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National Physical Laboratory

Heat Transfer in Polymers

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29 March 2006

Heat Transfer in Polymers - Summary

- Introduction
- Industrial Demonstrations: Corus, Zotefoams
- Thermal Conductivity
- Heat Transfer Coefficient
- Standards for Thermal Properties Measurement
- Future activities
- Summary

Heat Transfer in Polymers

Heat transfer is:

- key to polymer processing
- still inadequately understood / measured
- key to increasing throughput - process times dominated by the cooling phase
- significant in affecting product properties, e.g. warpage, inadequate melting, thermal degradation

Aims of the work

- To help companies measure and model heat transfer in polymer processing

- To enable measurement of more accurate data and encourage the use of improved models for numerical simulation software

- This should lead to:
  - Right first time design
  - Reduce cycle times / higher productivity (faster processing)
  - Energy saving
  - Fewer failures in service
  - Reduce waste- e.g. reduce warpage and hot spots during processing

Resulting in reduced costs and improved quality

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INDUSTRIAL TRIALS

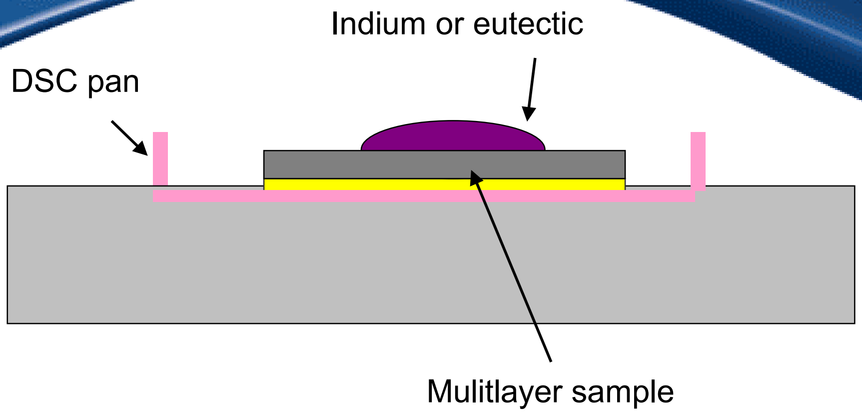
Corus & Zotefoams

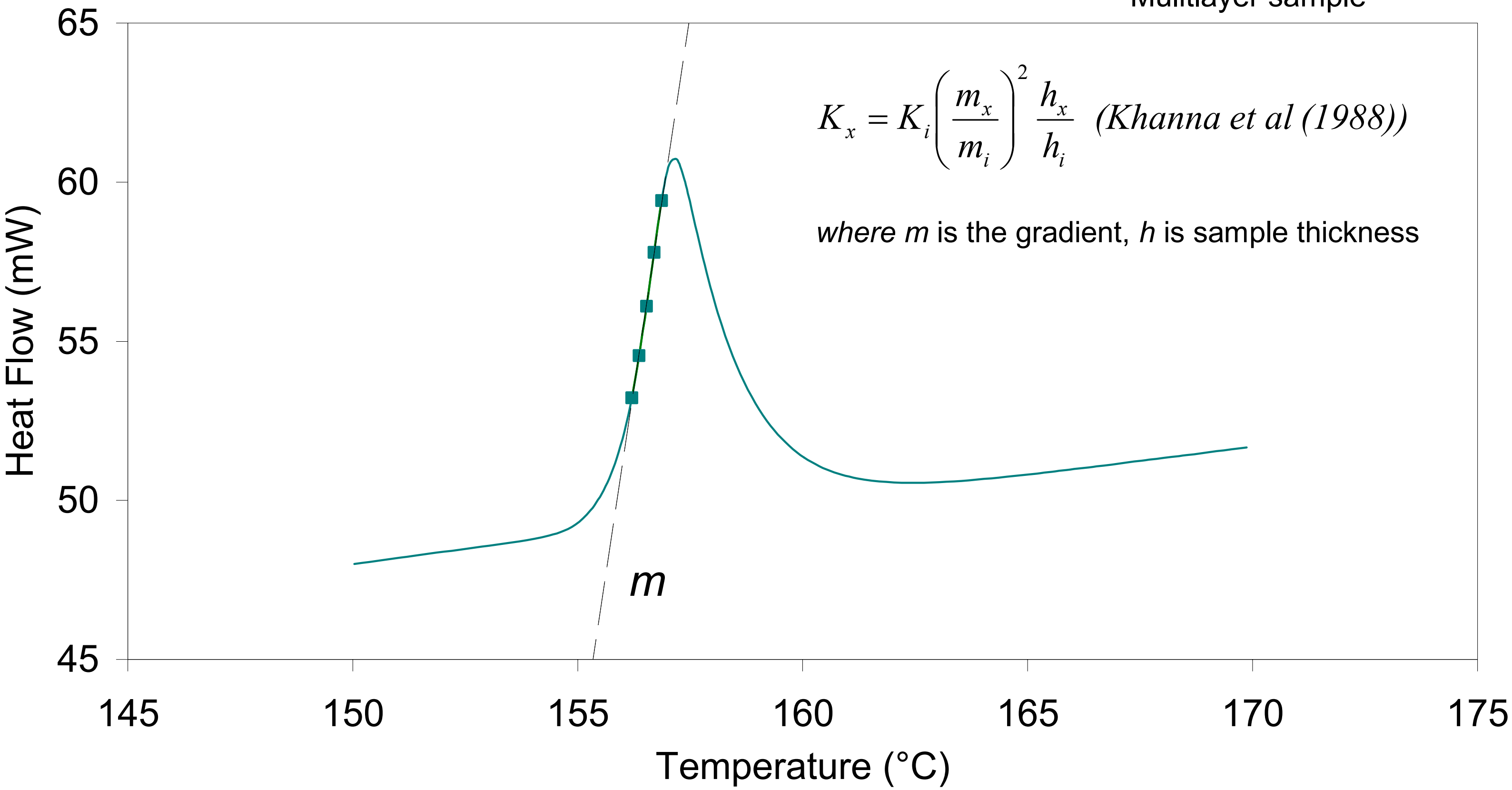
Industrial Demonstrations

Aim is to investigate DSC method and demonstrate practical benefits of heat transfer measurements and modelling

- Corus
  - Thermal conductivity of plastisol coated steel before and after solidification
- Zotefoams
  - Heat transfer during cooling of polyolefin foam

DSC method for thermal conductivity





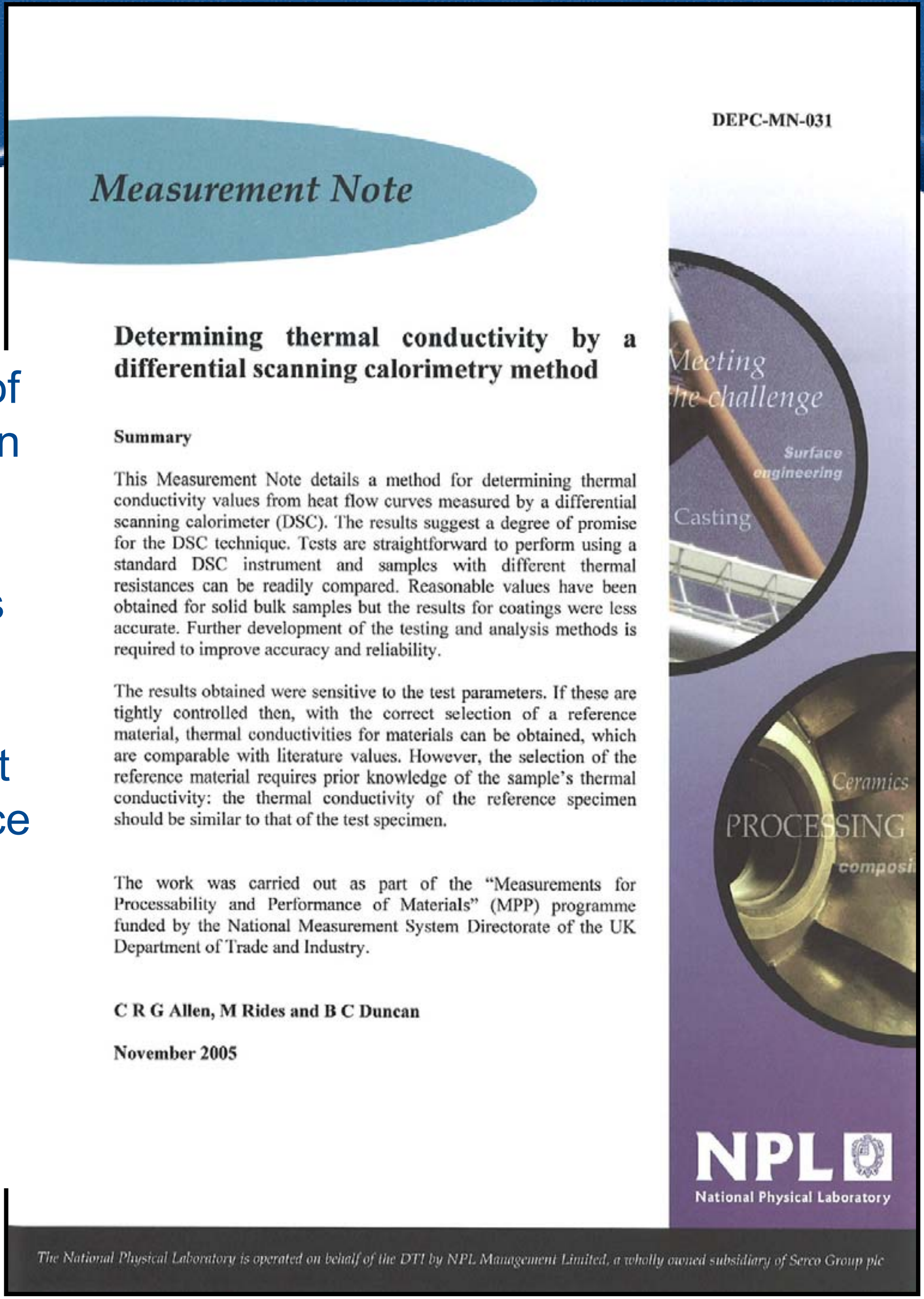
$$K_x = K_i \left(\frac{m_x}{m_i} \right)^2 \frac{h_x}{h_i} \quad \textit{(Khanna et al (1988))}$$

where m is the gradient, *h* is sample thickness

DSC method for thermal conductivity

- Essential to use reference specimen of similar thermal conductivity as specimen to be measured
- Repeatability 95% confidence levels up to approximately 25%
- Essential to carry out several repeat tests to improve on statistical significance of data
- Not appropriate for testing molten/liquid samples

