

Effect of Pressure on Thermal Conductivity of Polymers

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ABSTRACT

The effect of pressure on thermal conductivity of five commercial polymers has been investigated. The five materials were selected as representative of materials frequently used in industry. The materials were; a polypropylene, a high-density polyethylene, a polystyrene, a talc filled polypropylene and a glass filled polypropylene. A short review of thermal conductivity theory is presented and practical details of measurements at elevated pressure are described. For all materials the thermal conductivity was found to increase linearly with pressure, but the magnitude of the increase varied greatly between the materials. Results for ambient pressure, extrapolated from the elevated pressure values, were generally found to be higher than the values directly measured at ambient pressure. Possible explanations for this difference are offered and the implications for measurements are discussed. This report shows that for some commercial polymers the effect of pressure on thermal conductivity is important and can have a significant impact on processing parameters, such as predicted cycle times, derived from thermal conductivity values.

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Approved on behalf of the Managing Director, NPL
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1 INTRODUCTION

The thermal conductivity of a material is defined as the rate at which heat flows through it. The precise definition is given by Fourier's equation, shown below:

$$\frac{dq}{dt} = -\lambda A \frac{dT}{dx} \quad (1)$$

Where q is the heat energy flowing in the x direction through an area A during time t , dT/dx is the temperature gradient, and λ is the thermal conductivity of the material. These quantities are illustrated in Figure 1.

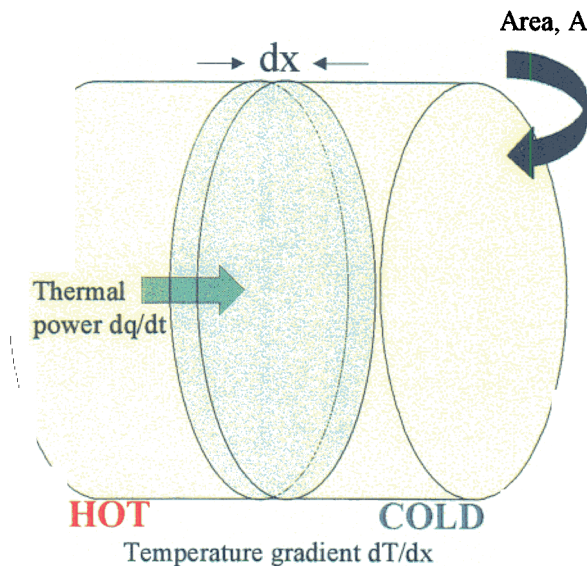


Figure 1 Schematic heat flow diagram

Knowledge of a material's thermal conductivity at different temperatures and pressures can be critical for modelling processing of polymers. Many modelling packages used to predict how a polymeric material will behave during moulding processes require a value for the thermal conductivity for accurate predictions. It is through these predictions that the processing conditions can be optimised to reduce wastage and increase productivity.

A material's thermal conductivity will change under different conditions of temperature and pressure, for example a semi-crystalline material shows a dramatic change in thermal conductivity through the glass transition and thermosets show differences between their cured and uncured phases. Therefore, it is important to measure the thermal conductivity over the processing range to ensure accurate modelling.

Measurements of thermal conductivity at elevated pressure are relatively unusual and in many cases the value at atmospheric pressure is used as there is no alternative. The limited research that has been conducted on the effect of pressure indicates that the effect of pressure can be significant, see for example [1], although the overall picture is far from clear. This report describes the measurement of thermal conductivity at elevated pressure and reports results for selected polymers.

2 MEASUREMENT OF THERMAL CONDUCTIVITY

All measurements were conducted using a pvT-100 machine manufactured by SWO with a thermal conductivity cell attachment. This equipment is capable of measuring the thermal conductivity of plastics, rubbers, oils and other types of materials as a function of both temperature and pressure. The equipment is based on the transient hot wire method for measuring thermal conductivity. A cross section of the apparatus is shown in Figure 2.

Within the thermal conductivity probe there is a heater and a thermocouple. These wires lie parallel to each other within the needle probe. With the specimen at a set temperature power is fed to the heater wire for a set time and the temperature rise is measured during this time with the thermocouple. The temperature rise is related to the thermal conductivity of the material in which the needle probe is inserted.

Pressures in the range of 15 MPa to 160 MPa can be applied to the material at temperatures from 25 °C to 280 °C. A typical thermal conductivity sample will be 50 mm long with a diameter of 9.8 mm.

