The mass production of polyurethane plastics has meant an increase in the requirements that these products have to meet and in the level of technology for their manufacture. Currently important is the problem of eliminating from the production process toxic compounds and those substances posing a threat to the environment. Another requirement is a reduction in production costs together with an improvement in the processing properties while retaining the right service properties of the products.

A predominant trend in the modern world is to restrict energy consumption. One of the ways of achieving this goal is to improve the thermal insulation of buildings, reactors, heating pipes and mains pipes. In many cases what is required is that the layers providing the heat insulation should be of restricted thickness, so for this reason in many applications an improvement in the insulation can be achieved by changing the insulating material or improving the insulating properties of the material already used. It appears that foams based on polyurethanes (PUR) can achieve the lowest coefficient of thermal conductivity among insulating materials, and thus efforts have concentrated on reducing this still further.

Rigid PUR foams are crosslinked materials and usually characterised by a low apparent density and high content of closed pores. For certain specialised applications such as sound-damping materials foams with open pores are prepared [1 – 5]. The quality of PURs is described on the basis of a determination of their physical and mechanical properties by standard methods [6]. These materials are normally employed for constructional or insulation functions [7]. Products made from PUR can be used in a temperature range from -50°C to about +90°C [6]. This beneficial characteristic results from the high durability of the urethane bond and specific features of the raw materials employed [8]. The properties of PUR foams depend largely on their density, which can vary in the range 10 – 600 kg/m³. In addition these materials shows high values for the softening point and glass transition temperature (>20°C) and good resistance to the action of many solvents [6, 7].

In the present article we shall present results of a study of the effect of the apparent density on the thermal conductivity of rigid PUR foams foamed with a mixture of pentanes. We have critically compared the suitability of the known models from the literature for determining the values of the coefficient of thermal conductivity of PUR foams.

EXPERIMENTAL

Materials
For the synthesis of the PUR foams we used the following base materials:

Polyols
- Polieterol D-24, a product obtained by the reaction of bisphenol-A with ethylene oxide, with a hydroxyl number of 260 mg KOH/g; produced by the Institute of Heavy Organic Synthesis in Kedzierzyn.
- Rokopol TD-34, an oxyalkylenated o-tolylenediamine with hydroxyl number 420 mg KOH/g; produced by Alfa Systems in Brzeg Dolny.
Isocyanate
- Supracec DNR, a polymeric diisocyanate diphenylmethane containing 31% by mass of free – NCO groups; produced by Imperial Chemical Industries Ltd., Belgium.

Surfactant
- SR-321, a silicone oil, produced by Union Carbide, USA.

Catalyst
- Texacat DMCHA, N,N'-dimethylcyclohexylamine; produced by Texaco Chemical Deutschland GmbH, Germany.

Blowing agent
- Industrial pentane – a mixture of 75% n-pentane and 25% isopentane, produced by Jedlicze Refinery.

MEASUREMENT OF THE COEFFICIENT OF THERMAL CONDUCTIVITY

The coefficient of thermal conductivity \( \lambda \) was measured using a Fox 200 made by Lasercomp. This makes it possible to determine the value of \( \lambda \) in the range 20 – 100 mW/m.K. The studied specimen measures 25 cm x 25 cm, and its thickness can be as much as 50 mm. The final condition for correctly carrying out the measurement is the complete filling of the measuring chamber. A diagram of the apparatus is shown in Figure 1.

The base of the chamber (4) is mounted in such a way that its position can be regulated using four independent stepped motors. This arrangement ensures accurate fitting of the specimen to the upper and lower wall of the chamber. The heat source and remover are attached to these walls. At a minimum distance from the specimen surface are placed detectors for measuring the temperature to an accuracy of 0.01°C. The Peltier modules used in the device (1 and 2) permit measurements to be made under conditions of heat flow in two directions – up and down. The method of measuring the value of the coefficient \( \lambda \) consists in determining the amount of heat flowing through the material in unit time during steady flow of the heat, when a temperature difference has been set up along opposite sides of the specimen.

The measurements are carried out in series of 512 at intervals of 0.5 s. After performing the set minimum number of series of measurements conditions of completion of the measurement are checked from the results of the three last measurements and if these are fulfilled the process is taken as being completed. The results and measurement parameters obtained are recorded in the form of a pack.

