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The Measurement of the Thermal Conductivity of Amorphous Polymers Above Glass Transition Temperature

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ABSTRACT

The polymer processing industry is sensitive to low labour cost competition. The industry needs to remain cost effective by improving efficiency when processing polymers into existing and newly developed products. A reduction in cycle times during the manufacture of an injection moulded product would lead to increased output rate of the final product and increased profit margins. Modelling is used to predict cooling times during the injection moulding cycle and to reduce them through improvements in mould design leading to shorter cycle times. For these models to be reliable the data input into the model has to be accurate. Polymers have low thermal conductivities and because of this, heat transfer data is key to predicting accurate cycle times.

The thermal conductivity behaviour of amorphous polymers at temperatures above the glass transition temperature (T_g) for the polymer is not well described. In the literature, different experimental techniques e.g. the line source probe and the hot plate technique produce conflicting data giving conflicting trends describing thermal conductivity behaviour above T_g nominally for the same polymer. A novel measurement instrument, the heat transfer coefficient (HTC) apparatus, has been designed and built in order to attempt to resolve the measurement issues for thermal conductivity of amorphous polymers above T_g . The instrument has an adjustable upper plate to allow good thermal contact with the specimen across a wide range of temperatures.

Thermal conductivity measurements have been made on poly(methyl methacrylate) (PMMA) to determine the repeatability and precision of the HTC instrument. The repeatability for PMMA tested at set temperature 60°C was determined as 1.5 %. The value compares with a repeatability of 8 % for the line-source probe technique. For PMMA at 60°C the mean thermal conductivity value of 0.189 W/(m.K) compares with an accepted standard value for the specimen of 0.192 W/(m.K) differing from the known specimen value by 1.6 %. Therefore the HTC instrument could be used to establish reliable thermal conductivity data for modelling predictions of cooling time during the injection moulding of amorphous polymers.

Experimental data used to form the current model predicting thermal conductivity behaviour for amorphous polymers above the T_g was reviewed. Thermal conductivities of PC and PS were measured from 53°C to 180°C and show an increase in thermal conductivity with temperature above the T_g for both polymers. This trend is in agreement with data from the line source probe technique. A model predicting an increase in thermal conductivity with increase in temperature above T_g was reviewed.

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Approved on behalf of the Managing Director, NPL,
by Dr M G Cain, Knowledge Leader, Materials Team,
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1 INTRODUCTION

The injection moulding process consists of injecting molten polymer under pressure into a water cooled mould. Shrinkage of the material during cooling is compensated for by injecting additional polymer into the mould after the initial injection. This step is known as 'packing'. The plastic part is ejected from the mould when it is sufficiently solid. The injection moulding process gives rise to a cycle time which is the key to productivity and profitability.

The thermal conductivity of polymers has a major influence on the rate at which mouldings cool, this is critical in determining cycle times. Since polymers have low thermal conductivities and relatively high specific heat capacities, heat transfer in the polymer is the rate determining part of the process. The major route for heat to be removed from the polymer during the injection moulding process is through the mould wall. The rate at which heat is transferred from the polymer through the mould wall depends on how good the contact is between the wall and the plastic. Therefore the measurement of data such as thermal conductivity of the polymer and the heat transfer coefficient at the polymer to mould wall interface is important. These two parameters are crucial to determining the heat transfer behaviour of the polymer during the injection moulding process.

Improved measurement, prediction and understanding of heat transfer in production processes could lead, for example, to improved processing equipment, materials design and reduced cycle times, so increasing productivity. Scrap rates could also be reduced through, for example, the elimination of hot spots that cause material degradation, or lead to internal stresses and hence unacceptable warpage of product.

There is increasing demand for accurate and relevant data for the thermal conductivity behaviour of polymers for use in design simulations. Thermal conductivity is the least accurately measured property of polymers, and yet it is one of the most important material properties for polymer processing. The thermal conductivity of amorphous polymers above the glass transition temperature has not been well characterised.

The glass transition temperature (T_g) is a property of amorphous polymers and it is at this temperature that the polymer undergoes a transition from a hard, brittle glass-like state where the polymer chains are 'locked' together to a rubber-like state where the polymer has elastic properties, softens and where the polymer chains are more mobile than in the glassy state. Conflicting data exists for amorphous polymers above the glass transition temperature and therefore the heat transfer behaviour of these polymers during processing is not as well known as it could be. This work will attempt to improve upon the characterisation of amorphous polymers.

The aims of the project are:

- To investigate discrepancies that occur between measurements of thermal conductivity of amorphous polymers above the glass transition temperature and a model used to predict thermal conductivity behaviour in this region
- To use a novel Heat Transfer Coefficient (HTC) instrument to determine thermal conductivities of amorphous polymers at elevated temperatures and

compare with thermal conductivity data obtained using a line source probe technique

- To review the model used to predict the shape of thermal conductivity curves for amorphous polymers

The HTC instrument is novel because it enables the measurement of thermal conductivity of polymers at steady state conditions (where temperature remains constant with time) at atmospheric and higher pressures. The instrument has been designed for this application by the incorporation of a containing guard ring and movable upper plate.

2 SUMMARY OF LITERATURE REVIEW

Data published by various groups of researchers shows conflicting trends in behaviour of the thermal conductivity of amorphous polymers above the glass transition temperature.

Technique	Steady State or Transient	Thickness Required In Calculation of Thermal Conductivity	Does calculation of results include correction for changes in specimen thickness during test?	Is surface contact between the specimen and the instrument an issue?	Does thermal conductivity of specimen increase or decrease with temperature above T _g ?
Hot Plate Methods	Steady state	yes	no	yes	decrease
Bicalorimeter	Transient	Not enough information in literature	Not enough information in literature	Not enough information in literature	decrease
Lee's Disc	Steady state	yes	no	yes	decrease
Line source probe	Transient	No. Specimen assumed to be infinite thickness	Not applicable. Specimen thickness assumed to be infinite.	Yes. Air entrapment in specimen and between specimen and probe is issue	increase
Laser flash	Transient	Yes.	Software makes correction for length change in specimen retrospectively.	Yes.	increase

Work carried out by Eiermann et al [1, 2, 3] and Hands, Lane and Sheldon [4] using the steady state hot plate technique and bicalorimetric techniques used by Bashirov et al [5] and use of the Lee's Disc technique by Sombatsompop and Wood [6] all show experimentally a decrease in thermal conductivity for amorphous polymers in the rubbery state.

However, work carried out by Underwood and McTaggart [7], Lobo and Cohen [8], Lobo and Newman [9], Oehmke and Wiegmann [10] and Dawson, Rides and Nottay [11] using the line source probe and use of the Laserflash measurements by Knappe [12] all show experimentally an increase in thermal conductivity for amorphous polymers in the rubbery state.

The thermal conductivity of polymers is an important fundamental property in understanding heat transfer behaviour during polymer processing.

Further research is required to try clarify the situation in order to obtain accurate thermal conductivity data to improve on modelling and predicting the polymer processing of amorphous materials more accurately.

Experimental work needs to be done to attempt to more clearly determine the thermal conductivity behaviour of amorphous polymers in the rubbery state, and once more clearly defined, to attempt to model this behaviour accurately.

3 EXPERIMENTAL DETAILS

3.1 OVERVIEW OF EXPERIMENTAL TECHNIQUE FOR HEAT TRANSFER COEFFICIENT (HTC) INSTRUMENT

A novel HTC instrument has been developed to study heat transfer through polymer specimens mounted between two plates.

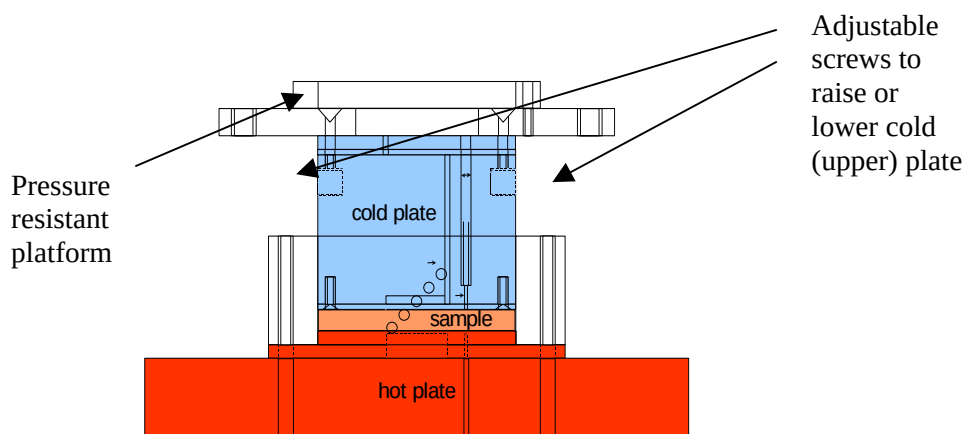


Figure 1 - Heat Transfer Coefficient Apparatus

The apparatus consists of two parallel, circular plates sandwiching the polymer specimen (Figure 1). The bottom plate (steel) is temperature controlled (electrically heated), and the top plate (aluminium) acts as a heat sink. Heat flux sensors and thermocouples are located in both upper and lower plates to measure heat fluxes and temperatures from which thermal conductivities are calculated.

Test specimens are moulded at or above the melt temperature from polymer granules using a compression moulding technique and left to cool to room temperature under pressure to minimise residual stress. The thickness x_s of the specimen is measured using a micrometer.

By placing the plates in contact the baseline thermal resistance R_{Baseline} for the HTC instrument is determined at the test temperature. This baseline accounts for interface heat transfer coefficients and plate thermal conductivities. The test specimen is then

inserted between the hot and cold plates. The hot plate is set to the required test temperature and the apparatus is left for 4 hours to achieve steady state conditions. Outputs from the upper and lower thermocouples and heat flux sensors are logged.

From rearranging the Fourier equation:

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

where Q is the rate of heat flow, Watts W , across a material of cross sectional area A (m^2) and thickness x (m) and of thermal conductivity λ , $W/(mK)$.

It is possible to calculate the thermal conductivity λ_j ($W.m^{-1}.K^{-1}$) for a layer of thickness x_j (m)

$$\lambda_j = \frac{q_j x_j}{T_B - T_T} \quad (2)$$

where q_j is heat flux at surface ($W.m^{-2}$) and T_B and T_T are the temperatures at the bottom and top of the layer respectively.

The heat transfer coefficient between two surfaces in contact, h , is defined by

$$h_i = \frac{q_i}{T_1 - T_2} \quad (3)$$

h = heat transfer coefficient ($W.m^{-2}.K^{-1}$) q_i = heat flux at surface ($W.m^{-2}$)
 T_1 = temperature on 'hot' interface side T_2 = temperature 'cold' interface side

For the specimen the total thermal resistance $R_{specimen}$ ($m^2.K.W^{-1}$) is the sum of the thermal resistances of the individual layers during the specimen test r_i - $R_{Baseline}$ and is given by

$$R_{specimen} = \frac{\delta T}{q} = \left[\sum r_i \right] - R_{Baseline} = \left[\sum_i \frac{1}{h_i} + \sum_j \frac{x_j}{\lambda_j} \right] - R_{Baseline} \quad (4)$$

where the subscript i represents the heat transfer coefficient at different interfaces. h_i and j represent the layers of thickness x_j (m) and thermal conductivity λ_j . ($W.m^{-1}.K^{-1}$).

The thermal conductivity of the specimen can be calculated by

$$\lambda_{specimen} = \frac{x_s}{R_{specimen}} \quad (5)$$

3.2 EXPERIMENTAL PROCEDURE FOR HTC INSTRUMENT

(i) Specimen Preparation

A steel mould comprising of a 100 mm diameter ring with a detachable bottom and lid is used to mould the polymer granules into a disc shaped specimen.

A fan oven is set to 210°C and switched on. The 100mm steel ring of the mould is placed over the steel bottom of the mould and pushed down until the bottom of the ring is in contact with the base of the steel mould bottom. A 100 mm diameter disc of fabric coated with release agent is then inserted into the assembly to cover the surface of the bottom of the mould.

14 ± 0.5 g of granules of the polymer to be tested are weighed and then transferred into the mould. The polymer granules are spread manually over the 'release fabric' disc to ensure as even a distribution as possible. A disc of 'release fabric' is then placed on top of the polymer granules in the mould. The steel top of the mould is then inserted into the mould ring and pushed down until the base of the top is in contact with the top of the mould ring. The granule/'release fabric' sandwich can then be pressurized.

The mould assembly is then placed into the oven at 210 °C and a 10 kg load is placed on top of the assembly. The load ensures that the sandwich packs down, the granules soften and trapped gases are eliminated.

After 3 hours the load and mould assembly is removed from the oven. The mould is left to slowly cool in air down to room temperature. Once the mould has cooled to room temperature then the two halves of the mould are separated and the polymer disc is removed from the mould.

The polymer disc is then cut down to a 80 mm diameter disc. The thickness of the disc is measured and recorded at 5 points equally spaced around the edge of the disc in order to determine its uniformity.

(ii) Measurement of Thermal Conductivity of Polymer Disc Specimens Using The HTC Instrument With Laser Scanning Micrometer (LSM)

A Mitutoyo LSM-3000/9602 is calibrated using two reference diameter standards 23.9999 mm and 1.0003 mm in diameter. The LSM is then configured to measure gap distances to a resolution of 0.00005 mm.

The LSM is set at a fixed position above the top of the upper piston housing of the HTC instrument. A metal reference rod is fixed into a set position in the laser beam by attaching the rod to a holder fixed to the support frame on which the laser emission unit and reception unit are mounted.