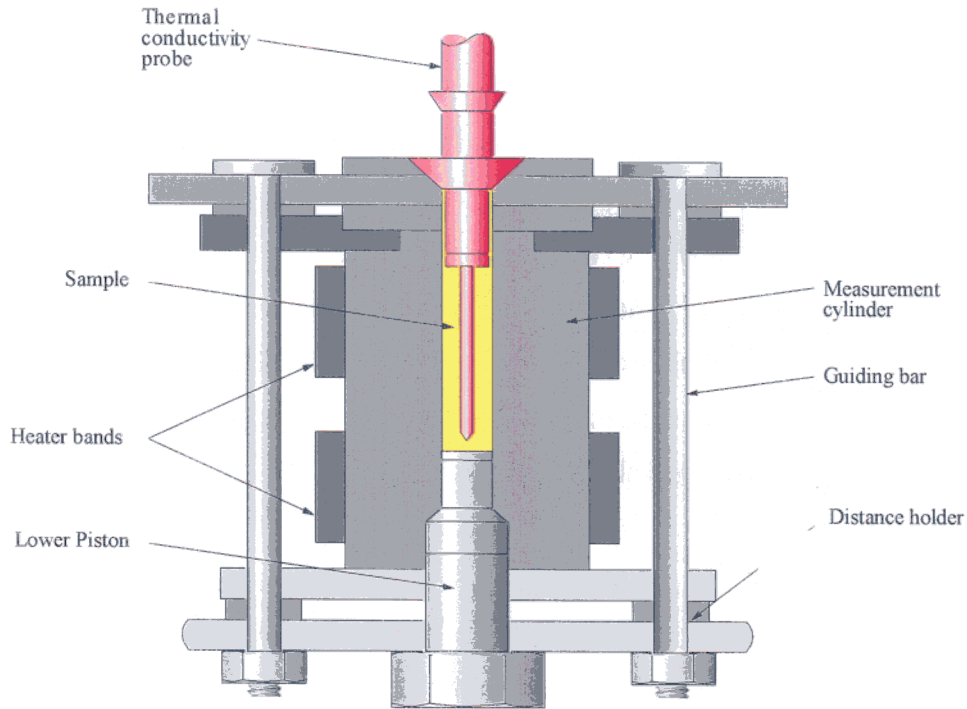


Figure 2 Thermal conductivity cell and probe

The thermal conductivity is calculated using a plot of temperature against the natural log of time. The equation used is given below [2]:

$$\Delta T = +\frac{q}{4\pi\lambda} \ln(t).B \quad (2)$$

Where ΔT is the temperature rise of the probe, q is the heat input per unit length, λ is the thermal conductivity of the material, t is the time and B is a correction factor. This correction factor is evaluated by calibration of the instrument with a glycerol sample of known thermal conductivity and is required to account for deviations from the idealised case used for the theoretical analysis.

The results presented in this Report were taken at a single temperature for each material and at pressure ranging from atmospheric to 160 MPa. Heat is supplied to the wire for thirty seconds during a measurement and the gradient of the line is evaluated for times between two and thirty seconds. Five separate measurements are taken for each pressure and the reported value is the average of the five measurements.

3 EFFECT OF PRESSURE ON UNFILLED POLYMERS

Three unfilled polymers were studied, polypropylene, high-density polyethylene and polystyrene. The thermal conductivity of each polymer was measured at a single temperature at pressures between 15 MPa and 160 MPa. Polypropylene and polyethylene were tested at 180 °C and the polystyrene was tested at 120 °C. The results are shown in Figure . The error bars represent the standard deviation of the five measurements taken at each pressure. It can be seen that all three polymers exhibit a linear trend with respect to pressure. The coefficients of the linear fit to the experimental results are given in Table 1.

Figure 1 and Table 1 show that the effect of pressure is different for each polymer. The polypropylene is most affected by pressure, thermal conductivity increases by more than 40 % across the range of pressures studied. The polyethylene exhibits much less of a pressure effect and the polystyrene hardly changes across the range of pressure.