MEASUREMENT RESULTS AND THEIR COMPARISON WITH LITERATURE DATA

A series of studies have been published which relate to the transport of heat in polyurethane foams under steady-state conditions [9 – 21]. In general terms the speed of this transport is described by the apparent thermal conductivity \( \lambda_z \), which combines several physical mechanisms (conduction via the solid phase of the polymer, conduction through the gaseous phase, thermal radiation, convection in the gaseous phase). The coefficient \( \lambda_z \) defined in this way can be described in the case of uniaxial steady transport of heat by the equation:

\[
\lambda_z = q / \frac{dT}{dx}
\]

(1)

where \( q \) is the density of the total stream of heat (W/m²) transported along the path x, and \( dT/dx \) is the temperature gradient in the direction of x.

Figures 2 and 3 show the curve of the dependence of the apparent coefficient of thermal conductivity on the density of the rigid PUR foam (RPURF). This relationship shows the minimum values of \( \lambda_z \) corresponding to density in the range 33 – 37 kg/m³.

Microscopic studies showed that foams with the lowest density values have cells with relatively large dimensions. It is known that large dimensions of the cells reduce the insulation properties of a porous material.

In the low case of a low wall density the intercellular ribs of the foams are built up from a small amount of polyurethane material, and thus present a weaker barrier during their penetration by infrared radiation. Cell walls of low thickness constitute a weaker barrier to the transport of heat. The form of the curve of the dependence \( \lambda_z = f(p) \) is probably due to the fact that in the very low density
region of the foams (and hence in the region of high translucency) the proportion of irradiation in the total mechanism of heat transport is high. It decreases with increase in density till it reaches the value \( \lambda_{z_{\text{min}}} \). Further increase in the density of the foam no longer gives rise, practically speaking, to a change in flow of heat transported by radiation, whereas there is an increase in the amount of conduction through the solid phase, mainly the ribs, since this is where the solid phase material is mainly located. This hypothesis is confirmed by calculations made using the Glicksman model [cf. equation (4)].

With increase in the apparent density of the RPURF there is an increase in the amount of PUR material per unit volume of the foam. Even a slight decrease in the average length of the cells in this density range means that an increase in the amount of polymer must give rise to an increase in thickness of the chamber walls and the ribs. In such a situation the amount of thermal energy conveyed in the form of radiation in the gaseous phase and the amount of convection in this phase should not change. On the other hand there is an increase in the amount of heat conveyed through the solid phase, which in foams with maximum density values is three times as great per unit volume as it is in RPURF of minimum density.

In studies described in refs. [9 – 21] attempts were made to separate the various mechanisms of transport, treating the apparent coefficient \( \lambda_z \) as being equal to the sum of the following coefficients:

\[
\lambda_z = \lambda_s + \lambda_G + \lambda_R + \lambda_K
\]

where the subscripts S, G, R and K correspond to transport of heat in the solid phase, transport of heat in the gaseous phase, by radiation in the gaseous phase and by convection in the gaseous phase respectively.

Taking equation (1) into account this also makes it possible to separate the density components of heat flow \( q \) in the same way, so that:

\[
q = q_s + q_G + q_R + q_K
\]

where the subscripts have all the same meanings as in equation (2).

In general what is important is that when there are gas bubbles present in the foam which are smaller than 1 mm the mechanism of convection transport in the gaseous phase can be ignored [10] and hence \( \lambda_K = 0 \) and \( q_K = 0 \).

In Table we have collected together the published relationships which can be used to determine the coefficients \( \lambda \) corresponding to the individual mechanisms.

The various symbols occurring in Table 1 have the following meanings:

- \( k \) is the extinction coefficient (1/m),
- \( C_d \) is the diameter of the cells (m),
- \( T \) is the temperature (K),
- \( \rho_f \) is the apparent density of the foam (kg/m\(^3\)),
- \( L \) is the thickness of the layer of the polyurethane foam (m),
- \( Y \) is the molar fraction,
- \( \eta \) is the gas viscosity (Pa.s),
- \( M \) is the molar mass,
- \( \varepsilon \) is the volume fraction of pores of the foam,
- \( \bar{\varepsilon} \) is the mass fraction of the polymer forming the ribs,
- \( \sigma \) is the Stefan-Boltzmann constant, amounting to 5.6705 \( \times 10^{-8} \) W/(m\(^2\).K\(^4\)),
- \( e \) is the transmittance of the cell walls,
- \( \lambda_p \) is the coefficient of heat transfer through the unfoamed PUR.

