THERMAL CONDUCTIVITY OF POLYMERS

D. R. ANDERSON

Sandia Corporation, Albuquerque, New Mexico 87115

Received March 3, 1966

CONTENTS

I. INTRODUCTION

Although the methods for measuring thermal conductivity of polymers vary greatly, published values do provide many insights into variations of thermal conductivity associated with molecular change. In this review of thermal conductivity, each section covers a general type of polymer: thermoplastics, rubbers, and thermosets. All foams are grouped under the thermosets since the dominant influence is the presence of the gas pocket in the polymer matrix. Molecular changes and their influence on the thermal conductivity of each type polymer are discussed in the separate sections.

II. NOTATIONS, DEFINITIONS, UNITS (23)

Heat conduction can take place only when bodies at different temperatures are in physical contact. The heat flow will be from the body at the higher to the body at the lower temperature.

Assume a section of a material with one face at a higher temperature (t_2) than another (t_1) (Figure 1). The direction of heat flow will be from t_2 to t_1 or left to right.

When the section has reached equilibrium (steady-state conditions), *i.e.*, when the temperature at any point within the sample remains constant with time, the amount of heat flowing through the section can be calculated from Eq 1 knowing the following parameters.

q, Q, or H = heat flow (input), g cal/sec
a or A = area, cm^2
d or l = thickness, cm
t_2 = temperature of hot surface, °C
t_1 = temperature of cold surface, °C
T = time, sec
λ, K, or k = coefficient of thermal conductivity, (g cal)(cm)/(deg)(cm^2)(sec)

$$K = \frac{Qd}{(t_2 - t_1)aT} = \frac{(\text{g cal})(\text{cm})}{(\text{deg})(\text{cm}^2)(\text{sec})} \qquad \text{(Eq 1)}$$

Other sets of units may be used also (see Table I).

Thermal conductivity (K) of a homogeneous material is then the time rate of heat flow, under steady-state conditions, through a unit area, per unit temperature gradient, perpendicular to an isothermal surface

$$K = \frac{qd}{a(t_2 - t_1)} \qquad \text{(Eq 2)}$$

Thermal conductance (C) of a substance between two surfaces is the time rate of heat flow between these surfaces, under steady-state conditions, divided by the difference of their average temperatures and by the area of one of the surfaces

$$C = \frac{q}{a(t_2 - t_1)} = \frac{K}{d} \qquad \text{(Eq 3)}$$

Table I

Conversion Factors[a] for Thermal Conductivities, *k*

g cal/(cm²) (sec) °C/cm	w/(cm²) °C/cm	w/(in.²) °C/in.	BTU/(ft²) (hr) °F/ft	(kg cal)/(m²) (hr) ° C/m	BTU/(ft²) (hr) °F/in.
1.0	4.186	10.63	241.9	360.0	2903.0
0.2389	1.0	2.540	57.8	86.00	693.5
0.09405	0.3937	1.0	22.75	33.86	273.0
4.134×10^{-3}	0.01730	0.0440	1.0	1.488	12.00
2.778×10^{-3}	0.01163	0.0295	0.672	1.0	8.064
0.344×10^{-3}	1.442×10^{-3}	3.663×10^{-3}	0.0833	0.1240	1.0

[a] The conversion factors above are based on 1 watt = 3.413 BTU/hr, 1 kg cal = 1/860 kw-hr.

Thermal resistance (resistivity) (R) is the reciprocal of the conductance

$$R = \frac{1}{C} = \frac{d}{K} \qquad \text{(Eq 4)}$$

In a solid, energy can be transferred by either of two mechanisms: coupling between the lattice vibrations, or electronic movement and collision with atoms. Since electrons are not free to move in a dielectric crystal, the contribution from the electronic conduction can be neglected. Debye (9) and Peierls (33) explain heat conduction in dielectric crystals by the concept of mean free path of thermal waves (quanta) called phonons. Thermal conductivity can be calculated by the following equation (21)

$$\lambda = \frac{1}{3} cvl \qquad \text{(Eq 5)}$$

where c = heat capacity per unit volume, cal/cm³/°C (possible units), v = average velocity of wave, cm/sec (possible units), l = mean free path of thermal waves of normal modes of vibrations (photons), cm (possible units).

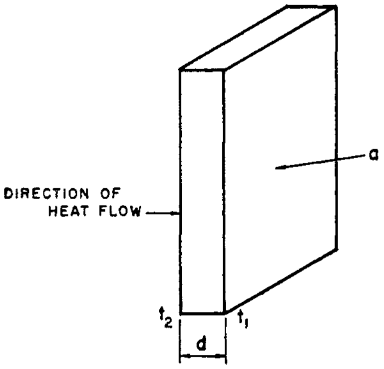

Figure 1.—Heat flow through a sample.

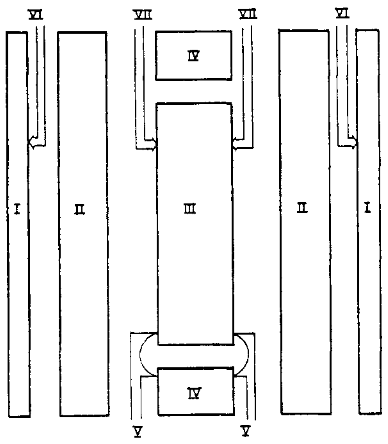

Figure 2.—Guarded hot plate: I, cooling units and surface plates; II, test samples; III, center heater and surface plates; IV, guard heater and surface plates; V, differential thermocouples; VI, cooling unit surface thermocouples; VII, heating unit surface thermocouples.

III. Methods for Measuring Thermal Conductivity

A. GUARDED HOT PLATE (AMERICAN SOCIETY FOR TESTING MATERIALS C177-63) (1)

The most accurate method for measuring equilibrium thermal conductivities of homogeneous samples of less than 10 BTU in./hr ft² °F uses a guarded hot plate. The general features of the metal-surfaced guarded hot plate are shown schematically in Figure 2. The unit consists of three sections: a central heating section (III), a guard heating section (IV), and a cooling section (I). Plates in these sections may be either round or square. The central section contains a heated and central surface plates. The guard section contains one or more guard heaters and guard surface plates. The guard section is used to ensure unidirectional heat flow from the central heater section and to eliminate any influences due to the edges of the sample. The noncorroding metal working surfaces of the heating and cooling plates (I) are smoothly finished and conform to a true plane as closely as possible. Thermocouples are placed at various places in the guarded hot plate to measure differential temperature between guard ring and central heater, temperature of the hot surface, and temperature of the cold surface.

Two identical samples are prepared for each test. Surfaces of test samples must be as near a plane as possible (0.003 in./ft) to assure intimate contact with hot plates and, thus, uniform heat flow. An appropriate force is applied to the hot plate sample assembly to further improve contact.

At the beginning of a test, the temperature difference between the hot and cold plates is adjusted to not less than 10°F; however, it is better to have a temperature gradient of 40°F/in. thickness. The central heating unit and the cooling units are adjusted until the temperature drop through the two sides does not differ by more than 1%, and the fluctuation over a time of 1 hr does not change by more than 0.5% of the temperature difference between hot and cold plates. After equilibrium has been attained the appropriate measurements are made of temperature difference across the specimens, the hot (t_2) and cold plate (t_1) temperatures, the center to guard temperature balance, and the electrical power (q) imput to the central heater. When four successive readings do not differ more than 1%, they may be used in the calculation of the thermal conductivity *via* Eq 1. Of course, the necessary dimensions of thickness (L) and area (A) are also needed.

B. SPLIT BAR (46)

The split bar method allows measurements over the same equilibrium conductivity range as the guarded hot plate. Although this method is not as well known and possibly not as accurate as the guarded hot plate method, it has the advantage of requiring a very small sample. While the guarded hot plate requires two samples several inches in diameter and approximately 0.5 in. thick, the split bar requires two wafer samples 1 in. or less in diameter, one approximately $^1/_{16}$, and one approximately $^1/_8$ in. thick. The general features of the split bar are schematically shown in Figure 3.

The unit consists of two sections of a round bar whose ends are flat and held parallel to each other. In each section are four small holes for differential thermocouples (I) and heater (II). One section of the bar (III) is held fixed; the other (movable) section (IV) has a heat sink (V). A hydraulic ram (VI) is used to assume proper and uniform thermal contact between the flat parallel faces of the rod and the parallel faces of the sample (VII).

