

The Thermal Diffusivity of Polymer Melts

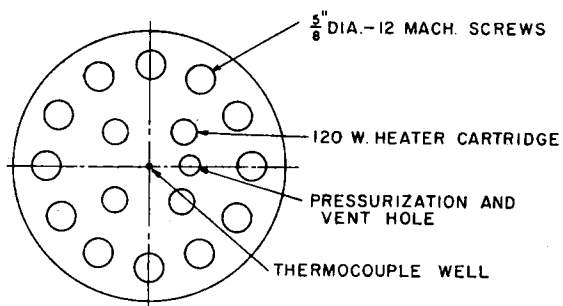
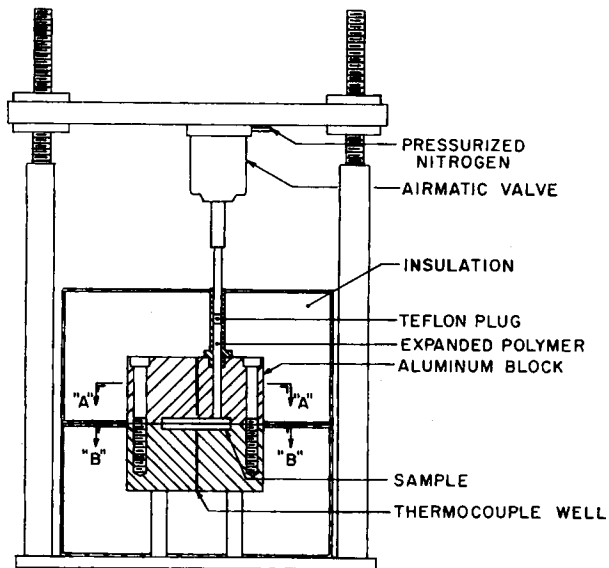
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Introduction

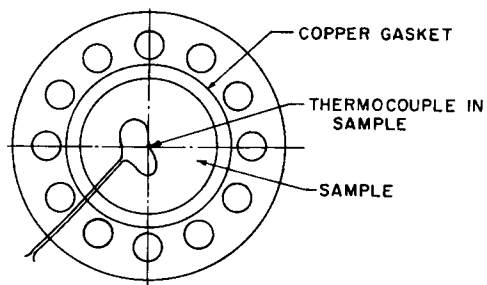
In any transient process which involves the flow of heat in a solid the physical property of the material which governs the time-dependent temperature distribution is the thermal diffusivity, i.e., the ratio of the thermal conductivity k to the product of the specific heat c_p , and the density ρ . The thermal diffusivity plays an important role in determining the cycle time in the injection molding of polymers, for example, and it is also important in annealing. However, the measurement of the thermal diffusivity of polymers has received relatively little attention, and apparently no direct measurements of the diffusivity of polymer melts have been reported. This lack of data probably stems from the fact that many investigators (Chung and Jackson,¹ for example) measure the temperature difference between two points in a solid immersed in a liquid; such methods can be used only as long as the solid retains its form stability. For the study of the thermal diffusivity of melts an apparatus has been constructed in these laboratories which can be used for the direct measurement of diffusivity at temperatures from 25 to ca. 325°C. The method is accurate only when the polymer can be forced by modest pressure to fill completely a cavity into which it fits fairly well as a solid. This generally restricts measurements to temperatures above the glass temperature of amorphous polymers and above the melt temperature of crystalline polymers, although in the case of polymers such as polyethylene the cavity is completely filled, because of thermal expansion, well before the melt temperature is reached. The technique and the results of measurements on a wide variety of thermoplastics are described in the following sections.

Experimental Method

The experimental method is a simple one. Two disks of polymer 3 in. in diameter and $\frac{1}{4}$ in. thick are either molded or machined from sheet and an iron-constantan thermocouple of No. 40 wire is placed between them in shallow grooves on their surfaces. This "wafer" is then placed in a cavity formed in two massive aluminum blocks, as shown in Figure 1, which are bolted securely together. The blocks are heated by eight 120 w. cartridges to a temperature some 20°C. above the glass (or melt) temperature of the polymer. A pressure of about 500 psi is applied to the material by admit-



SECTION A-A



SECTION B-B

Fig. 1. Apparatus for study of thermal diffusivity of melts.

ting nitrogen at low pressure to one side of a piston, the other side of which bears on a $\frac{3}{8}$ in. Teflon-capped steel rod in direct contact with the melt. The combination of thermal expansion and external pressure forces the polymer into excellent contact with the cavity walls. A period of about 15 min. is allowed for thermal equilibrium to be reached between the blocks and the sample, and then a step change in power input is applied to the heaters so that the block temperature rises almost linearly with time (this point is discussed further in Appendix B). By making periodic measurements of the block temperature and of the temperature difference between the block and the center of the disk, information can be obtained from which the thermal diffusivity can be calculated. Normally, the block temperature is raised linearly about 30°C. and then held constant (by reducing the power input) until the sample again comes to uniform temperature. Another step change in power input is then supplied, and another set of measurements is made during another 30°C. rise. After a temperature of ca. 325°C. has been reached in a series of steps the sample is discarded. With materials in which excessive degradation begins or the melt viscosity becomes quite low below 325°C. the test is stopped at a lower temperature.

