A REVIEW OF REQUIREMENTS FOR IMPROVED METHODS OF MEASURING THERMAL PROPERTIES OF POLYMERS

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ABSTRACT

A review of methods of measuring three main thermal properties (thermal conductivity, specific heat and latent heat) in polymer melts has been carried out. This has identified a number of relevant standards which would assist users. The purpose of this report is to evaluate current measurement methods for each of these properties and to propose the best currently available method(s) to meet industrial requirements and recommend improvements where needed. Moldflow simulations have also been carried out which illustrate the commercial importance of accurate thermal property data. For example, in an ABS hub cap a 20% variation in thermal conductivity leads to a 120% (54s) change in cooling time.
1 INTRODUCTION

Speed of production is critical in polymer processing for maximising profitability. The processing cycle is however limited by the amount of time needed to quench a plastic part into a frozen state in the mould and at the same time keeping the shrinkage and warpage values to within the specified tolerance limits. This becomes particularly complex as the part thickness increases, since most plastics have inherently poor thermal properties (e.g. the conductivity is about 100 times lower than metals).

Estimation of heat transfer is critical since the cycle time depends on the ability to predict minimum time a plastic part should remain in the mould (Figs. 1 and 2). This will allow the production rate to be maximum and the unit cost to be minimum (1). A recent report from Moldflow (2) stated a cost saving from shorter cycle times of 35p per part (–£60k pa) for Nippondenso using just the modelling data available today on an air filter unit. However the calculation of cooling time is difficult and is normally done by using the bulk average temperature of the melt; but this may lead to a considerable amount of uncertainty as the part thickness increases. Estimation of the frozen layer thickness of the part becomes complex as soon as the part is ejected and the interface changes from a metal heat sink to air or similar environment. (Figs. 1 and 2). The latent heat of crystallisation in the interior of the part is redistributed as the part continues to cool in the air at a much slower rate. This causes an increase in temperature in the part at the crystallisation front and may introduce part defects.

Plastic processing operations therefore, generally require understanding of the fluid flow and heat transfer phenomena from the core of the plastic moulding to the surface of the component (3). The heat transfer properties are functions of temperature, pressure and shear (flow) rate (Fig. 3). At the interface, the heat transfer phenomena may be affected by surface finish, pressure, additives such as mould release agents etc. Very few of these effects have been quantified so far. Heat transfer also has a strong influence on the viscosity of the polymer. An incorrect viscosity value may lead to hot spots, degradation and general increase in the scrap rate. Commercial software packages are available to assist design and to optimise production, but they all rely on access to reliable industrially relevant data (4,5). There is thought to be some uncertainty over the practiced measurement techniques and also over the significance of heat transfer parameters to industrial polymer processing. (Some of the causes of this uncertainty may include low pressure data that are used in high pressure industrial conditions, exclusion of latent heat of crystallisation in commercial simulation packages).

In order to demonstrate the benefits of good thermal property measurement, three main thermal properties (i.e. thermal conductivity, specific heat and latent heat) have been selected and have been reviewed in this report. The current measurement methods were also investigated to see if they provide industrially relevant experimental data. Heat transfer coefficients at surfaces and thermal diffusivity [= thermal conductivity / (density x specific heat)], although important for many industrial polymer processes, are not covered in detail in this report (see refs. 6-10 for further reading).