Figure 4 shows the values of \( \lambda \) obtained by calculation from the equations shown in Table 1. This Figure shows that the calculated amount of heat transported by radiation through one and the same foam varies within wide limits. The highest and lowest values differ by as much as one order. On the other hand the values of the coefficient of thermal conductivity calculated by various methods given in Table 1 applying to gases enclosed in the pores of the foam vary only slightly (Figure 5). Large difference occur again in the case of the coefficient of heat transfer
Table 1 Equations describing heat transfer through PUR foams

<table>
<thead>
<tr>
<th>Number</th>
<th>Suggested relationship</th>
<th>Authors</th>
<th>Notes and assumptions</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.1</td>
<td>( \lambda_R = \frac{16\sigma T^3}{3 \cdot k} )</td>
<td>Sinofsky and Glicksmann</td>
<td>Can be used only at a temperature of 75°C, corresponding to about 298 K</td>
</tr>
<tr>
<td>1.2</td>
<td>( \lambda_R = 4 \cdot \sigma \cdot e \cdot C_d \cdot T^3 )</td>
<td>Bhattacharjee and co-workers [11]</td>
<td></td>
</tr>
<tr>
<td>1.3</td>
<td>( \lambda_R = \frac{1.51 \cdot C_d \cdot \sigma \cdot T^3}{\left( \frac{\rho_1}{\rho_s} \right)} )</td>
<td>[12]</td>
<td></td>
</tr>
<tr>
<td>1.4</td>
<td>( \lambda_R = \frac{16 \cdot \sigma \cdot T^3 \cdot C_d}{2 - e} )</td>
<td>Cunningham and Sparrow [13]</td>
<td>It is assumed that ( e = 0.8 )</td>
</tr>
<tr>
<td>1.5</td>
<td>( \lambda_R = \frac{16\sigma T^3 C_d}{3 \cdot 3.68 \left( \frac{\rho_1}{\rho_s} \right)} )</td>
<td>Glicksmann and Torpey [14] and assumptions by Hotell and Sarofim [15]</td>
<td>Use is made of an analogy to the molecular theory of gases. It is assumed that the ribs can absorb and emit radiation. The cells and pentagonal dodecahedrons.</td>
</tr>
<tr>
<td>1.6</td>
<td>( \lambda = \lambda_a + \lambda_e = \lambda_a + \frac{4\sigma T L}{1 + \left( \frac{L}{C_f} \right) \left( \frac{1}{e} - 1 \right)} )</td>
<td>Williams and Aldao [16]</td>
<td></td>
</tr>
</tbody>
</table>

Transfer in gaseous phase comprising a mixture of gases

<table>
<thead>
<tr>
<th>Number</th>
<th>Suggested relationship</th>
<th>Authors</th>
<th>Notes and assumptions</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.1</td>
<td>( \lambda_G = \sum \left( y_i \cdot \lambda_i \right) )</td>
<td>According to ref. [17]</td>
<td>Can be used only when the values ( \lambda ) are close</td>
</tr>
<tr>
<td>2.2</td>
<td>( \lambda_G = \frac{1}{\sum \left( \frac{y_i}{\lambda_i} \right)} )</td>
<td>According to ref. [17]</td>
<td>Can be used only when the values ( \lambda ) are close</td>
</tr>
<tr>
<td>2.3</td>
<td>( \lambda_G = \sum_{i=1}^{n} \frac{y_i \lambda_i}{\sum_{i=1}^{n} y_i \lambda_i} )</td>
<td>Vassileva (according to ref. [18])</td>
<td>( \lambda ) is Vassileva’s function</td>
</tr>
<tr>
<td>2.4</td>
<td>( A_i = \left[ 1 + \frac{n_i}{n_i} \right]^{0.5} \left( \frac{M_i}{M} \right)^{0.85} \left( \frac{\gamma_i}{\gamma} \right)^{-0.75} )</td>
<td>Mason and Saxen (according to ref. [18])</td>
<td>One of the proposed descriptions of Vassileva’s function</td>
</tr>
</tbody>
</table>

Transfer in solid phase

<table>
<thead>
<tr>
<th>Number</th>
<th>Suggested relationship</th>
<th>Authors</th>
<th>Notes and assumptions</th>
</tr>
</thead>
<tbody>
<tr>
<td>3.1</td>
<td>( \lambda_s = \frac{2 - f}{3} - \frac{f}{3} \left( 1 - \varepsilon \right) \cdot \lambda_p )</td>
<td>Sinofsky and Glicksmann according to ref [10]</td>
<td>Authors’ assumptions: ( \varepsilon = 0.979; \ f = 0.8 ) – describes the position of the solid material in space</td>
</tr>
<tr>
<td>3.2</td>
<td>( \lambda_s = \lambda_p \left( 1 - \varepsilon \right) \cdot \varphi )</td>
<td>Sparks and Arvidson [20]</td>
<td>( \varphi ) - a spherical coefficient, associated with the orientation of the cells</td>
</tr>
</tbody>
</table>