The data can be treated in two ways. To calculate the diffusivity, one can use the information collected while the temperature difference between the block and the sample is changing rapidly with time, or one can wait until the temperature difference between the block and the center of the sample is essentially constant (when both temperatures are rising at the same rate). The latter calculation is simpler and somewhat more accurate, for reasons discussed more fully in Appendix A, where a complete treatment of the temperature distribution is given. One finds that during the "pseudo steady-state" period, when a constant temperature difference obtains, the thermal diffusivity is given by the equation

$$\kappa = hC^2/[2(\Delta\theta_0)]$$

where h is the rate of temperature rise of the aluminum block, C is the half-thickness of the sample, and $\Delta\theta_0$ is the temperature difference between the block and the center of the sample.

Materials

Most of the polymers examined are commercially available molding materials: the acrylics Plexiglas V-461 and Plexiglas VS-100 (Rohm & Haas), the rubber-modified acrylics Implex A and Implex R (Rohm & Haas), the styrenes Styron 683 and Styron 700 (Dow Chemical), the styrene-methyl methacrylate copolymer Zerlon 150 (Dow Chemical), the ABS material Cyclac T-1000 (Marbon Chemical), the styrene-acrylonitrile copolymer Bakelite C-11 (Union Carbide Plastics), the cellulose acetate butyrates Tenite H-3 and Tenite MH (Eastman Chemical Products) the polycarbonate Lexan (General Electric), the polyacetal Delrin (E. I. du Pont de

Nemours). All these materials were obtained as pellets; they were pre-dried, injection molded as disks, and stored over Drierite until used.

In addition to the injection-molded samples, five cast and one compression-molded material were tested. Geon 103 EP poly(vinyl chloride) (Goodrich Chemical), to which was added 2 parts per hundred of Advastab T-360 stabilizer (Advance Chemical), was milled into 0.050 in. sheets which were subsequently compression molded into $\frac{1}{4}$ in. sheets and then machined into disks. A cast sheet of Plexiglas II UVA, a cast sheet of polystyrene (Cast Optics), and three bulk-cast polymers—poly(isopropyl methacrylate), poly(*sec*-butyl methacrylate), and a 50 : 50 copolymer of methyl methacrylate and ethyl acrylate—were machined into disks and stored over Drierite.

The use of a large number of commercial polymers, in many cases not well characterized, might seem ill advised for an investigation of a basic material property. However, to anticipate a later discussion it should be noted that it became apparent quite early in the investigation that small differences in composition or molecular weight seemed to have no significant effect on the measured diffusivities of the melt. For this reason it was felt that commercial samples were suitable for the purpose of this work.

Results and Comparisons with Other Work

The data collected in these laboratories are presented in the following section. Where possible, they are compared with other results. Unfortunately, the comparisons with directly measured diffusivities are not abundant, and in some cases the data are given but not how they were obtained.² Although the diffusivity can be calculated from the thermal conductivity, specific heat, and density, it is almost impossible to find such data for the one material over a wide temperature range. Moreover, the calculated result suffers from a combination of the errors of its constituent parts. On the whole, it can probably be said that the comparisons with the better documented information serve to demonstrate the validity of the results obtained in the present work.

A few words are in order concerning the method of presentation. The figures have been labeled generically, i.e., Plexiglas and Lucite molding powders have been individually indicated as data points but all are placed on a plot for "poly(methyl methacrylates)," although it is known that small amounts of additives are present. Different specimens of a given material have been separately indicated by the use of distinctive symbols, because it is felt that this helps the reader to better assess the precision of the results. The precision is estimated as about 7% for reasons described in Appendix B.

Figure 2 shows the results of measurements on two samples of Plexiglas V-461 (red), three samples of Plexiglas VS-100 (clear) molding powder, and one sample of Plexiglas II UVA, with comparisons from the literature. Where they can be compared, the data are in good agreement with results for Lucite 140 molding power.² The thermal diffusivity shows a relatively

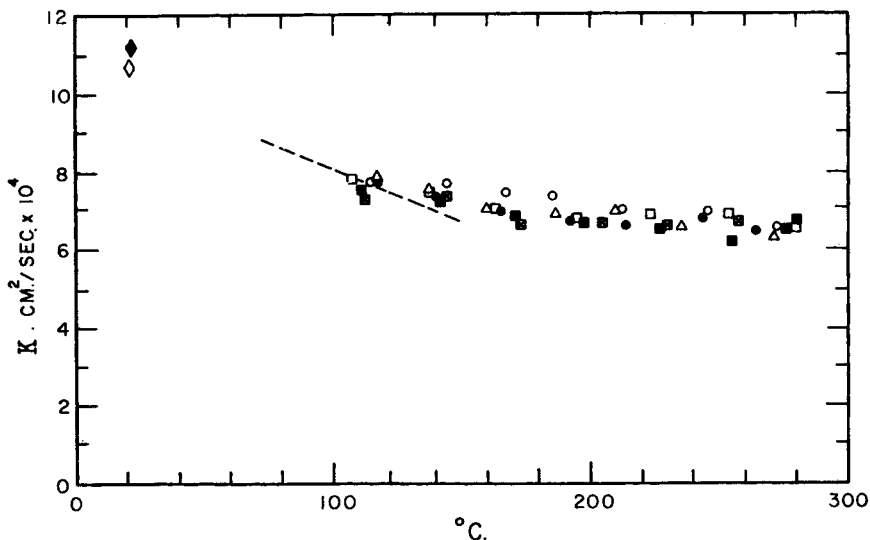


Fig. 2. Thermal diffusivities of polymethyl methacrylates; (Δ) Plexiglas II, UVA; (\circ , \bullet) Plexiglas V-461; (\square , \boxtimes , \blacksquare) Plexiglas VS-100; (\blacklozenge) Plexiglas sheet, ref. 1; (\diamond) Lucite rod, ref. 1; (---) Lucite 140 ref. 2.

rapid decrease as the temperature increases from room temperature to the glass temperature (ca. 105°C .) and a slower decrease at higher temperatures. Although V-100 and VS-100 molding powders show very significant differences in viscosity (as melts), their diffusivities are very similar. The cast methyl methacrylate sheet has a molecular weight of ca. 1,000,000 as against ca. 100,000 for the molding powders, but no effect of this variable on the diffusivity can be seen.

