, the thermal resistance between surfaces was negligible. This is extremely important because the contact resistance is generally load-dependent.

The information necessary for the calculation of the thermal conductivity is the temperature difference between two points along the heat flux axis and the heat flux rate, in addition to the dimensions of the samples under test. Temperatures were measured in the heater, the anvil and the ram at positions adjacent to the faces of the polymer. Chromel-constantan thermocouples were used for this purpose and were mounted in such a manner as to insure that the applied stress was not transmitted to them, since their output characteristics are stress dependent.

All testing was done in a vacuum environment in order to minimize edge losses and closely approximate one-dimensional axial heat flow. Such losses as occurred were mostly due to radiation and amounted to approximately 0.5% of the axial flow when the temperature difference across each specimen was about 1°C. The lack of lateral heat flow permits the use of a steady-state, one-dimensional heat flow equation which may be approximated by the following finite difference expression:

$$q = KA(T_1 - T_0)/L \quad (1)$$

where T_1 is the temperature of the anvil face, T_0 is the temperature of the heater face, L is the thickness of the specimen, A is the cross-sectional area of the specimen, q is the heat flux rate, and K is the thermal conductivity of the specimen. Since a similar equation may be written for the other specimen, the combined heat flow is given by:

$$q_0 = (KA/L)(2T_0 - T_1 - T_2) \quad (2)$$

where q_0 is the heater generation rate and T_2 is the temperature at the ram face. Equation (2) may be solved for the thermal conductivity as a function of the measured parameters of the system.

Results and Discussion

Tests performed on PMMA under zero load condition yielded the thermal conductivity at various temperatures as shown in Figure 1. Measurements made under uniaxial compressive loading demonstrate a considerable variation in the thermal conductivity as a function of load. The per cent increase in conductivity is shown in Figure 2 for various temperatures with compressive stress as the abscissa. The error is estimated to be approximately $\pm 3\%$ of the plotted value. It may be noted that the stress sensitivity is strongly temperature-dependent and that in one case the sensitivity decreases after achieving a maximum. Tests performed on samples of nylon and Delrin demonstrated somewhat less dependence on applied stress (Figures 3 and 4). In all cases the conductivity variation

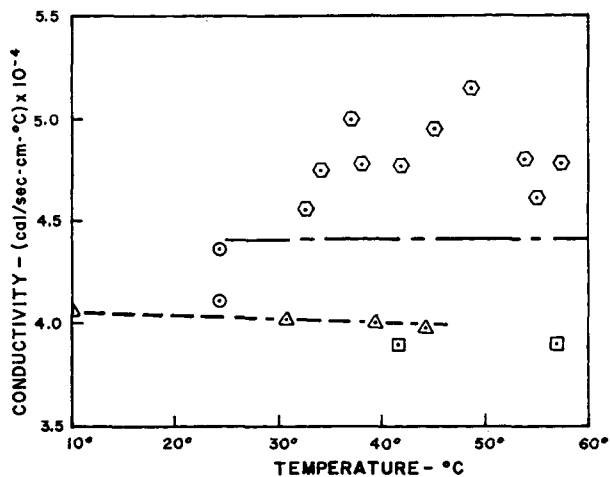


Fig. 1. Thermal conductivity of poly(methyl methacrylate) vs. temperature: (Δ) current investigation; (—) data of Shoulberg and Shetler;¹⁰ (\circ) data of Woodside and Wilson;¹¹ (\square) data of Bernhardt;¹² (\odot) data of Holzmuller and Munx.¹³

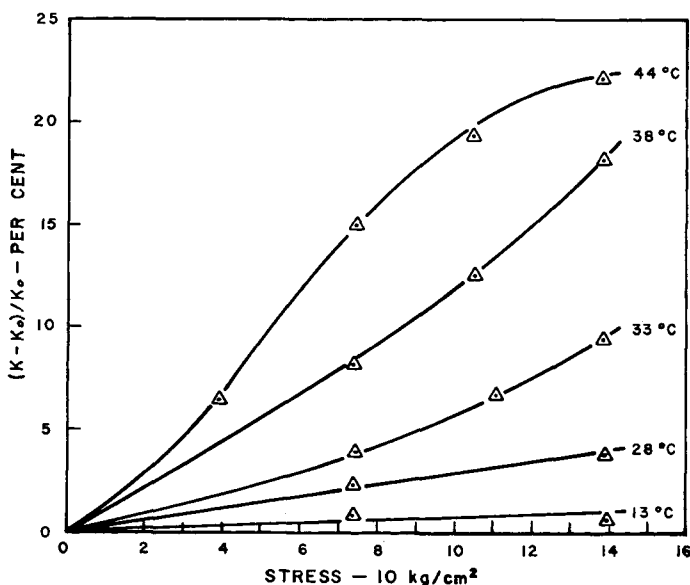


Fig. 2. Per cent increase in thermal conductivity vs. compressive stress for poly(methyl methacrylate) at various temperatures.

observed was found to be a reversible function of stress. There was, however, a time dependence which was probably associated with the viscoelastic nature of the material.