Since this method is not of the guarded design, it does not require the extra feedback circuits and heater controls. Heat losses, except those from the side walls of the sample, can be easily accounted for by measuring the thermal gradient at each rod face immediately fore and aft of the sample position. Heat loss through the side walls of a very thin sample is considered to be negligible. For each sample and temperature, the units must be allowed to reach an equilibrium condition. The numbers obtained from the differential thermocouple assemblies are graphed, and the thermal gradients at the sample faces are obtained by extrapolation. Since the thermal conductivity of the iron rods is known and the thermal gradient measured, the equilibrium heat flow through the sample may be calculated.

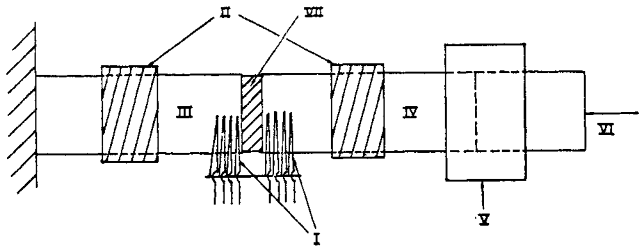

Figure 3.—Split bar: I, differential thermocouples; II, heaters; III, fixed section of bar; IV, movable section of bar; V, heat sink; VI, hydraulic ram; VII, sample.

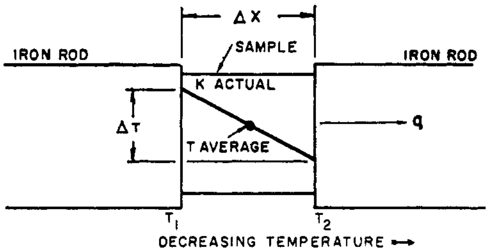

Figure 4.—Location of measurements on split bar.

Measurements on two samples of different thickness are required to eliminate the temperature drops due to the interfaces between the specimen and rod. The values obtained from graphs of Δt_1, Δt_2, q_1, and q_2 *vs.* T average for any temperatures are used in Eq 6 to calculate the actual thermal conductivity of the sample

$$K_{\text{actual}} = \frac{\Delta x_1 - \Delta x_2}{\dfrac{A_1 \Delta t_1}{q_1} - \dfrac{A_2 \Delta t_2}{q_2}} \qquad \text{(Eq 6)}$$

where K = actual thermal conductivity of the samples, Δx_1 = thickness of sample 1, Δx_2 = thickness of sample 2, Δt_1 = temperature difference between two faces of the rods for sample 1, Δt_2 = temperature difference between two faces of the rods for sample 2, A_1 = sample area normal to heat flow for sample 1, A_2 = sample area normal to heat flow for sample 2, q_1 = heat flow through sample 1, and q_2 = heat flow through sample 2 (Figure 4).

C. THERMAL CONDUCTIVITY PROBE (14)

This method of determining the thermal conductivity of a material differs from the other two discussed in that it does not require the attainment of thermal equilibrium (steady state). Since a steady-state condition is not necessary, this transient heat method is faster.

The general features of the probe are shown schematically in Figure 5.

The probe is inserted in the sample to be tested. The thermal conductivity is calculated from the amount of heat added per unit time through the heater coil and the increase in temperature measured by the

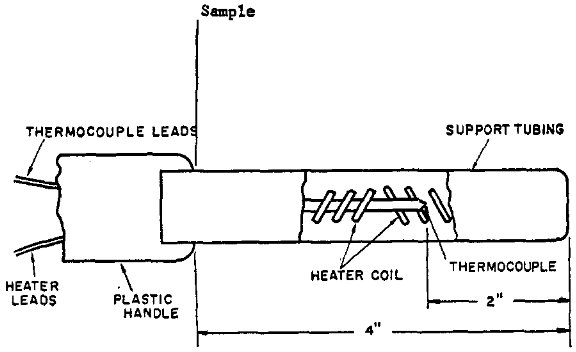

Figure 5.—Thermal conductivity probe.

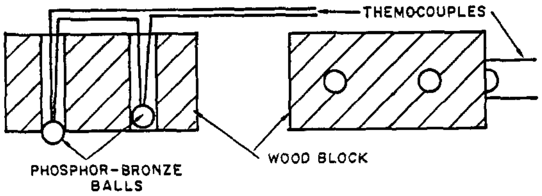

Figure 6.—Powell comparator.

thermocouple. A possible source of error might be the varied depths that the probe is inserted in the sample and the variable amount of sample to probe contact between samples.

The thermal conductivity is obtained by placing the appropriate measured values in the following equation

$$K = \frac{Q}{4\pi} \frac{\ln\left(\frac{t_2}{t_1}\right)}{\theta_2 - \theta_1} \qquad \text{(Eq 7)}$$

where K = thermal conductivity, Q = heat input per unit length per unit time, t_1 = time of measurement initiation, t_2 = time of measurement completion, θ_1 = temperature of probe at t_1, and θ_2 = temperature of probe at t_2.

The heat input can be obtained by measurement of the amount of watts of electricity used. The temperature rise is measured by the thermocouple in the probe.

D. POWELL COMPARATOR (5, 34)

Like the thermal conductivity probe, the Powell comparator is also a nonsteady-state method of measuring thermal conductivity. It requires a set of standards to obtain comparative thermal conductivities. However, the test is very rapid and can be obtained on almost any size or shape samples. The general feature of the comparator can be seen in Figure 6.

The wood block with its two balls, one contained and one exposed, and the attached thermocouples are equilibrated at some elevated temperature. The block is then immediately placed on the sample to be tested. After 10 sec, the temperature difference between the exposed and unexposed balls is read in microvolts from the potentiometer. The microvolt reading, when matched to a plot of thermal conductivity *vs.* microvolts for a group of several similar standards, yields the thermal conductivity. Possibilities for error in this method may arise from surface roughness, ball size, sample hardness, and lack of similarity of standards.

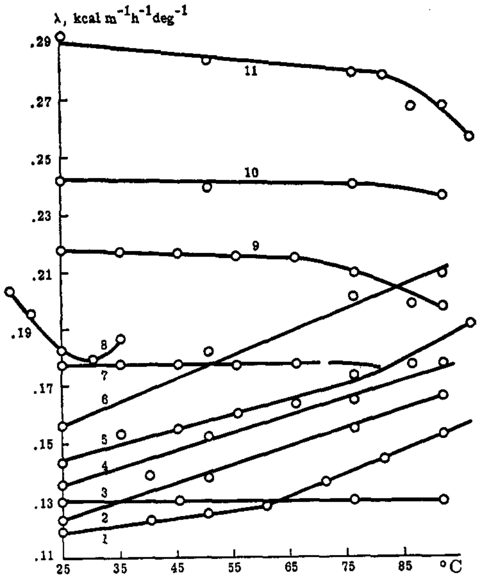

Figure 7.—Variation of thermal conductivity of polymers with temperature (6).

E. OTHER METHODS (7, 8, 10, 40)

Although there are many other methods of measuring thermal conductivity, these usually have been constructed to measure the conductivity of a certain specimen or specimens (very specific) and therefore will not be discussed in this paper.

IV. THERMOPLASTICS

A. MOLECULAR STRUCTURE AND ORDER

Several researchers (12, 13) have pointed out that the thermal conductivity of amorphous substances changes with temperature in a manner different from thermal conductivity of crystalline substances.

Theoretically, the thermal conductivity of amorphous substances below their T_g should remain the same or increase as temperature increases, whereas the conductivity of crystalline substances should decrease or remain the same as temperature increases. This generalization can be seen from Figure 7 where the top five lines, 7–11, are for crystalline materials and 1–6 are amorphous ones. The different conductivities have been explained in the case of amorphous polymers by an increased segmental mobility in the polymer chains. Other factors such as a reduction in density could offset this trend. In the case of crystalline

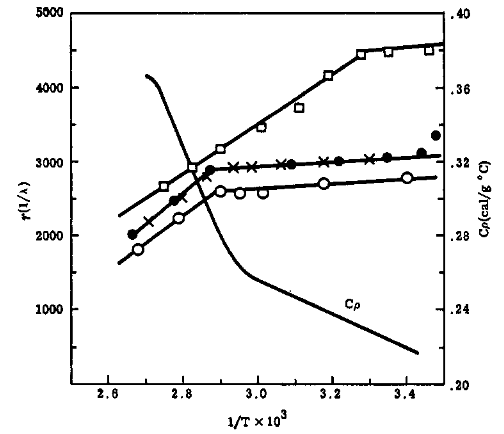

Figure 8.—Thermal resistivity of polyvinyl chloride and vinyl chloride–acetate copolymer and specific heat of polyvinyl chloride (21): ×, PVC-I; ○; PVC-II; ●, PVC-III; □, PVC-IV.