The data on the diffusivity of both molded and cast polystyrene appear in Figure 3, together with such information as the literature offers.^{1,2} The molecular weights have been estimated from reduced specific viscosity measurements on used samples as ca. 100,000 for the cast sheet, 130,000 for Styron 666, and 170,000 for Styron 700. No change in the diffusivity is apparent in this molecular weight range. Chung and Jackson's measurement at ca. 25°C . is about the same as their previously mentioned values for poly(methyl methacrylate) at the same temperature. In comparing Figures 2 and 3 one might conclude that polystyrene and poly(methyl methacrylate) have similar diffusivities as glasses but that polystyrene's diffusivity as a melt goes through a shallow minimum at about 210°C . and then increases slowly. The thermal diffusivity of Styrons 666 and 683 molding powders, as reported in Bernhardt, is in poor agreement with the other results. One can try to determine the more accurate set of data by calculating the diffusivity based upon separate measurements of k , ρ , and c_p . Ballman and Shusman³ have stated that the diffusivity of general-purpose polystyrene is between 7.85×10^{-4} and 8.3×10^{-4} cm.²/sec. in the temperature range of interest in injection molding; they based their values

of c_p upon those given by Bondy and Boyer,⁴ and their values of thermal conductivity upon unpublished work of McTaggart (presumably of Monsanto Chemical Co.). The values are in excellent agreement with those obtained in these laboratories at temperatures above about 125°C. For the

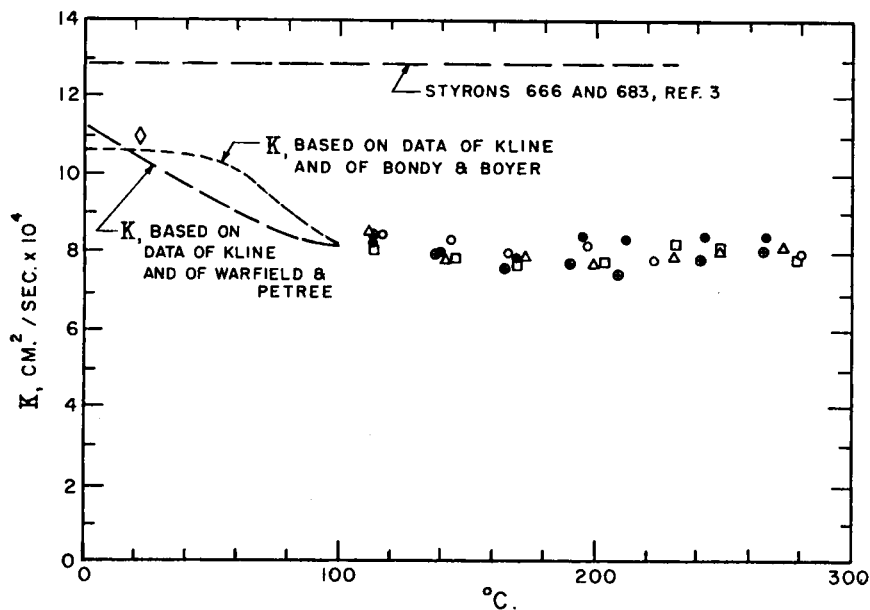


Fig. 3. Thermal diffusivities of molded and of cast polystyrene: (O, ●, ⊕) cast $\frac{1}{4}$ in. sheet; (Δ) Styron 683; (\square) Styron 700; (\diamond) polystyrene extruded rod, ref. 1.

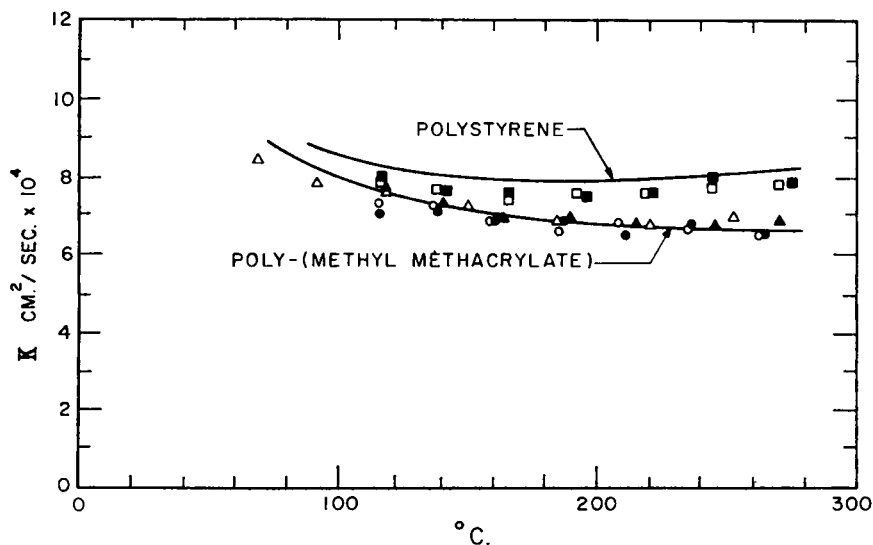


Fig. 4. Thermal diffusivities of some vinyl copolymers: (\square , \blacksquare) Bakelite C-11; (Δ , \blacktriangle) ethyl acrylate-methyl methacrylate; (O, ●) Zerlon 150.

range of 0–100°C. calculations have been made of the diffusivity based upon specific heats given by Bondy and Boyer and thermal conductivities of polystyrene according to Kline,⁵ with the use of a specific gravity of 1.04 at 100°C. and a thermal expansion coefficient of $0.53 \times 10^{-4}/^{\circ}\text{C}$. below 100°C.