This review includes a literature search on the above three thermal properties, since 1970, which identified 100 references on thermal conductivity, 134 references on specific heat and 58 references on latent heat. There are 2 standards for specific heat, 10 standards for thermal conductivity and one standard for latent heat measurement available in the literature. However, it is to be noted that by no means are all these references strictly relevant to polymer melts. Most of the reported work on polymers is on thermoplastic materials although there are references to a limited amount of work on reactive materials in some papers. The search also identified three databases: ATHAS (website: http://www.funnelweb.utcc.utk.edu/~athas) for specific heat of polymers (11), Moldflow database (website: http://www.moldflow.com/) containing thermo-physical properties of well over 4500 materials (12) and the CAMPUS database (website: http://www.campusplastics.com) containing information on plastics properties from over 40 leading material producers.
A survey of UK industrial requirements for heat transfer properties was carried out in July 1999 prior to this review, which confirmed the importance of heat transfer to polymer processing (comments are compiled in Annex 1). This has helped NPL to formulate the experimental work programme to ensure its relevance to industrial processing conditions. The survey received unanimous agreement from the industry on the importance of good data on heat transfer to maximise heat transfer rates and hence, production rates. 100% of respondents agreed that thermal conductivity and specific heat are significant heat transfer parameters, while 95% thought latent heat to be significant. Other parameters that were thought to be important in polymer processing were: thermal diffusivity, heat of reaction, viscous heating, rheology as a function of flow rate and cooling capacity of the cooling medium. 67% agreed that good heat transfer data would reduce degradation, while 77% believed it would also reduce distortion. 52% of respondents process/supply semi-crystalline materials while the rest (48%) are involved with amorphous materials. 47% make use of fillers and 50% thought orientation is an important aspect in their products. 44% use commercial process simulation software and nearly 50% have DSC equipment of their own. The majority (>85%) suggested the industrially relevant temperature and pressure ranges to be between 130°C to 280°C and between 3 MPa to 200 MPa respectively.

The UK measurement capabilities on thermal properties of polymers are believed to exist at the following principal centres in addition to NPL: Rapra Technology, Loughborough University, Bradford/Leeds Universities (IRC), Surrey University, Manchester University and DERA. However, almost all of the recently published literature reviewed in this work are from countries outside the UK. It is difficult therefore to comment on the exact state of the industrially relevant research work on polymer thermal analysis in the UK at present. Industrial need for reliable heat transfer data is however strong, as illustrated by the Moldflow simulation work reported in this document (e.g. Figs. 8 and 18). Making use of accurate relevant data is expected to aid the UK polymer processing industry to maximise profit and increase competitiveness in the medium to long term.

2 THERMAL CONDUCTIVITY (λ)

Thermal conductivity is the second most significant property (after viscosity) to influence temperatures and pressures in polymer processing. It is defined as the rate of heat transfer through a unit volume of the material by conduction and is usually expressed in W/m°C. It determines temperature distribution, controls flow characteristics and cooling rate, but in spite of such an important role it is also regarded to be one of the least accurately measured parameters (~50% variation within a grade and ~200% variation over the range of polymer studied, ref. 3). Accurate measurement is therefore crucial for reliable predictions of injection and blow moulding and downstream of the die in extrusion. Thermal conductivity data on PC/ABS used to design products like mobile phones, laptop, pager etc. were reported to vary between 0.11 to 0.22 W/m°C; this variation is considered to be the result of differences in measurement techniques rather than the material. On polyethylene, the thermal conductivity was reported to vary by ~80%. Moldflow have estimated that a 100% difference in thermal conductivity can lead to a 30 to 50% difference in pressure during processing (4). Considerable uncertainty also arises from the fact that most measurements are carried out at normal pressure (0.1 MPa) whereas polymer processing occurs at high pressure (up to 200 MPa). Even the temperature dependence of thermal conductivity is not well established since most conventional measurement methods require either a solid sample or a fluid that will not degrade during testing (note that λ of polyethylene may vary by ~50% between room temperature and 200°C). The effects of temperature and pressure on λ for a range of polymeric materials are shown in Figs. 4-7 and reported in refs. (13-21). Although temperature has a relatively small effect (10-20%) on thermal conductivity in most polymers in the melt state (160°C-280°C), a difference of 40% -100% in thermal conductivity value could be possible in many polymers due to pressure changes (up to 300 MPa).
Examples of Moldflow simulation work are shown in Figs 8a-8l which demonstrate the importance of thermal conductivity data in temperature and cooling time distributions in an injection moulded component (a hub cap). The effects of varying input thermal conductivity values (by introducing an error of ± 20% in the measurement) from the standard input value are shown at two pressure levels (30MPa and 60MPa). A difference of ~50% in cooling time distribution is seen (Fig. 8d) when a measurement error of -20% is introduced. The same very large change in cooling time is seen at 60MPa. Since a ± 50% difference in the measured thermal conductivity value is not uncommon in the literature, this exercise demonstrates very clearly the need for generating more accurate industrially relevant thermal conductivity data.

