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Thermal Conductivity Parameters for Semi-crystalline Polymers

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The nature and the form that the high temperature thermal conductivity model for semi-crystalline polymers should take have been modeled from a thermal conductivity response curve for isotropic polypropylene at 298 K and tested on the results of other polymers reported for other temperatures. The modeling of the experimental results of this study has led to a suggestion of a modified form of an existing composite model to make it relevant for the interpretation of the thermal conductivity behaviour of semi-crystalline polymers at high temperatures. Features of a mathematical model obtained confirm that although many models treat semi-crystalline polymers as composite materials, at high temperatures they behaves as if there are no distinct sharp boundaries between the crystallites and the amorphous matrix, suggesting that boundary effect terms which are relevant for other classes of composite materials is irrelevant in the case of semi-crystalline polymers at temperatures much greater than 100 K. It further confirms that, at high temperatures, thermal conductivity of a semi-crystalline polymer is independent of the thermal conductivity parameter for the crystalline phase but depends mainly on the thermal conductivity of the amorphous matrix, degree of crystallinity, size and distribution of the crystallites.

Key words: thermal conductivity, semi-crystalline polymers, composite model, boundary effect.

INTRODUCTION

Almost every existing thermal conductivity model for semi-crystalline polymers adopts a two-phase composite material picture, with many resulting from the modification of models meant for other classes of composite materials to make them relevant to polymer characteristics. However, due to high microstructural dynamics in polymers, resulting from their response to different parameters such as temperature, it has not been easy to get a form of mathematical model which would precisely simulate the corresponding influence of structural changes on the heat conduction mechanism in polymers. As a result, a number of inadequacies exist in a number of thermal conductivity models for semi-crystalline polymers and, while some of them have been resolved with time, a number have remained unresolved. The major concerns have been the kind and the number of parameters, which should be considered in formulating a thermal conductivity model for semi-crystalline polymers. The experimental results of this study have helped in identifying important terms and parameters for describing high temperature thermal conductivity of semi-crystalline polymers and this paper presents the form of a composite model which would be more relevant for isotropic semi-crystalline polymers at high temperatures. The proposed form is a modified from of equation 1, which is the general thermal conductivity equation for composite materials with spherical inclusions in a matrix proposed by Sangani & Yao (1988).

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\[
\frac{K}{K_m} = 1 + 2\phi \left( \frac{B - 1}{B + 1} \right) + \frac{2}{3} (\phi + 2\phi^3) \left( \frac{B - 1}{B + 1} \right)^2 + \Phi(\phi, \beta^n)
\] ........................... 1

Where
\[
\beta = \frac{B - 1}{B + 1}
\] and \( n = 3, 4, 5, \ldots \)

\( B \) – is a ratio of the thermal conductivity of the included particles to that of the matrix \( (K_p/K_m) \)

\( \Phi(\phi, \beta) \) - is a function of the volume fraction of the particles in the matrix and \( \beta \)

\( K \) – thermal conductivity of the material

\( K_m \) – is the thermal conductivity of the matrix

**Theory**

Maxwell (1973) proposed a form of expression for the thermal conductivity of composite materials of simple microstructures in which the volume fraction \( \phi \) of the particles in the continuous medium is very small but regardless of the size and spatial distribution of the particles, equation 2. Choy & Young (1977) later modified the Maxwell model to specifically fit semi-crystalline polymers when treated as two-phase composite materials, and they came up with the form expressed in equation 3.

\[
\frac{K}{K_m} = 1 + 3\phi \left( \frac{B - 1}{B + 1} \right) + \Phi(\phi^3)
\] ........................... 2

Where the parameters have the same meanings as in equation 1.

\[
\frac{K_o - K_a}{K_o + 2K_a} = \frac{\phi}{3}
\] ........................... 3

where
\( K_o \) - is the thermal conductivity of the isotropic semi-crystalline polymer

\( K_a \) - is the thermal conductivity of the matrix/the continuous medium

\( \phi \) - is volume fraction of the crystalline phase/inclusions in the matrix

Some similarities and differences exist between equations 1 and 2, in both equations the second term is a boundary effect term and the third term in equation 1 is for the size and distribution of the included particles. Equation 3, although a modified form of the Maxwell composite model for semi-crystalline polymers, does not show much similarity with the two expressions, although semi-crystalline polymers have also been treated as two-phase composite materials with spherical crystallites (spherulites) included as different entities in the amorphous phase Choy & Young (1977). While the two-phase composite picture is adoptable, sharp boundary effect may not be expected since the chain molecules run through both the crystalline and the amorphous phases and are known to provide the main pathways for heat conduction (Hansen & Barnier, 1972; Ochoo, 2003). As a result, it would not be expected that during heat conduction the phases should behave as if sharp boundaries exist between them, especially at higher temperatures. Similarity or difference between other classes of composite materials and semi-crystalline polymers, as far as the boundary effect is concerned, has not been well.
established. It may be argued that the existence of the first two-terms of equations 1 and 2 in any model and, hence, that of semi-crystalline polymers would be enough to reveal the extent of its similarity in thermal conductivity behaviour with other composite materials and, hence, a recognition of its composite nature.