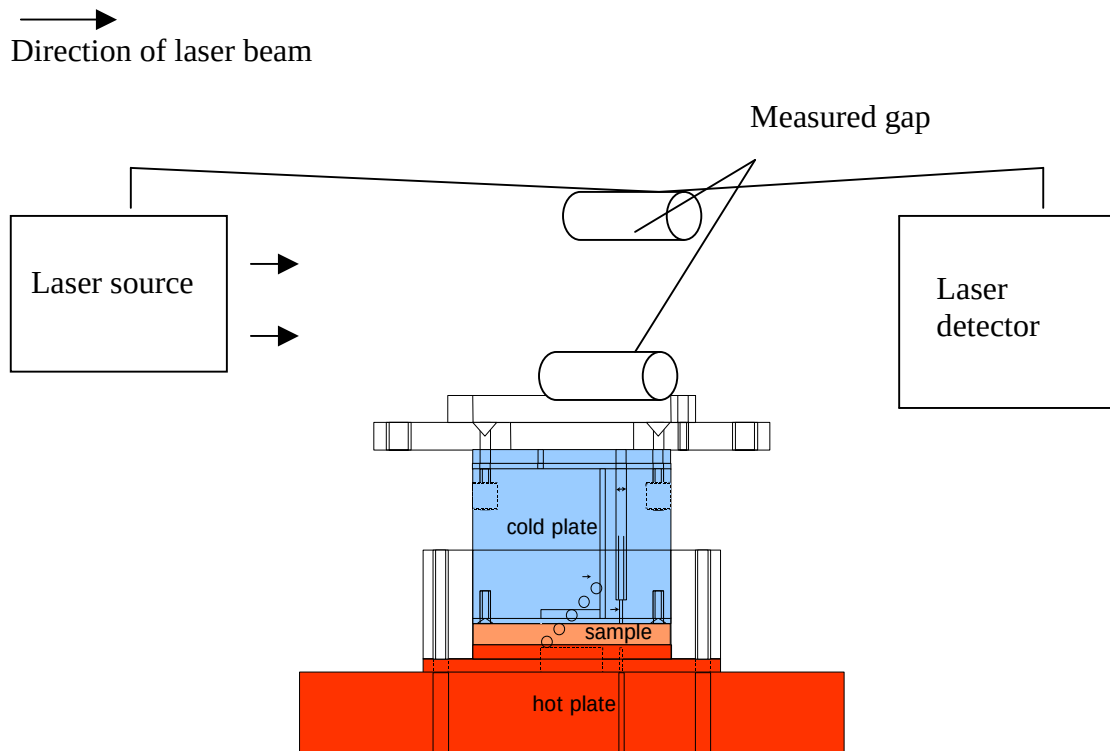


Figure 2 - HTC Instrument With LSM in position

A travelling metal rod is housed in a unit which is then located onto the top of the upper piston housing of the HTC instrument. The LSM then measures and records the gap distance between the fixed metal rod and the travelling metal rod (Figure 2).

A check is made that the correct top plate required for the test is in position within the upper piston and if it is not then the correct plate is selected and fitted.

Before the test is started, a check is made of the parallelism of the top and bottom plates by putting the top and lower sections of the instrument together and trying to rock the top section against the bottom. If a rocking motion occurs then that indicates that there may be a lack of parallelism in the plates.

The distance between the top and bottom plates can be controlled by three screws located within the top section of the HTC instrument.

At room temperature and with the screws raised to a neutral position, the top and bottom plates are brought together. The gap distance between the fixed rod and the travelling rod is then recorded. The temperature is noted. The screws are then lowered to raise the top section of the instrument to allow for the insertion of the specimen disc into the instrument between the plates. The screws are then raised back to a neutral position so that the specimen is fully in contact with the top and bottom plates. Again the gap distance between the fixed rod and the travelling rod is recorded. The thickness of the specimen at room temperature is the gap distance recorded at room temperature with the specimen in place subtracted from the gap distance recorded at room temperature with the two plates in contact.

The lower plate of the HTC instrument is set to the test temperature by adjusting the settings at the heater control box. Both the inner and outer temperatures of the bottom plate are set to the required test temperature. The logging systems to record the LSM data and the heat flux sensor and thermocouple data are switched on. The specimen is then left between the plates for 4 hours minimum to allow steady state conditions to be reached. At the end of this period the logged data is downloaded for calculation of the thermal conductivity value.

At temperatures approaching the T_g the material softens and begins to flow. This can be prevented by the use of a guard ring. The procedure would be the same except that a PTFE seal would be placed around the bottom heated plate and then the guard ring would be located on top of the PTFE seal and secured by six screws into the base of the HTC instrument. The top plate would then travel down inside the guard ring to contact either the bottom plate or a specimen disc.

Expansion of the top section of the HTC instrument has been accounted for by attaching thermocouples to the structure during tests where the bottom plate was set to different temperatures and from the mean temperature of the top section and the expansion coefficient of steel the expansion could be calculated.

(iii) Calculation of the Thermal Conductivity of a Polymer Disc Specimen From HTC Instrument Data

Three cases are presented:

- a. Calculation to calibrate the instrument without a guard ring in place
- b. Calculation to determine thermal conductivity of specimen without guard ring
- c. Calculation to determine thermal conductivity of specimen with guard ring in place

a) Calibration Using Reference Specimen

Determine the baseline thermal resistance R_{Baseline} by carrying out a plate:plate run at the test temperature quoted for the reference specimen.

$$R_{\text{Baseline}} = \frac{T_B - T_T}{q_B} \quad (6)$$

Where T_B is the temperature measured by the thermocouple in the bottom plate when the plates are together

T_T is the temperature measured by the thermocouple in the top plate when the plates are together

q_B is the heat flux at the bottom plate when the plates are together

For the reference standard specimen of known thermal conductivity the total thermal resistance

$$R_{\text{Total}} = \frac{T_B - T_T}{q_B} \quad (7)$$

Where T_B is the temperature measured by the thermocouple in the bottom plate when the reference specimen is between the plates

T_T is the temperature measured by the thermocouple in the top plate when the reference specimen is between the plates

q_B is the heat flux at the bottom plate when the reference specimen is between the plates

$$R_{\text{Reference Specimen}} = R_{\text{Total}} - R_{\text{Baseline}} \quad (8)$$

Also:

$$R_{\text{Total}} = h_{\text{steel:specimen}} + h_{\text{Al:specimen}} + h_{\text{hfs:Al}} + h_{\text{hfs:steel}} + R_{\text{steel}} + R_{\text{Al}} + R_{\text{specimen}} \quad (9)$$

The heat transfer coefficient is the same across each interface so therefore:

$$R_{\text{Total}} = 4 h + R_{\text{steel}} + R_{\text{Al}} + R_{\text{specimen}} \quad (10)$$

$$\text{As thermal conductivity for a specimen } \lambda = \frac{x}{R} \quad (11)$$

Where x is specimen thickness, mm and R is specimen thermal resistance then as the thermal conductivities of steel, Aluminium and the reference specimen are known then it is possible to calculate R_{steel} , R_{Al} , and R_{specimen} .

$$\text{Therefore } h = \frac{(R_{\text{Total}} - (R_{\text{steel}} + R_{\text{Al}} + R_{\text{referencespecimen}}))}{4} \quad (12)$$

The heat transfer coefficient is therefore “set” so that the HTC instrument will give the reference standard value for PMMA at this set test temperature.

b) Case Where A Guard Ring Is Not In Place

For the set test temperature the bottom plate heat flux and top and bottom plate temperature data can be obtained by interpolation of the trend line equations for the plate:plate baseline runs and from this data R_{Baseline} can be obtained.

The measured thermal resistance determined during a test with the test specimen between the plates of the HTC instrument is R_{Total} .

To determine the thermal resistance for the test specimen:

$$R_{\text{Specimen}} = R_{\text{Total}} - R_{\text{Baseline}} \quad (13)$$

For the test specimen thermal conductivity can then be calculated from:

$$\lambda_{\text{specimen}} = \frac{x_s}{R_{\text{specimen}}} \quad (14)$$

c) Case where guard ring is in place

The total thermal conductivity for a test specimen was measured :

$$\lambda_{\text{Total Specimen}} = \frac{x_{TS} q_B}{T_B - T_T} \quad (15)$$

where x_{TS} is the thickness of the test specimen

q_B is the heat flux at the bottom plate
 T_B is the temperature at the bottom plate
 T_T is the temperature at the top plate

The total thermal conductivity for a reference specimen of PMMA where the thermal conductivity is known at the test temperature was measured using the HTC instrument:

$$\lambda_{\text{Total Reference Specimen}} = \frac{x_{RS} q_B}{T_B - T_T} \quad (16)$$

where x_{RS} is the thickness of the reference specimen
 q_B is the heat flux at the bottom plate
 T_B is the temperature at the bottom plate
 T_T is the temperature at the top plate

A calibration factor was then determined for the HTC instrument:

$$f_{\text{calibration}} = \frac{\lambda_{\text{knownrefspec}}}{\lambda_{\text{total refspec}}} \quad (17)$$

The thermal conductivity of the test specimen could then be calculated:

$$\lambda_{\text{test specimen}} = f_{\text{calibration}} * \lambda_{\text{Total Test Specimen}} \quad (18)$$

4 RESULTS AND DISCUSSION

4.1 INITIAL ASSESSMENT OF MATERIALS

The glass transition temperatures of the four amorphous polymer specimens have been tested by DSC and determined to be 82.55°C for PVC, 84.37°C for PS and 138.19°C for PC (Figures 3 to 5, Table 1). The values obtained in the literature are 85°C for PVC [13], 80°C - 100°C for PS [14], and 150°C for PC [15].

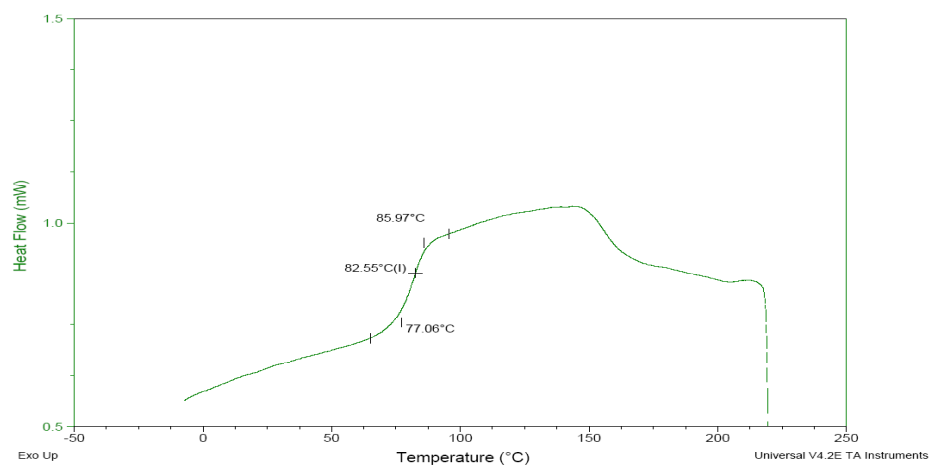


Figure 3. DSC plot for determination of T_g of PVC

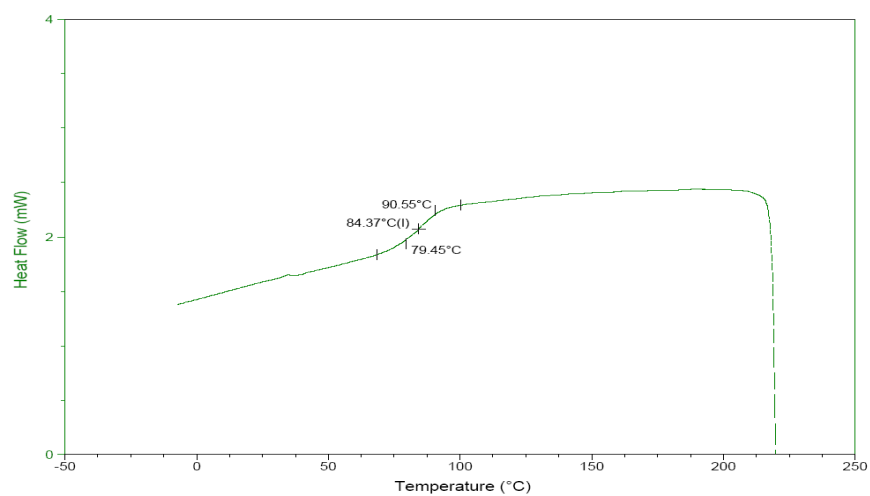


Figure 4. DSC plot for determination of T_g of PS

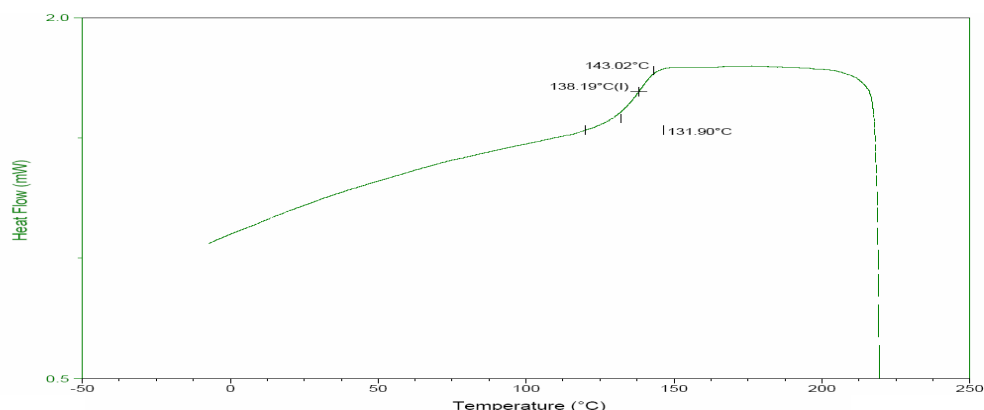


Figure 5. DSC plot of determination of T_g of PC

Although discrepancies between the experimental and literature glass transition temperature values are observed such differences are to be expected. The measurements are highly sensitive to thermal histories of the specimens, crystallinity, molecular weight and impurity contents of the specimens.

4.2 INITIAL ASSESSMENT OF REPEATABILITY AND PRECISION OF TECHNIQUE

An initial assessment of the repeatability error and precision of thermal conductivity measurements of polymer specimens by the HTC technique (set up without the guard ring) has been made.

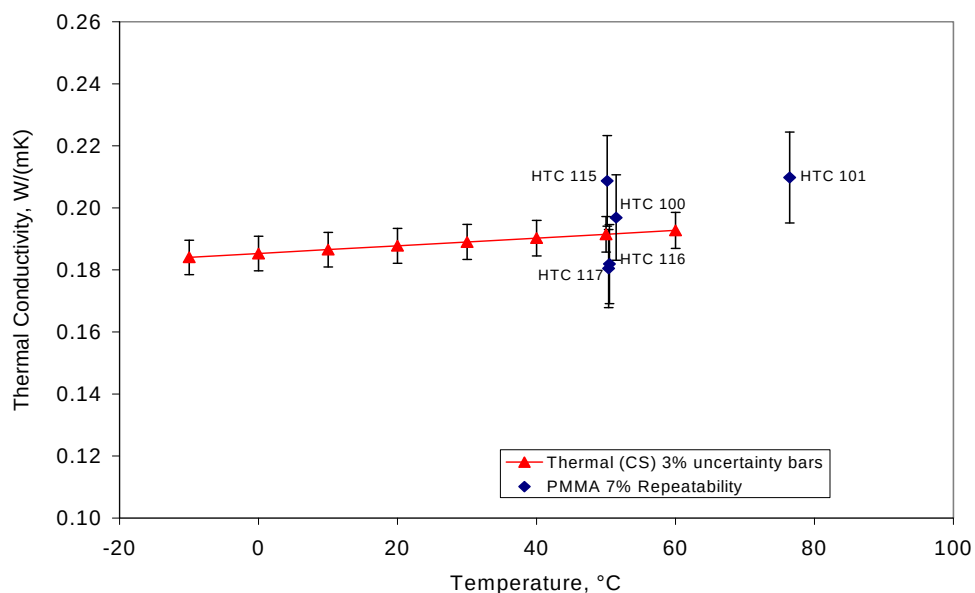


Figure 6. Thermal conductivity data for PMMA at 60°C and 95°C. (Tables 2 and 3).