Accurate thermal conductivity data are needed for material selection, heat flow calculations, for understanding the heat transfer mechanism and accurate cycle time predictions. In particular, there is a general lack of reliable published data on both semi-crystalline and amorphous polymer melts at high temperature, pressure and shear rate (flow rate). In addition, further complications arise as it becomes important to relate the thermal conductivity value to the deformation history of the material. Most of the published data are obtained on non-oriented samples. However, it should be noted that the molecular / fibre orientation might have a large influence on the thermal conductivity of polymeric materials (Figs. 9-12) i.e. thermal conductivity will increase in the longitudinal direction and will decrease in the transverse direction (3). Polymer molecular weights are also likely to make differences to thermal conductivity for the same type of polymer. Thermal conductivity has been reported to increase with increased molecular weight of the polymer (up to \( M_w = 100,000 \)) (3). The type of filler, its concentration, aspect ratio, continuous or non-continuous nature and orientation of fibres, all have considerable influence on the thermal conductivity value measured (22-29). A difference of a factor of ~10 in thermal conductivity between the draw direction and perpendicular to the draw direction has been reported in ref. 7. Theoretical work to estimate thermal conductivity values of polymers by mathematical modelling has also been reported in the literature (30-31).

The requirements identified for measuring the thermal conductivity of polymer melts are thus:

- need to measure highly viscous materials up to 280°C
- measurement times preferably to be of the order of minutes to avoid degradation (hence, transient methods to be first considered)
- preferably to be a direct measurement method
- no sharp, high temperature rises that may cause degradation
- ability to measure both temperature and pressure dependencies and if possible, ability to measure flowing melts (shear rate) and orientation dependency
- error to be better than ± 10%
- method(s) to be robust, rapid, cost effective and be easy to operate.

This survey has identified 16 measurement methods which are placed in 3 main categories (32-51)

<table>
<thead>
<tr>
<th>Category</th>
<th>Techniques</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>Transient methods</td>
<td>8</td>
<td>direct or indirect method, fast (1-10 minutes), measurement in non-equilibrium state.</td>
</tr>
<tr>
<td>Steady-state methods</td>
<td>4</td>
<td>accurate but slow (up to 36h) for equilibrium state, direct method, gives absolute value but degradation likely.</td>
</tr>
<tr>
<td>Non steady-state methods (periodic)</td>
<td>4</td>
<td>direct or indirect method, non-equilibrium techniques.</td>
</tr>
</tbody>
</table>

Steady state methods such as the parallel hot-plate / guarded hot plate (ASTM C518 and C177), concentric cylinder, axial heat flow and radial heat flow methods, require long periods, of the order of hours, to reach equilibrium temperature and are thus unsuited to polymers because of degradation problems.
Table 1 summarises the published thermal conductivity measurement options by transient methods both by direct and indirect routes (7). Of these transient techniques, the Line Source Probe and the Transient Hot Wire methods are recommended for polymeric materials.

In the Line Source Probe technique a heat source and a thermocouple are incorporated into a fine needle shaped probe which is inserted into the sample (Fig. 13). From measurements of the voltage and the current supplied to the heater, the electrical power and hence the heat energy being supplied to the probe can be determined. The temperature is measured as a function of time. The thermal conductivity is determined directly from the temperature measured at two different times (t₁ and t₂) from the equation:

\[
\lambda = \frac{Q \ln \left( \frac{t_2}{t_1} \right)}{4\pi (T_2 - T_1)}
\]

where, \( Q \) = a short pulse of known energy, \( T_1 \) and \( T_2 \) = initial and final temperatures.

The Line Source Probe technique is rapid, measures thermal conductivity directly, can be used under a range of conditions and has the added advantage of the probe being robust in design, easily calibrated and cleaned. Its principal disadvantage is that the accuracy is relatively poor compared to the Transient Hot Wire technique. A standard procedure (ASTM D5930-97) exists to assist users (but no ISO standard yet).

