

trapping layer ranging in depth from 0.7 μm to 2.2 μm from the surface. The presence of near surface traps have also been reported in Teflon FEP by Seggern¹⁶ from his t.s.c. experiments in electron bombardment and corona charged samples. The spatial depth of near surface trapping centres as reported by them are in the range of 0.5 μm to 1.8 μm from the surface. Our results are in close agreement with the reported ones. This method is now being used to study the effect of surface treatment on the spatial depth of traps in grafted FEP and positive results have been obtained which will be communicated in the near future.

Acknowledgements

The authors wish to express their thanks to Professor M. R. Bhiday and Professor A. S. Nigavekar for their interest in the work. Thanks to C.S.I.R for supporting the research.

References

- 1 Ioannou, D. E. *J. Phys. D. Appl. Phys.* 1980, **13**, 4, 611
- 2 Ioannou, D. E. and Davidson, S. M. *J. Phys. D. Appl. Phys.* 1979, **12**, 1399
- 3 Martin, E. H. and Hirsch, J. *Solid State Comm. (USA)* 1969, **7**, 10, 783
- 4 Gross, B., Sessler, G. M. and West, J. E. *Appl. Phys. Lett.* 1979, **34**, 555
- 5 Blumtrill, H. *Phys. Stat. Solidi* 1979, **55**, 611
- 6 Ansbacher, F. and Ehrenberg, W. *Proc. Phys. Soc.* 1951, **A64**, 362
- 7 Aris, F. C., Davies, P. M. and Lewis, T. J. *J. Phys. C. Solid State Phys.* 1976, **9**, 797; Aris, F. C., Borton, M., Lewis, T. J. and Toomer, R. IEE Conf. Publ. No. 129, 267 (1975)
- 8 Beckley, L. M., Lewis, T. J. and Taylor, D. M. *J. Phys. D. Appl. Phys.* 1976, **9**, 1355
- 9 Suzuyoki, Y., Mizutani, T. and Ieda, M. *Jpn. J. Appl. Phys.* 1976, **15**, 1665
- 10 Yoshino, K., Kyokane, J., Nishitani, T. and Inuishi, Y. *J. Appl. Phys.* 1978, **49**, 4849
- 11 Ehrenberg, W. and Ghosh, B. J. *J. Phys. C. Solid State Phys.* 1969, **2**, 152
- 12 Hirsch, J. and Martin, E. H. *J. Noncrystallogr. Solids* 1970, **4**, 133
- 13 Patridge, R. H. 'The radiation chemistry of macromolecules', p 195, Ed. M. Dole, Academic Press, New York, 1972
- 14 Mele, A., Dellesite, A., Bettinali, C. and Di Domenico, A. *J. Chem. Phys.* 1968, **49**, 3297
- 15 Gross, B., Sessler, G. M. and West, J. E. *J. Appl. Phys.* 1974, **45**, 7, 2841
- 16 Seggern, H. V. *J. Appl. Phys.* 1979, **50**, 2817

Thermal conductivity of polymers: A new correlation*

M. G. Kulkarni and R. A. Mashelkar

Department of Chemical Engineering, National Chemical Laboratory, Pune 411 880, India
(Received 10 September 1980; revised 24 February 1981)

Introduction

Study of transport properties of polymers is important from two view points. It provides an insight into the structure of the polymer and it helps to predict product performance during specific applications. A review of the literature reveals that the effects of such parameters as molecular weight, molecular weight distribution, crystallinity and orientation have been studied in great detail and empirical correlations have been established. Although thermal properties of polymers play an important role in polymer processing, in studying structure-property relationships and choosing materials for specific applications, thermal transport is still not clearly understood.

Theories of mechanism of heat transfer in polymers have not been well developed compared with the theories of mechanism of heat transfer in gases and liquids, primarily due to the lack of reliable data, which in itself has been attributed to difficulties involved in the experimentation. A qualitative description of the temperature dependence of thermal conductivity of polymers over a wide range has been given by Hands¹.

In view of the lack of experimental data and difficulties involved in accurate measurements, approximations are often used. A number of correlations associating such structural variables as molecular weight of the polymer, crystallinity, orientation etc. with the thermal conductivity have been proposed²⁻⁵. Thus Luba *et al.*⁵ proposed empirical correlations for thermal conductivity of amorphous polymers in the temperature ranges above and below T_g as well as for semicrystalline polymers above and

below T_m . The thermal conductivity of amorphous polymers at 173K was correlated with the refractive index of the polymers. It is not clear as to whether the same relationship would be valid at other temperatures as well, since the authors themselves have stressed the need to establish the correlation at temperatures other than 173K.