MATERIALS AND METHOD

Commercial isotactic polypropylene labeled as PPH 30605 and melt index 1.7 were supplied by East Africa Bag and Cordage Co. Ltd. in pellets form. The pellets were melted in specially designed cylindrical mould of diameter 1.5 cm and 6 cm long, evacuated of air and kept in the temperature range of 180-240°C in an oven. The mould was then allowed to cool at a controlled rate in the oven.

Samples formed were annealed under different conditions, constant temperature but varying time to vary the degree of crystallinity. Density of the samples were determined using a graduated density gradient column method, the degree of crystallinity was determined from Perkin-Elmer IR spectrometer model 500 and the Beer-Lambert law. Cylindrical samples of diameter 0.5-0.6 cm and length 0.95 cm, were machined from the annealed samples for the thermal conductivity measurements. They were enclosed in a specially designed cell, lagged with fiber glass to minimize radial heat losses. A 500 watt flash bulb was used in a transient method to generate heat on one face of the sample and the rate of thermal diffusion to the opposite face of the sample monitored through thermocouples connected to a data logger, measuring the rate of temperature build up.

RESULTS AND DISCUSSION

Characteristic temperature versus time graphs similar to Figure 1 were obtained and used to determine rate of thermal diffusivity ($\alpha$) in samples, according to the procedure and equation given by Carslaw & Jeager (1959), where the straight portion of the curve is extrapolated to the time axis, to obtain the time axis intercept, $t_x$, required in the expression

$$
\alpha = \frac{0.48L_o^2}{\pi^2 t_x} \quad \text{where } L_o \text{ is the length of the sample.}
$$
The thermal conductivity of a sample was then calculated from $k = C_p \alpha \rho$, where $\rho$ is the density of the material, (Hall, 1986; Ochoo, 1990). According to Frank (1970), for isotactic polypropylene the specific heat capacity $C_p$ varies with temperature according to the expression

$$C_p = 4.184 \left( 0.3669 + 0.00242 T \right) \text{J/g K}$$

Table 1 and Figure 2 show the results obtained in this study for the variation of thermal conductivity of isotropic isotactic polypropylene with temperature, it is linear over a range of about 35°C. This suggests that whatever is happening at one temperature would replicate at any other temperature or, in other terms, follow the law of superposition.

**Figure 1.** Variation of the back surface temperature with time, for isotactic polypropylene sample of volume fraction crystallinity $\phi = 0.64$ at 298 K.
Figure 2. Variation of thermal conductivity of isotropic polypropylene with temperature, for volume fraction crystallinity $\phi = 0.64$.

Table 1. Variation of thermal conductivity of isotropic isotactic polypropylene with temperature.

<table>
<thead>
<tr>
<th>Temperature /K</th>
<th>Thermal Conductivity $\times 10^{-1}$ w/m K</th>
</tr>
</thead>
<tbody>
<tr>
<td>293</td>
<td>1.500</td>
</tr>
<tr>
<td>298</td>
<td>1.502</td>
</tr>
<tr>
<td>303</td>
<td>1.565</td>
</tr>
<tr>
<td>313</td>
<td>1.625</td>
</tr>
<tr>
<td>323</td>
<td>1.675</td>
</tr>
<tr>
<td>333</td>
<td>1.720</td>
</tr>
</tbody>
</table>

Variation of thermal conductivity with crystallinity results, at 298 K, are as shown in Figure 3 and Table 2.
Attempts to obtain volume fraction crystallinity (\(\phi\)) below 0.4 was not successful due to the required conditions which could not be achieved easily. As a result, the experimental thermal conductivity values for those values of crystallinity could not be determined. However, because the thermal conductivity for purely amorphous polymer \(K_a\), that is, when \(\phi = 0\), was significant to the interest of this investigation, it became necessary to obtain the thermal conductivity of amorphous phase at 298K by extrapolation, following the procedure described by Choy & Young (1977). The value obtained was \(8 \times 10^{-2}\) w/mK and was used to draw the curve in figure 3. The curve shows a non-linear relationship between thermal conductivity and volume fraction crystallinity. Its shape became of much interest because it resembles a quadratic curve in part and mostly because such curves are described by two parameter power functions of the form (Microcal Software, Inc., 1995).

\[
y = a(1 + x)^b \quad \text{where } b > 1
\]

Considering \(b = 2\), because of its resemblance to a quadratic curve, \(y\) takes the form.
where \( y = K_o \) - thermal conductivity for an isotropic sample

\( x = \phi \) - the volume fraction crystallinity.