The Transient Hot Wire technique works on a similar basis except that the heat source and thermocouple are provided for by a single fine platinum wire, which is suspended in the sample (Fig. 14). The temperature of the wire may be inferred from its resistance which varies characteristically with temperature. The Transient Hot Wire technique is also rapid, accurate, measures thermal conductivity directly and under various conditions of pressure, temperature and shear (flow) rate. The main problem with this method is that the fine platinum wire is fragile, with the consequence that the preparation of the sample and cleaning the polymer off from the wire may present practical difficulties. In addition, the method is dependent upon a small heat-emitting area and therefore, small bubbles, imperfections or non-wetted sections on the wire may have a significant effect on the results. In order for this technique to be used as a standard, appropriate methods should be developed for preparing the sample and removing polymeric residues from the wire without damaging it. Thicker wires may be used, but to the detriment of the accuracy of the technique.

3 SPECIFIC HEAT (\( C_p \))

The specific heat capacity (\( C_p \)) is the heat required to raise unit mass of material by 1°C at constant pressure and is usually expressed in J/g°C. It is regarded to be an important macroscopic material property (52-54) which enables other thermodynamic functions to be derived (e.g. in the calculation of thermal diffusivity, shear heating etc). Like thermal conductivity, specific heat also exhibits (Figs. 15-17) variations from room temperature to processing temperature (50-70% variation in amorphous polymers is common). In particular, during melting, the specific heat can increase very significantly (5). By contrast, the pressure reduces the specific heat values in polymers by as much as 15% in the range 1-35MPa (Figs. 16, 17).

A number of published measurement techniques for measuring specific heat are presented in Table 2 with measurement uncertainties quoted where available (55-75). Most of the reported work were on
thermoplastic materials although some included a limited amount of work on thermoset materials primarily for the purpose of studying the cure kinetics/the heat of reaction. The table includes the traditional adiabatic calorimetry method and its various modifications (76) as well as the popular and accurate DSC (Differential Scanning Calorimetry) method and its modified version i.e. Temperature Modulated Differential Scanning Calorimetry (TMDSC) (77-84). The thermal diffusivity and the heat capacity can be successfully measured by a laser flash method (ASTM C2141), although this may not be a particularly suitable method for all polymeric materials due to degradation problems (85). Other measurement methods which are available in the literature include: Micro-Calorimetric method (86), Heat Pulse technique (61) and the Drop method (81).

The DSC and its variation are by far the most widely used techniques for measuring specific heat in polymer melts because of the high accuracy (<1% error), reliability and the ease of operation. A small sample weight (<100mg) is required which can be tested between -100°C to in excess of 700°C with high reproducibility and at different cooling/heating rates. Many makes of commercial equipment are now available. A standard procedure (ASTM E1269) exists to assist users.

The measurement of specific heat of polymers under pressure is a complex area and only a few published results are available (87-90). Conventional calorimetric methods are difficult to use because of the large heat losses in a high pressure apparatus. Modern DSC equipment can however be modified with a simple attachment which would then allow pressure dependant measurement up to 10 MPa. A technique called the “Heat Wave Method” has been reported to determine specific heat and thermal diffusivity in polymers such as PTFE, PMMA, PS and PP at pressures of 0-30 kbar (16,17). Mathematical models to predict specific heat and thermal conductivity under pressure and temperature have also been reported (17, 91).

Examples of Moldflow simulation work are shown in Figs 18a-18l which demonstrate the importance of specific heat data in temperature and cooling time distributions in an injection moulded component (a hub cap) at pressures of 30MPa and 60MPa. The effects of varying input specific heat values (by introducing an error of ± 20% in the measurement) from the standard input value show that a difference of ~50% in cooling time can occur (Fig. 18f). The same trend is obtained when the pressure is doubled to 60MPa. Since a ± 20% difference in the measured specific heat value (e.g. due to pressure differences) cannot be ruled out, this exercise demonstrates the need for generating accurate industrially relevant specific heat data (including pressure dependent data) for use in computer simulation software in the future.

Specific heat of filled polymers (amorphous and semi-crystalline) can be determined in the same way as for unfilled polymers. A few papers have been published on the effect of filler on specific heat. The results from filled PS and PMMA are discussed in ref. (92). The effects of fibre content on the specific heat in filled epoxy have been reported in ref. (93).