The thermal conductivity of a PMMA specimen disc was tested four times with the bottom plate set to 60 °C and once with the bottom plate set to 95°C, both temperatures being below the glass transition temperature of the polymer. The thermal conductivity values obtained for the specimen have been plotted along with accepted reference standard values for PMMA (Tables 2 and 3, Figure 6). The accepted standard values were obtained using the guarded hot plate technique at the National Physical Laboratory, UK.

The repeatability error of the thermal conductivity values for PMMA obtained from the HTC instrument at 60°C was calculated to be 7.0 %. The mean thermal conductivity value for PMMA at 60°C obtained using the HTC instrument was calculated to be 0.192 W/(mK) differing from the reference standard value of 0.192744 W/(mK) by 0.4%.

The thermal conductivity of a PS specimen disc was tested five times using the HTC instrument with the bottom plate set to 180°C and once with the bottom plate set to 60°C, 95°C and 200°C respectively. The tests where the plate is set to 180°C and 200°C are tests carried out at temperatures above the glass transition temperature of the polymer. The thermal conductivity values obtained for the specimen tested using the HTC instrument have been plotted alongside thermal conductivity values extrapolated to 0 bar from line source probe data for the PS polymer obtained at high pressures (Tables 4 and 5, Figure 7).

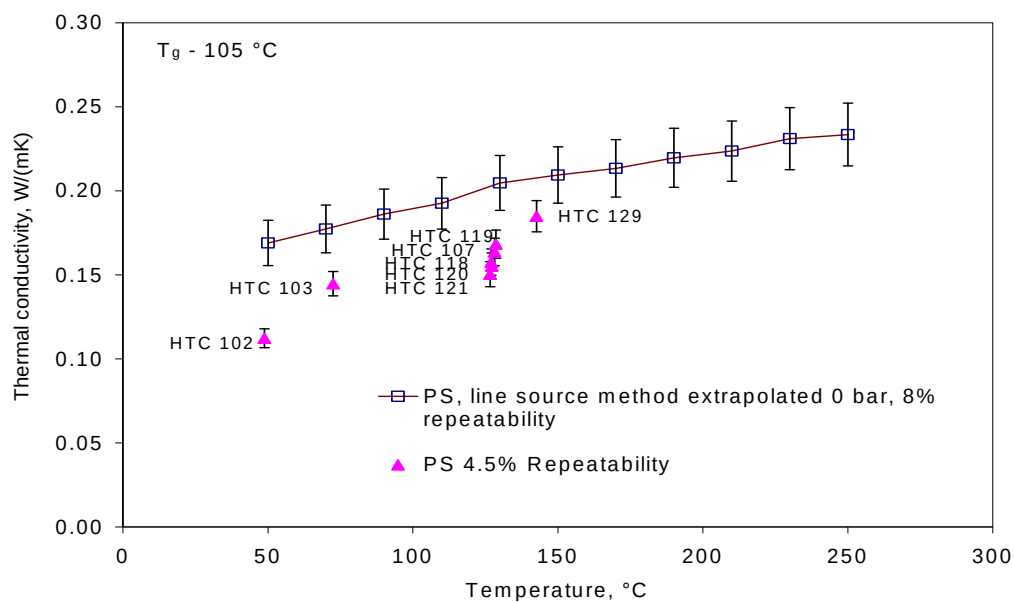


Figure 7. PS using HTC instrument compared with line-source probe extrapolated to 0 bar [11]. Test temperatures were set at 60°C, 95°C, 180°C and 200°C. (Tables 4 and 5).

The repeatability error of the thermal conductivity values for PS obtained from the HTC instrument at 60°C was calculated to be 4.4 %. Taking the extrapolated line source thermal conductivity values for PS of 0.213 W/(mK) at 170°C and 0.220 W/(mK) at 190°C then a thermal conductivity value of 0.217 W/(mK) could be expected at 180°C

for the PS (Table 5). The mean thermal conductivity value obtained at 180°C by the HTC instrument method is 0.159 W/(mK) (Table 4). Therefore there is a 36.5% difference between the experimental thermal conductivity value for PS at 180°C obtained using the HTC instrument and the thermal conductivity value for PS at 180°C obtained from extrapolating the line source probe data to 0 bar.

The differences in repeatability error for PMMA 7.0 % at 60°C and PS 4.4% at 180°C is most likely to be due to thermal contact issues. At 60°C which is below the glass transition temperature for PMMA, the PMMA specimen disc remains in a glass-like state with a hard and rigid surface. Therefore if the surface of the specimen disc has protrusions then these will remain for the duration of the tests and so could possibly prevent repeatable contact on each loading of the specimen into the HTC instrument. At 180°C set temperature for the bottom plate, which is above the glass transition temperature for PS, the PS specimen disc softens and this softening process could improve the thermal contact of the specimen with the upper and lower plates of the HTC instrument.

The PMMA thermal conductivity values obtained by testing using the HTC instrument are within 0.4% of the accepted reference standard thermal conductivity value for PMMA. This gives an indication of the degree of precision of the thermal conductivity data obtained using the HTC instrument. The extrapolation method may account for the 36.5 % difference between the thermal conductivity values for PS obtained from tests using the HTC instrument and the extrapolated line source probe thermal conductivity values. An assumption has been made during the extrapolation process of a linear relationship between the thermal conductivity values for PS at higher pressures and the thermal conductivity of PS at 0 bar.

4.3 INITIAL DETERMINATION OF THE THERMAL CONDUCTIVITY OF PS USING THE HTC INSTRUMENT

Initial thermal conductivity data for PS was obtained in heating mode using the HTC instrument with the bottom plate set in the temperature range from 60°C to 200°C (Figure 8 and Table 6).

The data for PS shows an overall increase in thermal conductivity with increasing temperature across the test temperature range. However, a decrease in thermal conductivity with increasing temperature is observed over the set temperature range 125°C to 180°C. Over this range the actual specimen temperature ranges from 92°C to 114°C. This temperature range coincides with the literature values quoted for the glass transition temperature 80°C to 100°C. The decrease in thermal conductivity with increase in temperature observed from 92°C to 114°C is assumed to occur as the result of the PS under going a transition from a glassy to an elastic state.

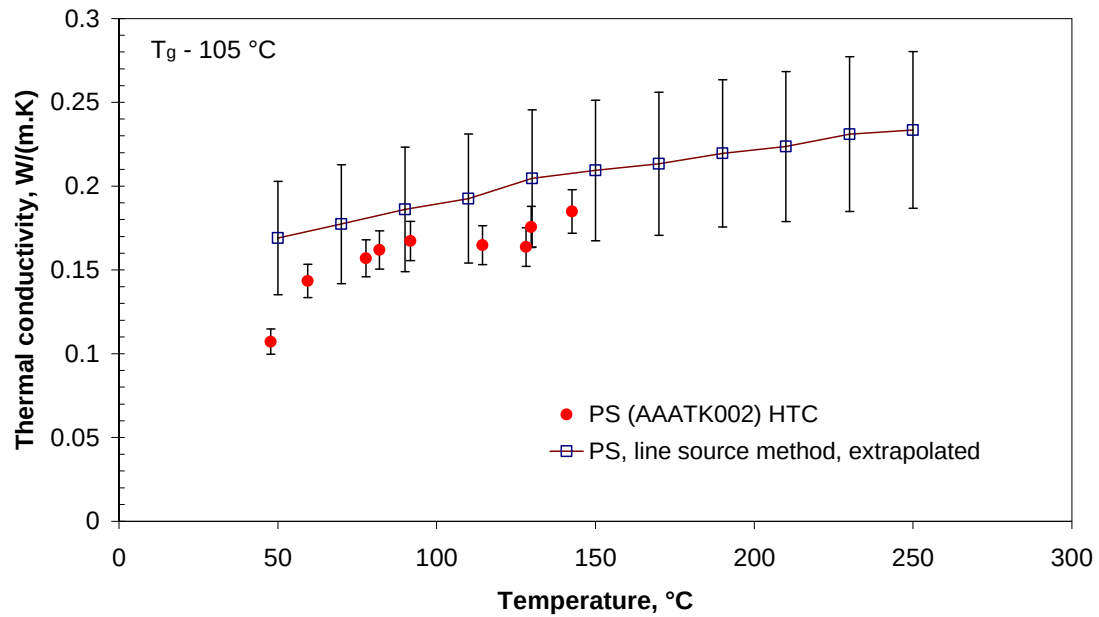


Figure 8. PS using HTC instrument compared with NPL line-source probe data extrapolated to 0 bar. Test temperatures set across range 60°C to 200°C. (Table 6).

The accuracy of the absolute values of the data for PS obtained using the HTC instrument could be improved upon in this case. The thickness measurement of the specimen was assumed to remain constant (for convenience) throughout the duration of the tests and across the test temperature range. However, the thickness measurement does vary due to thermal expansion during each test, and it is a key parameter in calculating the thermal conductivity of a specimen. Therefore an accurate technique for measuring the thickness of a specimen during the course of a test is needed. The baseline values for each set of measurements at the set temperature were taken as the values obtained from a run with the plates together at 180°C. For the most accurate results, the temperature of the lower plate of the HTC instrument should be set to the same temperature to which the lower plate is set during the specimen run.

4.4 FACTORS AFFECTING THE REPEATABILITY AND PRECISION OF THE HTC THERMAL CONDUCTIVITY MEASUREMENT TECHNIQUE

From equation (2), to calculate a thermal conductivity value for a specimen using the HTC instrument then specimen thickness, heat flux and temperatures of the bottom and top plates have to be known. Therefore these parameters have to be measured as accurately as possible.

(i) Measurement of specimen thickness

Initially a hand held micrometer was used to measure specimen thickness. The thickness readings for two different operators using a hand held micrometer to measure a PMMA disc of nominally 1mm thickness were plotted (Figure 9). The percentage error for the thickness measurements for both sets of operators was calculated to be <1% (Table 7). However, the hand held micrometer cannot be used to measure the

thickness of the specimen once it is placed between the top and bottom plates of the instrument. Other measurement techniques were investigated to provide the thickness data required for the specimen between the plates of the instrument at the test temperatures.

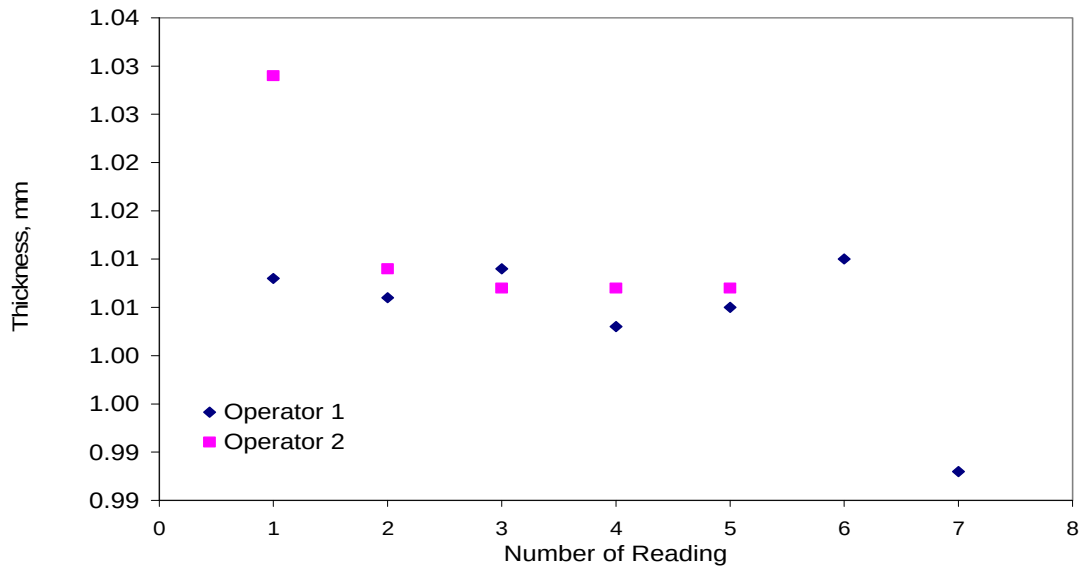


Figure 9. Variation of hand held micrometer readings for two operators measuring reference PMMA disc nominally 1mm thick (Table 7).

Two techniques were tried to measure the thickness of the specimen between the top and bottom plates of the HTC instrument, Vernier callipers and a dial gauge.

Vernier callipers were used to measure the distance between the bottom steel flange of the HTC instrument and the top aluminium section of the instrument. The distance of travel between these points is equivalent to the thickness of specimen when it is inserted into the HTC instrument and heated during the tests.

A dial gauge was mounted at the top of the instrument to measure the distance of travel of the top plate from which the thickness of the specimen could be determined. The dial gauge measures the retraction of a plunger in contact with the top surface of the instrument above the top plate. As the top plate moves upwards due to the expansion of the specimen due to heating, the plunger retracts and the distance of travel of the plunger is equal to the specimen thickness and instrument expansion. The expansion of the instrument must be taken into account and subtracted from the dial gauge reading.

Thermal conductivity measurements for PS were also made using the HTC instrument at test temperatures over the range 60°C to 200°C. Vernier calliper and dial gauge methods were used to obtain the specimen thickness at each test temperature (Figure 10 and Table 8). The overall trend observed across the range of test temperatures was for an increase in thermal conductivity with increase in test temperature.