(e.g. plastisols) – need constant and known sample thickness



DEPC-MN-031

Measurement Note

Determining thermal conductivity by a differential scanning calorimetry method

Summary

This Measurement Note details a method for determining thermal conductivity values from heat flow curves measured by a differential scanning calorimeter (DSC). The results suggest a degree of promise for the DSC technique. Tests are straightforward to perform using a standard DSC instrument and samples with different thermal resistances can be readily compared. Reasonable values have been obtained for solid bulk samples but the results for coatings were less accurate. Further development of the testing and analysis methods is required to improve accuracy and reliability.

The results obtained were sensitive to the test parameters. If these are tightly controlled then, with the correct selection of a reference material, thermal conductivities for materials can be obtained, which are comparable with literature values. However, the selection of the reference material requires prior knowledge of the sample's thermal conductivity: the thermal conductivity of the reference specimen should be similar to that of the test specimen.

The work was carried out as part of the "Measurements for Processability and Performance of Materials" (MPP) programme funded by the National Measurement System Directorate of the UK Department of Trade and Industry.

C R G Allen, M Rides and B C Duncan

November 2005

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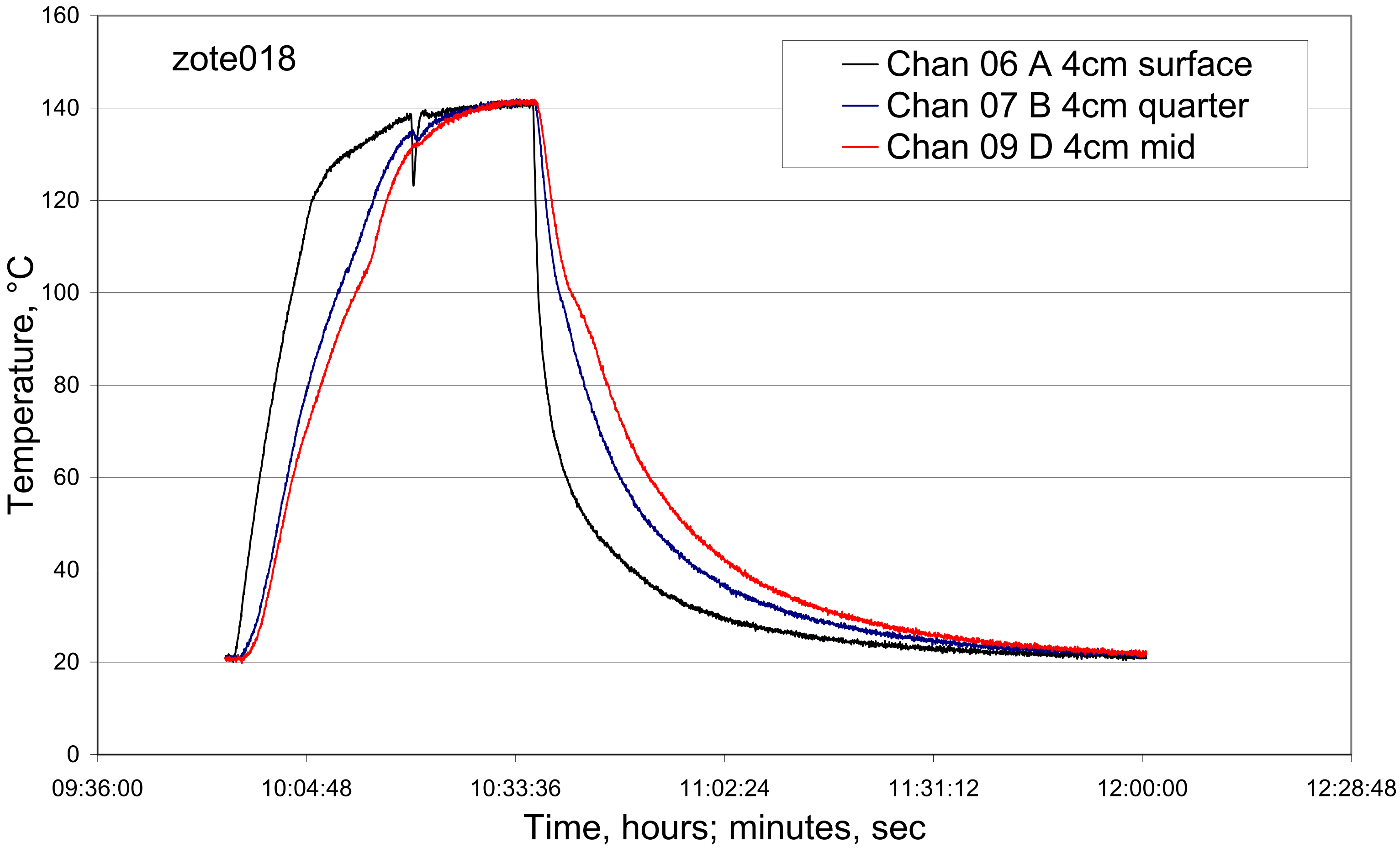
Thermal issues in foams