The ATHAS (Advance Thermal Analysis System) database (11, 94-97) is a good source for acquiring specific heat capacity data (website: http://www.funnelweb.utcc.utk.edu/~athas). The CAMPUS (website: http://www.campusplastics.com) and Moldflow databases (website: http://www.moldflow.com/) (12) are also two valuable sources containing information on plastics properties. Other databases are also available in the open literature (51, 98-102).
4 LATENT HEAT

The latent heat is defined as the total amount of heat required to melt a unit mass of material and is normally expressed in J/g. The latent heat and the specific heat are therefore closely related:

\[ \int C_p \, dt = \text{latent heat} \]

where, \( t_1 \) = temperature at the start of melting
and \( t_2 \) = temperature at the end of melting

A special case of heat transport is when a material undergoes a first order phase transition with emission or absorption of heat such as crystallisation. An essential feature of crystallisation is the existence of a moving interface at which the latent heat of fusion is liberated or absorbed (Figs. 19, 20). In some materials this interphase at which the transformation occurs follows the isotherm of the melting point of the substance (103-111). This results in the liquid phase being substantially super cooled or the solidified phase being super heated. This is the case for polymers. Piorkowaska and co-workers have shown (112, 113) that it is possible to determine the influence of the latent heat of fusion evolving during polymer crystallisation on the temperature distribution near the crystallisation front. First-order phase transitions are accompanied by the release or the absorption of latent heat of fusion (Fig.19). Hence, the initial temperature distribution inside the material undergoing melting or solidification will change. The process of transformation is then controlled by heat dissipation; hence the position of the interphase boundary is deduced to be proportional to the square root of time. Several treatments to this problem are available (112, 113). Second order transitions (such as the glass transition) do not evolve or absorb heat and thus have no latent heat. Therefore, the effects of this thermal parameter are only relevant to semi-crystalline polymers.

A limited amount of information on this parameter is available in the literature (114-118). The DSC and the TMDSC are the two principal techniques that are capable of determining this property experimentally (104, 118). Some theoretical work has also been reported to derive this value in various polymers (105, 106, 114). The effects of pressure and filler type and content on latent heat have not been reported specifically though much work has been done on the effect of additives (e.g. nucleating agents) and the effect of pressure on crystallisation kinetics. Previous work at NPL (118) indicated a potential way of measuring latent heat of crystallisation in polymer melts at high pressure using PVT equipment (Fig.20).

A standard (ASTM D3417 - 97, “Enthalpies of fusion and crystallisation of polymers by DSC”) exists to assist users.

5 CONCLUSIONS

5.1 COOLING TIME

Cooling time predictions appear to be very sensitive to thermal conductivity and specific heat input values. Measurement errors of ± 20% from current methods could be considered typical, yet a 20% variation in input data has been shown to lead to a 120% change in cooling time. This has major implications for the accurate prediction of cycle times.
5.2 THERMAL CONDUCTIVITY

Two principal methods of measuring this parameter are: the Transient Hot Wire method and the Line Source Probe method. Both are capable of making temperature and pressure dependant measurements. The Transient Hot Wire method is stated to be more accurate, but the Line Source Probe method is more practical for polymers.

5.3 SPECIFIC HEAT

Undoubtedly, the DSC and its extension (TMDSC) are the most popular choices for the measurement of specific heat in polymers. The DSC technique is fast, accurate and generally regarded to be reliable. The technique can be modified at a relatively low cost to measure pressure dependant properties up to 10 MPa.

5.4 LATENT HEAT

The only method reported for the measurement of latent heat is the DSC and its extension (TMDSC). This survey revealed no previous work on pressure dependency or the effects of filler type and content on latent heat in polymers.

It is recommended that the effects of industrially relevant temperature, pressure and shear (flow) rate on all 3 thermal parameters (reviewed in this report) be investigated in filled and unfilled polymers. As a first step, it is important therefore to consider whether the accuracy can be improved if careful choices of measurement technique and procedure are made. The improved accuracy on thermal property measurements could help to develop more reliable computer simulated prediction packages, which in turn should benefit the polymer processing industry to achieve reduced cycle times and low scrap rates in production. It should be noted that major software packages, such as Moldflow, require a similar investigation on “heat transfer coefficients” and “no-flow temperature” parameters, which are further critical input parameters to their heat transfer software packages. Future investigation of these two parameters are therefore also recommended.