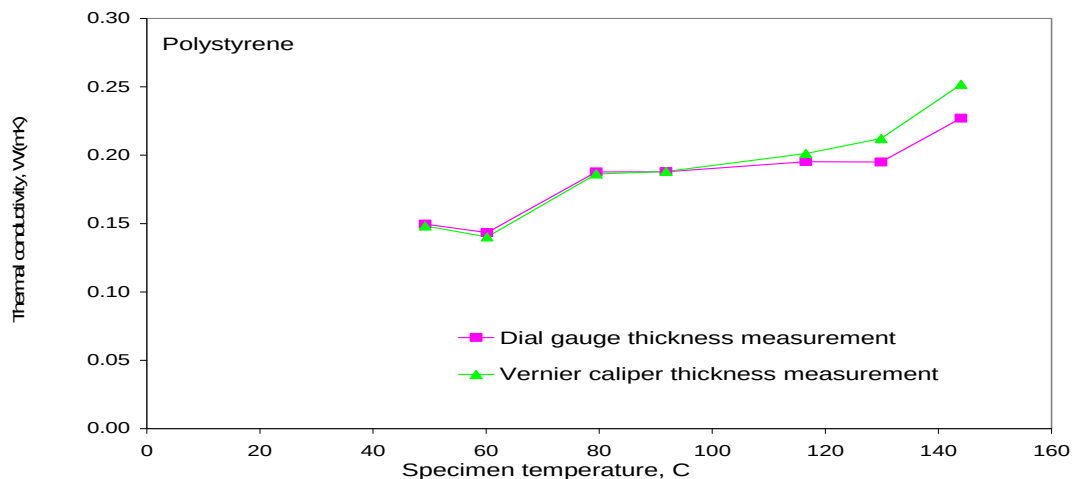


Figure 10. Thermal Conductivity values for PS. Thickness of the specimen measured during the tests using dial gauge and Vernier calliper methods (Table 8)

Measurements using Vernier callipers were taken of the phenolic base thickness, aluminium bottom base section with insulation thickness and the distance from the bottom steel flange to the top aluminium section of the instrument at room temperature and 170°C. These measurements were carried out independently by two operators and the overall expansion for the instrument then calculated (Table 9). Operator 1 determined an overall contraction of -0.16mm and operator 2 determined an overall expansion of 0.31mm for the HTC instrument sections heating up from room temperature to 170°C. Therefore the Vernier calliper measurement technique for determining thickness was found to be unreliable due to operator error and was discarded as a method for determining the thickness of the specimen between the plates of the HTC instrument during testing.

An analysis of the dial gauge thickness measurements for the PS specimen (Figure 11 and Table 10) shows that the thickness of the specimen increases with temperature across the set test temperature range of 60°C to 200°C. However, there is a significant increase in thickness between the specimen temperature of 91.83°C and 116.53°C. This temperature region spans that where the glass transition temperature of the PS occurs where the polymer goes from being hard and glassy to soft and elastic. However, it is also possible that the sudden change in thickness observed is not real as the dial gauge exhibited 'slip/stick' characteristics during testing. The plunger would 'stick', not rising up into the barrel of the dial gauge, giving a falsely low reading. This would then be followed by the plunger 'slipping', rising up into the barrel of the dial gauge in one step, giving a falsely high thickness reading. Therefore due to the 'stick/slip' phenomenon exhibited by the dial gauge this technique was discarded as a way of determining the thickness of a specimen between the plates of the HTC instrument during a test.

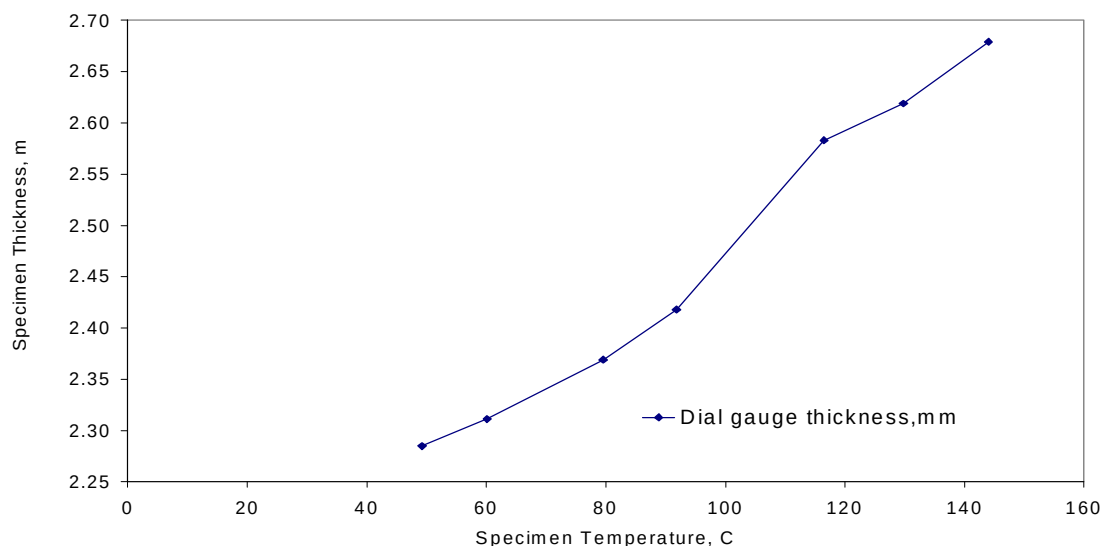


Figure 11. Thickness of specimen measured using dial gauge measurement during the thermal conductivity testing of PS using the HTC instrument (Table 9)

A LSM was set up to read the distance across a gap and calibrated. The gap consisted of a upper rod in the laser beam fixed at a set height above the laboratory bench with a lower rod secured onto the top surface of HTC instrument. When the top section of the HTC instrument moved upwards due to insertion of the specimen or increases in the thickness of the specimen then the gap measured by the LSM between the upper and lower rods would decrease. The gap at test temperature for the specimen was subtracted from the gap measured at room temperature for the specimen and a correction was made for the expansion of the upper section of the HTC instrument (Figure 12 and Table 11). Expansion of the upper section of the instrument was found to increase linearly with increasing temperature.

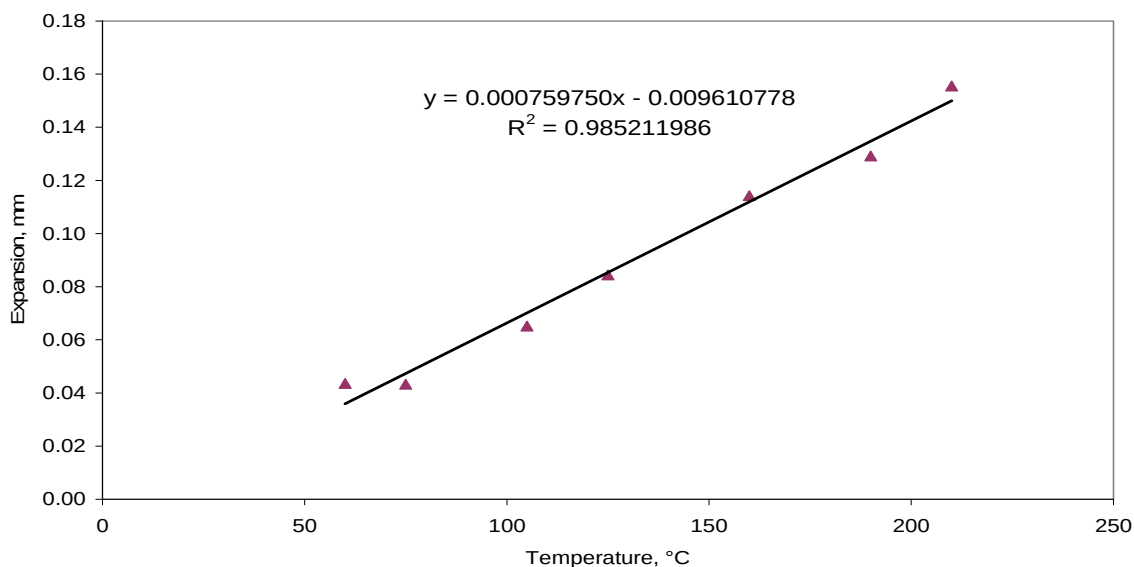


Figure 12. Expansion of upper section of the HTC instrument measured by LSM

Thickness measurements using the LSM method eliminated operator error and provided a recordable method measuring thickness to 4 decimal place accuracy. It will be shown later on that the LSM thickness measurement technique contributed to reducing the repeatability error for determination of thermal conductivity of polymer specimens using the HTC instrument (Figure 19).

(ii) Duration Time of Test

The thermal conductivity of PS specimens were tested at different test temperatures and held at the test temperature for sufficient time to achieve steady state conditions (where the temperature does not change with time, Table 12) or insufficient time so that only non-steady state conditions (where the temperature does change with time, Table 13) were achieved. The thermal conductivities of the PS measured under the two sets of conditions are plotted in Figure 13. There are differences between the thermal conductivity of PS specimens measured at the same test temperature but under steady state and non-steady state conditions. Therefore to reduce the repeatability error for the measurement of thermal conductivity using the HTC instrument, a minimum time of test should be determined that will give steady state conditions.

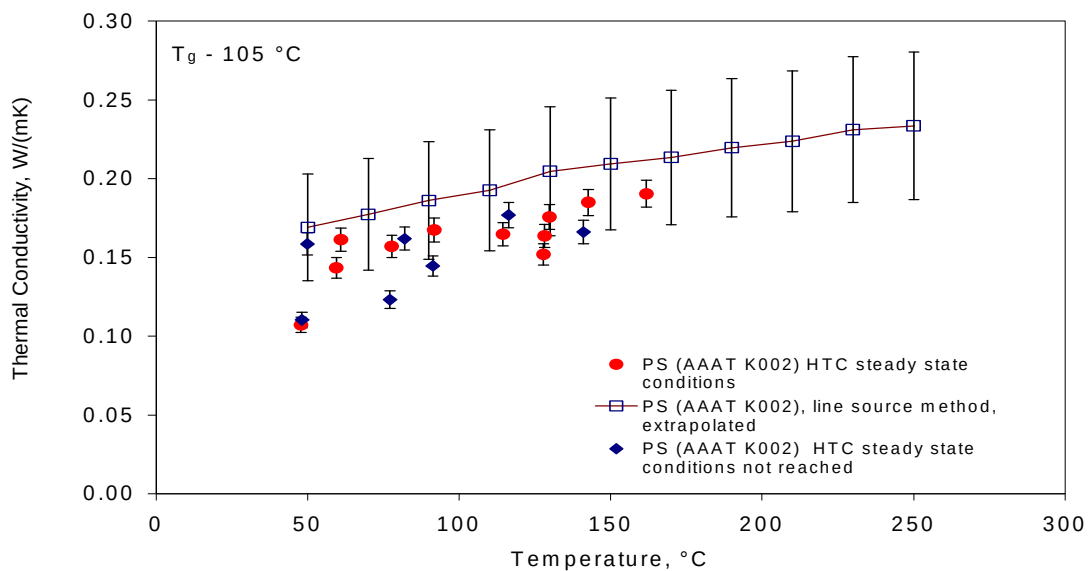


Figure 13. Measurement of thermal conductivity of PS using HTC instrument across set temperature range from 60°C to 225°C under steady state and non steady state conditions

The absolute difference in thermal conductivity measured at test temperatures achieved under steady state conditions was plotted against time (Figure 14 and Table 14). From this figure it can be seen that the difference in thermal conductivity values obtained at a test temperature reduces with the increasing time that the specimen is held at this temperature. Therefore holding the specimen at test temperature for longer periods should minimise the repeatability error for the use of the HTC instrument to measure thermal conductivity. The optimum length of time in terms of test time required to hold the specimen to produce the smallest difference in thermal conductivity was determined to be 14358 seconds which is to the nearest hour, 4 hours.

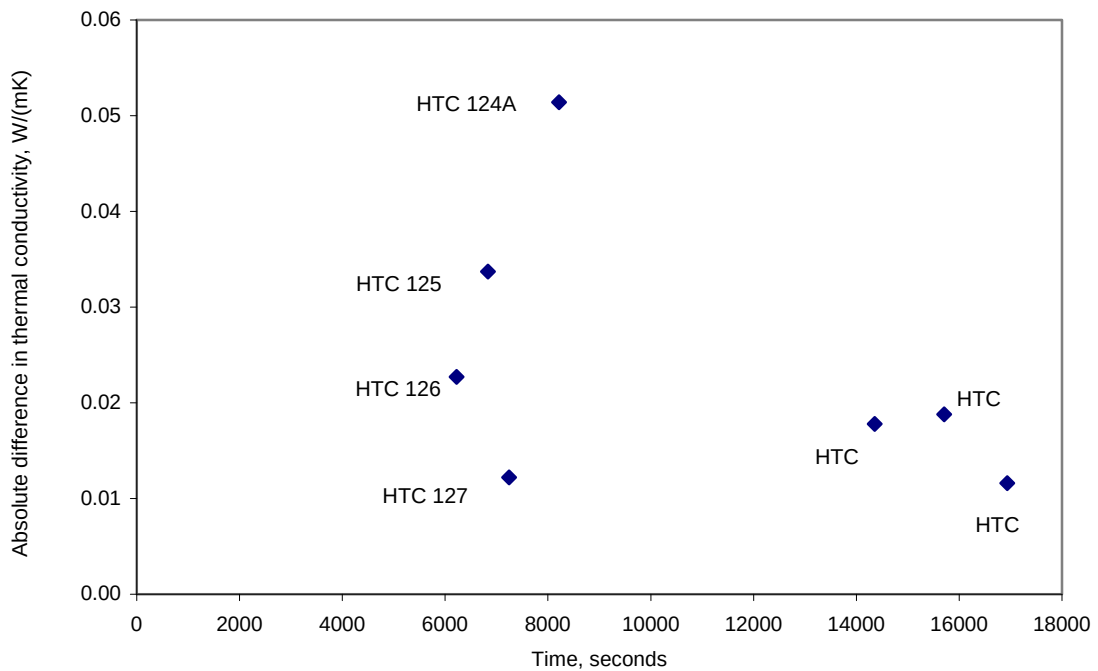


Figure 14. Comparison of effect of holding time at test temperature on thermal conductivity value of test compared to thermal conductivity test result obtained under steady state conditions at test temperature

(iii) Heat Flux and Temperature Measurements

A typical plot of the moving average (period 2) of the output signals from the top and bottom heat flux sensors and top and bottom thermocouples during a HTC instrument test is shown in Figure 15. There is some noise associated with each signal and therefore the value taken for each signal is the mean value for the final 500 seconds of each test (Table 15). This process was applied to all HTC tests to provide repeatability to the tests in terms of the noise of the heat flux and temperature signals.

The noise expressed as a percentage error associated with the thermocouples for the test (0.376 % top and 0.333 % bottom) was determined to be less than the noise associated with the heat flux sensors (10.030 % top and 3.002 % bottom). During these HTC tests only the bottom heat flux sensor value and the top and bottom thermocouple temperatures are used to calculate the thermal conductivity therefore minimising the percentage error associated with the heat flux sensor reading. The larger percentage error associated with the top heat flux sensor is due to the lower heat flux at the top plate compared with the bottom plate.