Problem: waviness in foams – thermal issue

Heating & cooling of foam block



Thermal measurements in foams

Summary:

- quantified uneven cooling of foam sheet
- resulting in demonstrated variation in shrinkage with position
- causing waviness of sheets
- modelling activity in support of experimental activity

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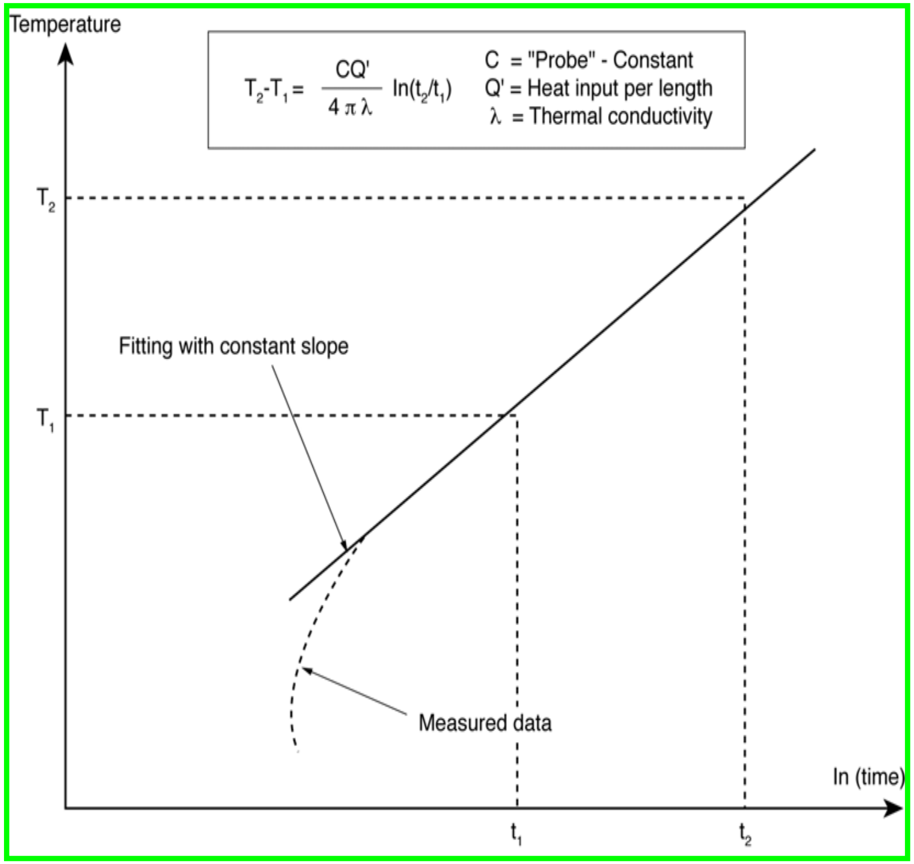
Thermal conductivity measurements

Angela Dawson

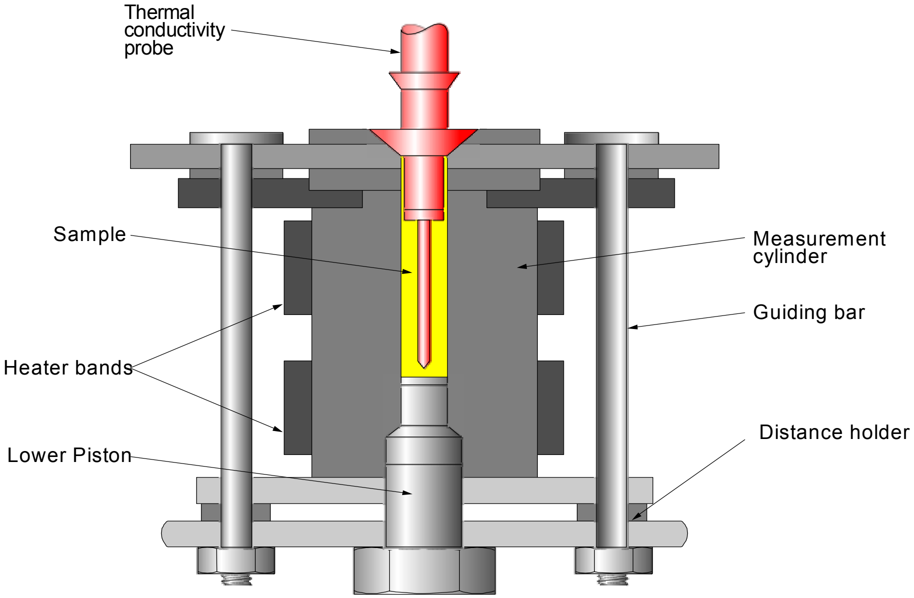
29 March 2006

Line source probe apparatus



$$T_2 - T_1 = \frac{CQ'}{4\pi\lambda}\ln(t_2/t_1)$$

C = "Probe" - Constant
Q' = Heat input per length
λ = Thermal conductivity



Measures thermal conductivity at industrially relevant processing pressures and temperatures

