

# Correlating and Predicting Polymer Thermal Conductivities

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## Synopsis

General correlations were developed to estimate polymer thermal conductivities for four cases—amorphous polymers above the glass temperature; amorphous polymers below the glass temperature; semicrystalline polymers above the melting temperature, and semicrystalline polymers below the melting temperature. The correlations based on readily available parameters (mer weights, densities at 25°C, specific heats) yielded calculated thermal conductivities that deviated by only 1%–2% from experimental values.

The transfer of heat is an important aspect of every polymer processing operation. Such processes cannot be properly controlled, evaluated, or optimized unless the heat transfer is clearly delineated. An inherent part of understanding this heat transfer is the necessity of having acceptable thermal conductivity data.

A number of investigators<sup>1–15</sup> have measured such data for both solid and molten polymers. These data, while making a valuable contribution to the body of knowledge, do not completely satisfy the needs of the polymer scientist or engineer. In order to meet this need, correlations must be used.

Several such correlations have been presented in the review papers of Anderson,<sup>16</sup> Knappe,<sup>17</sup> and Van Krevelen.<sup>18</sup> However, they require in most instances data that are not always available for a given polymer. For example, it was shown<sup>18</sup> that the ratio of  $k_T/k_{T_g}$  correlated with the ratio  $T/T_g$ , where  $T_g$  is the glass temperature in °K and  $k_T$  and  $k_{T_g}$  are the thermal conductivities at  $T$  and  $T_g$ , respectively. However, unless  $T_g$  and  $k_{T_g}$  (or a  $k_T$  at a given  $T$ ) were known, the correlation could not be used. Likewise, Eiermann<sup>19,20</sup> correlated semicrystalline solid behavior with the ratios  $k_c/k_a$ ,  $\rho_c/\rho_a$ , and percent crystallinity, where  $k_c$  and  $k_a$  were the thermal conductivities of pure crystalline and amorphous polymers, respectively, and where  $\rho_a$  and  $\rho_c$  were densities of amorphous and crystalline polymers. This required that the percent crystallinity and three of the four quantities  $k_a$ ,  $k_c$ ,  $\rho_a$ , and  $\rho_c$  be known. A somewhat different approach was taken by Hands, Lane, and Shelton<sup>21</sup> who showed that thermal conductivities for amorphous solid polymers appeared to correlate with densities. These authors<sup>21</sup> point out that this represents a first approximation.

Hence, use of the existing correlations generally requires that certain data be available. If these data are not available, the correlations cannot be used. The present study was undertaken to provide more general correlations of the type that used parameters readily available.

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The four cases considered were (1) amorphous polymers below  $T_g$ ; (2) amorphous polymers above  $T_g$ ; (3) semicrystalline polymers above their melting point; (4) semicrystalline polymers below their melting point.

For amorphous polymers at temperatures greater than  $1.1T_g$ , the following relation was found to hold:

$$k = \frac{6.3 \times 10^{-3}[1 - 0.00015(T - T_g)]}{T_g^{0.0216}M^{0.3}} \quad (1)$$

where  $k$  is thermal conductivity in cal/cm-sec-°C,  $T_g$  is the glass transition temperature in °K,  $T$  is the temperature in °K, and  $M$  is the polymer weight. This relation is similar to a form found appropriate for liquid thermal conductivities by Sheffy and Johnson.<sup>23</sup> The basic difference is in the constants and the use of  $T_g$  rather than the melting temperature. Calculated values for poly(methyl methacrylate)<sup>9</sup> and polystyrene<sup>9</sup> deviated generally about 1%–2% from experimental values with the maximum single deviation being 4.6%.

The situation for amorphous polymers below  $T_g$  was not as simply resolved. It appears, however, that for methacrylic polymers<sup>10</sup> and polystyrene,<sup>10</sup> a correlation with refractive index<sup>22</sup> seems to be possible (see Fig. 1) for 173°K, the given temperature which was chosen to be both well below  $T_g$  and also to have thermal conductivity values for a number of polymers together with appropriate refractive index data. Again it would be necessary to reestablish the correlation at temperatures other than 173°K.

Semicrystalline polymers above their melting point can be handled with an

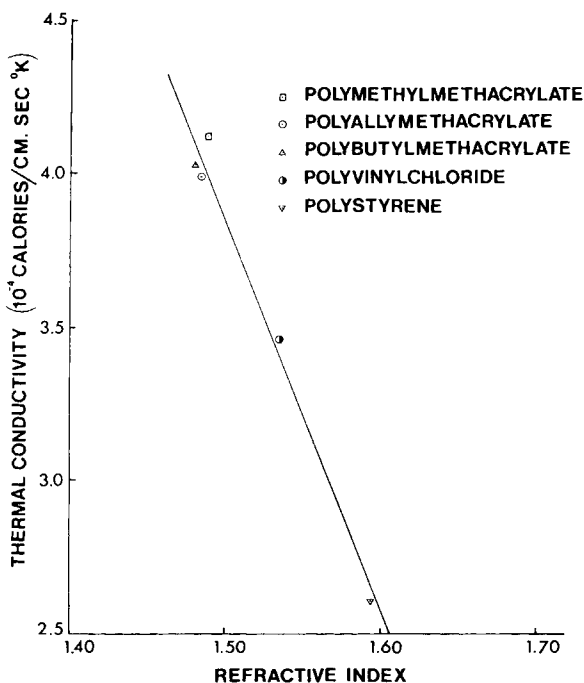


Fig. 1. Amorphous polymer thermal conductivities (at 173°K) vs refractive index.