6 ACKNOWLEDGEMENTS

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Table 1: Summary of transient thermal conductivity and diffusivity methods

<table>
<thead>
<tr>
<th>Method</th>
<th>Estimated error</th>
<th>Direct measure of conductivity</th>
<th>Comments (also see notes)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Concentric cylinder</td>
<td>5%</td>
<td>No</td>
<td>Measurement during flow</td>
</tr>
<tr>
<td>Transient hot wire</td>
<td>3%</td>
<td>Yes</td>
<td>Accurate method, fragile wire</td>
</tr>
<tr>
<td>Line source probe</td>
<td>10% [2]</td>
<td>Yes</td>
<td>Rapid, robust method</td>
</tr>
<tr>
<td>Laser flash / flash radiometry</td>
<td>10%</td>
<td>No</td>
<td>Possible degradation at polymer surface</td>
</tr>
<tr>
<td>Forced Rayleigh scatter</td>
<td>10%</td>
<td>No</td>
<td>Used to examine anisotropy of solids and flowing melts</td>
</tr>
<tr>
<td>Differential scanning calorimetry</td>
<td>20%</td>
<td>Yes</td>
<td>Poor accuracy</td>
</tr>
<tr>
<td>Radial temperature wave</td>
<td>10%</td>
<td>Yes</td>
<td>Reference to measurement of solids only</td>
</tr>
<tr>
<td>Plane temperature wave</td>
<td>12%</td>
<td>Yes</td>
<td></td>
</tr>
</tbody>
</table>

Notes

[1] Estimates of errors obtained from the literature except see [2].
[3] "No" indicates that the method measures diffusivity \( \alpha \) from which thermal conductivity \( \lambda \) can be determined using \( \lambda = \rho C_p \alpha \), where \( \rho \) is the density and \( C_p \) the specific heat capacity. However this introduces an additional source of error, that may be as much as 8-10% due to errors in \( \rho \) and \( C_p \).
<table>
<thead>
<tr>
<th>Method</th>
<th>Estimated Error (1)</th>
<th>Comments</th>
</tr>
</thead>
<tbody>
<tr>
<td>Differential Scanning Calorimetry (DSC) and Temperature Modulated</td>
<td>1% or less</td>
<td>fast, temperature to 700°C, sample weight &lt;100 mg, pressure studies</td>
</tr>
<tr>
<td>Differential Scanning Calorimetry (TMDSC)</td>
<td></td>
<td>possible.</td>
</tr>
<tr>
<td>Differential Thermal Analysis (DTA)</td>
<td>5% or less</td>
<td>equivalent to DSC, ref. material</td>
</tr>
<tr>
<td>Adibatic Calorimetry</td>
<td>1% or less</td>
<td>slow, up to 330°C</td>
</tr>
<tr>
<td>Continuous heating fast calorimetry</td>
<td>5%</td>
<td></td>
</tr>
<tr>
<td>Drop Calorimetry</td>
<td></td>
<td>gives average value</td>
</tr>
<tr>
<td>Isothermal Calorimetry</td>
<td>3%</td>
<td>works under vacuum for high</td>
</tr>
<tr>
<td>Plane temperature wave technique</td>
<td>3.5%</td>
<td>temperature testing</td>
</tr>
<tr>
<td>Pulsed Photothermal Radiometry (Flash radiometry)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Heat Pulse Technique</td>
<td>20%</td>
<td></td>
</tr>
<tr>
<td>Cryostat Thermometry</td>
<td>10%</td>
<td></td>
</tr>
</tbody>
</table>

1. claimed by authors reporting their results
Temperature Profile During Air-Cooling (only half-thickness shown). Conditions: Air Temperature = 18.3°C, Air Velocity = 0.61 m/sec., emissivity = 0.9. Temperature profiles are shown in 10-second increments.

Fig. 1  (ref. 1)

Skin Thickness Results for Various Cooling Times in a 1.27 cm (½ in.) rectangular bar

Fig. 2  (ref. 1)
Smoothed thermal conductivity and heat capacity data vs. temperature, obtained at six different pressures. The pressure for each isobar is given in bars (1 bar = 100 kPa).

Fig. 3 (ref. 7)

Summary of results on the thermal conductivity vs. pressure

Figs. 4 a & b (ref. 16)
Thermal conductivities of polypropylene.