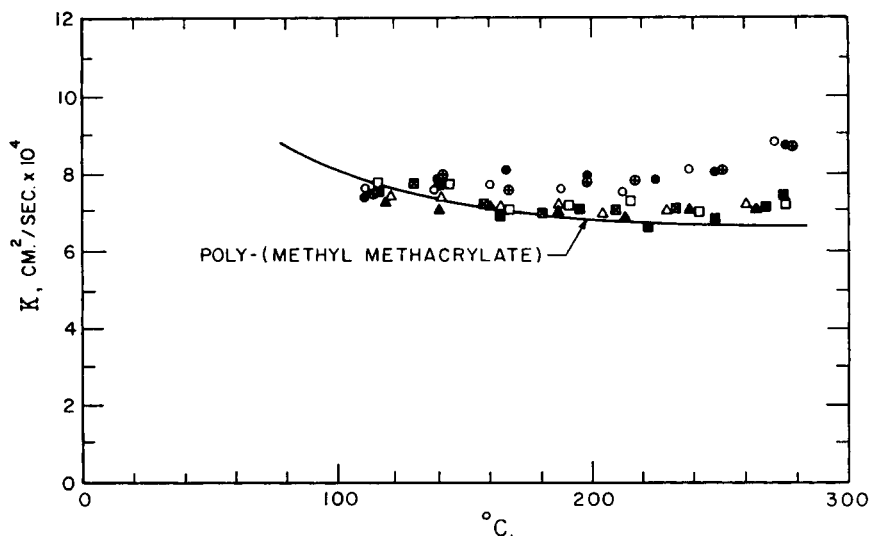


Fig. 5. Thermal diffusivities of some rubber-resin blends: (O, ●, ⊕), Cyclac T-1000; (Δ, ▲) Implex A; (□, ■, ⊞) Implex R.

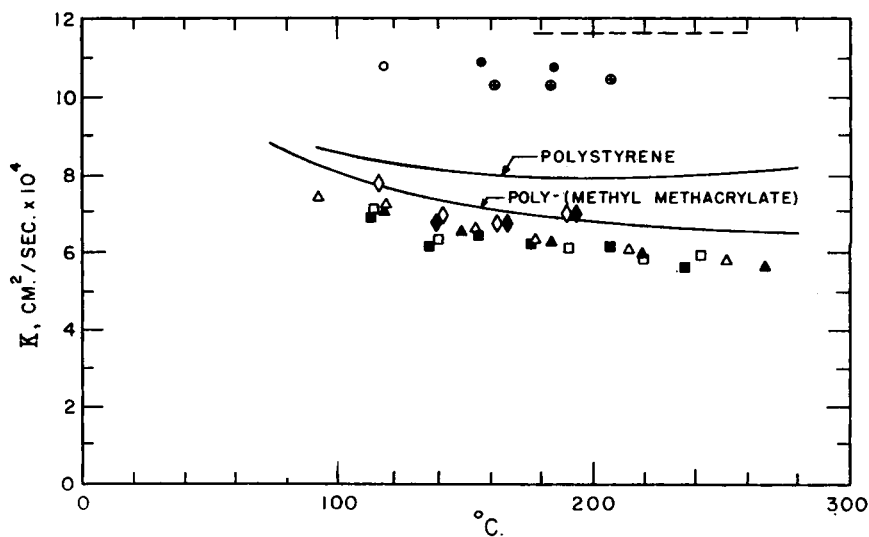


Fig. 6. Effect on thermal diffusivities of adding pendant groups of different sizes to carbon-carbon backbone of vinyl polymers: (◇, ◆) poly(vinyl chloride), Geon 103 EP; (O, ●, ⊕) polyethylene, Marlex 6000, Type 9; (□, ■) poly(isopropyl methacrylate); (Δ, ▲) poly(*sec*-butyl methacrylate); (---) polyethylene, low density (Dow Chemical), ref. 2.

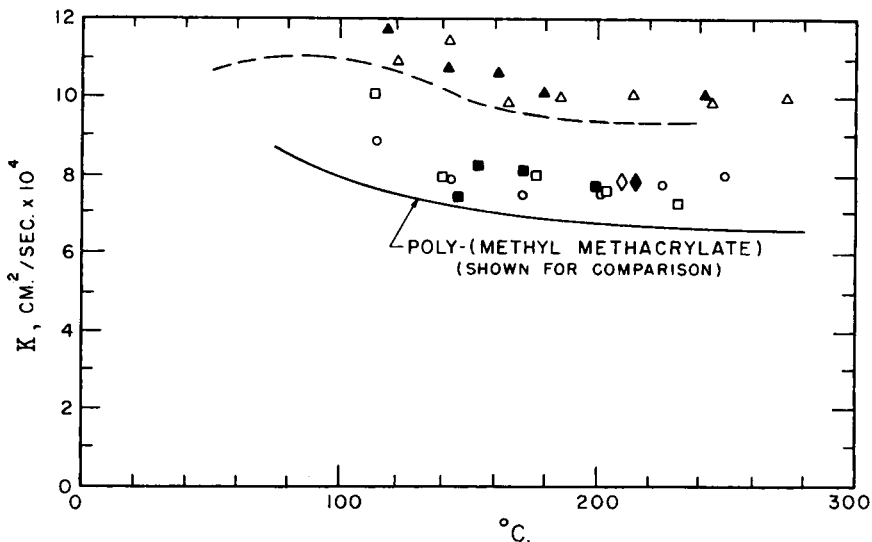


Fig. 7. Thermal diffusivities of nonvinyl polymers: (Δ , \blacktriangle) Lexan; (\diamond , \blacklozenge) Delrin; (\circ) Tenite butyrate MH; (\square , \blacksquare) Tenite butyrate H-3; (---) α -cellulose, ref. 7.