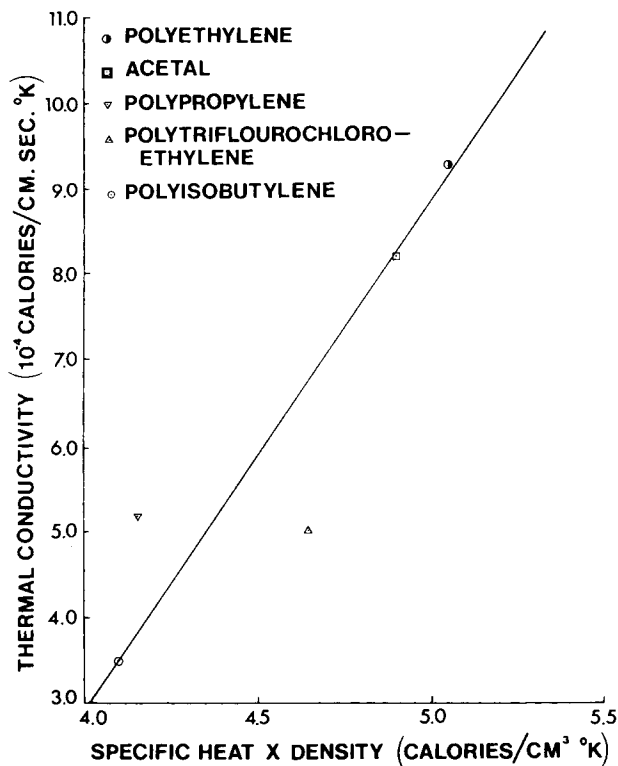


Fig. 2. Semicrystalline polymer thermal conductivities (at 173°K) vs product of density and specific heat.

expression similar to that used for amorphous polymers above  $T_g$ . This result is

$$k = \frac{1.2 \times 10^{-2}(C_p)(\rho)^{1.33}}{T_m^{0.216}M^{0.300}} \quad (2)$$

where  $k$  is the thermal conductivity in cal/cm-sec-°C,  $T_m$  is the melting point in °K,  $M$  is the mer weight,  $C_p$  is the specific heat of the melt at the temperature desired, and  $\rho$  is the polymer density at 25°C in g/cm<sup>3</sup>.

Values of  $k$  calculated from eq. (2) were generally within 1% of experimental values for various polyethylenes,<sup>6</sup> nylon,<sup>9</sup> and penton.<sup>9</sup> The maximum deviation was 2.6%.

For temperatures below the melting point, the situation is less well-defined for semicrystalline polymers. Here, however, there appears to be a relationship between thermal conductivity and the product of specific heat and density (both at 25°C). A plot of this type is shown in Figure 2. As can be seen,  $k$  data (at 173°K) for polypropylene,<sup>17</sup> polyisobutylene,<sup>17</sup> poly(chlorotrifluorethylene),<sup>7</sup> acetal,<sup>17</sup> and polyethylene<sup>7</sup> all fall on a curve. This correlation at a given temperature appears to be a reasonable technique for estimating or correlating thermal conductivities of semicrystalline polymers below their melting temperatures.

The physical significance of the terms in eqs. (1) and (2) can be considered in terms of the work of others, mainly in the area of liquid thermal conductivities. For example, the Sheffy and Johnson equation on which eq. (1) was based is

empirical but nonetheless is related to a theoretical equation utilizing vibrational frequencies and intermolecular distances. Equation (2) is of a form similar to an empirical equation developed by Weber,<sup>24</sup> which was verified by the theoretical treatments of Bridgman<sup>25</sup> who used a lattice model, by Predvoditelev,<sup>26</sup> who assumed a mixed gas–solid model, by Vargaftik,<sup>27</sup> who allowed for intermolecular association, and by McLaughlin,<sup>28</sup> who used a lattice structure together with a Lennard-Jones potential distribution. In any case, while eqs. (1) and (2) are empirical, they have solid roots in a number of theoretical sources.

The correlations developed in this work represent general forms that can easily be used with a minimum of required data. In addition, the deviations between calculated and experimental values for eqs. (1) and (2) are of the order of 1%–2%. In essence, then, these correlations could be useful to the polymer scientist and engineer in estimating polymer thermal conductivities.

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