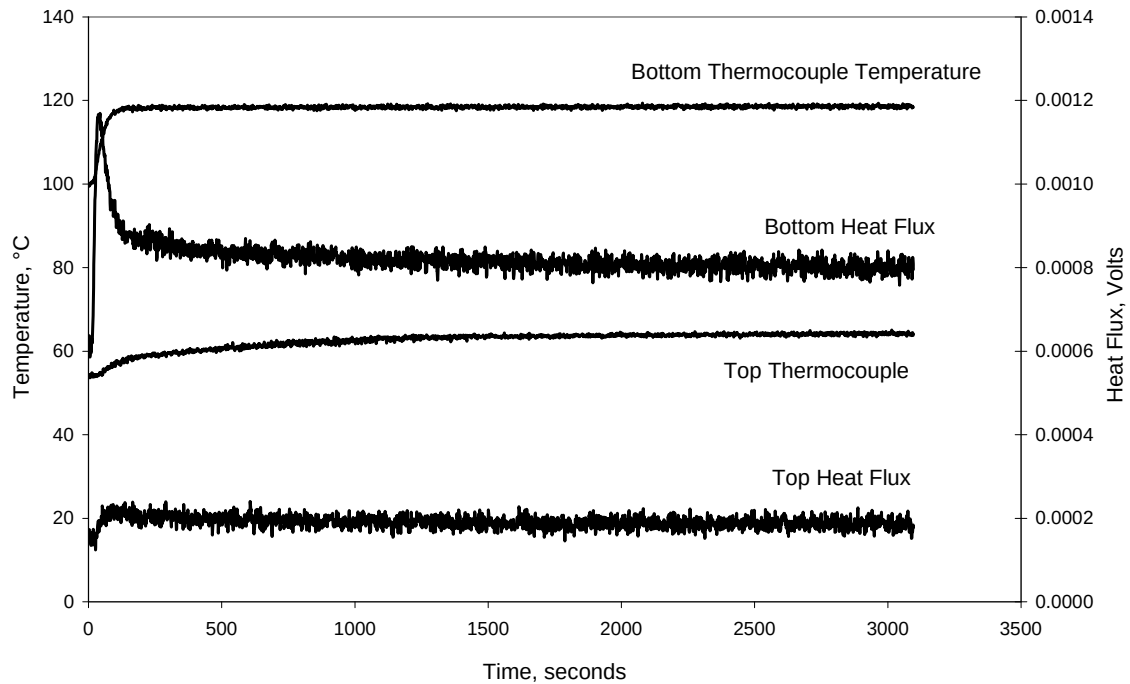


Figure 15. Typical Moving Average (Period 2) of Heat Flux Sensor and Thermocouple Outputs during a HTC Instrument Measurement of Thermal Conductivity. Bottom plate temperature set to 125°C.

Calculations of the thermal conductivity of a material under test using the HTC instrument taking the heat flux value at the bottom plate only. The heat flux across the specimen is then assumed to remain constant at this value due to steady state conditions being maintained. However, from the measurement of heat flux at the top plate it can be seen that heat is lost between the top and bottom plates. Therefore the assumption of constant heat flux across the specimen is not a correct assumption. Heat flow through the specimen is not unidirectional and heat losses at the specimen edge could be taking place. Therefore the design of the instrument could be modified in order to maximise the unidirectional heat flow through the specimen, for example by providing additional heating around the edge of the specimen to try to prevent edge heat losses.

(iv) Specimen Preparation

Different densities of PVC discs were compression moulded at London Metropolitan University using PVC powder in a compression moulding tool with hydraulic press. It can be seen that thermal conductivity increases with density of specimen for the PVC specimens tested (Figure 16 and Table 16). Therefore it is important to mould specimen discs of uniform density in order to obtain repeatability during thermal conductivity testing by the HTC instrument technique.

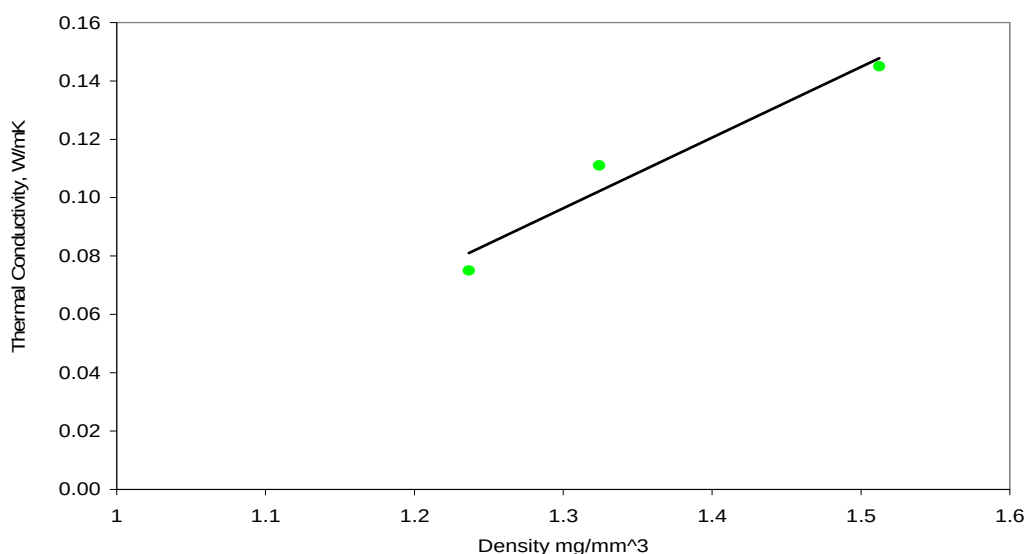


Figure 16. Effect of density variations for PVC specimens on thermal conductivity

For the HTC measurement technique to give the lowest repeatability error possible for thermal conductivity measurements then the specimen discs have to be moulded to give repeatable densities, thicknesses and plane parallel surfaces. One technique that can be used to do this is compression moulding. A powdered polymer should be used so that air can be easily eliminated from the mould. The compression moulding technique is repeatable down to a known shot weight (weight of polymer loaded into mould) and because any excess polymer will ‘flash’ i.e. will be forced out of the mould into an overflow channel then a repeatable density of specimen can be produced. Compression moulding specimen preparation gives specimens that are very low in internal stresses. Generally compression moulded specimens are less stressed than injection moulded specimens. They do not form a skin layer of polymer at the surface unlike specimen discs produced by injection moulding.

Close contact between the surface of the test specimens and the top and lower plates of the HTC instrument are key to obtaining repeatable thermal conductivity measurements. If specimens cannot be produced by compression moulding of polymer powder then the surface of the test specimens should be made plane by means of a mechanical technique such as grinding. The specimen faces should be parallel over the surface area of the face and be flat.

It may be possible to use the HTC instrument as an compression moulding tool to mould specimen discs ‘in situ’ in a hydraulic press.

4.5 REPEATABILITY AND ACCURACY OF THERMAL CONDUCTIVITY MEASUREMENTS USING A LSM TO MEASURE SPECIMEN THICKNESS UNDER STEADY STATE CONDITIONS

The thermal conductivity of a PMMA specimen disc was tested four times with the lower plate set to 60°C. This temperature is below the glass transition temperature of

the polymer. The thermal conductivity values obtained for the specimen have been plotted along with the accepted reference standard values for PMMA (Tables 3 and 17, Figure 17).

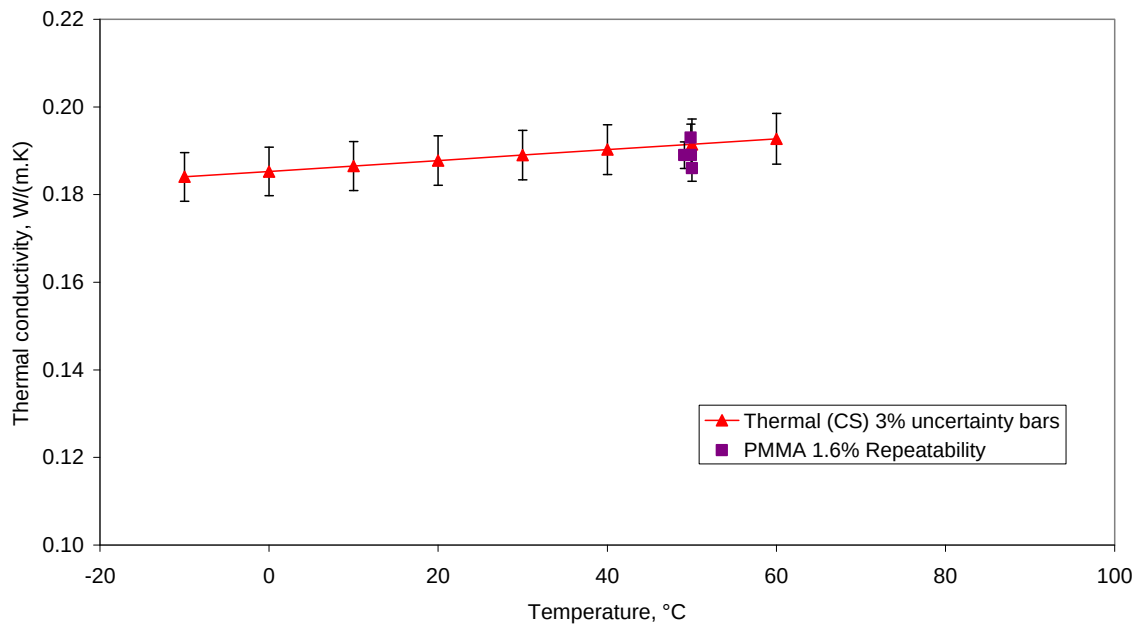


Figure 17. Repeatability of PMMA 1.6% when thickness measured by LSM under steady state conditions

The repeatability error of the thermal conductivity values for PMMA obtained from the HTC instrument at 60°C was 1.5 %. The mean thermal conductivity value for PMMA at 60°C obtained using the HTC instrument was 0.189 W/(mK) differing from the reference standard value of 0.192744 W/(mK) by 1.6 %.

This improvement in the repeatability of the thermal conductivity data has been made by measuring thickness by LSM and taking the measurements under steady state conditions. The decrease in mean thermal conductivity value to 0.189 W/(mK) may be due to an increase in the temperature difference across the specimen due to the maintenance of steady state conditions.

4.6 THERMAL CONDUCTIVITY MEASUREMENTS ON PC AND PS ACROSS TEMPERATURE RANGE FROM 53°C TO 180°C WITH GUARD RING IN PLACE

To calculate the thermal resistance for the specimen, data with the two plates in contact is necessary at the required set temperature in order to determine the thermal resistance for the instrument.

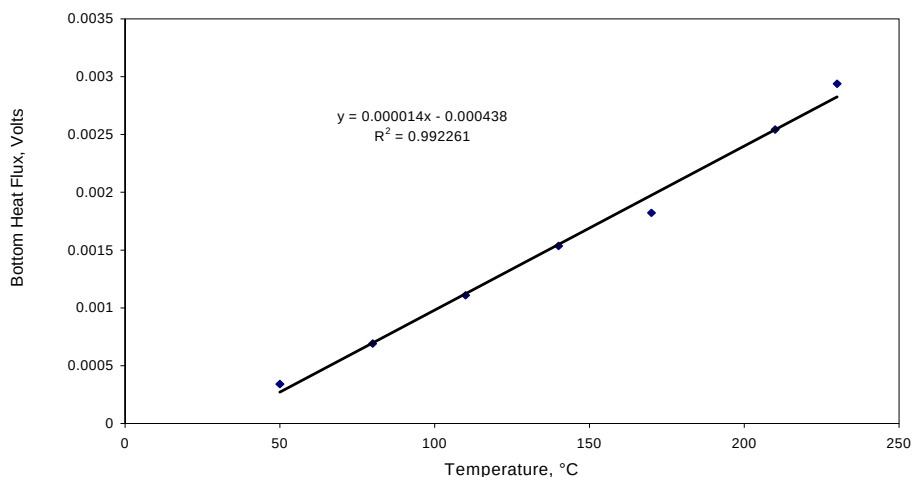


Figure 18. Heat flux sensor output, Volts increasing with increasing temperature for plate to plate runs without a guard ring in place

It has been observed in Figure 18 that there is a linear relationship between the heat flux sensor signal and the set test temperature where a guard ring is not used. Therefore it is possible to interpolate the plotted heat flux signal (Volts) vs. set temperature data and so obtain heat flux sensor data at set temperatures that have not measured experimentally. There are also linear relationships (Figure 19) between the bottom plate temperature vs. set temperature and top plate temperature vs. set temperature enabling interpolations to be made.

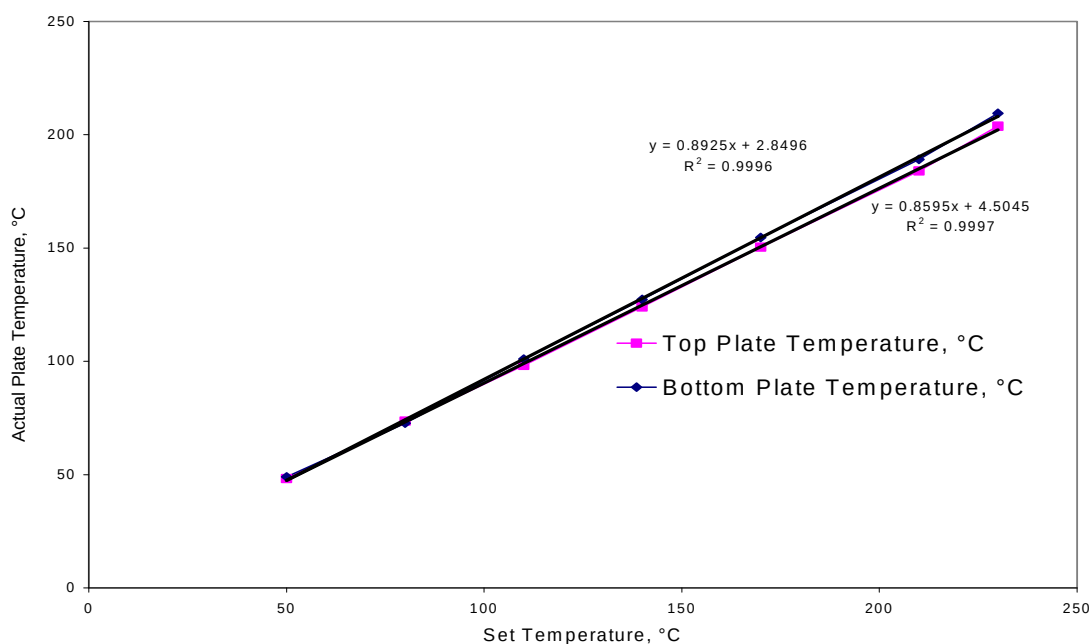


Figure 19: Plate temperatures during plate to plate baseline runs without guard ring in place

The heat flux signal at the bottom plate when the guard ring was fitted (Figure 20) was lower than for the bottom plate without the guard ring across the range of temperatures measured experimentally. (Heat flux signal (Volts) without guard ring at 140°C set temperature is 0.0022V but with guard ring at 150°C heat flux signal (Volts) is 0.0011V). The difference between the temperature of the bottom and top plates was also greater when the guard ring was in place. The temperature of the top plate was much lower than expected compared with the bottom plate when the guard ring was in place (Figure 21). Consequently the baseline data for cases when the guard ring was in place could not be reliably calculated. The guard ring may be acting as a preferred route to heat transfer and so conducting heat away from both the bottom and top plates.