These values, which are plotted in Figure 4, constitute a transition to the higher diffusivity of the melts measured in these laboratories. If the recently reported c_p values of Warfield and Petree⁶ are used instead of Bondy and Boyer's data, somewhat different values of κ are found between 0 and 100°C., although the values at 100°C. are identical and those at 0°C. agree within about 5%. Thus the relatively high constant value of κ for Styron 683 reported in Bernhardt's book seems to be definitely inaccurate.

Zerlon 150, a copolymer of methyl methacrylate and styrene, has the values of κ shown in Figure 4, where it is compared with curves indicating approximately the data for poly(methyl methacrylate) and polystyrene shown in the preceding two figures. Two other copolymers are also shown in Figure 4: Bakelite C-11, a styrene-acrylonitrile copolymer, and a cast methyl methacrylate-ethyl acrylate (50 : 50) copolymer. Zerlon and the methyl methacrylate-ethyl acrylate copolymer show diffusivities very similar to that of poly(methyl methacrylate). The addition of acrylonitrile to styrene seems to cause a slight reduction of the diffusivity throughout a wide temperature range.

In Figure 5 are shown the diffusivities of some rubber-modified acrylics and of an ABS type of polymer, Cylolac T-1000. Implex A and Implex R have slightly higher diffusivities than does poly(methyl methacrylate), while Cylolac T-1000 has a value of κ close to that of polystyrene.

In Figure 6 data have been displayed to show the effect on the thermal diffusivity of adding pendant groups of different sizes to the carbon-carbon backbone of vinyl polymers. Of all the vinyl polymers examined, linear polyethylene (Marlex 6000, high density, melt index 0.9) has the highest diffusivity. The open triangle standing alone on the left in Figure 6

shows a measurement made after considerable thermal expansion, but below the crystalline melting point, of the sample. The sample cavity was completely filled, and thermal contact between the polymer and the aluminum surface was probably excellent; the other data points are above the melt temperature. These data are in fair agreement with data on low-density polyethylene.² The substitution of side groups more bulky than hydrogen in all cases reduces the diffusivity, and in general the thermal diffusivity of the melt decreases with increasing bulkiness of the side groups, the large pendant groups of poly(isopropyl methacrylate) and poly(*sec*-butyl methacrylate) associated with the polymers having the lowest diffusivities. Poly(vinyl chloride) is lower than might be expected on this basis; that this may result from its polar character is suggested by the fact that a copolymer of styrene and the strongly polar acrylonitrile has a lower diffusivity than styrene.

Figure 7 shows some data on nonvinyl polymers, with the curve for poly(methyl methacrylate) added for ease in comparing the data with those of vinyl polymers. The data of Martin⁷ on α -cellulose are for sheets; the polymer is not thermoplastic. However, the data are shown for comparison with the data on the Tenite butyrates. The data for the polycarbonate Lexan include some points below the glass transition temperature (ca. 154°C.), to show that the diffusivity of the glass is higher than that of the melt. Only a few points are shown for the polyacetal Delrin, because of the relatively limited temperature range between the melt temperature and the temperature at which degradation was observed during the tests.

Discussion and Conclusions

Remarkably little has been written about the thermal properties of polymer melts, perhaps because analytical treatment of the processing of melts is still in an early stage. From the point of view of the analyst, the data of the preceding section should be welcome, because it appears that (1) the thermal diffusivities of a wide variety of polymer melts differ by less than a factor of 2, and (2) although the diffusivity generally decreases in the passing from glassy state to melt, the melt diffusivity of any given polymer is surprisingly constant over a wide range of temperature (in the absence of degradation).

The decrease in κ for amorphous polymers in the region near the glass temperature (T_g) is not surprising. If one examines the curve of specific heat as a function of temperature for such materials as presented by, say, Wunderlich,⁸ one notes a relatively rapid increase in c_p near T_g , followed by a slow increase of c_p with temperature for the melt. But the thermal conductivity of amorphous polymers shows only a slight change in its temperature coefficient at T_g , and although the thermal expansion coefficient undergoes an increase at T_g , the actual density change of the polymer between any two temperatures in the region near T_g is small. Thus the decrease of κ near T_g essentially reflects the influence of changes in c_p . The constancy of κ for the melt can also be explained. The specific heat undergoes a slow

rise with increasing temperature which is partially counterbalanced by the decreasing density. The thermal conductivity above T_g increases with temperature for many amorphous polymers, according to Cherkasova,⁹ but for poly(methyl methacrylate) it decreases above T_g , at least between 105 and 160°C.¹⁰ In any event, the conductivity changes quite slowly, and for most amorphous polymers, the increases in k and c_p and the decrease in ρ tend to result in an almost constant value of κ . In contrast to the reduction of κ near T_g , it is interesting to note that the diffusivity of the linear polyethylene is almost the same on both sides of the crystalline melting point. Cherkasova suggests that the thermal conductivity should fall as the crystalline regions disappear; the crystalline melting is accompanied by a significant decrease in density, and these two effects appear to counterbalance each other.