Complex models

<table>
<thead>
<tr>
<th>Number</th>
<th>Suggested relationship</th>
<th>Authors</th>
<th>Notes and assumptions</th>
</tr>
</thead>
<tbody>
<tr>
<td>4.1</td>
<td>( \lambda_{S1,G} = \lambda_G + \frac{2}{3} \left( 1 - \varepsilon \right) \lambda_p )</td>
<td>Schuetz and Glicksmann [21]</td>
<td>Assumption: the cells are cubes</td>
</tr>
<tr>
<td>4.2</td>
<td>( \lambda_{S2,G} = \lambda_G + \frac{2}{4} \left( 1 - \varepsilon \right) \lambda_p )</td>
<td>Schuetz and Glicksmann [21]</td>
<td>The upper limit of conductivity of actual foams</td>
</tr>
<tr>
<td>4.3</td>
<td>( \lambda_{S3,G} = \lambda_G + 0.8 \left( 2 \frac{f}{3} \right) \left( 1 - \varepsilon \right) \lambda_p )</td>
<td>Schuetz and Glicksmann [21]</td>
<td>The lower limit of conductivity of actual foams</td>
</tr>
</tbody>
</table>
calculated according to equations for complex models (\(\lambda_{SG}\)) (Figure 6).

The calculations relating to the initial data corresponding to the foams used for the studies, and analysis of the equations from Table 1 confirm our opinion that the model corresponding most closely to the results of our tests is the Glicksman model described by equations 1.1 and 4.1 in connection with equation 2.3 referring to the heat transport in the gaseous phase. This is shown in Figure 7. The line which best described the results obtained (3 days from the time of synthesis of the foam) is the broken line in this Figure. This can be described by an equation which is the sum of equations 1.1, 4.1 and 2.3:

\[
\lambda_z = \frac{16 \cdot \delta \cdot T^6}{3 \cdot K} + \frac{2}{3} (1 - \varepsilon) \cdot \lambda_p + \lambda_G
\]

(\(\lambda_G\) according to equation 2.3 in Table 1).

Figure 8 shows the contributions of the various flows to the transport of heat through RPURF of differing densities, as calculated from equation (4). The changes in the percentage contributions of the various mechanisms in the coefficient \(\lambda_z\) (describing the total heat transport) with increase in the densities of the foams are converted as follows:

- Transport in the solid phase: increases from about 7 to about 20%.
- Transport in the gaseous phase: minimum increase from about 53 to about 57%.
- Radiation: initially decreases from about 40% to about 23%, but in foams with the highest density increases slightly to about 28%.

**Figure 9** shows the dependences as in **Figure 8** but with an additional two curves describing the maximum and minimum values of the coefficient $\lambda_z$ determined from the dependences in **Table 1**.

The maximum values of the coefficient $\lambda_z$ are only slightly higher than the values seen from the experimental data, whereas the minimum values are clearly lower than the measured values. The dependences in **Table 1** were worked out for polyurethane foams prepared using freons as blowing agents. In our present study we used pentanes as the blowing agents [22 and 23], which have higher thermal conductivity values in the gaseous phase, $\lambda_G$, which means that the RPURF obtained using them are characterised also by a higher coefficient of thermal conductivity $\lambda_z$. This fact may also explain why the calculated maximum values of $\lambda_z$ in **Figure 8** are only slightly lower than the experimental values.

**CONCLUSIONS**

The value of the apparent coefficient of thermal conductivity – which contains all the possible mechanisms of heat transport – of rigid polyurethane foams foamed with a hydrocarbon blowing agent shows a minimum in the density range $33 - 37\ \text{kg/m}^3$, where it is about 25 mW(m.K). This variability of the coefficient $\lambda_z$ as a function of the density of the foams ($\rho$) is similar in the case of foams studied 3, 10, and 183 days after their preparation.

Of all the models published in the literature and quoted in the present study, and the equations describing them only the Glicksman model describes with satisfactory accuracy the dependence $\lambda_z = f(\rho)$ for foams 3 days after their preparation.

Although it did not prove possible experimentally to separate the various mechanisms of heat transport in the case of polyurethane foams, nevertheless the measured apparent coefficient $\lambda_z$ shows good agreement with equation (4) describing the Glicksman model.

**REFERENCES**


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