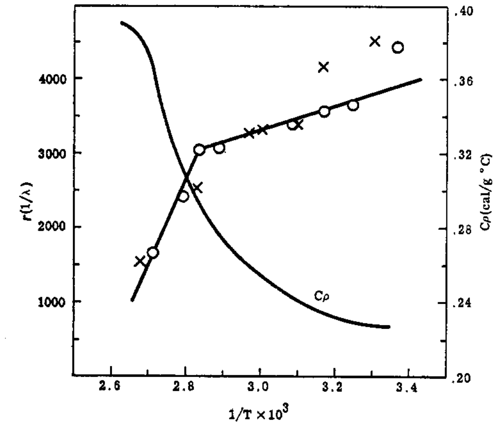

Figure 9.—Thermal resistivity and specific heat of polystyrene (21): ○, PS-I; ×, PS-II.

polymers the decrease in conductivity is due to decrease and breakup of the crystalline portions of the polymer after which the conductivity of the amorphous polymer should increase. Other workers (25a, 27a, 37a) have found that with some amorphous polymers decreases in conductivity with increased temperature are observed. These occurrences, contrary to the theory, usually are due to measurements made above the glass transitions (large volume and density changes) or other transitions which break the smooth conductivity curves. In these areas the volume must increase and decrease the thermal conductivity faster than the increased segmental motion increases it.

Ueberreiter (42) estimated the thermal conductivity of fractionated polystyrene samples by measuring specific heat, specific volume, and thermal diffusivity. Pasquine (32a) found that the thermal conductivity *vs.* temperature curve of commercial polystyrene changed abruptly at the glass transition temperature. Hattori (21) showed in Figures 8 and 9 that thermal resistivity of the polymers increased with $1/T$, as for glasses, up to the glass transition temperatures. At this point, there was an abrupt change in the resistivity.

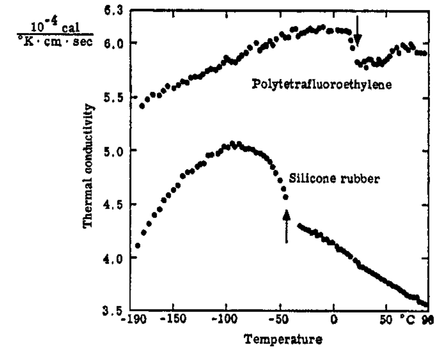

Figure 10.—Thermal conductivity of polytetrafluoroethylene and silicone rubber (11).

Table II shows compositions of the polymers in Figures 8 and 9. For polyvinyl chloride the change is near 70°, with the exception of the 85:15 copolymer, and for polystyrene it occurs at 80°. The specific heat curves are also shown in the figures for polyvinyl chloride and styrene (Figures 8 and 9). A standard method of obtaining the glass transition temperature (T_g), *i.e.*, a discontinuous change of slope in the specific heat curves also shown in Figures 8 and 9, places the T_g at approximately the same temperature as the break in the $r - 1/T$ curves. Hattori (21) states that "the T_g temperature may be considered as the temperature at which micro-Brownian motion of polymer molecules is excited. Assuming then that each polymer has a constant mean free path over the range of temperatures of the measurement, the discontinuous change of conductivity at the T_g could be attributed to the additive effect of the increase of inner mobility of the polymer chain molecules resulting from the excitation of micro-Brownian motion." According to this process the thermal conductivity is lowered; thus, the weak increase of the thermal conductivity with increased temperature is more than compensated for above the T_g (38). In partially crystalline materials, however, no uniform behavior is found.

First-order transitions cause a break in the thermal conductivity curve. Figure 10 shows the melting of the crystalline part of silicone rubber at approximately −50°. In polytetrafluoroethylene (Figure 10) a lat-

Table II (21)
Test Specimens

Sample	Polymer	Degree of polymerization
PE-I	Polyethylene	MW 21,000
PE-II	Polyethylene	
PE-III	Polyethylene	MW 70,000–80,000
PE-IV	Polyethylene	
PVC-I	Polyvinyl chloride	1,000
PVC-II	Polyvinyl chloride	1,300
PVC-III	Copolymer, *ca.* 95:5	1,500
PVC-IV	Copolymer, *ca.* 85:15	800
PS-I	Polystyrene	770
PS-II	Polystyrene	1,000

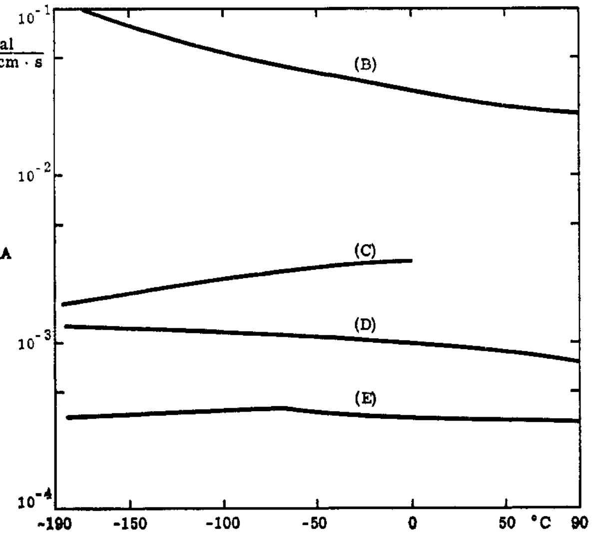

Figure 11.—Heat conductivity of nonmetallic solids (10): A, heat conductivity; B, quartz crystal; C, quartz glass; D, low-pressure polyethylene; E, natural rubber.

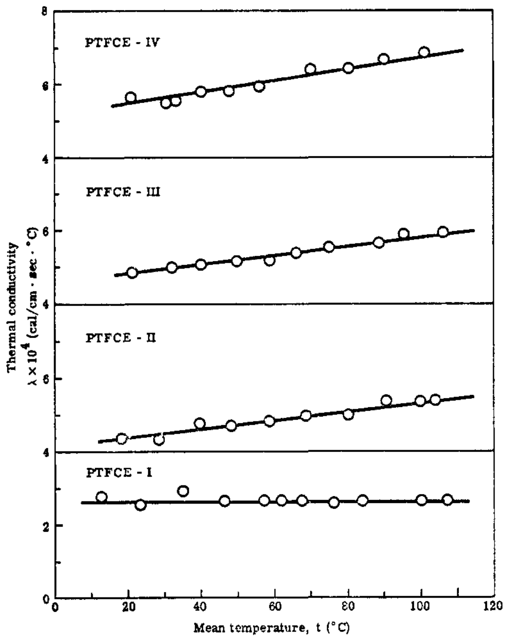

Figure 12.—Thermal conductivity of polytrifluorochloroethylene (22).

tice transformation of the crystalline part and the corresponding break in the thermal conductivity occur at 20°.

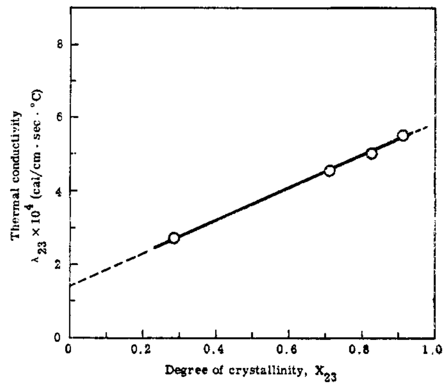

Figure 13.—Relation between thermal conductivity and degree of crystallinity of polytrifluorochloroethylene at 23° (22).

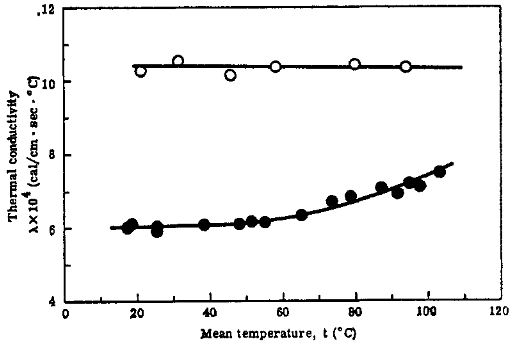

Figure 14.—Thermal conductivity of polytetrafluoroethylene: ●, PTFE-1 (quenched); ○, PTFE-II (annealed) (22).