Search for a new correlation

Attempts to explain the temperature dependence of the thermal conductivity of polymers on theoretical considerations have not been successful. Uberreiter and Nens⁶ assumed that thermal energy is transferred along the length of the polymer chain and the transverse waves set up above the glass transition temperature tend to dampen the process of transfer, resulting in decreased conductivity above the glass transition temperature. The concept is analogous to that proposed by Eucken⁷ to explain the temperature dependence of the thermal conductivity of low molecular weight amorphous materials. According to Eucken⁷ such a material can be looked upon as a quasi-lattice structure. Thermal conduction in such a structure takes place as a result of excited coupled intermolecular and intramolecular vibrations of the quasi-lattice structure. An increase in the temperature when the structure is much below its T_g results in an increase in population density of these interactions resulting in an increase in thermal conductivity. However, an increase in temperature also leads to an increase in the free volume which disrupts the lattice and the propagation of the vibrations. The net result of the two opposing effects is a decrease in the thermal conductivity. With a further increase in temperature, the population density of excited

* NCL Communication No. 2658

coupled vibrations continues to increase whereas a further disruption of the network is not possible. As a result, thermal conductivity increases with temperature above T_m . Eiermann⁸ considered the amorphous polymer as a network of resistances in which the primary valence forces offered a negligible resistance to transfer of thermal energy in comparison with that offered by the secondary valence forces.

Sheldon and Lane⁹ considered thermal conduction in polymers as a result of molecule to molecule transfer of energy by either translational, rotational and/or vibrational modes. These processes are diffusional in nature. Thus, with an increase in temperature, density of the polymers decreases whereas the segmental mobility increases. The observed temperature dependence of thermal conductivity would therefore depend upon the relative magnitudes of the two factors. Similar views were expressed in subsequent studies on thermal conductivity of melts^{10,11}. The theories are suggestive of the fact that segmental motion might play an important role in thermal conduction in polymers.

Segmental motion in polymers governs a large number of polymer properties such as modulus, viscosity, diffusivity etc. The role of segmental motion on transport properties will depend upon two parameters viz. the available free volume and the ease of rotation around the carbon-carbon bond. Frisch and Rogers¹² speculated that mass, momentum and energy transport in polymers should be affected by free volume in an identical manner. Although the importance of free volume was noted, the data were correlated in terms of the critical temperature. Thus plots of λ/λ_{\max} vs T/T_c were found to have a maximum at T_g . This was explained on the basis of Eucken's theory of quasi-lattice model of amorphous polymers. The critical temperature T_c was defined as:

$$T_c = T_{\max} \left(\frac{T_{\text{crit}}}{T_{\max}} \right)_{\text{polyethylene}} \quad (1)$$

where T_{\max} denotes the temperature at which thermal conductivity reaches a maximum and T_{crit} denotes the critical temperature of polyethylene of infinite molecular weight. It is difficult to visualize free volume in polymers at the critical temperature. Furthermore, it would seem more appropriate to correlate the thermal conductivity, which is governed by free volume in terms of free volume

at the glass transition temperature, as has been done in the past to correlate viscosity and diffusivity data. To our knowledge no previous efforts have been made to correlate the thermal conductivity of polymers within the framework of the WLF equation. We shall now examine the possibility of establishing such a correlation.

WLF equation for thermal conductivity of polymers

The shift factor a_T in the WLF equation is defined as:

$$a_T = \frac{\eta T_0 \rho_0}{\eta_0 T \rho} \quad (2)$$

where η denotes viscosity, and ρ denotes density. In general the vertical shift $\frac{T\rho}{T_0\rho_0}$ is negligible, and we have

$$a_T = \frac{\eta(T)}{\eta(T_g)} \quad (3)$$

we therefore defined the shift factor for thermal conductivity as:

$$a_T = \frac{\lambda(T)}{\lambda(T_g)} \quad (4)$$

and write

$$\ln \frac{\lambda(T)}{\lambda(T_g)} = \frac{-C_1(T - T_g)}{C_2 + (T - T_g)} \quad (5)$$

For the present discussion we identify three temperature ranges pertaining to: Thermal conductivity (1) of molten polymers, (2) in the glass transition region and (3) below the glass transition temperature.

Reliable and reasonably extensive data are available in region (1) and region (3). However, only limited data are available in the intermediate region (2). Therefore we shall first examine the data in regions (1) and (3).