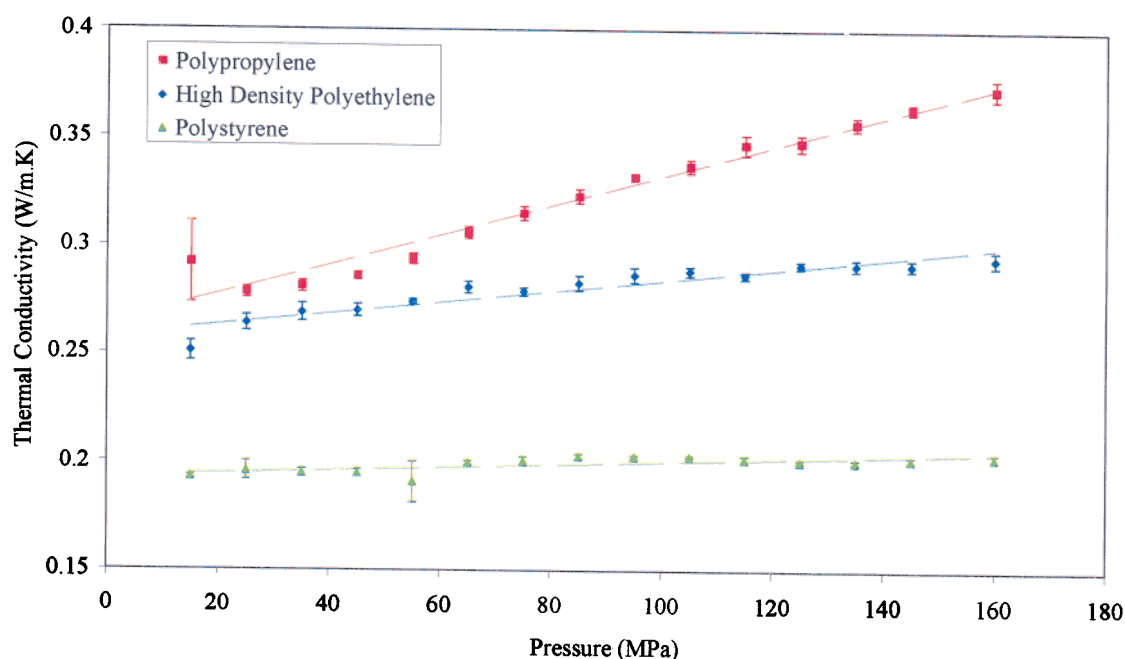


Figure 1. Effect of pressure on thermal conductivity of three unfilled polymers.

Table 1. Coefficients of fit for thermal conductivity against pressure data

Material	Gradient (W/m.K.MPa)	Intercept (W/m.K)	R ²
Polypropylene	6.87×10^{-4}	0.264	0.961
Polyethylene	2.61×10^{-4}	0.258	0.889
Polystyrene	7.07×10^{-5}	0.193	0.610

4 EFFECT OF PRESSURE ON FILLED POLYMERS

Glass and talc filled polypropylenes were tested across the same pressure range as the unfilled materials (15 to 160 MPa). Again, each material was tested at a single temperature, both the glass and talc filled polypropylene were tested at 200 °C. The data for both the filled materials, together with the data for unfilled polypropylene, are shown in Figure 2. As with the unfilled materials, the thermal conductivity appears linear with respect to pressure and the coefficients of the linear fit are shown in Table 2.