\( a, b \) and \( c \) are constants which can be determined from the graph

For \( x = \phi = 0 \), \( c \) is the thermal conductivity of purely amorphous polypropylene. The values ‘\( a \)’ and ‘\( b \)’ in the equation were obtained from the curve, leading to equation 4.

\[
K_o = (0.8 + 0.451\phi + 0.929\phi^2) \times 10^{-1} \text{ w/mK}
\]

………………… 4

On dividing both sides by \( K_a \) which is \( 0.8 \times 10^{-1} \text{ w/mK} \), the expression becomes

\[
\frac{K_o}{K_a} = 1 + 0.564\phi + 1.161\phi^2
\]

………………… 5

Equation 5 has similar features to equation 1, especially the existence of \( \phi^2 \), suggesting that factors leading to the term containing \( \phi^2 \) for composite materials are also in play in polypropylene. At higher temperatures the ratio of the thermal conductivity of crystalline phase (\( K_c \)) to that of the amorphous phase (\( K_a \)) is believed to be much greater than one where as at very low temperatures \( K_c/K_a \approx 1 \) (Choy & Young 1977; Ochoo, 1990). If higher terms (\( n \geq 3 \)) in equation 1 are ignored for the semi-crystalline polymers, i.e ignoring other aspects of thermal conductivity the higher terms stand for in a composite material so as to consider the boundary effect, particle size and distribution aspects only and using the assumption that the ratio \( K_c/K_o \gg 1 \), then terms in equation 1 reduce to those in equation 6, where \( K_c/K_a = B \).

\[
\frac{K_o}{K_a} = 1 + 2\phi + \frac{2}{3} (\phi + 2\phi^2)
\]

………………… 6

A reasonable similarity and agreement is found to exist between equations 6 and 5 if the second term containing \( 2\phi \) in equation 1 is omitted on the ground of the expected not-so-sharp crystalline-amorphous boundary, in which the boundary effect term is irrelevant. It then suggests that the variation of thermal conductivity of an isotropic semi-crystalline polymer (\( K_o \)) with crystallinity, at high temperatures, is not influenced by the amorphous-crystalline boundary and the experimental results would be expected to satisfy the condition

\[
\frac{K_o}{K_a} \leq 1 + \frac{2}{3} (\phi + 2\phi^2)
\]

………………… 7

Indeed, a big variation was realized between the experimental results and equation 6 due to the presence of the second term. In decimal form, the condition set in equation 7 comes out as
In this form it is easy to see that each of the remaining terms in the composite model approximates well to the terms in the experimental one, equation 5. Thus, the results not only predict the absence of the second term in equation 1, for the high temperature thermal conductivity, but also shows that it is in the absence of the second term that a very good agreement between the experimental values and equation 1 can be realized. The theoretical values from expression 7, which is equation 1 without the second term, are shown in Table 2 and plotted in Figure 3. They show good agreement with the experimental values than the modified Maxwell model, equation 2.

The need to remove the second term in the composite model of equation 1, in itself suggests the valid terms and form for the high temperature thermal conductivity composite model for isotropic semi-crystalline polymers. This is supported by good agreement between the composite model (before and after its modification) and the thermal conductivity results of other polymers at other temperatures, as shown in Tables 3 and 4. At low temperatures the unmodified form of the composite model, with the higher terms still ignored but $K_c/K_a \approx 1$, accurately predicts the thermal conductivity values. It failure at temperatures much greater than 100 K, unless the second term in the model is removed is a justification of the need to modify the model for it to agree well with the results of polymers. This observation not only justifies the modification of the model but also justifies existence of pronounced boundary-effect at low temperatures, which vanishes at high temperatures, and that the thermal conductivity of an isotropic semi-crystalline polymer becomes independent of the thermal conductivity of the crystalline phase (the term $K_c$) at high temperatures.

Table 2. Variation of thermal conductivity with crystallinity results at 298 K.