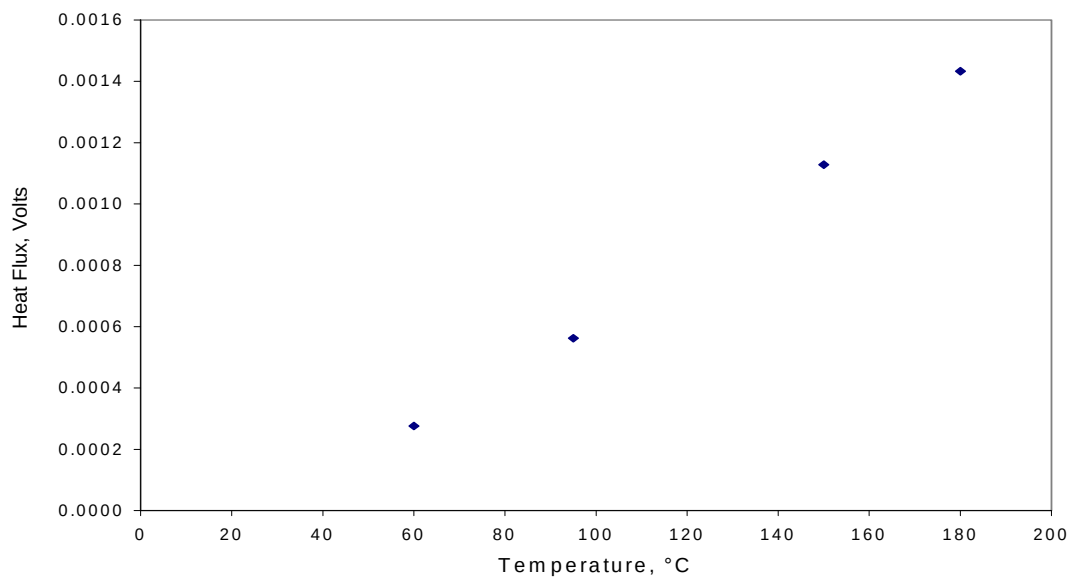


Figure 20. Bottom heat flux sensor output, Volts increasing with increasing temperature for plate to plate runs with guard ring in place

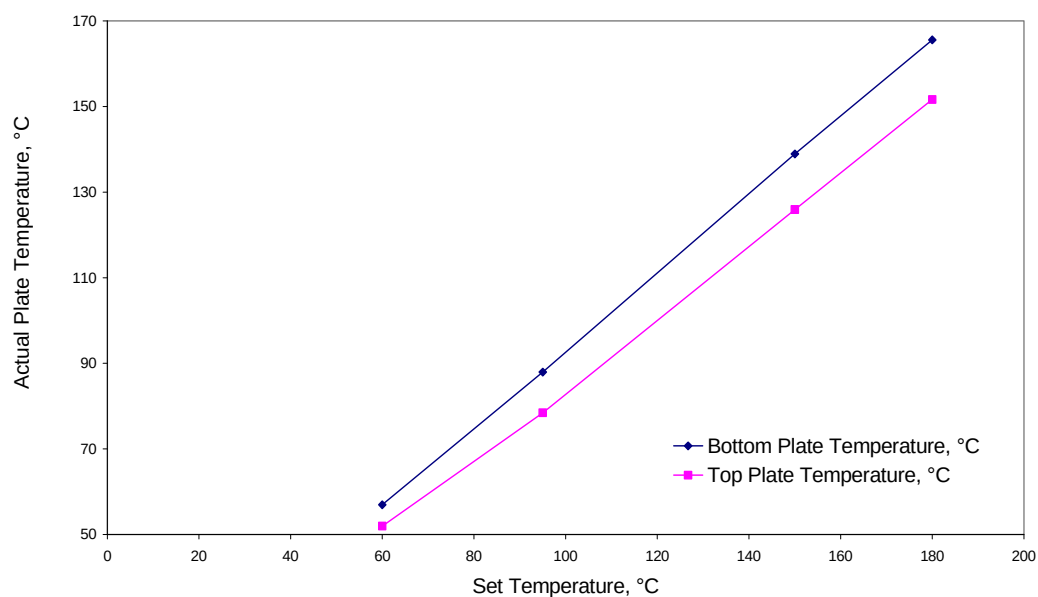


Figure 21: Plate temperatures during plate to plate baseline runs with guard ring in place

In order to obtain experimental data for specimens using the guard ring system the thermal conductivity of the PMMA reference specimen was calculated by measuring the top and bottom plate temperatures of the HTC instrument with the specimen inserted between the plates at set temperature 60°C for the bottom plate. The bottom heat flux and the thickness of the PMMA specimen were also measured. A calibration factor for the instrument was then calculated by dividing the reference thermal conductivity value for PMMA measured at 60°C by the experimentally determined value of thermal conductivity for PMMA at 60°C. The thermal conductivities of PS and PC were then measured by the same method and the thermal conductivity for the polymer was obtained by multiplying the experimentally determined thermal conductivity value for the material by the calibration factor.

The thermal conductivities of PS and PC measured using the HTC instrument both show an increase in thermal conductivity with increasing temperature across the test temperature range (Figure 22). The thermal conductivities of PS and PC measured by comparison to the reference standard PMMA value at 60°C do not take into account the temperature dependence of the thermal resistance of the instrument. Therefore the thermal conductivity values for PC and PS measured with the guard ring in place are not absolute values but do show the overall trend in thermal conductivity behaviour with increasing temperature.

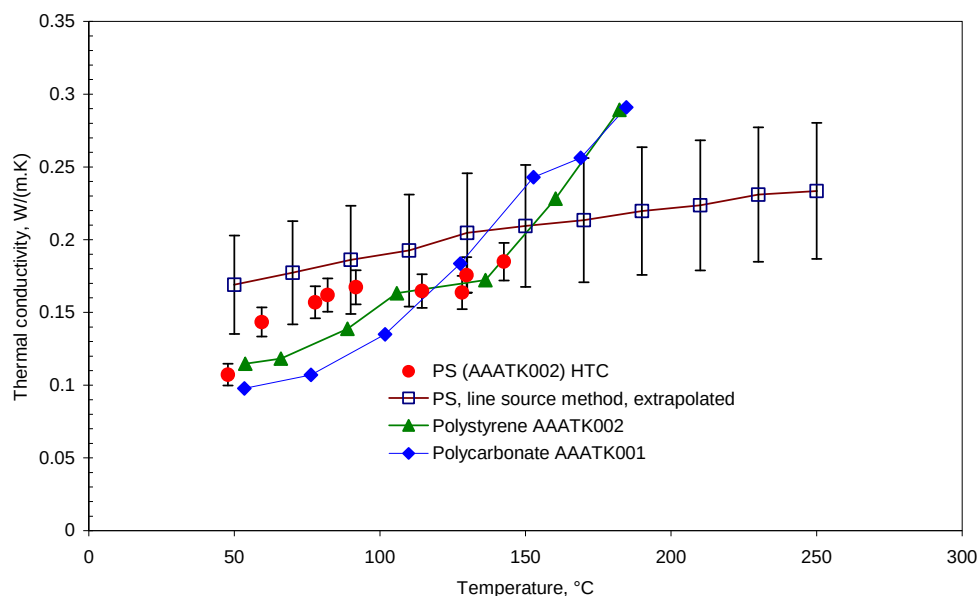


Figure 22. Thermal conductivity data for PS and PC in heating mode using HTC instrument with guard ring fitted

For both PS and PC decreases in gradient of the thermal conductivity vs. temperature curve are observed in the temperature range where the glass transition temperature might be expected to occur. For PS this decrease in gradient of the curve is observed in

the temperature range 105.80°C to 136.22°C. For PC this decrease is observed in the temperature range 152.73°C to 168.95°C. The glass transition temperatures for PS and PC measured by DSC are 84.37°C and 138.19°C respectively. Differences between the data measured using DSC and HTC instrument techniques could explain the differences in potential glass transition regions observed:

- DSC measurements were made in cooling mode whereas the HTC instrument was operated in heating mode
- Specimens may have been of differing densities
- Specimen size required for the HTC instrument is approximately 100 times larger than for the DSC (approximately 1.5g compared with 15.0 mg) which could affect the time taken for each specimen to undergo a transition from a glassy to rubbery state
- Measured T_g is highly sensitive to heating/cooling rate

Both PS and PC have lower measured thermal conductivity values than expected at lower temperatures. This could be due to poor thermal contact between specimen and bottom plate. When the guard ring is in place it is not possible to see whether good contact has been established between the specimen disc and the bottom plate

4.7 COMPARISON OF THERMAL CONDUCTIVITY DATA FOR PS AND PC OBTAINED BY HTC INSTRUMENT AND LINE SOURCE PROBE TECHNIQUES AT ELEVATED TEMPERATURES.

Thermal conductivity increases with increasing temperature for both PS and PC polymers tested by the HTC instrument technique and for PS tested by the line source probe technique. For PS and PC tested by the HTC instrument there is a gradient change in the thermal conductivity curve in the temperature range where a glass transition temperature would be likely to occur. A similar gradient change is also observed for the data from the line source technique.

The absolute values of thermal conductivity for PS tested by the line source probe technique and the HTC instrument technique differ. This may be due to errors in the line source probe data introduced by the linear extrapolation process or errors introduced into the HTC instrument data by use of the guard ring. The HTC instrument has been shown to have repeatability errors to within 1.5 % and precision errors to within 1.6 % when testing without the guard ring but there may be greater errors introduced by the use of the guard ring.

4.8 INVESTIGATION INTO DISCREPANCIES BETWEEN EXPERIMENTAL AND MODELLED THERMAL CONDUCTIVITY DATA FOR AMORPHOUS POLYMERS ABOVE T_g

The current model, described by Van Krevelen [16], used to predict thermal conductivity behaviour for amorphous polymers above the glass transition temperature predicts a decrease in thermal conductivity with increase in temperature for temperatures above the glass transition temperature of the polymer. The model is based around the correlation between the speed of sound in a material (sound velocity) and the

chemical structure of the material. From this it was found that a direct proportionality exists between the thermal diffusivity and the sound velocity.

The model involves the multiplication of the polymer specific heat capacity c_p , density ρ , and the longitudinal velocity of elastic waves (sound velocity) μ_{Long} with average free path length (distance between the molecules in adjacent thermal layers) L which gives the expected thermal conductivity λ .

$$\frac{\lambda}{c_p \rho} = L \mu_{Long} \quad (19)$$

$$\text{where } \mu_{Long} = \left(\frac{U_R}{V_{mol}} \right)^3 \left[\frac{3(1-\nu)}{1+\nu} \right]^{1/2} \quad (20)$$

U_R is the molar sound velocity function also known as the Rao Function $(\text{cm}^3/\text{mol})(\text{cm/s})^{1/3}$.

V_{mol} is the molar volume (cm^3/mol)

ν is an elastic parameter for the polymer [16]

$\nu =$ PS 0.35
PVC 0.35
PMMA 0.34

Data used to develop the model is taken from the steady state hot plate methods used by Eiermann [1, 2], Eiermann and Hellwege [3] and Hands, Lane and Sheldon [4]. The thermal conductivity data obtained by the hot plate methods rely on good thermal contact between the test specimen and the plates of the instrument.

Lee's Disc technique [6] is another steady state technique which relies on good thermal contact between the specimen and the plates of the instrument.

In calorimetric techniques [17, 5] there is contact between the specimen and the vertical, concentric inner and outer circular metal plates. However, there is insufficient experimental detail in the literature to determine whether poor specimen/plate contact may contribute to the decrease in thermal conductivity with increase in temperature observed above the glass transition temperature for data produced from calorimetric techniques.

The HTC instrument has been designed with a moveable upper plate to maintain contact with the specimen when the thickness of the specimen changes at temperatures above the glass transition temperature and with a guard ring to contain the specimen if flow of the material occurs.

The line source probe, laser flash and HTC instrument are techniques where data from tests has indicated an increase in thermal conductivity with increasing temperature above glass transition temperature. The line source probe is in contact with the specimen at temperatures above the glass transition temperature throughout the test and

contact is independent of the viscosity of the specimen. Due to the movable upper piston the plates of the HTC instrument are in contact with the specimen at temperatures below and above the glass transition temperature and the thickness of the specimen can be measured at all temperatures.

The laser flash technique is a non contact method and would appear to operate independently of specimen thickness. The thermal diffusivity of a specimen is measured and then the thermal conductivity calculated by:

$$\lambda_{\text{specimen}} = c_p * \rho * \alpha \quad (21)$$

specific heat capacity of specimen c_p

density of specimen ρ

thermal diffusivity of specimen α

4.9 REVIEW OF MODELS TO PREDICT THE THERMAL CONDUCTIVITY BEHAVIOUR OF AMORPHOUS POLYMERS

Data from several thermal conductivity measurement techniques, developed more recently than the hot plate methods, appears to show an increase in thermal conductivity with increasing temperature above the glass transition temperature. For these more recent methods, specimen thickness measurement and containment issues have largely been resolved or were not originally an issue with the technique. The model published by Van Krevelen does not predict a trend where there is an increase in thermal conductivity with increasing temperature above the glass transition temperature. Therefore there is a need for a model that predicts an increase in thermal conductivity with increasing temperature above the glass transition temperature.

A new model has been proposed by Zhong and Yang [18] to predict the thermal conductivity and pressure dependence of thermal conductivity of polymer melts. The model requires an atmospheric thermal conductivity datum for the polymer at each temperature to be modelled as well as Tait equation parameters to calculate the thermal conductivities for polymer melts at high pressures. However, the 0.1MPa thermal conductivity at a certain temperature can be predicted by a group contribution theory. Therefore to model thermal conductivity, λ , at higher pressures, P , the following relationships can be used:

$$\lambda(T,P) = \lambda(T,0.1\text{MPa}) \frac{1 - f(T,0.1\text{MPa})}{1 - f(T,P)} \quad (22)$$

$$f(T,P) = \frac{1}{15} \left\{ \frac{1}{C} - 1 - \ln \left[1 + \frac{P}{B(T)} \right] \right\} \frac{C \ln[1 + P/B(T)]}{1 - C \ln[1 + P/B(T)]} \quad (23)$$

where λ is in W/(m.K) and P is in MPa

B_0 and B_1 are Tait equation parameters:

	Temperature Range, K	Pressure Range, MPa	B_0 MPa	B_1 $\times 10^3/^\circ\text{C}$
PMMA	509-569	0-196	412.62	4.5203
PS	388-469	0-200	216.9	3.319
PC	424-613	0-177	310.0	4.078

C is taken to be a temperature and pressure-independent constant equal to 0.0894.