Data from literature were analysed to test the validity of equation 5. A wide range of polymers were investigated over the temperature range of 100K to 600K. In total about 60 data points were examined. The systems investigated have been summarised in Tables 1 and 2.

Table 1 Thermal conductivity of polymers above T_m

Polymer	Temperature range	C_1	C_2	Remark	Reference
Polystyrene	473–573K	2.1299	1445	Increase with temperature	Fuller and Fricke (1971)
Nylon-6	490–570K	2.2192	776.06	"	"
Nylon-6,10	460–570K	1.6051	413.24	"	"

Table 2 Thermal conductivity of polymers up to T_g

Polymer	Temperature range	C_1	C_2	Remark	Reference
Polyvinylchloride	150–353K	0.3711	657.5	Increase with temperature	Eiermann (1961)
Polymethylmethacrylate	120–373K	0.0785	334.89	"	Eiermann (1965)
Polycarbonate	120–420K	0.3560	467.00	"	Eiermann (1965)
Polyethyleneterephthalate	120–340K	0.8674	417.60	"	Eiermann (1965)
Polystyrene	273–353K	0.3875	426.6	"	Pasquino (1964)

Thermal conductivity of molten polymers

Figure 1 shows a typical WLF type plot for the polymers summarised in Table 1. Appropriate values of thermal conductivity at the glass transition temperature were obtained by extrapolating the relevant data to the glass transition temperature. The shift factor was defined as the ratio of thermal conductivities at the two temperatures. It is clear from the figure that an excellent fit results in the range investigated. This clearly demonstrates that segmental motion plays an important role in the thermal transport.

Thermal conductivity below the glass transition temperature

Although the principle of reduced variables is strictly applicable in zones in which contributions to viscoelastic properties of polymers involve the same friction coefficient, the WLF equation, in a more restricted sense, has been applied to semicrystalline polymers^{13,14} and for polymers below the glass transition temperature¹⁵.

Based on similar considerations, we applied the WLF equation to correlate thermal conductivity of polymers below glass transition temperature¹⁶⁻¹⁸. However, in the present case T_g itself was used as the reference temperature. Plots shown in Figure 2 indicate that a good fit is observed in this region also.

Thermal conductivity in the glass transition region

Conflicting trends have been reported in the literature regarding the temperature dependence of thermal conductivity in the transition region. Thermal conductivity of polytrichlorofluoroethylene¹⁹ increased with temperature whereas that of natural rubber²⁰, polyvinyl chloride⁹, and polyethylene²¹ decreased with temperature. It must be noted here that these polymers are semicrystalline in nature. The thermal conductivity of these polymers has two contributory factors (1) from the crystalline fraction and (2) from the amorphous fraction. The observed temperature dependence of the thermal conductivity would therefore depend on temperature dependence of the thermal conductivity of the two fractions. Analysis of temperature dependence of the thermal conductivity of polyethylene²¹ shows that the thermal conductivity of the crystalline fraction decreases while that of the amorphous fraction increases. This analysis further substantiates our

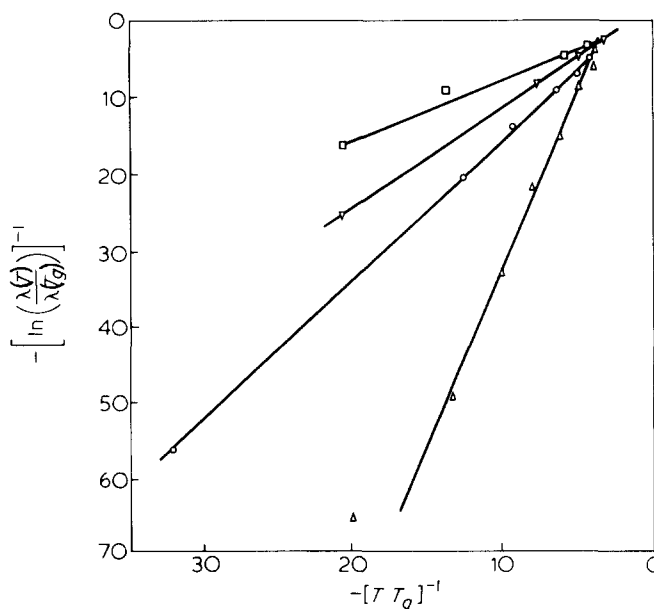


Figure 2 Thermal conductivities of polymers below transition temperature: Polyvinylchloride, (○); Polymethylmethacrylate, (△); Polycarbonate, (▽); Polyethyleneterephthalate, (□); (Data from references 20, 21)

hypothesis that segmental motion plays an important role in the mechanism of thermal transport in amorphous polymers.