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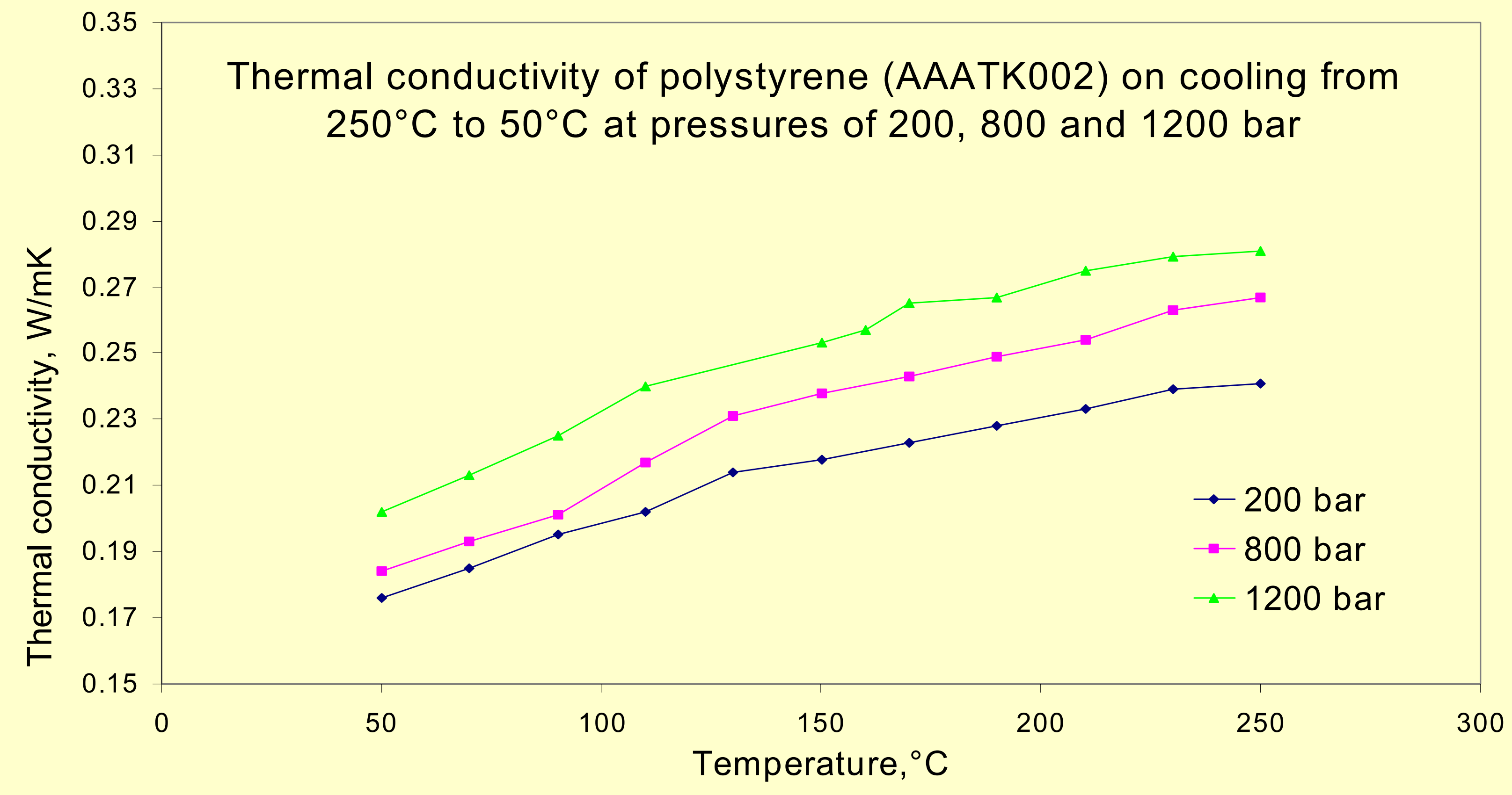
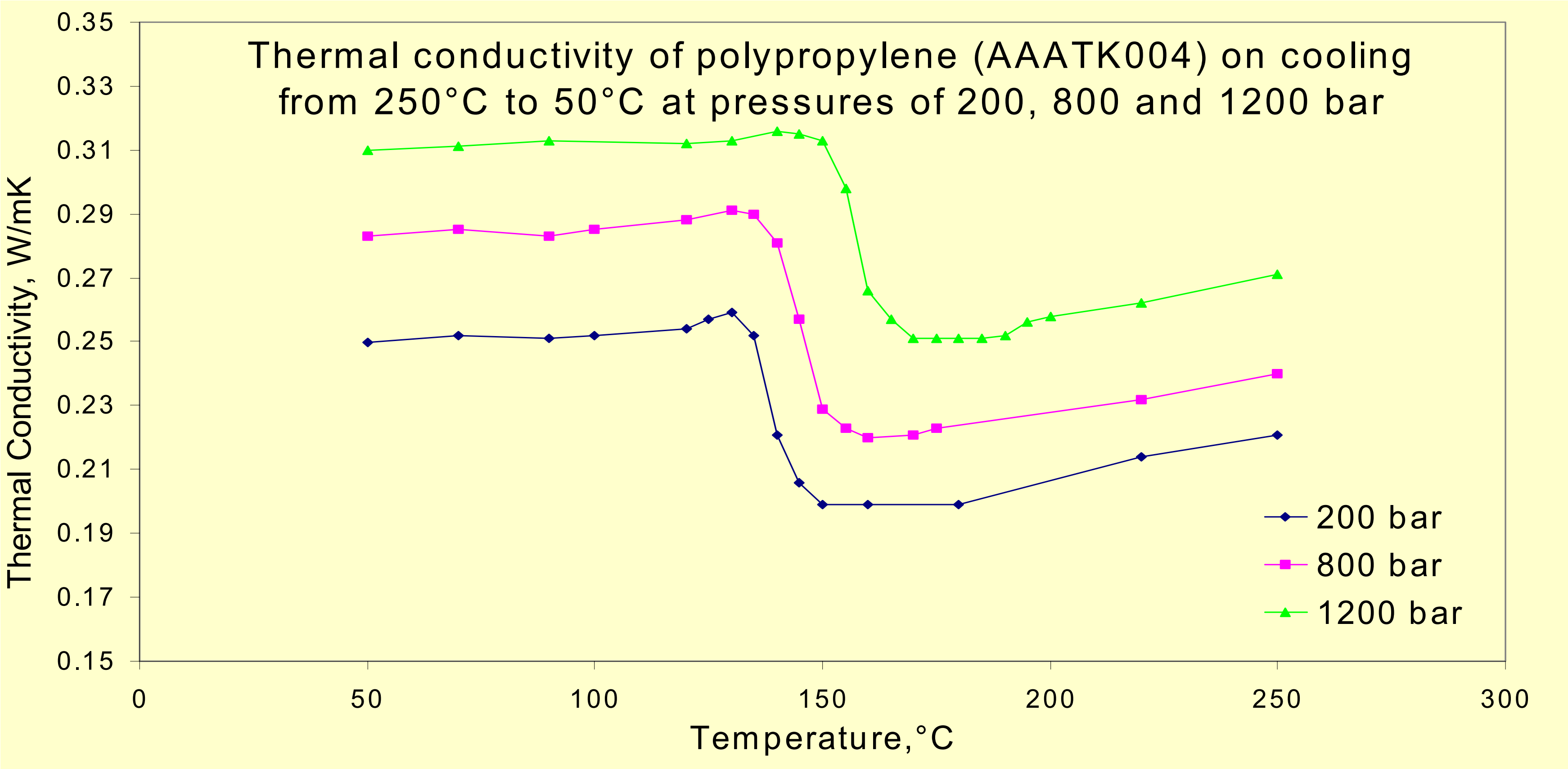
Thermal conductivity