Although in a real crystal the mean free path is limited by various imperfections which cause scattering of the phonons, in an ideal crystal lattice the mean free path is infinite. These imperfections, which decrease the symmetry or order, lower the thermal conductivity of the sample. Since amorphous substances have a more disordered structure than partially crystalline ones, amorphous substances would be expected to have lower conductivities. That thermal conductivity decreases as disorder increases can be seen in Figure 11. Quartz crystal (B) has a higher conductivity and order than quartz glass (C). Low-pressure polyethylene (D), though it is partially crystalline, has yet a lower conductivity due to the replacement of some of the primary bonds by secondary ones. Natural rubber (E) has the lowest conductivity and also the highest amount of disorder.

In partially crystalline polymers of like structure, a good comparison of the amount of order or crystallinity between samples is the comparison of densities: the higher the crystallinity, the higher the density and also the higher the thermal conductivity. Data obtained by Hattori (22) on polytrifluorochloroethylene (Figures 12, 13, and 14, and Table III) illustrate this correlation.

Table III
Density and Degree of Crystallinity of Polytrifluorochloroethylene Specimens (23)

Specimen	Density, g/cm³	Degree of crystallinity[a]
PTFCE-I	2.116	0.286
PTFCE-II	2.140	0.716
PTFCE-III	2.147	0.841
PTFCE-IV	2.151	0.913

[a] Fraction of the bulk polymer which is in the crystalline form.

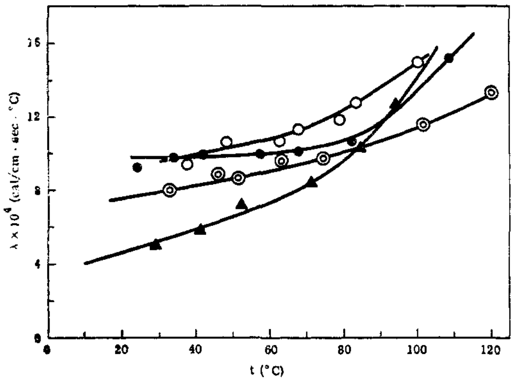

Figure 15.—Thermal conductivity of polythylene (21): ▲, PE-I; ●, PE-II; ◎, PE-III; ⊖, PE-IV.

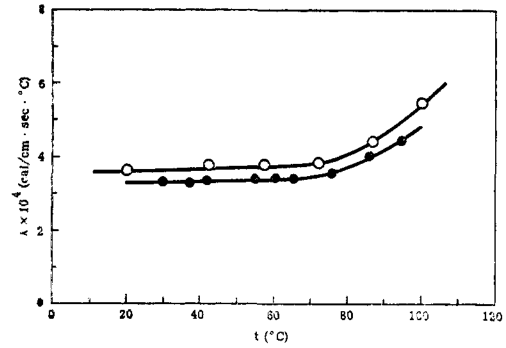

Figure 16.—Thermal conductivity of polyvinyl chloride (21): ●, PVC-I; O, PVC-II.

The probable effect of increasing the size of any substituent connected to a hydrocarbon chain or to any polymer backbone is increased disorder and, thus, decreased conductivity, according to data obtained by Hattori (21) (Figures 15, 16, and 17). Polyethylene, which contains only hydrogen as the substituent and has a strong tendency to crystallize, has a much higher conductivity ($\approx 8 \times 10^{-4}$ cal/cm sec deg) than either polyvinyl chloride ($\approx 3.5 \times 10^{-4}$ cal/cm sec deg) or polystyrene ($\approx 2.7 \times 10^{-4}$ cal/cm sec deg). Going from chloride in polyvinyl chloride to phenyl in polystyrene, the size of the bulky group, and thus disorder, increases and thermal conductivity decreases. X-Ray diffraction data indicate that polystyrene has an irregularly folded structure with almost no evidence of crystallinity. However, it seems that even in amorphous substances with highly disordered structures, the geometrical factors or the regularity of the structural aggregate are still important in affecting the conduction of heat. Furthermore, conductivity and order are both decreased as two or more different groups are placed along the backbone of a polymer molecule. This decrease is shown in Figure 18 for the copolymers of vinyl acetate–vinyl chloride. For the exact composition of each copolymer, see Table II.

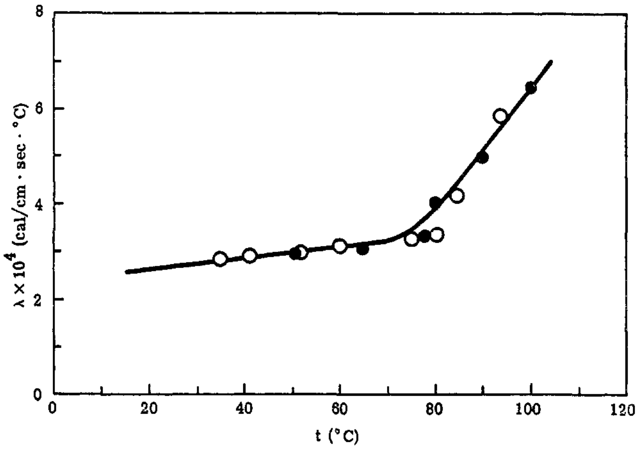

Figure 17.—Thermal conductivity of polystyrene (21): ●, PS-I; O, PS-II.

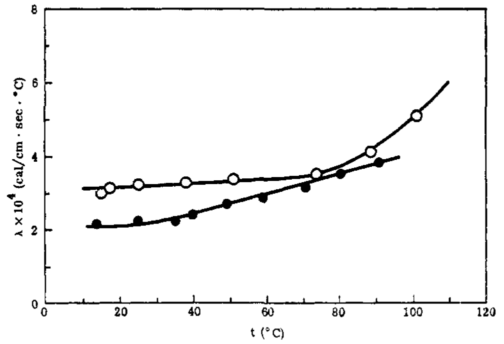

Figure 18.—Thermal conductivity of vinyl chloride–acetate copolymer (21): O, PVC-III; ●, PVC-IV.

Hattori (20, 21) states that "since the conductivity along the main chain is higher than that between chains, it is expected that a polymer having higher molecular weight will have higher conductivity values." Eiermann's (10) experiment on the thermal conductivity of stretched amorphous polymers discussed below furnishes proof of this.

According to Ueberreiter (42, 44) the thermal conductivity of a polymer with short chains is smaller than one with long chains, apparently because a larger number of energy transactions must take place between molecules in a substance with shorter chains. Figures 16 and 17, however, show that for amorphous polymers, a change in thermal conductivity with chain length is not appreciable. For polyethylene (Figure 15) the observed variation in thermal conductivity could be due to the differences in degree of crystallization with molecular weight. More recently, Hansen (18) has observed a linear dependence of thermal conductivity on the $^1/_2$ power of the weight-average molecular weight for molten linear polyethylene. This relationship does not hold true above molecular weights of 100,000.

B. STRETCHING

In an attempt to increase order and conductivity in an amorphous polymer, Eiermann (10) attempted

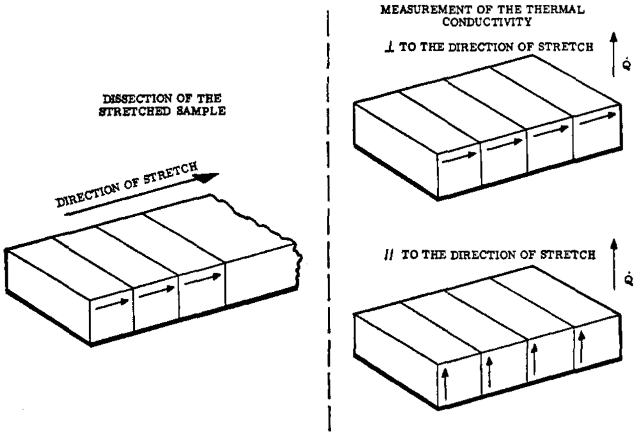

Figure 19.—Measurement of the thermal conductivity of stretched samples (11).