The thermal diffusivity appears to be rather insensitive to molecular weight. In this respect it is interesting to note that κ for liquid octane at 30°C. is about 9.3×10^{-4} cm.²/sec.,¹¹ whereas "liquid" polyethylene has a diffusivity of about 10.4×10^{-4} cm.²/sec.; from this comparison alone one can speculate that the effect of molecular weight should be small.

Although the data indicate that there is a general decline of κ for the melts of the vinyl polymers as the length and size of pendant groups increase, it is not easy to try to elucidate the cause of this decline. Considerably more data than are presently available for the thermal conductivity and specific heat of polymer melts will be required for this purpose.

Appendix A. Transient Temperature Distribution in the Sample Disk

Consider the temperature distribution in a disk of material, originally at uniform temperature, whose surface temperature is made to rise linearly with time, starting at time zero. Let the material have properties which are independent of temperature and let the disk have a radius a and a thickness $2b$, with the origin of coordinates at the center of the disk and extending in the radial (r) and axial (z) directions. If the rate of temperature rise of the surface is h degrees per unit time and the thermal diffusivity is κ , the temperature θ , as a function of time t at any point (r, z), can be expressed as:¹²

$$\theta = ht - \frac{8h}{\pi\kappa} \sum_{m,n=1}^{\infty} \frac{1}{(2m-1)R_n} [R_n/a^2 + (2m-1)^2\pi^2/4b^2] J_1(R_n) \times J_0(R_n r/a) \sin(2m-1)\pi(z+b)/2b (1 - \exp\{-\kappa[R_n^2/a^2 + (2m-1)^2\pi^2/4b^2]t\}) \quad (1)$$

where the R_n 's are the roots of $J_0(r) = 0$. For the case of an infinite flat plate of thickness $2c$, the temperature at any distance z from the midplane is given by:

$$\theta = ht + h(z^2 - c^2)/2\kappa + \frac{16hc^2}{\kappa\pi^3} \sum_{n=0}^{\infty} \frac{(-1)^n}{(2n+1)^3} \exp\{-\kappa(2n+1)^2\pi^2 t/4c^2\} \cos(2n+1)\pi z/2c \quad (2)$$

By the use of eq. (1) the dimensionless temperature θ_0/ht at the center of a disk having a diameter/thickness ratio of 6 has been calculated as a function of the dimensionless time $\kappa t/b^2$; with eq. (2), it has been calculated as a function of $\kappa t/c^2$ for an infinite flat plate. For values of $\kappa t/c^2 > 0.6$ the values differ by less than 1%, so that subject to this restriction a disk, say, 3 in. in diameter and $1/2$ in. thick shows a negligible effect *at its center* from heat transfer through its cylindrical outer surface. Since the test pieces used in the thermal diffusivity apparatus have these dimensions, the basic equation of interest is eq. (2); for conditions at $z = 0$, it can be written as:

$$\theta_0/h = t - (c^2/2\kappa) + 16c^2/\kappa\pi^3 \sum_{n=0}^{\infty} (-1)^n/(2n+1)^3 \exp\{-\kappa(2n+1)^2\pi^2 t/4c^2\} \quad (3)$$

Let $A = \kappa\pi^2 t/4c^2$ and let the infinite series of eq. (3), exclusive of its coefficient, be $S(A)$. Then one can write (after rearrangement):

$$\theta_0/ht = (1/A)[A - \pi^2/8 + (4/\pi)S] \quad (4)$$

If one calculates S as a function of A , a single measurement of θ_0 at a known time t enables one to calculate κ , assuming h and c are known. In practice it is important to note that as t (and therefore A) becomes large, S approaches zero and the temperature difference between surface and center becomes constant. One could then write:

$$\kappa = hc^2/2(ht - \theta_0) = hc^2/2(\Delta\theta_0) \quad (5)$$

Both eq. (4), the more general solution, and eq. (5), the pseudo steady-state solution, can be used to calculate κ . However, as indicated by the data, κ has a value of about 0.003 ft.²/hr. for many polymers, so that the restriction $\kappa t/c^2 > 0.6$ limits one to measurements made at least 5 min. after a linear surface temperature rise begins. On the other hand, at times long after the start of the linear surface temperature rise, θ_0/ht approaches unity, and A , and therefore κ , become difficult to determine accurately with eq. (4). In practice, therefore, the asymptotic solution represented by eq. (5) has proved more useful.

Appendix B. Precision of the Measurements

The similarity in the magnitudes of many of the calculated diffusivities and the spread of some of the data may cause some skepticism about the precision of the entire measuring technique. Errors in the final calculated results can arise from several causes, which will be reviewed separately, beginning with those which probably give rise to the largest errors.