Although the data obtained here are limited, it is possible to make certain preliminary conjectures concerning the origin of this phenomenon. In the case of PMMA, the maximum per cent thermal conductivity change

observed was about two orders of magnitude greater than the corresponding strain. This effectively rules out chain orientation as a means of explaining the observations. Similarly, a relative displacement of scattering centers, as presented in the model of Hanson and Ho,⁴ would yield con-

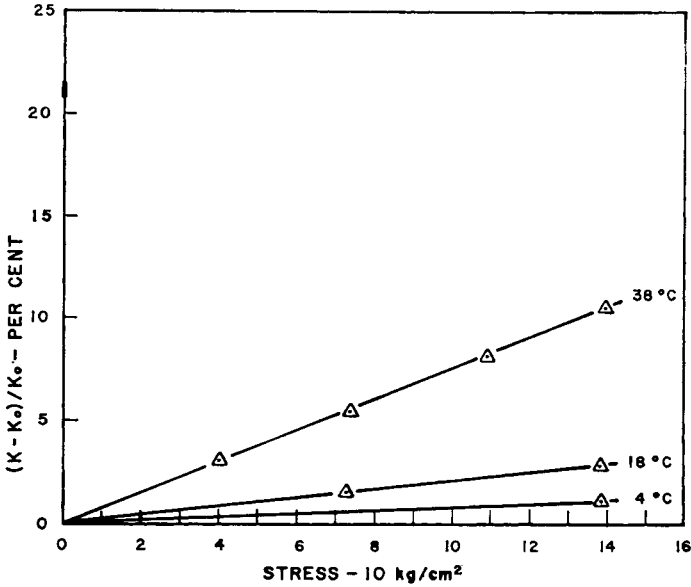


Fig. 3. Per cent increase in thermal conductivity vs. compressive stress for nylon at various temperatures.

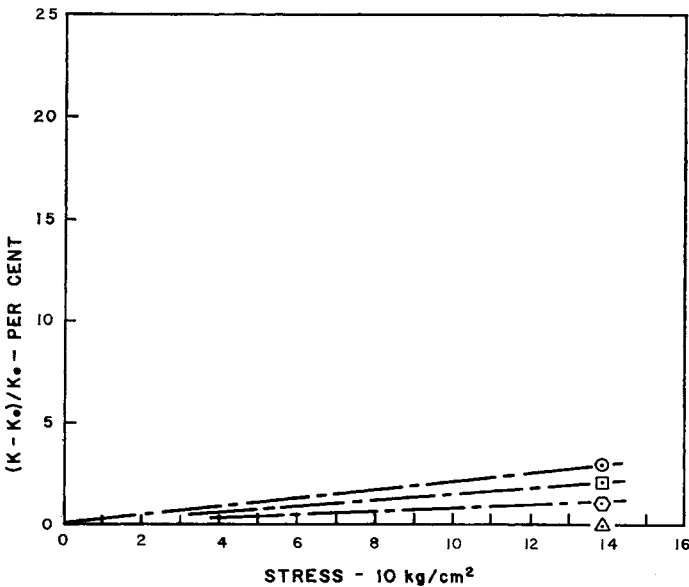


Fig. 4. Per cent increase in thermal conductivity versus compressive stress for Delrin at various temperatures: (\circ) 27°C.; (\square) 38°C.; (\odot) 13°C.; (\triangle) 3°C.

ductivity variations of the same order as the strain, and hence must also be rejected from consideration. Even with the small variety of polymers tested, there seems to be sufficient evidence to rule out increased crystallinity as a cause of the observations. PMMA, found to be the most sensitive to stress, is generally highly amorphous and should possess less tendency to crystallize than nylon or Delrin. A model patterned after that of Kincaid and Eyring,⁵ would seem to yield a behavior more suitable to explanation of the data.

As a very crude approximation, consider a polymer consisting of hard-shell cylindrical molecules with segments oriented alternately in the x , y , and z directions. Further, restrict the examination only to thermal energy transported between molecules rather than along them, i.e. the interchain contribution to the thermal conductivity. The net velocity of transport between molecular centers may be obtained⁵ by considering the energy to travel at infinite velocity across the cylinder and at some characteristic velocity between the surface of the cylinders. This approach yields a transport velocity of:

$$U_t = U_c(d/d_f) \quad (3)$$

where U_t is transport velocity, U_c is characteristic velocity, d_f is the separation of surfaces, and d is the center-to-center distance. Ignoring the Poisson effect for the moment, a macroscopic strain will result in a corresponding transformation of molecular centers. This yields:

$$\epsilon = (d - d_0)/d_0 \quad (4)$$

where d_0 is initial separation and ϵ is strain. The actual change in the center-to-center distance all takes place in the free distance: therefore;

$$d_f - d_{f0} = d - d_0 \quad (5)$$

where d_{f0} is initial free distance. Equation (5) can be rearranged:

$$(d_f/d_0) = (d_{f0}/d_0) + [(d - d_0)/d_0] \quad (6)$$

Combining eq. (6) with eq. (4) yields:

$$d_f/d_0 = d_{f0}/d_0 + \epsilon \quad (7)$$

When eq. (7) is substituted in eq. (3), the transport velocity becomes:

$$\begin{aligned} U_t &= U_c \left(\frac{d}{d_0} \right) / \left[\left(\frac{d_{f0}}{d_0} \right) + \epsilon \right] \\ &= U_c(1 + \epsilon) / [(d_f/d_0) + \epsilon] \end{aligned} \quad (8)$$

The ratio of the transport velocity in the strained state to the transport velocity in the initial unperturbed condition is simply:

$$U_t/U_{t0} = (d_f/d_0)(1 + \epsilon) / [(d_f/d_0) + \epsilon] \quad (9)$$

where U_{t0} is initial transport velocity.