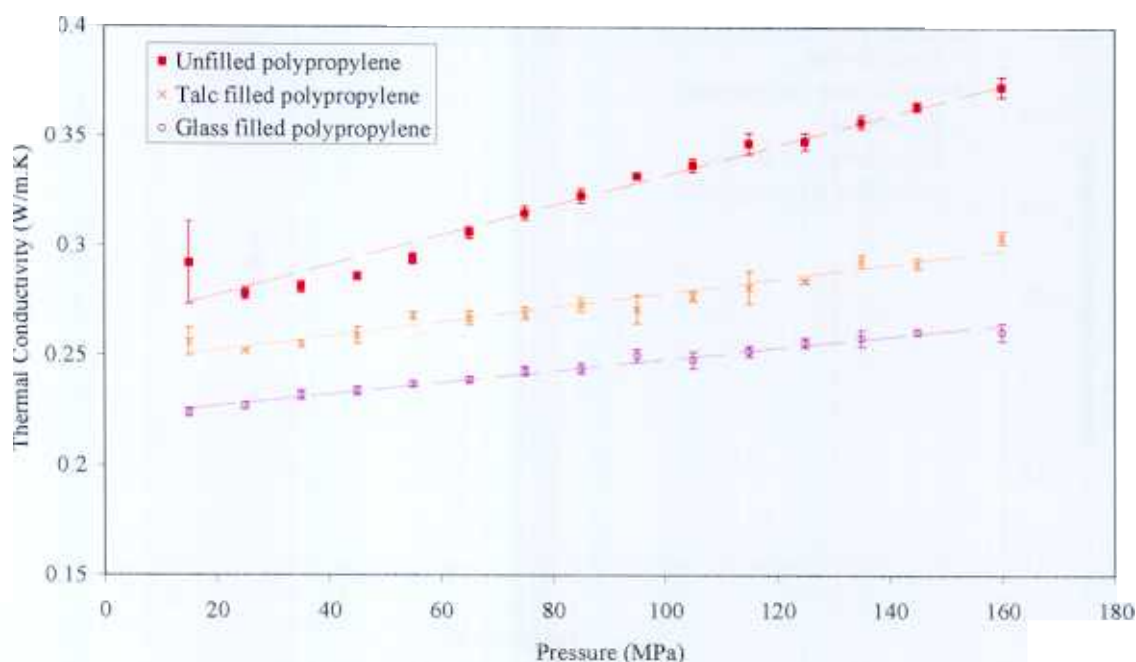
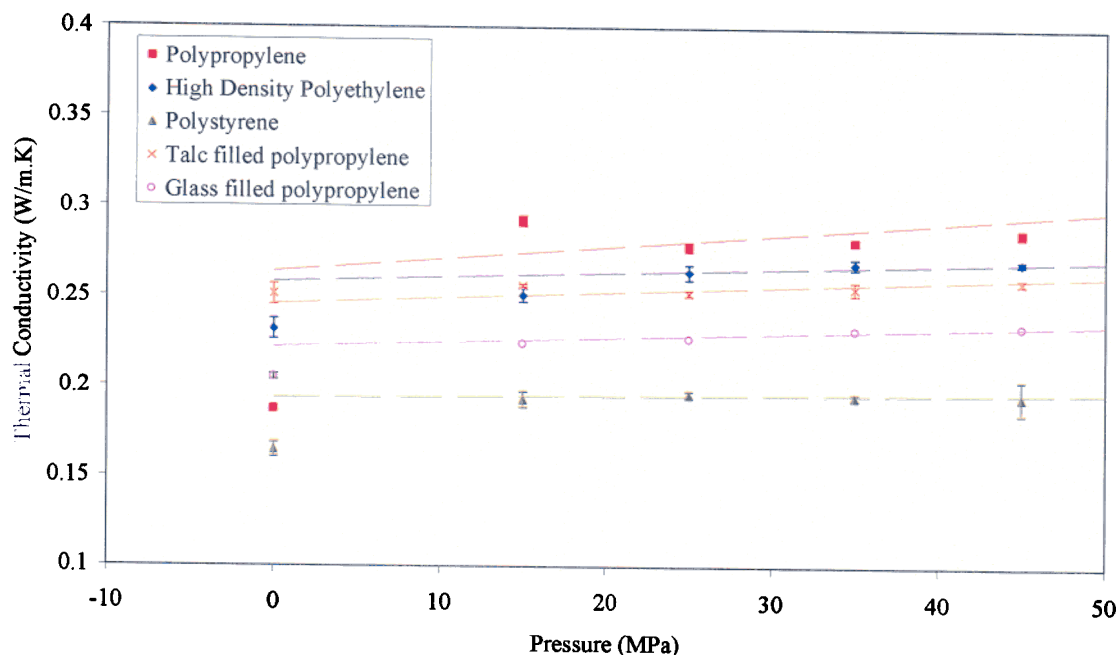
**Figure 2. Effect of pressure on thermal conductivity of filled polypropylene.**

Table 2. Coefficients of fit for thermal conductivity against pressure data

Material	Gradient (W/m.K.MPa)	Intercept (W/m.K)	R ²
Unfilled polypropylene	6.87×10^{-4}	0.264	0.961
Talc filled polypropylene	3.28×10^{-4}	0.245	0.951
Glass filled polypropylene	2.64×10^{-4}	0.222	0.984

5 MEASUREMENTS AT AMBIENT PRESSURE

A further effect that is of interest is an apparent offset between results measured at elevated pressure extrapolated to atmospheric pressure and measurements taken at atmospheric pressure. This effect is illustrated in Figure 3. The same data as presented in Figures 1 and 2 are presented and the linear fit is extrapolated to zero pressure. Also shown are values of thermal conductivity measured at atmospheric pressure. (Atmospheric pressure has been taken as zero pressure, although it is actually around 0.1 MPa.)

**Figure 3. Comparison of thermal conductivity at ambient and elevated pressure.**

It can be seen from Figure 3 that the measured thermal conductivity at atmospheric pressure is generally lower than the extrapolated values. These differences have been

tabulated and are presented in Table 3. The offset has been calculated in absolute terms and as a percentage.