The theoretical analysis (presented in Appendix A) is based upon a model in which the thermal diffusivity of the material is assumed independent of temperature and the outer surfaces of the sample are assumed to increase in temperature at a linear rate with time. In practice, the rate of

temperature rise of the outer surface is approximately linear for periods of about 10 min. (which correspond to temperature increases of ca. 25°C. for most of the measurements), but falls off gradually because the rate of power input is held constant while heat losses to the atmosphere gradually increase as the surface temperature of the apparatus increases. It is also difficult to make the temperature of the surfaces rise linearly at time

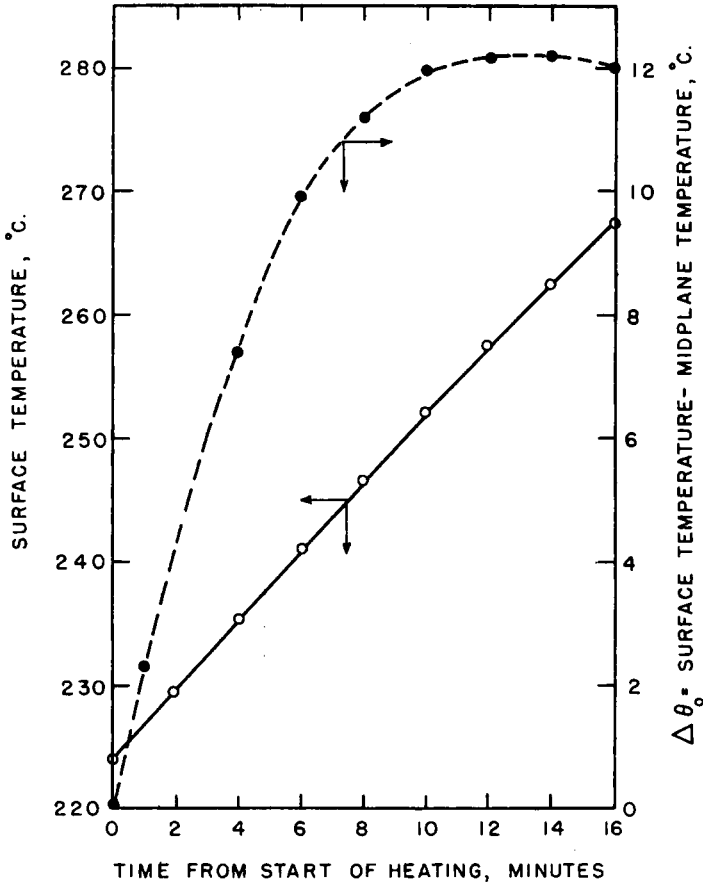


Fig. 8. Typical records of surface temperature and $\Delta\theta_0$ as functions of time, for calculating thermal diffusivity.

“zero” because the heaters are separated from the sample surface by aluminum, which has a high, but not infinite, thermal diffusivity. Figure 8 shows typical records of surface temperature and of $\Delta\theta_0$ as functions of time. Although it is theoretically possible to calculate the diffusivity for an arbitrary surface temperature variation, such as that shown here, it is extremely tedious, and the diffusivities have been calculated by determining the average rate of temperature increase, h , at the time when the

temperature difference between the block and the center of the sample becomes essentially constant. It is felt that the resulting error in h is not greater than 5%. This is probably a considerably larger error than that caused by neglecting the temperature dependence of the diffusivity in the analysis, since it is clear that this dependence is usually small at temperatures where the polymer is indeed a melt. Only in regions near the glass temperature, where the diffusivity seems to decrease relatively rapidly with increasing temperature, would this lead to a significant error, and this error is believed to be a maximum of 2 or 3%.

Errors could also result from heat conduction along the thermocouple wires or from errors in the position of the thermocouples. The former potential difficulty has been removed by bending the wires into a loop which lies in an isothermal plane, as shown in Figure 1. The second possible source of error is not easy to assess. Initially, the thermocouple is very accurately centered in the sample. But volumetric expansion of the material causes polymer to rise in the vent tube, and some displacement of the couple occurs. Examination of samples after they have been used occasionally shows some distortion of the loop but no significant movement of the junction out of the midplane. However, as the sample cools before the aluminum blocks are unbolted, contraction occurs and displacements may be reversed. Fortunately, small movements of the couple in the midplane of the disks would be unimportant since a large central area of the midplane is almost isothermal. Movement of the couple closer to a wall could introduce serious errors, although at the midplane $\partial\theta/\partial z$ is zero, and a movement of 0.025 in. would cause an error of only 1%. It is the reproducibility of data for samples in which the loops of wire are not identical, as well as visual examination of the used samples, which provides grounds for doubting that any significant thermocouple displacement occurs.

The effect of heat transfer by natural convection on the calculated data is difficult to calculate. However, the effect, if any, would be most significant at the higher temperatures, where the polymer viscosity becomes low. As a matter of interest it may be noted that the viscosity of poly-(methyl methacrylate) of ca. 100,000 molecular weight is about 500 cpoises at 288°C. and very low shear rates, according to measurements in these laboratories. One might be concerned that under these conditions natural convection would have some effects, although this is certainly not a low viscosity. However, if natural convection affected the results for Plexiglas V-461, the diffusivity at high temperatures would be expected to be higher for V-461 than for the Plexiglas II UVA cast material, which has a much higher molecular weight ($M_w \approx 1,700,000$) and such a high bulk viscosity that the two halves of our sample did not fuse at 315°C. and 500 psi. Since no differences were observed in the calculated diffusivity (see Figure 2), it is presumed that natural convection plays an insignificant role in the heating process.

The potentiometer used was a Leeds and Northrup model having a resolution of 0.001 mv. Since the temperature differences measured corre-

sponded to voltages of about 0.5 mv., negligible errors are introduced from this source.

An overall estimate of the maximum error caused by lack of precision in the calculated value of the thermal diffusivity is 7%. An examination of the data points shows that the scatter about mean curves is within this range.

This investigation was started at the suggestion of Mr. W. F. Bartoe; he was of much assistance in the design of the measuring apparatus. Most of the data were collected by Messrs. J. A. Shetter and L. L. Shaner.