<table>
<thead>
<tr>
<th>Volume fraction</th>
<th>Thermal Conductivity Experimental value $\times 10^1$ w/mK</th>
<th>Thermal Conductivity Modified composite model equation 7 $\times 10^1$ w/mK</th>
<th>Thermal Conductivity Maxwell model equation 2 $\times 10^1$ w/mK</th>
</tr>
</thead>
<tbody>
<tr>
<td>Crystallinity</td>
<td>Thermal Conductivity</td>
<td>Thermal Conductivity</td>
<td>Thermal Conductivity</td>
</tr>
<tr>
<td></td>
<td>Experimental value</td>
<td>Modified composite model equation 7</td>
<td>Maxwell model equation 2</td>
</tr>
<tr>
<td>0</td>
<td>0.8</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>0.201</td>
<td>-</td>
<td>0.928</td>
<td>0.971</td>
</tr>
<tr>
<td>0.300</td>
<td>-</td>
<td>1.056</td>
<td>1.067</td>
</tr>
<tr>
<td>0.435</td>
<td>1.172</td>
<td>1.234</td>
<td>1.207</td>
</tr>
<tr>
<td>0.483</td>
<td>1.207</td>
<td>1.306</td>
<td>1.261</td>
</tr>
<tr>
<td>0.521</td>
<td>1.354</td>
<td>1.367</td>
<td>1.304</td>
</tr>
<tr>
<td>0.590</td>
<td>1.494</td>
<td>1.486</td>
<td>1.388</td>
</tr>
<tr>
<td>0.640</td>
<td>1.502</td>
<td>1.578</td>
<td>1.451</td>
</tr>
<tr>
<td>0.690</td>
<td>1.669</td>
<td>1.676</td>
<td>1.517</td>
</tr>
<tr>
<td>0.730</td>
<td>1.804</td>
<td>1.758</td>
<td>1.572</td>
</tr>
</tbody>
</table>

*thermal conductivity value for the amorphous phase estimated according to procedure outlined by Choy & Young (1977).
Table 3. Thermal conductivity of PE reported by Choy & Young (1977), $K_s = 2.4 \times 10^{-1}$ w/mK.

<table>
<thead>
<tr>
<th>Material</th>
<th>Temperature K</th>
<th>Volume fraction crystallinity</th>
<th>Experimental thermal conductivity $\times 10^{-1}$ w/mK</th>
<th>Equation 6.1 $\times 10^{-1}$ w/mK</th>
<th>Percentage error %</th>
</tr>
</thead>
<tbody>
<tr>
<td>Polyethylene (PE)</td>
<td>323</td>
<td>0.69</td>
<td>4.89</td>
<td>5.03</td>
<td>2.9</td>
</tr>
</tbody>
</table>

Table 4. Thermal conductivity of semi-crystalline polymers at low temperatures reported by Choy & Greig (1999), tested against the composite model before modification.

<table>
<thead>
<tr>
<th>Material</th>
<th>Temperature K</th>
<th>Volume fraction crystallinity</th>
<th>Experimental thermal conductivity $\times 10^{-1}$ w/mK</th>
<th>Equation 1 $\times 10^{-1}$ w/mK</th>
<th>Percentage error %</th>
</tr>
</thead>
<tbody>
<tr>
<td>PP</td>
<td>100</td>
<td>0.65</td>
<td>1.80</td>
<td>1.84</td>
<td>2.2</td>
</tr>
<tr>
<td>PET</td>
<td>70</td>
<td>0.29</td>
<td>1.74</td>
<td>1.77</td>
<td>1.7</td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.39</td>
<td>1.88</td>
<td>1.86</td>
<td>1.1</td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.51</td>
<td>2.02</td>
<td>2.00</td>
<td>1.0</td>
</tr>
</tbody>
</table>

CONCLUSION

The results of this study have confirmed that while semi-crystalline polymers exhibit behaviour significant enough to make them be treated as composite materials, whose thermal conductivity can be analyzed using composite model by Sangani & Yao (1988) the crystalline-amorphous boundary effect which defines the composite nature, however, is more pronounced at low temperatures but vanishes at temperatures much greater than 100 K and that the parameter for the thermal conductivity of the crystalline phase ($K_c$) also becomes irrelevant. As a result, without modification, the composite model may be used to analyze thermal conductivity behaviour of semi-crystalline polymers, at temperatures around 100 K and below but when dealing with temperatures much greater than 100 K the boundary effect term be considered irrelevant.
REFERENCES