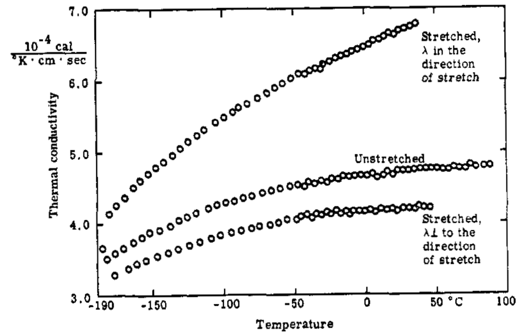

Figure 20.—Thermal conductivity of polymethyl methacrylate: unstretched and stretched to 375% (11).

to make measurements on a stretched polymer. Conductivity measurements were made parallel and perpendicular to the direction of stress. Anisotropy of the thermal conductivity was found as Figures 19 and 20 indicate. It was found from the experiment that the thermal conductivity of the stretched polymethyl methacrylate increased in the direction of stretch, whereas it decreased perpendicular to the direction of stretch. Pasquine (32a) also found a decrease in conductivity perpendicular to the direction of orientation for polystyrene. Eiermann (10) also states that "the increase in heat conductivity in the stretch direction cannot be due to crystallization because in this case the heat conductivity would also increase perpendicular to the direction of stretch." Apparently thermal energy is transported more easily along the main chain valences than along secondary valences and van der Waals bindings.

V. Rubbers

A. MOLECULAR STRUCTURES AND ORIENTATION (36)

Mueller (31) has suggested that thermal conductivity is related to the strength of the interatomic binding forces; *e.g.*, the great strength of this binding force in metals is supposed to account for high thermal conductivity, while the relative weakness of this binding force in organic polymers accounts for correspondingly low thermal conductivities. This weakness also accounts for asymmetry which will be discussed later. Also on the basis of binding forces, Mueller says that "a polymer should resemble an organic liquid rather than a solid." Rubberlike and liquid materials do have much in common: similarity of X-ray patterns, changeability of shapes under small deforming forces, and mobility of atoms in molecules. From these and other data came the proposal that a rubber be regarded as a "solid in one direction and a liquid in the other two dimensions" (29). Rehner (35) states that "the crux of this analogy (rubberlike liquid) lies in determining whether properties of rubberlike substances are describable by laws known to hold for liquids." Rehner then attempts to determine if they do compare by studying sound velocity in rubbers using equations derived and used for the study of liquids such as the equation below.

$$K_{\text{liq}} = 0.931\left(\frac{C_v}{C_p}\right)^{1/2} 3k_B\left(\frac{N}{V}\right)^{2/3} V \qquad \text{(Eq 8)}$$

where K = thermal conductivity, C_v and C_p = specific heats, k_B = Boltzmann constant, N/V = number of molecules/cc, and V = velocity of sound in liquid.

Since several of the needed parameters were not obtainable experimentally, *i.e.*, C_p and coefficient of compressibility, these were calculated for four rubbers. Resulting velocities of sound are shown in Table IV.

Equation 8 was found by Rehner to be inapplicable to the rubbers studied.

Several important points on molecular structure are indicated in Table IV. In the fifth column, the correction for rotational energy included in C_p for polyisobutylene at the Debye temperature is almost zero, indicating a very stiff molecule. Correlation has also been pointed out by several other investigators (15, 16). Since the corrections for Hycar-OR and natural rubber are roughly equal, the two polymers must be quite alike with respect to their rotational freedoms. Thus vinyl and nitrile groups are about the same size as the methyl group and have similar rotational properties. Compressibility data in column six indicate that as the amount of methyl substitution along the backbone is increased the compressibility is decreased; thus, the repulsion between substituent groups must be directly related to freedom of rotation.

B. STRETCHING

Dauphinee (7, 8) measured thermal conductivities perpendicular to the direction of stretch on two rubbers, natural and GR-S. The outstanding feature of the thermal conductivity of natural rubber is its double nature (Figures 21 and 22). In both Figures 21 and 22 the upper line appears to be continuous

TABLE IV

THERMAL AND MECHANICAL PROPERTIES OF RUBBERLIKE POLYMERS (35)

Polymer	Characteristic Debye temp, °K	Specific heat at 300°K, cal/g		Specific heat correction for rotation, cal/g	Coefficient of compressibility × 10^4, cm²/kg	Density at 300°K, g/cm³	Thermal diffusivity × 10^3 at 300°K, cm²/sec	Velocity of sound, m/sec		
		C_p	C_v					From equation	From mechanics[a]	Experimental[b]
Polyisobutylene	500	0.470	0.268	0.00	13.0	0.91	1.1	16.000 19,000[c]	2900	
Hycar-OR	1050	0.473	0.360	0.0464	9.6	1.00	1.3	16,600	3230	
Natural rubber	1000	0.452	0.386	0.0406	53.7	0.906	1.2	15,800	1430	37
Methyl rubber W	650	0.47	0.355	0.039	34.8	0.913				

[a] For a compression wave in an infinite medium. [b] For a longitudinal wave in a finite bar. [c] Corresponding to the assumption of completely free and completely hindered rotation, respectively.

throughout the whole range; the lower part of the graphs, however, consists of two sections, one for temperatures below and one for temperatures above −60°. Below −70°, for all degrees of stretch, the points occur about halfway between the upper and lower curves. Dauphinee (8) states "that it seems probable that these points represent the average conductivity when one of the paired samples is in the state corresponding to the upper curve and the other sample in the state corresponding to the lower curve." The degree of stretch, however, did not seem to change the thermal conductivity (32), *i.e.*, 0%, 3.5; 50%, 3.7; and 100%, 3.7. The outstanding feature observed with the GR-S rubber is the complete hysteresis loop that appears in the region of the second-order transition (Figure 23). The conductivity of both GR-S and natural rubbers at 0% stretch lies in the range of 3.5–4.0 × 10^{-4} cal/cm sec deg. With both rubbers, stretching increases the rate of change of conductivity with temperature; however, here the similarity ends. Whereas thermal conductivity of natural rubber remains constant with stretch, thermal conductivity of GR-S rubber decreases under all cure conditions. At some temperatures the decrease is as much as 50%.

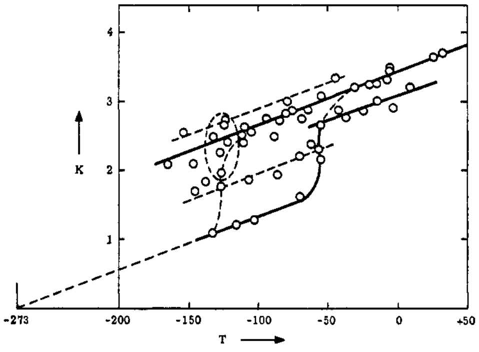

Figure 21.—Natural rubber, unstretched (8).

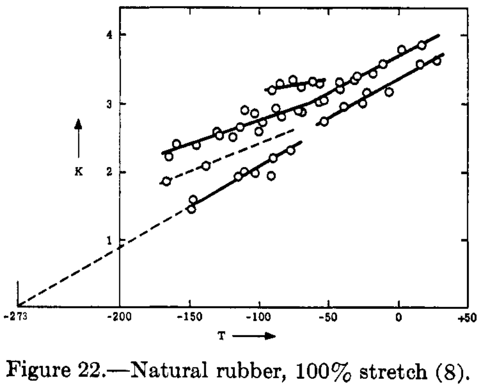

Figure 22.—Natural rubber, 100% stretch (8).

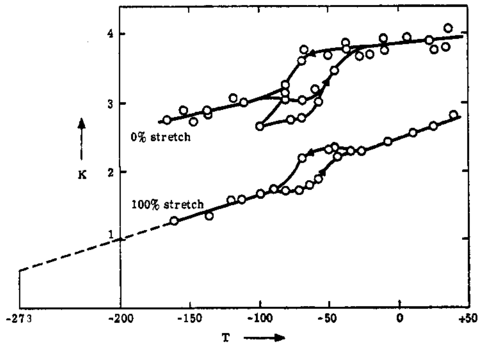

Figure 23.—GR-S, optimum cure, 0 and 100% stretch (8).