References

1. Chung, P. K., and M. L. Jackson, *Ind. Eng. Chem.*, **46**, 2563 (1954).
2. Bernhardt, E. C., Ed., *Processing of Thermoplastic Materials*, Reinhold, New York, 1959.
3. Ballman, R., and T. Shusman, *Modern Plastics*, **37**, 126 (1959).
4. Bondy, R. H., and R. F. Boyer, *Styrene, Its Polymers, Copolymers, and Derivatives*, Reinhold, New York, 1952, p. 479.
5. Kline, D. E., *J. Polymer Sci.*, **50**, 441 (1961).
6. Warfield, R. W., and M. C. Petree, *J. Polymer Sci.*, **55**, 497 (1961).
7. Martin, S. B., *J. Appl. Phys.*, **31**, 1101 (1960).
8. Wunderlich, B., *J. Phys. Chem.*, **64**, 1052 (1960).
9. Cherkasova, L. N., *Russian J. Phys. Chem.*, **33**, 224 (1959).
10. Shoulberg, R. H., *J. Appl. Polymer Sci.*, **6**, S32 (1962).
11. McAdams, W. H., *Heat Transmission*, 3rd ed., McGraw-Hill, New York, 1954.
12. Williamson, E. D., and L. D. Adams, *Phys. Rev.*, **14**, 99 (1919).

Synopsis

A study of the thermal diffusivity of polymer melts as a function of temperature over the range 25–325°C. is described. Measurements were carried out with an apparatus especially designed and constructed for this purpose; this apparatus and the theoretical treatment of data obtained with it are treated in detail. The polymers examined include polystyrene, poly(methyl methacrylate), some of their copolymers, poly(vinyl chloride), linear polyethylene, polyacetal, polycarbonate, cellulose-acetate-butyrate, some "high-impact" polymer blends and terpolymers, and some higher methacrylates. The thermal diffusivities of the melts vary from about 11×10^{-4} cm.²/sec. (for linear polyethylene) to about 5×10^{-4} cm.²/sec. (for poly(*sec*-butyl methacrylate)). In general the thermal conductivity of an amorphous polymer decreases as it passes from the glassy state to a melt, but remains quite constant over a wide temperature range in the melt state. On the basis of a limited amount of data one might tentatively conclude that the thermal diffusivities of the melts of vinyl polymers become lower as larger or longer groups are added to the carbon-carbon backbone. As regards molecular weights equal to those common for molding powders, molecular weight seems to have no effect on the thermal diffusivity.

Résumé

On étudie la diffusion thermique de polymères fondus en fonction de la température dans un domaine allant de 25 à 325°C. Les mesures ont été effectuées à l'aide d'un appareillage spécialement conçu et réalisé dans ce but; cet appareillage et le fondement théorique des résultats obtenus sont discutés en détail. Les polymères examinés comprennent le polystyrène, le polyméthacrylate de méthyle, certains de leurs copolymères, le chlorure de polyvinyle, le polyéthylène linéaire, le polyacétal, le polycarbonate,

l'acéto-butyrate de cellulose, certains mélanges de polymère à impact élevé, des terpolymères et certains polyméthacrylates d'alcoyle plus élevé. La diffusion thermique de polymères à l'état fondu varie de 11×10^{-4} cm²/sec (pour le polyéthylène linéaire) jusque 5×10^{-4} cm²/sec (pour le polyméthacrylate de butyle secondaire). En général la conductivité thermique d'un polymère amorphe diminue lorsqu'il passe de l'état vitreux à l'état fondu, mais reste tout à fait constante dans un large domaine de température à l'état fondu. Sur la base d'une quantité restreinte de résultats, on peut essayer de conclure que la diffusion thermique de polymères vinyliques à l'état fondu diminue avec la grandeur ou la longueur des groupements fixés sur la chaîne carbonée principale. Pour les poids moléculaires habituels dans les poudres utilisées pour le moulage, le poids moléculaire n'exerce aucun effet sur la diffusion thermique.

Zusammenfassung

Die thermische Diffusionsfähigkeit von Polymerschmelzen wurde als Funktion der Temperatur im Bereich von 25 bis 325°C untersucht. Die Messungen wurden mit einem eigens für diesen Zweck gebauten Apparat ausgeführt; dieser Apparat und die theoretische Behandlung der damit erhaltenen Ergebnisse wird genau beschrieben. Folgende Polymere wurden vermessen: Polystyrol, Polymethylmethacrylat und einige Copolymere; Polyvinylchlorid; lineares Polyäthylen; Polyacetal; Polykarbonat; Celluloseacetat-Butyrat; einige "stossfeste" Polymermischungen und Terpolymere; einige höhere Methacrylate. Die thermische Diffusionsfähigkeit der Schmelzen liegt im Bereich von etwa 11×10^{-4} cm²/sek (für lineares Polyäthylen) bis etwa 5×10^{-4} cm²/sek (für Poly-*sek*-butylmethacrylat). Im allgemeinen nimmt die Wärmeleitfähigkeit eines amorphen Polymeren beim Übergang vom Glaszustand zur Schmelze ab, bleibt aber im geschmolzenen Zustand über einen grossen Temperaturbereich ziemlich konstant. Auf Grund einer beschränkten Zahl von Versuchsergebnissen könnte man den vorläufigen Schluss ziehen, dass die thermische Diffusionsfähigkeit der Schmelzen von Vinylpolymeren um so niedriger wird, je grössere oder längere Gruppen sich an der Kohlenstoff-Kohlenstoffhauptkette befinden. Bei den für Presspulver üblichen Molekulargewichten scheint das Molekulargewicht keinen Einfluss auf die thermische Diffusionsfähigkeit zu haben.

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