Amorphous polystyrene (PS) under pressure



Thermal conductivity

Semi-crystalline polypropylene (PP) under pressure



Thermal conductivity: implications of results

- Increase in pressure gives increase in thermal conductivity and increase in crystallisation temperature for semi-crystalline polymers

- Thermal conductivity data strongly dependent on both pressure and temperature:
  - 50% over range 50°C to 250°C
  - 43% over range 200 bar to 1200 bar

  Implies single-point thermal conductivity value may be in error by up to 50%

- Important to use pressure and temperature dependent thermal conductivity data for accurate process modelling – will improve, for example, warpage and hot-spot prediction

- More accurate data based on industrial processing conditions - improvements in commercial modelling packages -– possible cost benefits

Paper accepted by ‘Polymer Testing’

The Effect of Pressure on the Thermal Conductivity of Polymer Melts

A. Dawson, M. Rides and J. Nottay

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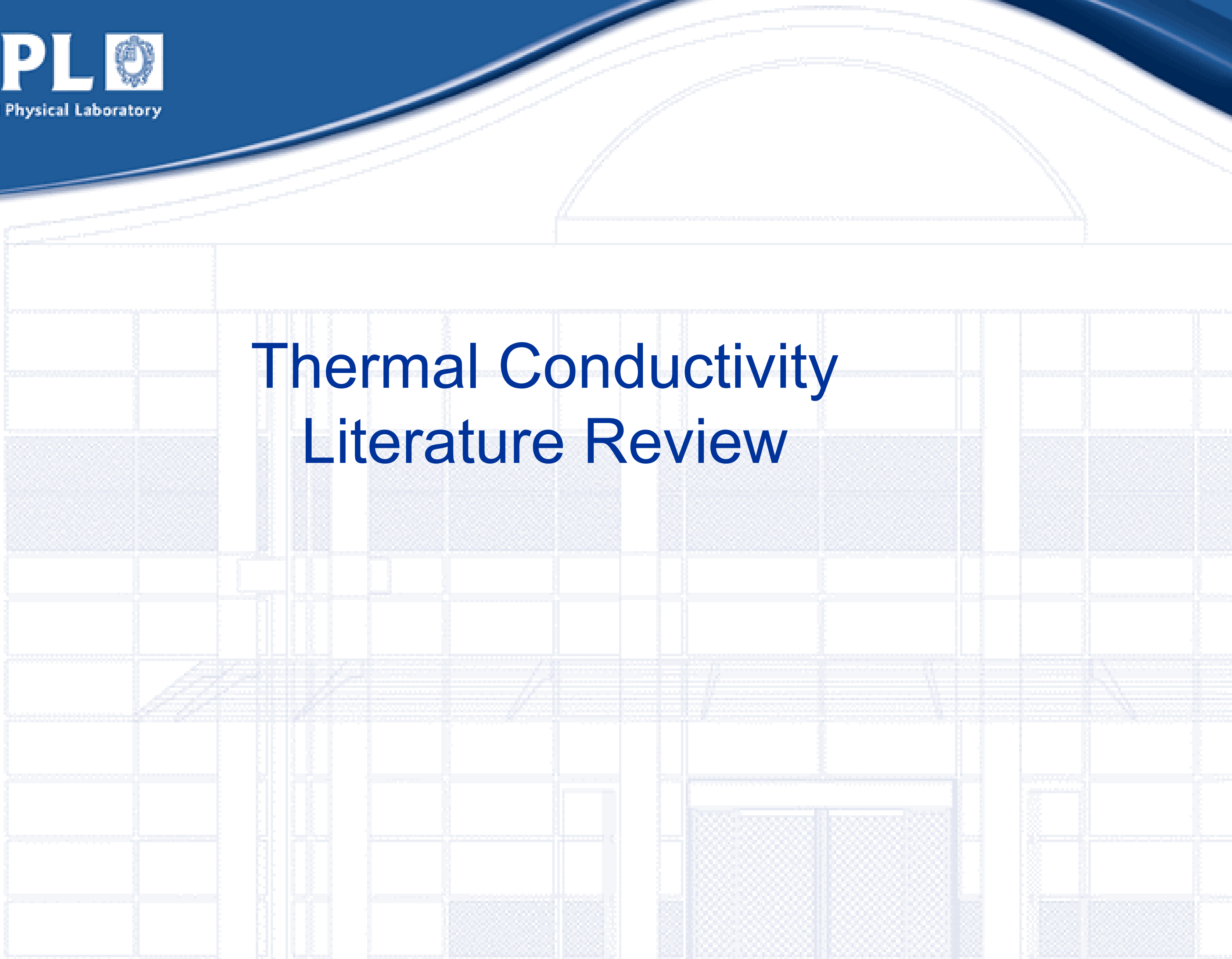
National Physical Laboratory,
Teddington, Middlesex, TW11 0LW, UK