Fig. 5  (ref. 14)

Thermal conductivity plotted against temperature for PIB-85000 at pressures of 0.1 MPa, 0.19, and 0.29 GPa.

(ref. 18)

Thermal conductivity plotted against pressure for PIB-28000 at temperatures of 297 and 450 K.

(ref. 18)
Figure 8a  Temperature distribution when thermal conductivity is decreased by 20% at 30MPa

Figure 8b  Temperature distribution for standard thermal conductivity at 30MPa

Figure 8c  Temperature distribution when thermal conductivity is increased by 20% at 30MPa
Figure 8d  Cooling time distribution when thermal conductivity is decreased by 20% at 30MPa

Figure 8e  Cooling time distribution for standard thermal conductivity at 20MPa

Figure 8f  Cooling time distribution when thermal conductivity is increased by 20% at 30MPa
Figure 8g  Temperature distribution when thermal conductivity is decreased by 20% at 60MPa

Figure 8h  Temperature distribution for standard thermal conductivity at 60MPa

Figure 8i  Temperature distribution when thermal conductivity is increased by 20% at 60MPa
Figure 8j  Cooling time distribution when thermal conductivity is decreased by 20% at 60MPa

Figure 8k  Cooling time distribution for standard thermal conductivity at 60MPa

Figure 8l  Cooling time distribution when thermal conductivity is increased by 20% at 60MPa
The effect of pressure on the thermal conductivities of polypropylene and its composites at constant temperature of 230°C.

Fig. 9  (ref. 14)

Thermal conductivities of the composite with 10.88 wt % glass fiber content.

Fig. 10  (ref. 14)
Thermal conductivity of the composites.

**Fig. 11** (ref. 28)

Thermal conductivity versus temperature for composites of glass beads. From top to bottom: composite [100 : 50] (●), composite [100 : 30] (○), and resin per se (○). Lines are theoretical values from the Maxwell equation, except observed value for resin per se.

**Fig. 12** (ref. 51)
Fig. 13

Line source probe

Fig. 14

Transient hot wire
Heat capacity per unit volume plotted against temperature for PPG-85000 at pressures of 0.1 MPa and 0.29 GPa.

Fig. 15  (ref. 18)

Summary of results on the specific heat vs. pressure

Fig. 16  (ref. 16)

Specific heat scans as a function of temperature for PS pressurized at 0 (--), 100 (---), 300 (---), and 400 (---) MPa

Fig. 17  (ref. 89)
Figure 18a  Temperature distribution when specific heat is decreased by 20% at 30MPa

Figure 18b  Temperature distribution for standard specific heat at 30MPa

Figure 18c  Temperature distribution when specific heat is increased by 20% at 30MPa
Figure 18d  Cooling time distribution when specific heat is decreased by 20% at 30MPa

Figure 18e  Cooling time distribution for standard specific heat at 30MPa

Figure 18f  Cooling time distribution when specific heat is increased by 20% at 30MPa
Figure 18g  Temperature distribution when specific heat is decreased by 20% at 60MPa

Figure 18h  Temperature distribution for standard specific heat at 60MPa

Figure 18i  Temperature distribution when specific heat is increased by 20% at 60MPa
Figure 18j  Cooling time distribution when specific heat is decreased by 20% at 60MPa

Figure 18k  Cooling time distribution for standard specific heat at 60MPa

Figure 18l  Cooling time distribution when specific heat is increased by 20% at 60MPa
Effect of Pressure on Crystallisation Temperature for High Density Polyethylene at 200 and 1600 bar Cooled at 5 °C/minute

Temperature Deviation Due to Latent Heat of Crystallisation

Fig. 20 (ref. 118)
Results Of Questionnaire on Heat Transfer in Polymer Processing

The results reported below are the replies given by the delegates who completed the questionnaire on July 7th 1999 at the new programme launch meeting. Twenty-two questionnaires were filled in but not all the questions were answered by all the delegates.

1. 100% believed that heat transfer is an important aspect of polymer processing (21 responded).