As in the case of the WLF correlation for other transport properties, it should be possible to correlate the constants C_1 and C_2 with the micro-characteristics of the

system. Thus, $C_1 = \frac{B}{2.303f_g}$ and $C_2 = \frac{f_g}{\alpha_f}$ where f_g denotes the free volume at the glass transition temperature, α_f denotes the coefficient of thermal expansion of free volume above the glass transition temperature and B is a parameter in the Doolittle equation which is close to unity. We did not attempt this since the available data were insufficient for any such correlation. However, the success of the WLF correlation demonstrated that this communication should hopefully pave the way for building sounder and predictive correlations and also developing additional theoretical frameworks where the role of segmental motion in thermal transport can be more clearly understood.

References

- 1 Hands, D. *Rubber Chem. Technol.* 1977, **50**, 480
- 2 Anderson, D. R. *Chem. Revs.* 1966, **66**, 677
- 3 Knappe, W. *Adv. Polym. Sci.* 1971, **7**, 477
- 4 Van Krevelin, D. W., Hofstjer, P. J., 'Properties of Polymers', Elsevier, Amsterdam, 1972, 233
- 5 Luba, M., Pelt, T., Griskey, R. G. *J. Appl. Polym. Sci.* 1979, **23**, 55
- 6 Uberreiter, K. and Nens, S. *Kolloid. Z.* 1951, **123**, 92
- 7 Eucken, A. *Ann. Phys.* 1911, **34**, 185
- 8 Eiermann, K. *Rubber Chem. Technol.* 1966, **39**, 841
- 9 Sheldon, R. P. and Lane, K. *Polymer* 1965, **6**, 77
- 10 Fuller, T. R. and Fricke, A. L. *J. Appl. Polym. Sci.* 1971, **15**, 1729
- 11 Ramsey, J. C., Fricke, A. L., Caskey, J. A. *J. Appl. Polym. Sci.* 1973, **17**, 1597
- 12 Frisch, H. L. and Rogers, C. E. *J. Polym. Sci.* 1966, **C12**, 297
- 13 Faucher, J. A. *Trans. Soc. Rheology.* 1959, **3**, 81
- 14 Nagamatsu, K., Yoshihoni, T. *J. Colloid. Sci.* 1959, **14**, 377
- 15 Iwayanagi, S. *J. Sci. Res. Inst., Tokyo*, 1955, **49**, 4
- 16 Eiermann, K. *Kunststoffe* 1961, **51**, 512
- 17 Eiermann, K. *Kunststoffe* 1965, **55**, 335
- 18 Pasquino, A. D., Pilsworth, M. N. *J. Polym. Sci. Lett.* 1964, **2**, 253
- 19 Hatoori, M. *Bull. Univ. Osaka Perfect Ser. A* 1960, **9**, 51
- 20 Eiermann, K. and Hellwege, K. -H. *J. Polym. Sci.* 1962, **57**, 99
- 21 Hansen, D. and Ho, C. C. *J. Polym. Sci.* 1965, **A3**, 659

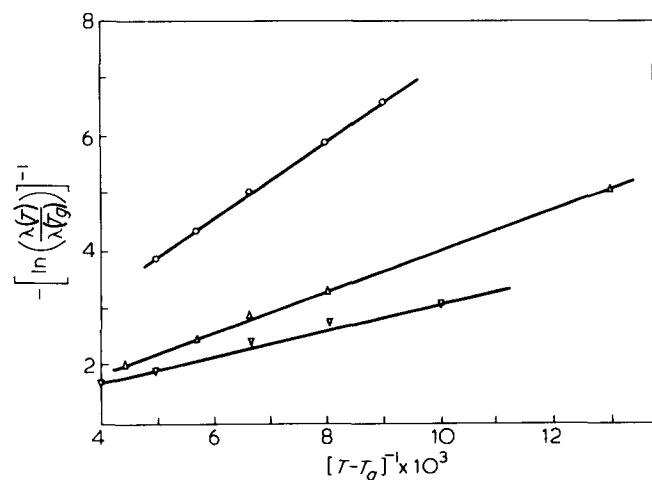


Figure 1 Thermal conductivities of polymer melts: Polystyrene (○), Nylon-6, (△), Nylon-6,10, (▽); (Data from reference 10)