http://www.npl.co.uk/materials/polyproc/iag



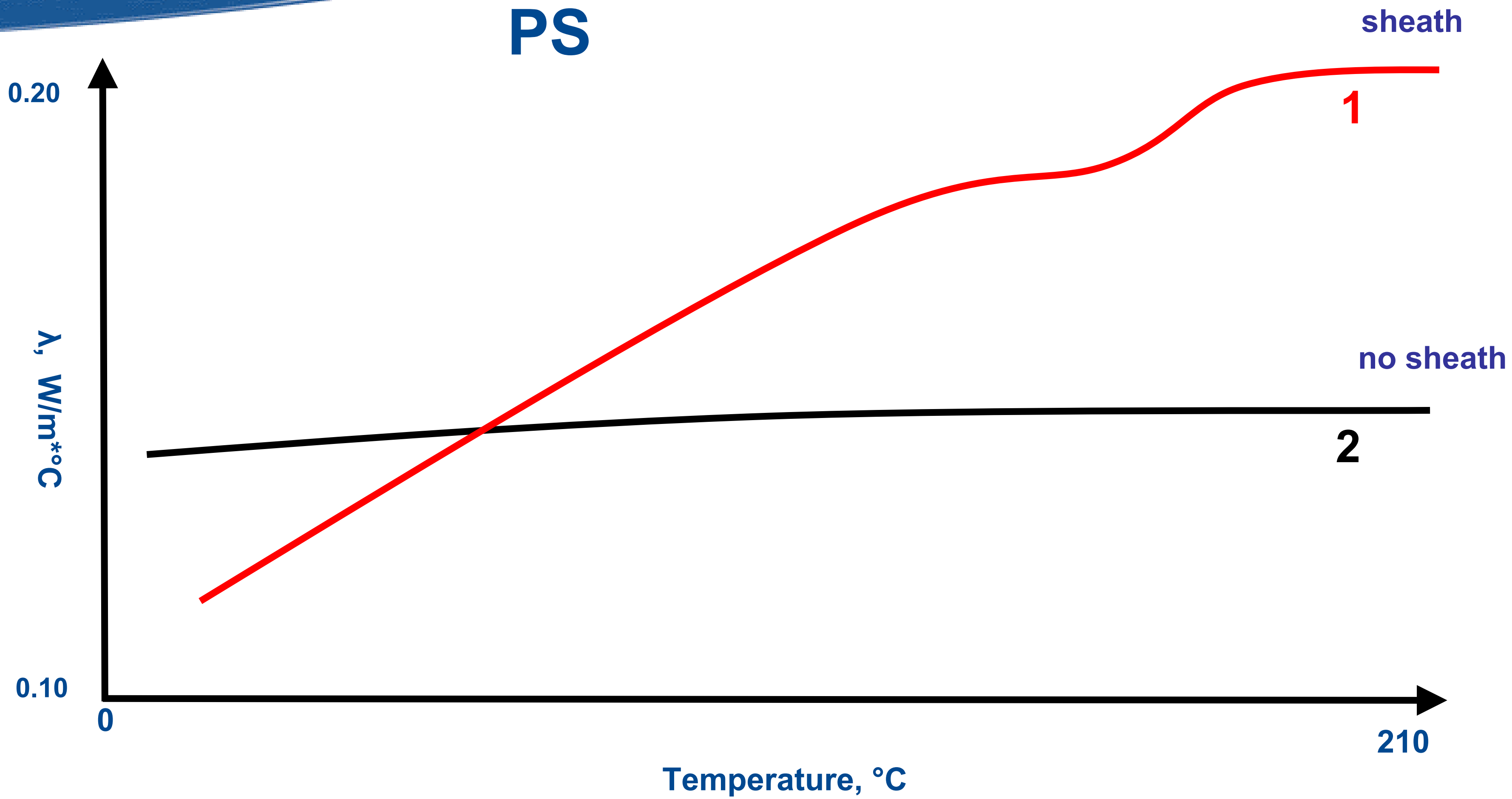
Thermal Conductivity Literature Review

Line Source Technique

H. LOBO and C. COHEN 1990[1]
W.UNDERWOOD and
R. McTAGGART 1960[2]

Heating / cooling ?