Tantz (40), on the other hand, measured the change of thermal conductivity with stretch on a number of rubber vulcanizates parallel to the direction of stretch. In all materials (Figure 24) investigated, a consider-

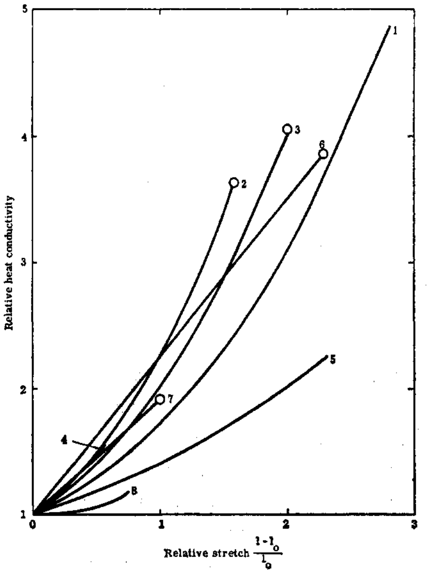

Figure 24.—Behavior of thermal conductivity (with reference to the conductivity of the nonelongated sample), as a function of elongation (40).

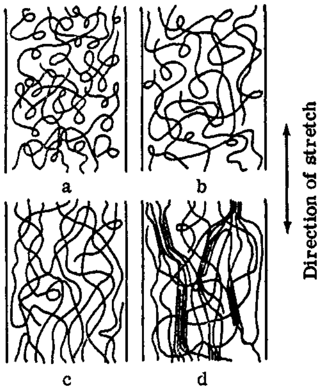

Figure 25.—Arrangement of filament molecules in an elongated high polymer (strongly schematic) (40): (a) without elongation; (b–d) showing increasing elongation.

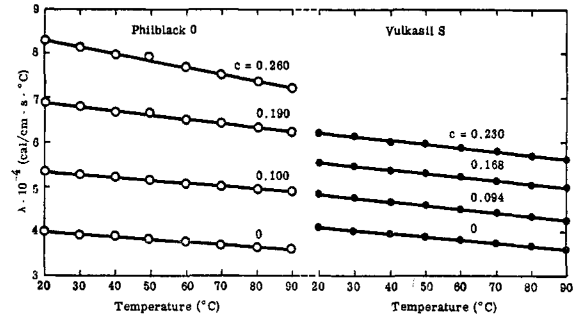

Figure 26.—Temperature dependence of the thermal conductivity in slightly cross-linked (polymerized) natural rubber with various fillers (parameter *C*: filler in volume per cent) (37).

able increase in the thermal conductivity with elongation was observed. With strongly vulcanized rubber, the increase was least while with polybutylenes the increase was greatest. Natural rubber lies in between. Mueller (32) found, however, that natural and silicone rubbers when stretched show little anisotropic heat conductivity.

Tantz (40) indicates that the rise in thermal conductivity is to be ascribed to a more pronounced orientation of molecular chain segments in the elongation direction (also the direction of thermal flow). A secondary cause of the increased heat conductivity can be found in a decreasing number of diffusion or scattering centers for the thermal waves. This phenomenon is shown schematically by Figure 25.

The second-order transition T_g in natural or GR-S rubber observed by Bekkedahl (3) in his specific heat measurements shows great similarity to the hysteresis loops found *via* thermal conductivity. It has been suggested (27) that the second-order transition in elastomers may actually be the result of a series of λ points spread over a considerable temperature range because of the great diversity in size of the molecular segments. The increase in C_p where these transitions begin would be maintained afterward by the continuous absorption of energy as each successive length reached

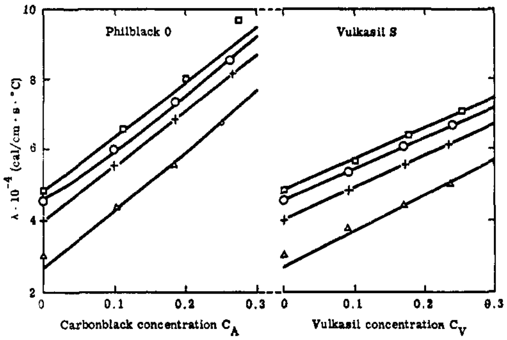

Figure 27.—The thermal conductivity of various elastomers as a function of the filler concentration (volume per cent) at 20° (37): □, Perbunan N2810; ○, Buna Hüls 152; +, natural rubber; △, Enjay Butyl 365.

its λ point. This idea may explain the fact that though the changes in specific heat and thermal conductivity begin at the same temperature, the thermal conductivity is over a much wider range. The specific heat variation would be a function of the number of segments undergoing transitions, while variation of the conductivity could be a function of the total number of segments that have undergone transitions and thus would extend over a wider temperature range.

C. FILLER (4, 30, 39)

In all cases of the addition of fillers to rubbers the thermal conductivity is increased; however, the increase varies with the filler used (Figure 26). For a given filler and rubber, however, there is a straight-line relationship between the plotted thermal conductivity and the filler concentration (Figure 27).

In rubbers the greater the sulfur content the greater is the maximum intensity of the thermal effects (47). Carwile (5a) has compiled a list of selected thermal conductivity values for soft vulcanized natural rubber covering the above subtopics. The information is in agreement with that discussed for other rubbers.

VI. THERMOSETS

A. CELLULAR MATERIALS

The apparent thermal conductivity of cellular materials is the sum of heat transfer by conduction, convection, and radiation. Conduction is the transfer of heat energy due to microscopic molecular motion and vibrations in the solid and gas. In high molecular weight molecules, the energy is transferred by movement of parts of the large molecule, possibly by oscillation. The convection is the transfer of heat energy by a mass transfer of more energetic molecules and is limited to mobile molecules such as gases and liquids. Radiation is the transfer of energy between two points at different temperatures by means of massless particles, called photons. Radiation is only important when the cell walls of the material are very thin.

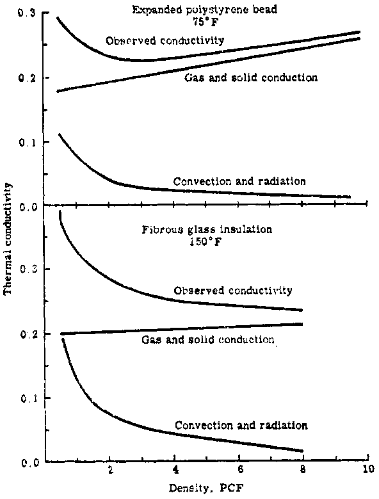

Figure 28.—Contribution of convection and radiation to thermal conductivity.

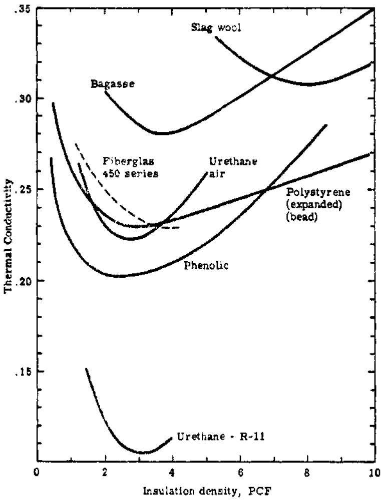

Figure 29.—Thermal conductivity of insulations *vs.* density (17).

Vershoor and Greebels (45) showed that the contribution of radiation and convection to the apparent thermal conductivity of a porous material becomes appreciable at density below 2 lb/ft.^{3} At a density of 0.5 lb/ft^3, radiation contributed 32% and convection 15% of the observed conductivity (Figure 28).

The relationship between apparent thermal conductivity and density for a number of materials is presented in Figure 29. All foam insulation materials show a minimum point in the thermal conductivity curve at some density, unlike the straight or gradually curved lines found in solids. The increase in thermal conductivity at lower densities must be due to factors other than conduction through the solid or gas structure. Harding (19) states "Surface chemistry predicts that the cells of low density foams should be regular dodecahedral. Microscopic studies indicate that this polyhedral structure is approximated in practice but the cells are elongated in the direction of the foam rise."

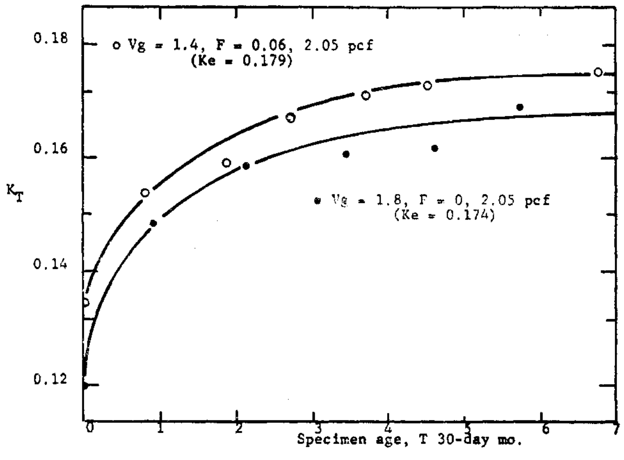

Figure 30.—Parallel K_1-T correlation *vs.* experiment.