2. The following reasons for obtaining good data on heat transfer were regarded as important:
   a) ensuring that degradation does not occur    Yes: 67%  No: 4%  Maybe: 29% (21 responded).
   b) ensuring uniform cooling to minimise distortion    Yes: 77%  No: 4%  Maybe: 19% (22 responded)
   c) maximising heat transfer rates to maximise production rates    Yes: 100% (20 responded)
   d) Other reasons added were to improve accuracy of modelling software and to ensure materials have the same thermal history.

3. The temperature range used for processing covered 80°C to 300°C, with 94% falling in the range 130°C to 280°C and 60% falling in the range 130°C to 250°C (15 responded).

4. The pressure range used for processing covered atmospheric pressure to 210 MPa, with 86% in the range 3 to 200 MPa (6 responded).

5. 52% of respondents processed or supplied semi-crystalline polymers and 48% amorphous (21 responded).

6. The main materials stated as being important were:
   - Polypropylene 15
   - Polyethylene 10
   - PVC 9
   - Nylon 6
   - Polystyrene 6
   - ABS 4.
   Other materials included filled PP (4), PC (3), PET (3), PPE (2), PBT (2), filled nylon (1), PVDF (1), PEEK (1) and PPO (1). It was also stated that the materials selection should include semi-crystalline, amorphous, filled and unfilled materials.

7. 47% of respondents make use of fillers, and 53% do not (17 responded).
   a) examples of fillers were calcium carbonate (5) glass fibre (2) and glass flake (2).
   b) 75% of respondents thought fillers could help solve heat transfer problems (16 responded)
   c) 58% thought that the effect of fillers on heat transfer was not well understood, 37% were uncertain and 5% thought the effect was well understood (19 responded)
8. For 50% of respondents orientation was an important aspect in their products, for 40% orientation was not important and for 10% it might be important (20 responded).
   a) 64% thought fibre orientation could effect heat transfer and 36% thought it might (14 responded)
   b) 50% thought molecular orientation could effect heat transfer 4% thought it would not and 44% thought it might (16 responded)
   c) Nobody thought the effects of orientation on heat transfer were well understood, 69% thought it was not well understood and 31% were uncertain (16 responded).

9. 44% used process simulation software. The following responses were given to the question relating to their source of data:
   a) materials suppliers data sheets Yes:100% ( 13 responded)
   b) default values in the software Yes: 56% No: 44% ( 9 responded)
   c) by measurement Yes: 80% No: 20% ( 10 responded)
   d) from the open literature Yes: 67% No: 33% ( 9 responded)
   e) from Campus Yes: 57% No: 43% ( 7 responded)
Two respondents thought international standards were used in the measurement of the data (7 responded).

10. 100% of respondents thought thermal conductivity and specific heat were significant heat transfer parameters (19 responded). One respondent did not think latent heat of crystallisation was significant, the rest (95 %) thought latent heat was significant. (18 responded). Other parameters that were thought to be important were diffusivity (2), heat of reaction, viscous heating, flow rate rheology and cooling capacity of the cooling medium.

11. Ten respondents had DSC equipment. Other equipment relevant to heat transfer parameters was thermo-gravimetric analysis, thermo-mechanical analysis and thermal diffusivity measurement equipment.

In the light of the feedback received the main materials to be studied in the project will be:

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<th>2</th>
<th>3</th>
<th>4</th>
<th>5</th>
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</thead>
<tbody>
<tr>
<td>Thermal Conductivity</td>
<td>PP</td>
<td>filled PP</td>
<td>HDPE</td>
<td>PVC</td>
<td>filled PVC</td>
</tr>
<tr>
<td>Latent heat</td>
<td>PP</td>
<td>filled PP</td>
<td>HDPE</td>
<td>nylon 6</td>
<td></td>
</tr>
<tr>
<td>Specific heat</td>
<td>PP</td>
<td>filled PP</td>
<td>PS</td>
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This plan fits the consensus view that semi-crystalline polymers, amorphous polymers, filled and unfilled should be included. The PP filler will be calcium carbonate. The PP grades will properly be supplied by Montell. The HPPE will probably be from Durapipe, the PVC (filled and unfilled) from Volex, the nylon 6 from Nylacast the PS from Linpac. In addition to these it is expected that ABS will be measured as part of a trial with Nokia mobile phones. Other materials can be measured (up to three day’s work) at the request of paid up members of the Polymer Processing Measurement Club.