The model gives a good method to predict the thermal conductivity of polymer melts for a wide temperature and pressure range using only PVT data.

The Tait equation is used to present PVT data for polymers and is well established. The general form of the Tait equation [18] is:

$$V(P,T) = V(0,T) \{1 - C \ln[1 + P/B(T)]\}$$

$$\text{Where the zero pressure isotherm is } V(P,T) = V_{00} \exp(\alpha T) \quad (24)$$

V_{00} is the volume at zero pressure and absolute zero temperature.

$$\text{The Tait parameter is } B(T) = B_0 \exp(-B_1 T) \quad (25)$$

α is the thermal expansion coefficient of the polymer

B_0 and B_1 are Tait equation parameters

C is taken to be a temperature and pressure-independent constant equal to 0.0894.

A predictive relationship between thermal conductivity and specific volume for an amorphous polymer over a temperature range including solid and melt states was developed by Rides, Dawson and Nottay [11].

Both the temperature dependence and pressure dependence have been modelled using an exponential form. An additional exponential temperature term has been included to give a temperature dependence to the pressure dependence factor:

$$\nu = \nu_0 [\exp(k'(\theta - \theta_0))] [\exp(\ell' \theta (p - p_0))] \quad (26)$$

$$\lambda = \lambda_0 [\exp(k'(\theta - \theta_0))] [\exp(\ell' \theta (p - p_0))] \quad (27)$$

where ν_0 (cm^3/g), k and ℓ are constants of the specific volume equation,

λ_0 ($\text{Wm}^{-1}\text{K}^{-1}$) k' and ℓ' are constants of the thermal conductivity equation

θ is temperature (K)

p is pressure (MPa)

θ_0 (K) and p_0 (MPa) are a reference temperature and reference pressure respectively

v_o and λ_o are the specific volume and thermal conductivity values (constants) at temperature θ_o and pressure p_o

Therefore the thermal conductivity for an amorphous polymer can be modelled using specific volume data and the relationship:

$$\lambda = v \frac{\lambda_o}{v_o} [\exp((k - k')(\theta - \theta_o))]^{-1} [\exp(\theta(\ell - \ell')(p - p_o))]^{-1} \quad (28)$$

Although the data produced by the model shows a good fit with the experimental data, the data produced by the model does not describe the slight change in gradients observed for the experimental data for PS. The change in gradient of the thermal conductivity vs. temperature plot at approximately 100 °C is possibly due to the glass transition temperature (T_g) of PS ($T_g = 100$ °C).

5 CONCLUSIONS

The HTC instrument can be used to produce accurate and repeatable thermal conductivity measurements for amorphous polymers in the solid state and melt states and the glass transition temperature region. This data could eventually be used to provide more accurate models in order to improve the design of injection moulds. This in turn could increase efficiency and hence profitability by reducing injection moulding cycle times as well as improving the quality of the product by reducing warpage and shrinkage in the finished plastic part.

An increase in thermal conductivity with increasing temperature is observed at temperatures above the glass transition temperature for amorphous polymers tested using the HTC instrument. This trend supports experimental thermal conductivity data from the line source probe and laser flash thermal conductivity measurement techniques.

A new model has been reviewed that predicts the thermal conductivity behaviour of amorphous polymers where there is an increase in thermal conductivity of the polymer with increasing temperature at temperatures above the glass transition temperature.

6 AREAS FOR FURTHER WORK

Compression moulding specimens in a compression moulding press from powder could lead to improvement in the homogeneity and parallelism of the specimens, giving reproducible specimens with low internal stress.

The effect of the guard ring on test results for polymers should be investigated and the guard ring redesigned if necessary. The accuracy and repeatability of test data obtained with the guard ring in place should then be determined.

Once guard ring issues have been resolved then thermal conductivity data for amorphous polymers using the guard ring could be obtained across a temperature range from where the polymers are in the solid state through to temperatures where the polymers are in the melt state. Counterpart tests should be carried out at the same set

temperatures where the top and bottom plate are in contact with each other. Reference specimen PMMA tests should then be carried out at these temperatures to calibrate the instrument at each test temperature with reference to PMMA.

Testing of amorphous polymer specimens over a wide range of test temperatures using the HTC instrument under pressure in a hydraulic press and with the guard ring in place could give data produced under conditions similar to those in injection moulding and so could be fed into modelling applications.

7 ACKNOWLEDGEMENTS

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APPENDIX A LITERATURE REVIEW

A Review of Thermal Conductivity Measurement and Behaviour of Amorphous Polymers at Temperatures Above the Glass Transition Temperature (T_g)

A.1 INTRODUCTION

The importance of the thermal conductivity of polymers in the injection moulding process is given by Cracknell [19]. It is possible to estimate the cooling time for a polymer moulding given a set of injection moulding conditions as long as values for the thermal conductivity, density and specific heat capacity of the polymer and section thickness of the moulding are known.

These calculations depend on accurate data for thermal conductivity, specific heat and density of polymers being available for a wide range of temperatures. Brown [20] has reported that a 50% increase in the thermal conductivity of a polymer, when input into injection moulding simulation software can lead to a reduction of the predicted time to freeze for a component of 33%. Therefore, if the thermal conductivity value is erroneously high then the part will be removed too early in the cycle. Warpage and shrinkage of the part could then occur.

A.2 MECHANISM OF HEAT TRANSFER

Three mechanisms of heat transfer have been described in the literature:

A.2.1 Convection

The mechanism for convection and method for quantifying the contribution of convection to the overall heat transfer process is well known and explained by Winterton [21] and Redford [22]. Briefly, when a heated surface heats the material in contact with it, then a layer of less dense material is formed. The less dense material will rise and be replaced by cooler more dense material. Therefore convective heat transfer is likely to be the boundary condition applicable at the surface of a solid object.

A.2.2 Radiation

A concise account of radiation as a heat transfer mechanism involving the emission of electromagnetic radiation by a hot body and where changes to the properties of the medium occur only if the medium absorbs some of the radiation is given by Sprackling [23].

The contribution of radiation to the heat transfer mechanism at a heat transfer surface has been accounted for within the heat transfer coefficient for convection [22].

A.2.3 Conduction

a) Steady State Conditions

The steady state condition for conduction occurs when the temperature field remains constant with time and the stored energy does not increase or decrease [22]. In this case then Fourier's Law, which is commonly reported in the literature, applies:

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

where Q is the rate of heat flow, Watts W, across a material of cross sectional area A (m^2) and thickness x (m) and of thermal conductivity λ , W/(mK).

b) Transient Conditions

If the temperature within a specimen changes with time then the conditions are said to be in a transient state.

Winterton [21] considered the situation in terms of a box of x, y, z dimensions:

If heat is generated at a rate u Wm^{-3} then the temperature rise ∂T caused by the supply of heat in time ∂t , where c is specific heat capacity $J Kg^{-1}K^{-1}$ then:

$$\text{where} \quad \nabla^2 T = \frac{\partial^2 T}{\partial x^2} + \frac{\partial^2 T}{\partial y^2} + \frac{\partial^2 T}{\partial z^2} \quad (2)$$

$$\text{therefore} \quad \nabla^2 T + \frac{u}{\lambda} = \frac{\rho c}{\lambda} \frac{\partial T}{\partial t} \quad (3)$$

where λ , W/(mK) is thermal conductivity.

A.3 Experimental Methods and Models Where Thermal Conductivity Decreases With Increasing Temperature At Temperatures Above T_g

A.3.1 Steady State Hot Plate Technique

Initial work on measuring the thermal conductivity of polymers using this technique was carried out in Germany by Eiermann [1]. The technique described was based on Fourier's steady state heat flow equation (1) where the thermal conductivity is determined from Fourier's Law. The specimen is placed between a top heated plate and a bottom cold plate. The apparatus was maintained in a possibly pressurized, helium filled atmosphere to maintain good thermal contact between the specimen and the two plates. This was particularly important at temperatures below the glass transition temperature when the specimens became brittle. The thermal conductivity can be obtained from measurement of the heat flux through the specimen and the temperature gradient across the specimen. Results were reported for PMMA using this technique from ambient temperature up to a maximum temperature of 100°C.

This work was extended in a further paper by Eiermann [2] where the thermal conductivities of PC and PMMA were measured from ambient temperature to 150°C again using the steady state technique. Results indicated an increase in thermal conductivity of the polymer with increasing temperature up to the glass transition temperature, typically 149°C for PC and 105°C for PMMA. There was then a decrease in thermal conductivity of the polymer with increase in temperature at temperatures above the glass transition temperature for PMMA. The maximum temperature of 150°C was not high enough to reach the T_g for the PC specimen.

An attempt was made by Eiermann and Hellwege [3] to explain the results from the two steady state technique papers. The break in thermal conductivity at the second-order (glass) transition temperature was interpreted by them as being connected with a break in the volume versus temperature curve.

However, Hands, Lane and Sheldon [4] compared results from their own work with that of Eiermann [1, 2, 3] for thermal conductivity in terms of the concept of a mean free path for heat transfer by elastic waves. In this case the quanta of energy transferred is the phonon. The number of phonons, which is temperature dependent, determines the number of phonon-phonon collisions and so there is a decrease in mean free path length with increase in temperature as collisions become more frequent.

For polymers below the glass transition temperature, the mean free path, Hands, Lane and Sheldon [4] postulated, is determined by structural scattering which is largely temperature independent. Therefore a small increase in thermal conductivity with temperature for polymers in the glassy state would be expected. At temperatures above the glass transition temperature a decrease in thermal conductivity with temperature is predicted due to the dominant effect of the change in density that occurs.

A generalized dependence for the thermal conductivity of amorphous polymers was put forward in a paper by Arutyunov [24]. Although the relationships for the increase in thermal conductivity with temperature below glass transition temperature and the decrease in thermal conductivity with temperature above glass transition temperature can be derived separately, a relationship for the thermal conductivity behaviour of amorphous polymers across the whole temperature range was also derived. This is done for a homologous series of polymers using a dimensionless function and the measured temperature and glass transition temperature respectively as well as the thermal conductivity coefficients at the measured temperature and glass transition temperatures respectively.

The experimental work using the steady state technique was taken further by Barker, Chen and Frost [25] investigating the effect of pressure on the glass transition temperature for PMMA. The thermal conductivity of PMMA was measured across the temperature range – 60°C to 30°C and at 1560 bar and 2030 bar pressures. It was again observed that there was an increase in thermal conductivity with temperature below the glass transition temperature for the polymer and a decrease in thermal conductivity with increase in temperature above the glass transition temperature. The thermal conductivity and glass transition temperature were shifted to higher values under pressure.

The Barker, Chen and Frost [25] findings agreed with the work carried out by Hands, Lane and Sheldon [4] that the main mechanism of heat transfer in a polymer is due to phonon –phonon collisions. The effective mean free path for phonons in PMMA is calculated to be 15 Angstroms by Barker, Chen and Frost. For amorphous polymers Barker, Chen and Frost [25] conclude that the main source of thermal resistance is therefore structural scattering. This work agrees closely with the work of Hands, Lane and Sheldon [4] in confirming that a small increase in thermal conductivity with temperature for polymers in the glassy state would be expected. At temperatures above the glass transition temperature a decrease in thermal conductivity with temperature is expected due to the dominant effect of the change in density that occurs.

Piorkowska and Galeski [26] reported that at temperatures close to absolute zero there is a linear relationship between thermal conductivity and temperature for amorphous polymers. Again an increase in thermal conductivity is observed with increase in temperature up to the glass transition temperature and a decrease in thermal conductivity is observed with increase in temperature above the glass transition temperature.

A.3.2 Calorimetric Techniques

The use of the bicalorimetric technique, a transient technique, was reported by Bashirov and Shermergor [17]. However there is a lack of experimental information. The technique measures the thermal diffusivity of materials from which the thermal conductivity can be calculated, as reported by Naziev, Bashirov and Abdulagatov using a tricalorimetric technique[5].

Results are presented for PS and PMMA in the temperature range from 300K to 513K at ambient pressure and at pressures $1 \times 10^8 \text{ N/m}^2$, $1.5 \times 10^8 \text{ N/m}^2$, $2 \times 10^8 \text{ N/m}^2$ and $0.4 \times 10^8 \text{ N/m}^2$. For both polymers there is an increase in thermal conductivity with increase in temperature until the glass transition temperature is reached. At temperatures above the glass transition temperature a decrease in thermal conductivity with glass transition temperature is observed. There is also a shift to the right along the temperature axis of the glass transition temperature with increase in pressure. Thermal conductivity increases with increasing pressure.

The overall trend of the thermal conductivity behaviour of the polymers shows good agreement with the results from the work carried out by Eiermann.

An explanation of the effect of pressure on thermal conductivity is given as increasing pressure reduces the free volume and increases the intermolecular interaction within the polymer leading to an increase in heat transfer rate and therefore increase in thermal conductivity. However, decreases in thermal conductivity are observed above the glass transition temperature where a decrease in segmental mobility of the polymer chains and the packing processes after relaxation slow down the rate of heat transfer and therefore decrease the thermal conductivity of the polymer. Therefore the decrease in segmental motion has a greater effect on thermal conductivity than the reduction in free volume.

A.3.3 Lee's Disc Technique

The Lee's Disc apparatus allows the determination of the thermal conductivity of a specimen under steady state conditions. The specimen is placed between two copper plates and an electric heater between the middle and a third outer copper disc. The thermal conductivity of the specimen can be calculated if parameters such as current, voltage, area of plates, specimen thickness and disc temperature are determined experimentally.

The thermal conductivity of PS was measured using this technique and reported by Sombatsompop and Wood [6]. The temperature range was 40°C to 300°C. Thermal conductivity increased with increasing temperature up to approximately 100°C, the T_g for the polymer was stated to be 97°C. The thermal conductivity of the PS decreased with increasing temperature at temperatures above 100°C (above T_g).

Sombatsompop and Wood [6] described the increase in thermal conductivity with temperature in the glassy state as being due to increases in intermolecular energy transfer and so increases in molecular movement with increasing temperature. They thought that energy transfer in the rubbery state is thought to be poorer due to an increase in free volume and therefore greater molecular separation.

A.4 Experimental Methods and Models Where Thermal Conductivity Increases With Increasing Temperature At Temperatures Above T_g

A.4.1 Line Source Technique

In the line source technique, a test probe is inserted into the polymer melt contained between two PTFE seals in a heated specimen chamber. The chamber can be set to the required test temperature. The probe contains a heater wire and a thermocouple.