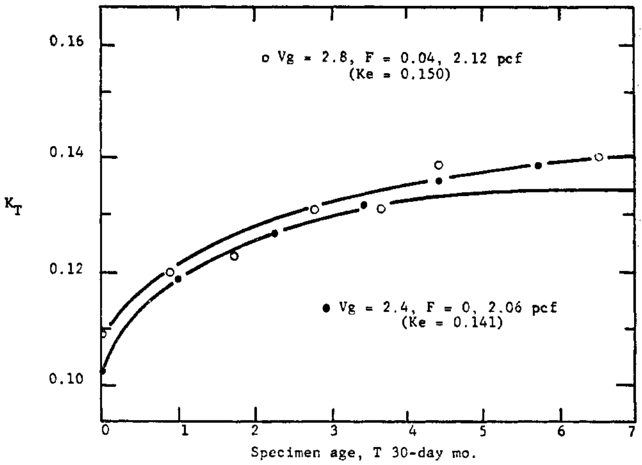

Figure 31.—Perpendicular K_1-T correlation *vs.* experiment.

This cell elongation is an important consideration in thermal conductivity measurements as shown by Figures 30 and 31. Heat passage in the direction perpendicular to the rise of the molded foam was about 20% less than in the parallel orientation. The extent of difference in other foams, however, will be a function of mold dimensions, cell size, and manufacturing technology. Harding (19) also states that "thermal conductivities were independent of foam density, except as chemistry affected cell structure." Data are presented for the conductivity of polystyrene foam at a density of 1.5 lb/ft^3 over the cell size range of 0.0037 to 0.18 in Table V.

Figure 32 shows that thermal conductivity decreases with cell size (28) because there are more heat flow barriers per unit thickness, and thus the heat transfer due to gaseous convection is decreased. Equation 9 (17), which is a modification of the Topper equation (41)

$$K_f = K_g + \frac{(D_f - D_g)}{(D_s - D_g)} (K_s - K_g) + 1.2C \qquad \text{(Eq 9)}$$

[where K_g, K_s, K_f = thermal conductivity (BTU, in./

Table V
Effct of Cell Size on Thermal Conductivity of Polystyrene Foam at 70°F (17)

Type of sample	Density, lb/ft³	Cell size, in.	Thermal conductivity
Extruded foam^a	1.5	0.18	0.45
Extruded foam^a	1.61	0.046	0.28
Extruded foam^a	1.52	0.040	0.325
Extruded foam^a	1.5	0.039	0.284
Extruded foam^a	1.7	0.023	0.275
Extruded foam^a	1.54	0.012	0.251
Expanded bead	1.37	0.012	0.252
Expanded bead	1.37	0.0061	0.239
Expanded bean	1.61	0.0037	0.243

[a] Styrofoam–Trademark Dow Chemical Co.

hr ft² °F) of gas, solid, cellular material; D_g, D_s, D_f = density (lb/ft³) of gas, solid, cellular material; C = cell size in inches] points out the importance of knowing the starting gas composition and cell size when reporting thermal conductivities of cellular materials, since density, and thus conduction of a gas, is proportional to molecular weight (Figure 34).

Since a unit of heat might travel three times as far crossing a polyhedral cell through its polymer envelope as it would travel crossing the enclosed gas, the conductivity of the gas becomes of great importance. A 100% difference may exist between the conductivity of closed cell and open-celled foams (Figure 33). Thus the best insulating properties are obtained from the foam with the most closed cells. Therefore, the relation of the molecular weight and the thermal conductivity of gases used for blowing agents should be studied (Figure 34). The larger the molecule (higher molecular weight), the lower the thermal conductivity of the gas. Thus, to decrease the conductivity of the foam to a minimum, gaseous blowing agents with the highest possible molecular weights should be used. Although this relationship (increasing conductivity to decreasing molecular weight) has been known for a long time, only recently has its importance become sufficient to warrant overcoming the difficulty of using the higher molecular weight gases.

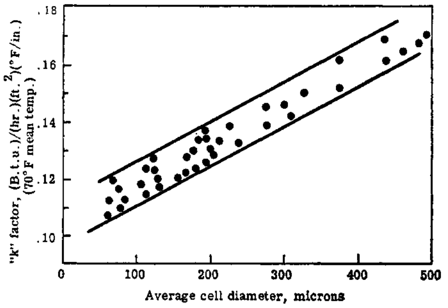

Figure 32.—Effect of cell size on "k" factor of fluorocarbon-expanded urethane foam (26).

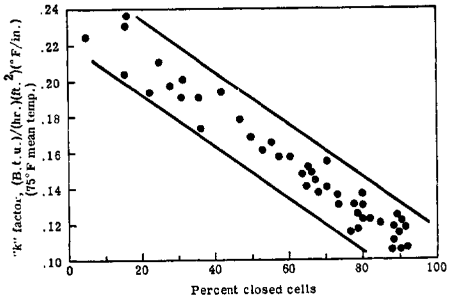

Figure 33.—Effect of closed cells on "k" factor of fluorocarbon-expanded rigid urethane foam (26).

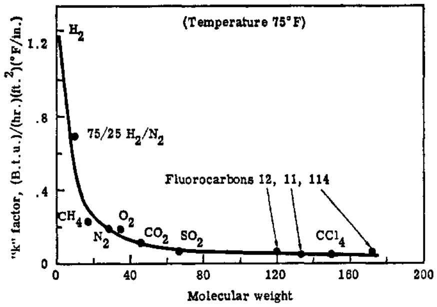

Figure 34.—Thermal conductivity of gases as a function of molecular weight (26).

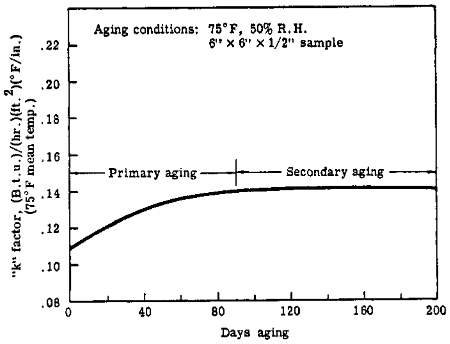

Figure 35.—Aging of cut surface fluorocarbon-expanded rigid urethane foam (26).

The difference between foams of similar density but different gaseous components can be seen in Figure 29. The urethane containing air is more than twice as thermally conductive as the one containing R-11 (a Freon, CCl_3F).

B. AGING OF CELLULAR MATERIALS (2)

Aging of a foam seems to relate mostly to what happens to the gas within the cells rather than to the polymer matrix. Since the insulating qualities of a foam are due to encapsulation and containment of the entrapped gas under all conditions, an air-blown foam should not show any appreciable change.

Figure 35 shows the two typical stages of aging, primary and secondary, which occur on a cut foam filled (blown) with a low-thermal-conducting gas. Primary aging is due to air diffusion into the foam cells until equilibrium conditions are established. With thin samples prepared for thermal conductivity measurements from a urethane blown with a fluorocarbon gas,

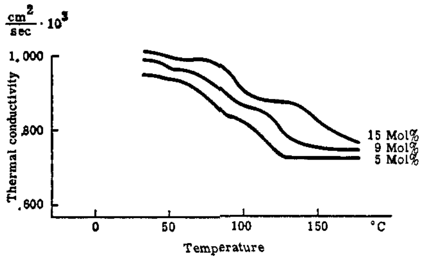

Figure 36.—Temperature conductivity *a* of polystyrenes with 5, 9, and 15 mole % divinylbenzene (43).