The thermal conductivity for amorphous substances is proportional to the transport velocity and the number of emitters per unit cross-section. For an incompressible material undergoing small deformations, the error introduced by ignoring the change in the number of emitters per cross-section due to Poisson's effect, is of the order of the strain and will be neglected in this analysis. Hence, the ratio of the conductivity under strain to the initial conductivity is simply:

$$K/K_0 = (1 + \epsilon)/[1 + (d/d_f)_0\epsilon] \quad (10)$$

In order to determine whether the mechanism discussed above is capable of producing conductivity changes of the order of magnitude observed in the experiments, some approximate values will be substituted into eq. (10). If it is assumed that on the average the free volume is dispersed uniformly throughout the solid, the ratio of the distance across the free volume to the center-to-center separation can be obtained from consideration of the geometry. If a value for the free volume fraction of the glass temperature of $1/40^{14}$ is chosen, the resulting free distance fraction is approximately $1/60$. Substituting this into eq. (10) along with a value of strain of 0.4% obtained for PMMA at the maximum loading yields an increase in conductivity of 32% . The maximum conductivity change actually observed for PMMA was 22% . Thus, the model, although crude, at least suggests results of the proper order of magnitude and offers encouragement for a more valid approach necessitating simultaneous consideration of interchain and intrachain transport and a statistical analysis of the molecule configurations.

By employing the simple model discussed above, the variation of the increase in conductivity with temperature for a particular value of stress may be explained in the following manner. As the temperature of a polymer decreases, less microbrownian movement is possible, and hence, the strain occurs more and more within a polymer chain rather than between chains. The straining of the chain itself is produced by variation in the valence angles and interatomic distances, neither of which effect would be expected to significantly increase the thermal transport rate. The lesser sensitivity of the nylon and Delrin may be due to more highly conductive crystalline areas which effectively short-circuit thermal transport around stress sensitive amorphous zones. If such is the case, an increase in the conductance of the amorphous zones which account for the bulk of the total strain, would be observed only to a lesser degree in the overall conductance. The applied stress would have little effect on the conductance of a crystalline zone, because the strong bonding would favor strains in the relatively weakly bonded amorphous zones.

Conclusions

The thermal conductivities of certain commercial polymers in the glassy state have been demonstrated to be stress dependent in compression. Previous observations in this field have been concerned with either rubbery

or plastic deformations and have indicated weaker dependencies than those presented herein. Whereas an explanation based upon chain orientation and alignment has generally sufficed for previous studies, this approach is inadequate for the data obtained in the current investigation. The approximate analysis presented indicates that the thermal transport models of Kincaid and Eyring⁵ and Sakiadas and Coates⁶ may be suitable points of departure for an understanding of the strong dependency observed in these tests.

Taken from the dissertation submitted to the Faculty of the Polytechnic Institute of Brooklyn in partial fulfillment of the requirements for the degree of Doctor of Philosophy, 1966.

References

1. H. Tautz, *Kolloid-Z.*, **174**, 128 (1961).
2. K. Eiermann and K. H. Hellwege, *J. Polymer Sci.*, **57**, 99 (1962).
3. K. H. Hellwege, J. Hennig, and W. Knappe, *Kolloid-Z.*, **188**, 121 (1963).
4. D. Hanson and C. C. Ho, *J. Polymer Sci. A*, **3**, 659 (1965).
5. J. F. Kincaid and H. Eyring, *J. Chem. Phys.*, **6**, 620 (1938).
6. B. C. Sakiadas and J. Coates, *AIChE J.*, **3**, 121 (1957).
7. C. Kittel, *Phys. Rev.*, **75**, 972 (1949).
8. P. W. Bridgman, *The Physics of High Pressure*, G. Bell Ltd., London, 1931, p. 307.
9. H. Jeffreys, *Proc. Cambridge Phil. Soc.*, **24**, 19 (1928).
10. R. H. Shoulberg and J. A. Shetter, *J. Appl. Polymer Sci.*, **6**, 532 (1962).
11. W. Woodside and A. G. Wilson, *ASTM Spec. Pub. No. 217*, 32 (1957).
12. E. C. Bernhardt, Ed., *Processing of Thermoplastic Materials*, Reinhold, New York, 1959.
13. W. Holzmuller and M. Munx, *Kolloid-Z.*, **159**, 25 (1958).
14. F. Bueche, *Physical Properties of Polymers*, Interscience, New York, 1962, p. 106.

Received April 26, 1967

Revised August 1, 1967