The measurement consists of applying a known voltage to the heater element in the probe for a set time. The thermocouple within the probe records the temperature transient during this process. The thermal conductivity of the material is obtained from the gradient of a plot of temperature versus $\ln(\text{time})$ [27].

An early version of the line source probe apparatus was described by Underwood and McTaggart [7]. Thermal conductivity of the PS increased with the temperature of the polymer both in the glassy and rubbery states for the polymer from 30°C to 210°C. The trend of these results was confirmed by work carried out by Lobo and Cohen [8]. Polymer in the amorphous melt state was observed to have a thermal conductivity independent of temperature. The effect of T_g was not clear and other effects such as cooling rate and shrinkage of the specimen were considered.

This work was extended, further measurements being made on PS and measurements made on PMMA and PC using the line source probe technique in the temperature range of 20°C to 200°C for PMMA and PS and 60°C to 240°C for PC by Lobo and Newman [9]. PS exhibited an increase in thermal conductivity with increase in temperature below T_g , through the T_g and above T_g whereas PMMA and PC exhibited an increase in thermal conductivity with increase in temperature below T_g , at T_g but hardly any variation above T_g .

Pressure was applied to line source probe testing of PS by Oehmke and Wiegmann [10]. The thermal conductivity of PS was seen to increase across the test temperature range from 60°C to 220°C. Pressures of 20 MPa, 80 MPa and 120 MPa were applied to the specimen and an increase in thermal conductivity was observed with increase in pressure.

An attempt to explain the trends observed during the measurement of thermal conductivity of polymers has been made by Dashora and Gupta [28]. Behaviour has been categorised into three categories- a) polymers showing a maximum at T_g b) polymers showing a plateau at T_g with positive or negative gradient before or after T_g and c) polymers showing a linear increase with slope in both glassy and rubbery regions but with a gradient change at T_g . They reported that in the glassy state, structural scattering dominates phonon scattering and that thermal conductivity can be predicted by quantifying these two parameters for a particular temperature. Above the glass transition temperature it is reported that the formation of voids due to expansion of the polymer can scatter phonons, as can increasingly dominant chain moments. These two mechanisms would be competing in the scatter of phonons and thermal conductivity in the rubbery state can be predicted by quantifying these two effects.

A model has been proposed for predicting the pressure dependence of thermal conductivity of polymer melts above the glass transition temperature that requires only atmospheric thermal conductivity data and Tait equation parameters, Zhong and Yang [18]. The model uses pvT data to predict thermal conductivity of polymer melts for a wide temperature and pressure range.

Thermal conductivity data was obtained at 20 MPa, 80 MPa and 120 MPa across the temperature range 50°C to 250°C using a line source probe for PS and PC, Dawson, Rides and Nottay [11]. For both polymers there was an increase in thermal conductivity with temperature in both the glassy and rubbery states for all the polymers.

A comparison of this experimental data was carried out with modelled thermal conductivity behaviour of PS across the same pressure and temperature. The model was based on specific volume data and used an exponential form. There was a close correlation between the modelled data and the experimental data across the temperature and pressure ranges.

A.4.2 Laserflash Technique

The temperature rise that occurs when a plane-parallel specimen of polymer is heated from the front by a short light pulse from a Xenon flash lamp can be measured, Knappe [12]. The rise is recorded at the back of the specimen with respect to time. The thermal diffusivity can then be determined and the thermal conductivity calculated if specific heat and density of the specimen are known.

The thermal conductivity data obtained for PC by this method shows a steady increase with increase in temperature across the testing range (20°C to 300°C) for both the glassy and rubbery states.

APPENDIX B: TABLES**Table 1. Glass transition temperature determinations of polymer specimens by DSC method**

Specimen	Glass Transition Temperature Determined By DSC, °C
PS	84.37
PC	138.19
PVC	82.55

Table 2: Thermal conductivity test results using HTC instrument for PMMA at 60°C and 95°C

Run Number	Set Temperature, °C	Specimen Temperature, °C	Thermal Conductivity, W/(m.K)
HTC 100	60	51.46	0.197
HTC 115	60	50.17	0.209
HTC 116	60	50.48	0.182
HTC 117	60	50.37	0.180
		Average Thermal Conductivity	0.192
		Standard Deviation	0.013
		Coefficient of Variation	6.981 %
HTC 101	95	76.43	0.210

Table 3: Thermal conductivity test results for NPL accepted reference standard PMMA supplied by Thermal Metrology Team using the NPL guarded hot plate apparatus

Temperature, °C	Thermal Conductivity of PMMA Standard Reference Specimen, W(mK)
-10	0.184036
0	0.185280
10	0.186524
20	0.187768
30	0.189012
40	0.190256
50	0.191500
60	0.192744

Table 4: Thermal conductivity test results using HTC instrument for PS at 60°C, 95°C and 200°C set test temperatures

Run Number	Set Temperature, °C	Specimen Temperature, °C	Thermal Conductivity, W/(mK)
HTC 107	180	128.20	0.164
HTC 118	180	127.03	0.158
HTC 119	180	128.61	0.168
HTC 120	180	127.16	0.155
HTC 121	180	126.61	0.150
		Average Thermal Conductivity	0.159
		Standard Deviation	0.007
		Coefficient of Variation	4.417 %
HTC 102	60	48.81	0.112
HTC 103	95	72.51	0.145
HTC 129	200	140.99	0.166

Table 5: Thermal conductivity test results for PS obtained from the extrapolation of NPL line source probe thermal conductivity data obtained under elevated pressures to 0 bar

Temperature, °C	PS thermal conductivity values, W/(mK) (NPL line-source technique)
50	0.169
70	0.177
90	0.186
110	0.193
130	0.205
150	0.209
170	0.213
190	0.220
210	0.224
230	0.231
250	0.234

Table 6: Thermal conductivity test results for PS using HTC instrument. Thickness of specimen assumed as constant over the test temperature range. Plates measured in contact only at 180°C.

Run Number	Set Temperature, °C	Specimen Temperature, °C	Thermal Conductivity, W/(mK)
HTC106	60	47.75	0.107
HTC107	180	128.20	0.164
HTC108	125	91.73	0.167
HTC109	110	82.02	0.162
HTC110	75	59.42	0.143
HTC111	105	77.49	0.157
HTC112	180	129.77	0.176
HTC113	160	114.44	0.165
HTC114	200	142.61	0.185

Table 7: Variation of hand held micrometer readings for two operators measuring reference PMMA disc nominally 1 mm thick. All measurements are in mm.

Reading Number:	Hand Held Micrometer Thickness Measurement of Disc of PMMA Nominally 1mm Thickness.	
	M. Rides	A. Dawson
1	1.008	1.029
2	1.006	1.009
3	1.009	1.007
5	1.003	1.007
6	1.005	1.007
7	1.001	
8	0.988	
Mean	0.997	1.012
Standard Deviation	0.022	0.010
Percentage Error	0.748	0.954

Table 8: Thermal conductivity values for PS obtained by the HTC instrument method where thickness of the specimen during the tests has been measured using a Vernier calliper and a dial gauge. All measurements are in mm.

Run number	Specimen Temperature, °C	Thermal Conductivity, W/(m.K) calculated using dial gauge thickness measurement	Thermal Conductivity, W/(m.K) calculated using Vernier calliper thickness measurement
HTC134	49.23	0.150	0.148
HTC135	60.14	0.143	0.140
HTC136	79.51	0.188	0.186
HTC137	91.83	0.188	0.188
HTC138B	116.53	0.195	0.201
HTC139	129.85	0.195	0.212
HTC140	144.01	0.227	0.252

Table 9. Variability of Vernier calliper measurements between two operators while determining the expansion behaviour of the HTC instrument. All measurements are in mm.

Instrument Components	Mean OP1	Mean OP2	Std Dev OP1	Std Dev OP2	OP1			OP2		
Phenolic Base 1-0										
Room Temperature	25.45	25.40	0.12	0.11	25.32	25.54	25.50	25.37	25.52	25.31
170°C	25.19	25.44	0.08	0.16	25.23	25.25	25.10	25.26	25.58	25.47
Change low to hot	-0.26	0.04								
Al+insulating material 2-1										
Room Temperature	41.85	41.57	0.06	0.10	41.91	41.80	41.84	41.54	41.49	41.68
170°C	41.83	41.90	0.23	0.11	42.09	41.74	41.66	42.03	41.82	41.85
Change low to hot	-0.02	0.33								
Top Al-bottom steel flange 3-2										
Room Temperature	67.71	67.72	0.05	0.03	67.76	67.67	67.71	67.71	67.70	67.76
170°C	67.84	67.67	0.23	0.13	68.09	67.64	67.78	67.52	67.76	67.72
Change low to hot	0.12	-0.06								
Expansion, mm	-0.16	0.31								

Table 10. Thickness values for PS measured by a dial gauge during a series of thermal conductivity tests using the HTC instrument

Run number	Specimen Temperature, °C	Dial gauge thickness measurement, mm
HTC134	49.23	2.285
HTC135	60.14	2.311
HTC136	79.51	2.369
HTC137	91.83	2.418
HTC138B	116.53	2.583
HTC139	129.85	2.619
HTC140	144.00	2.679

Table 11. Expansion of upper section of HTC instrument measured by LSM

Run Number	Set Temperature, °C	Expansion, mm
HTC170	60	0.0436
HTC171	75	0.0433
HTC172	105	0.0652
HTC173	125	0.0844
HTC174	160	0.1143
HTC175	190	0.1292
HTC176	210	0.1555

Table 12. Thermal conductivity of PS measured using HTC instrument held at temperature for time long enough to achieve steady state conditions

Run number	Set Temperature, °C	Specimen Temperature, °C	Thermal Conductivity, °C
HTC 106	60	47.75	0.107
HTC 110	75	59.42	0.143
HTC 124B	75	60.94	0.161
HTC 111	105	77.79	0.156
HTC 108	125	91.73	0.167
HTC 113	160	114.44	0.165
HTC 107	180	128.20	0.164
HTC 112	180	129.77	0.176
HTC 114	200	142.61	0.185
HTC 128	180	127.77	0.152
HTC 130	225	161.77	0.190

Table 13. Thermal conductivity of PS measured using HTC instrument held at temperature for insufficient time to achieve steady state conditions

Run number	Set Temperature, °C	Specimen Temperature, °C	Thermal Conductivity, °C
HTC 124A	60	49.90	0.159
HTC 131	60	48.13	0.110
HTC 125	105	77.17	0.123
HTC 109	110	82.02	0.162
HTC 126	125	91.37	0.145
HTC 127	160	116.30	0.177
HTC 129	200	140.99	0.166

Table 14. Examination of the effect of the time holding a specimen at test temperature during the test has on the thermal conductivity result measured using the HTC instrument

Run Number	Set test temperature, °C	Thermal conductivity of PS, W/(mK), steady state conditions	Thermal conductivity of PS, W/(mK), steady state or non-steady state conditions ('examined' values)	Absolute difference between steady state value for thermal conductivity of PS and 'examined' value	Time, seconds specimen held at temperature to give 'examined' value for thermal conductivity
HTC 106	60	0.107			
HTC 124A			0.159	0.051	8217
HTC 110	75	0.143			
HTC 124B			0.161	0.018	14358
HTC 111	105	0.157			
HTC 125			0.123	0.034	6831
HTC 108	125	0.167			
HTC 126			0.145	0.023	6221
HTC 113	160	0.165			
HTC 127			0.177	0.012	7245
HTC 107	180	0.164			
HTC 128			0.152	0.012	16935
HTC 114	200	0.185			
HTC 129			0.166	0.019	15710

Table 15: Determination of noise in heat flux and thermocouple signals 500 seconds from end of test. Bottom plate set temperature 125°C.

HTC 173	Mean Value	Standard Deviation	% Error
Heat Flux Top, V	0.000168280	0.000016879	10.03008213
Heat Flux Bottom, V	0.000539602	0.000016199	3.002098033
Temperature Top, °C	94.30	0.355014336	0.376486859
Temperature Bottom, °C	117.30	0.390709891	0.333055279

Table 16. Thickness and thermal conductivity used to determine the relationship between density and thermal conductivity for 50mm PVC P130/1 discs

Run No:	Specimen mass/mg	Diameter of disc/mm	Thickness of disc/mm	Volume of disc/mm³	Density of disc/mg/mm³	Thermal conductivity of disc/W/mK
HTC199	5957.900	50.000	2.006	3939.560	1.512	0.145
HTC200	4959.100	50.000	1.907	3745.170	1.324	0.111
HTC201	2991.300	50.000	1.884	3699.220	1.236	0.075

Table 17. Repeatability data for PMMA where thickness measured using LSM and where steady state conditions maintained

Run No.	Specimen Temperature, °C	Thermal Conductivity, W/mK
HTC155	49.87	0.193
HTC156	49.12	0.189
HTC157	49.92	0.189
HTC158	50.01	0.186
	Average Thermal Conductivity	0.189
	Standard Deviation	0.003
	Coefficient of Variation	1.518 %

Table 18. Heat flux measured at temperatures from 60°C to 180°C for plate to plate baseline without guard ring

	Set Temperature, °C	Bottom Plate Heat Flux Signal, V	Bottom Plate Temperature, °C	Top Plate Temperature, °C
HTC143B	50	0.00034216	49.03	48.27
HTC143B	80	0.000692074	72.73	73.64
HTC143B	110	0.001109384	101.07	98.26
HTC143B	140	0.001536037	127.37	124.04
HTC143C	170	0.001821412	154.65	150.40
HTC143C	210	0.002543434	189.17	184.04
HTC143C	230	0.002939189	209.51	203.78

Table 19. Heat flux measured at temperatures from 60°C to 180°C for plate to plate baseline with guard ring

	Set Temperature, °C	Heat Flux Signal, V	Bottom Plate Temperature, °C	Top Plate Temperature, °C
HTC166	60	0.00027617	56.96	51.98
HTC167	95	0.000562312	87.96	78.43
HTC168	150	0.001128057	138.91	125.90
HTC169	180	0.001432834	165.56	151.61

Table 20. Thermal conductivity data for PS tested using HTC instrument with guard ring fitted

Run No.	Temperature, °C	Thermal Conductivity, W/mK
HTC170	53.78	0.115
HTC171	65.97	0.118
HTC172	88.86	0.137
HTC173	105.80	0.163
HTC174	136.22	0.172
HTC175	160.29	0.228
HTC176	182.25	0.289

Table 21. Thermal conductivity data for PC tested using HTC instrument with guard ring fitted

Run No.	Temperature, °C	Thermal Conductivity, W/mK
HTC177	53.42	0.098
HTC178	76.32	0.107
HTC179	101.75	0.135
HTC180	127.59	0.184
HTC181	152.73	0.243
HTC182	168.95	0.256
HTC183	184.63	0.291