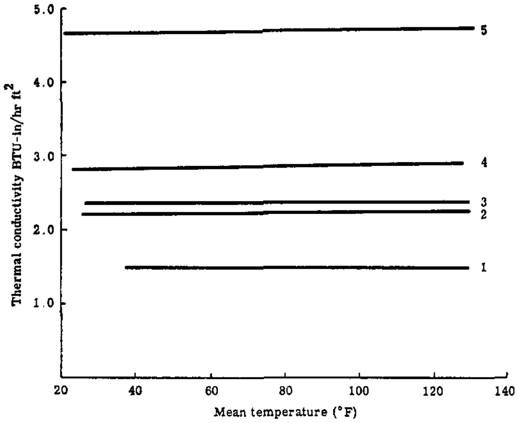

Figure 37.—Thermal conductivity of epoxy resins: 1, 89.3% Shell 828, 10.7% dicthand amine (DEA); 2, 71.4% Shell 828, 8.6% DEA, 20.0% mica filler; 3, 69.6% Shell 828, 8.4% DEA, 22.0% mica; 4, 62.5% Shell 828, 7.5% DEA, 30.0% mica; 5, 44.6% Shell 828, 5.4% DEA, 50.0% mica.

this equilibrium is reached within 70–100 days (26). The thermal conductivity is generally increased 30 to 35%. Secondary aging occurs slowly and is due to gradual loss of the gaseous component from the foam cells.

As would be expected, the higher the closed cell content and the smaller the cell size, the lower the thermal conductivity because of the larger amount of gas trapped and the greater number of barriers which stop convection and diffusion of the gas.

C. SOLIDS

Very little data have been published on solid thermosets. Ueberreiter (42–44) measured the thermal conductivity of polystyrene with three different amounts of divinylbenzene to study the influence of cross linking (Figure 36). He found three breaks in the thermal conductivity *vs.* temperature curve for all concentrations of divinylbenzene (cross links). These breaks are attributed to the following: first, Δa_3, the principal network material with a mesh spacing which corresponds approximately to the stoichiometric composition of the monomer mixture; second, Δa_2, a wide-spaced secondary network of quantitatively small extension; and third, Δa_1, the network fringes. The greater the number of cross links, the higher was the thermal conductivity for the polystyrene divinyl benzene copolymers.

Janssen (24) and Evans and Palanys (15) found that attempts to increase the cross linking of an epoxy resin by post cure, or by γ radiation up to 10^8 roentgens, only increased the conductivity from the "as-cast" condition by 5%. Janssen also found, as others have (25, 37), that thermal conductivity can be increased several times through the choice of filler (Figure 37).

ACKNOWLEDGMENT.—This work was supported by the United States Atomic Energy Commission. Reproduction in whole or in part is permitted for any purpose of the U. S. Government.

VII. REFERENCES

(1) Am. Soc. Testing Mater., *ASTM Std.*, C 177-63, Part 14, 15–26 (1965).
(2) Barringer, C. M., U. S. Patent 3,080,329 (1963).
(3) Bekkedahl, N., *J. Res. Natl. Bur. Std.*, **13**, 411 (1934).
(4) Bunish, S., and Witthoft, H. C., U. S. Patent 2,558,929 (1951).
(5) Carlson, H. S., and Jaeger, J. C., "Conduction of Heat in Solids," Clarendon Press, Oxford, 1947, p 345.
(5a) Carwile, L. C. K., and Hoge, H. J., *Symp. Thermophys., Properties, Papers, 3rd, Lafayette, Ind., 1965,* 320 (1965).
(6) Cherkasova, L. N., *Zh. Fiz. Khim.*, **33**, 224 (1959).
(7) Dauphinee, T. M., Ivery, D. G., and Smith, T., *Phys. Rev.*, **71**, 487 (1947).
(8) Dauphinee, T. M., Ivery, D. G., and Smith, H. D., *Can. J. Res.*, **28A**, 596 (1950).
(9) Debye, P., in "Vorträge über die Kinetische Theorie der Materie und Elektrizstät," M. Planck, *et al.*, Ed., B. G. Teubner, Leipzig, 1932.
(10) Eiermann, K., *Kunststoffe*, **51**, No. 9, 512 (1961).
(11) Eiermann, K., and Hellwege, K. H., *J. Polymer Sci.*, **57**, 97 (1962).
(12) Eiermann, K., *Kolloid-Z.*, **180**, 163 (1962).
(13) Euken, A., *Ann. Physik*, (4) **34**, 185 (1911).
(14) Eustachio, D. D., and Schreiver, R. E., *Trans. Am. Soc. Heating Ventilating Engrs.*, 331 (1952).
(15) Evans, A. G., and Palanys, M., *Nature*, **152**, 738 (1943).
(16) Flory, P. J., *J. Am. Chem. Soc.*, **65**, 372 (1943).
(17) Guenther, F. O., *SPE* (Soc. Plastics Engrs.) *Trans.*, **2**, 243 (1962).
(18) Hansen, D., and Ho, C. C., *J. Polymer Sci.*, **A3**, 659 (1965).
(19) Harding, R. H., and James, B. F., *Mod. Plastics*, **39**, No. 17, 133 (1962).
(20) Hattori, M., and Kamiike, O., *Kobunshi Kagaku*, **15**, 285 (1958).
(21) Hattori, M., *Bull. Univ. Osaka Prefect. Ser. A*, **9**, No 1, 51 (1960).
(22) Hattori, M., *Kolloid-Z.*, **185**, 27 (1962).
(23) Hodgman, C. D., "Handbook of Chemistry and Physics," 42nd ed, Chemical Rubber Co., Cleveland, Ohio, 1960, p 3080.
(24) Janssen, J. E., and Torborg, R. H., "A.S.M.E. Thermodynamics and Transport Properties of Gases, Liquids, and Solids," McGraw-Hill Book Co., Inc., New York, N. Y., 1959, pp 284–290.
(25) Kline, D. E., *J. Polymer Sci.*, **50**, 441 (1961).
(25a) Knappe, W., *Kunststoffe*, **51**, 707 (1961).
(26) Knox, R. E., *Am. Soc. Heating, Refrig., Air-Cond. Engrs. J.*, **4**, No. 10, 43 (1962).

(27) Kraemer, E. O., "Advances in Colloid Science," Vol. 2, Interscience Publishers, Inc., New York, N. Y., 1946, p 10.

(27a) Lake, P., *Kolloid-Z.*, **303,** 115 (1965).

(28) Mark, H., *Am. Scientist*, **31,** 97 (1943).

(29) Meyer, K. H., "National and Synthetic High Polymers," Interscience Publishers, Inc., New York, N. Y., 1942, p 159.

(30) Momin, A. N., Shankar, U., and Suryanarayana, N. P., *J. Sci. Ind. Res.* (India), **19A,** 215 (1960).

(31) Mueller, F. H., and Houwink, R., "Chemie und Technologie der Kunststoffe," Vol. I, Akademie-Verlag, Leipzig, 1942, p 226.

(32) Mueller, F. H., and Hellmuth, W., *Kolloid-Z.*, **185,** No. 2, 159 (1962).

(32a) Pasquine, A. D., and Pilsworth, M. N., *Polymer Letters*, **2,** 253 (1964).

(33) Peierls, R., *Ann. Physik*, (5) **3,** 1055 (1929).

(34) Powell, R. W., *J. Sci. Instr.*, **34,** 485 (1957).

(35) Rehner, J., *J. Polymer Sci.*, **2,** 263 (1947).

(36) Rehner, J., *Rubber Chem. Technol.*, **21,** 82 (1948).

(37) Schilling, H., *Kautschuk Gummi*, **16,** 84 (1963).

(37a) Sheldon, R. P., and Lane, K., *Polymer*, **6,** 205 (1965).

(38) Shoulberg, H., and Shetter, J. A., *J. Appl. Polymer Sci.*, **6,** 532 (1962).

(39) Tanaka, J., and Wakae, M., *Rept. Ind. Res. Inst., Osaka Prefect.*, **3,** No. 3, 26 (1951).

(40) Tantz, H., *Kolloid-Z.*, **174,** 128 (1961).

(41) Topper, L., *Ind. Eng. Chem.*, **47,** 1377 (1955).

(42) Ueberreiter, K., and Nens, S., *Kolloid-Z.*, **123,** 92 (1951).

(43) Ueberreiter, K., and Otto-Laupenmühlen, E., *Kolloid-Z.*, **133,** 26 (1953).

(44) Ueberreiter, K., and Otto-Laupenmuhlen, E., *Z. Naturforsch.*, **8A,** 664 (1953).

(45) Vershoor, J. D., and Greebels, P., *Trans. ASME*, **74,** 961 (1952).

(46) Wright, G., private communication.

(47) Zanemonets, N. A., and Fogel, V. O., *Kanchuk i Rezina*, **18,** No. 2, 21 (1959); *Chem. Abstr.*, **53,** 17553*b* (1959).