Table 3. Comparison of measurements at ambient pressure with extrapolated values from elevated pressure measurements

Material	λ at ambient pressure (W/m.K)	Intercept (W/m.K)	Difference (W/m.K)
Polypropylene	0.187	0.264	0.077 (41 %)
Polyethylene	0.232	0.258	0.026 (11 %)
Polystyrene	0.165	0.193	0.028 (17 %)
Talc filled polypropylene	0.251	0.245	-0.006 (-2 %)
Glass filled polypropylene	0.205	0.222	0.017 (8 %)

It can be seen from Table 3 that the differences can be considerable and generally the measurement at atmospheric pressure is lower than the extrapolated value. It is possible that this offset is due to the poorer thermal contact between the polymer and the probe at atmospheric pressure.

6 DISCUSSION

There is limited scientific literature available on the effect of pressure on thermal conductivity of polymers. However, the pressure dependence of a range of polymers has been studied [3-5]. In every case thermal conductivity increases with pressure. A second effect that has been noted is that the dependence on pressure decreases at higher pressures. However, this effect was observed at pressures higher than those normally experienced in polymer processing. The maximum pressure for the measurements presented in this Report is 160 MPa, which is sufficient to include most conventional polymer processes. Hence, it is reasonable to conclude that the thermal conductivity is linear with respect to pressure for polymer processing and that a linear regression fit is appropriate for interpolation and extrapolation of thermal conductivity values with respect to pressure.

It has been observed that there is an offset between values measured at elevated pressure extrapolated to atmospheric pressure and values measured at atmospheric pressure. This may be due to reduced thermal contact between the probe and the sample at atmospheric pressure. This is an important point as it may account for the variability of thermal conductivity values reported in the literature. Indeed, heat transfer at interfaces does not seem to be well quantified with respect to polymer processing.

view was confirmed at a meeting of the NPL Industrial Advisory Group on Measurements Relating to Processing of Plastics [6], where it was suggested that this topic should be investigated in future work.

A possibly related observation is that the filled polypropylene materials exhibited a lower thermal conductivity than the unfilled polypropylene. It would be reasonable to expect that the filled polymers would exhibit a higher thermal conductivity, since both talc and glass fibre have a higher thermal conductivity than polypropylene. This observation may be a result of poor compounding leading to a lower heat transfer coefficient at the interface of the polymer and filler.

Thermal conductivity is essential for modelling the processing of polymers. It has been shown that thermal conductivity is important in determining cooling times and filling pressures [7, 8]. Neglecting the effect of pressure on thermal conductivity can also result in inaccurate predictions of warpage and shrinkage in the final part, as well as hot spots leading to degradation, which result from errors in modelling temperature distribution [9].

7 CONCLUSIONS

Thermal conductivity of a range of polymers was measured at pressures between 15 and 160 MPa. The dependence of thermal conductivity varied significantly between the polymers studied. Polypropylene exhibited a 42 % increase in thermal conductivity across the pressure range studied, while polystyrene showed hardly any increase. For all the materials studied, the thermal conductivity was found to be a linear function of pressure, at the range of pressure studied. Therefore, a linear regression fit may be used for extrapolation. The observed difference in the thermal conductivity extrapolated to

atmospheric pressure and values measured at atmospheric pressure suggests that the role of the interface between the metal probe and the polymer may be important.

REFERENCES

1. Chakravorty, S. and Brown, C. S. The significance of thermal material parameters in polymer processing. NPL Report DMM(A)167, April 1995.
2. Tye, R. P. Thermal conductivity - Volume 1, London, Academic Press, 1969.
3. Andersson, P. and Sundqvist, B. Pressure dependence of the thermal conductivity, thermal diffusivity and specific heat of some polymers. *Journal of Polymer Science*, 1975, **13**, 243-251.
4. Sandberg, O. and Bäckström, G. Thermal conductivity and heat capacity of liquid and glassy poly(vinyl acetate) under pressure. *Journal of Polymer Science*, 1980, **18**, 2123-2133.
5. Yen, C. L. Tseng, H. C. Wang, Y. Z. and Hsieh, K. H. Thermal conductivity of glass fiber reinforced polypropylene under high pressure. *Journal of Applied Polymer Science*, 1991, **42**, 1179-1184.
6. Chakravorty, S. (editor) Minutes of the 6th Meeting of the Industrial Advisory Group on Measurement Methods relating to the Processing of Plastics, Leicester, UK, July 2001.
7. Rides, M. The effects of thermal conductivity and heat transfer coefficients
8. Brown, C. S. and Percio, S. Heat transfer in polymer processing: The importance of accurate measurement. *Proceedings of Polymer Rheology 2001*, Shrewsbury, UK, April 2001.
9. Michaeli, W. and Niggemeir, P. New results of material characterization for the improved calculation of shrinkage and warpage. *Journal of Polymer Engineering*, 2001, **21**(2-3), 263-279.