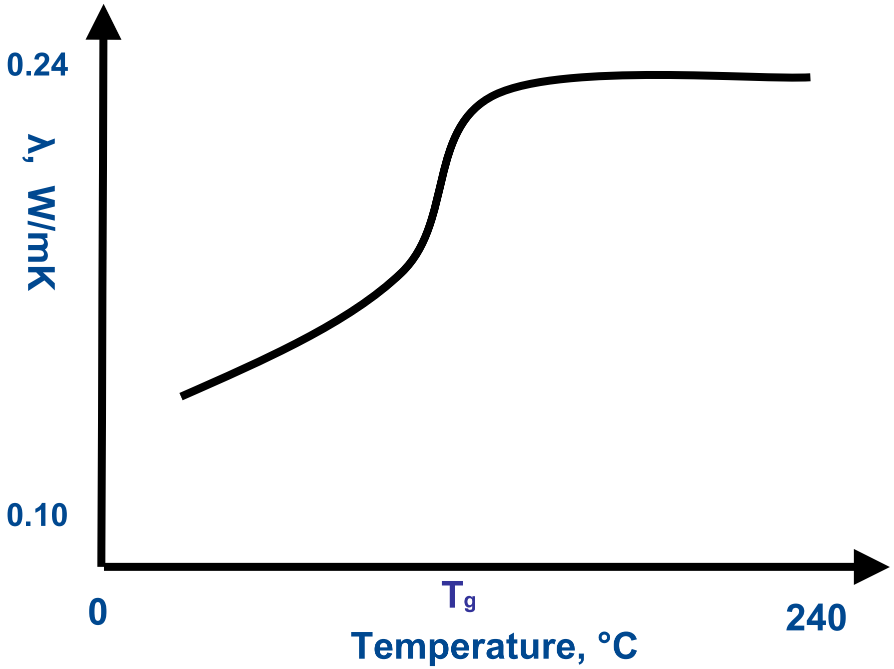
PS



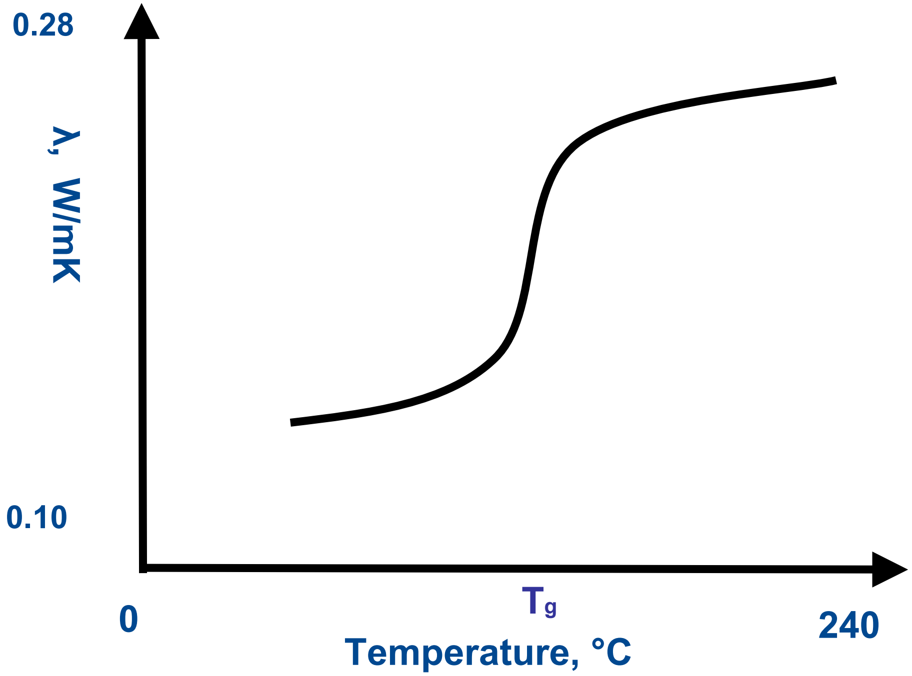
1- Poly. Eng and Sci. 30 (1990), p65-70
2- Chem. Eng. Prog. Sym. Series 56, 30 (1960) p261

Line Source Probe
H. LOBO and R. NEWMAN 1990

PMMA
Heating and cooling



PC
Cooling?

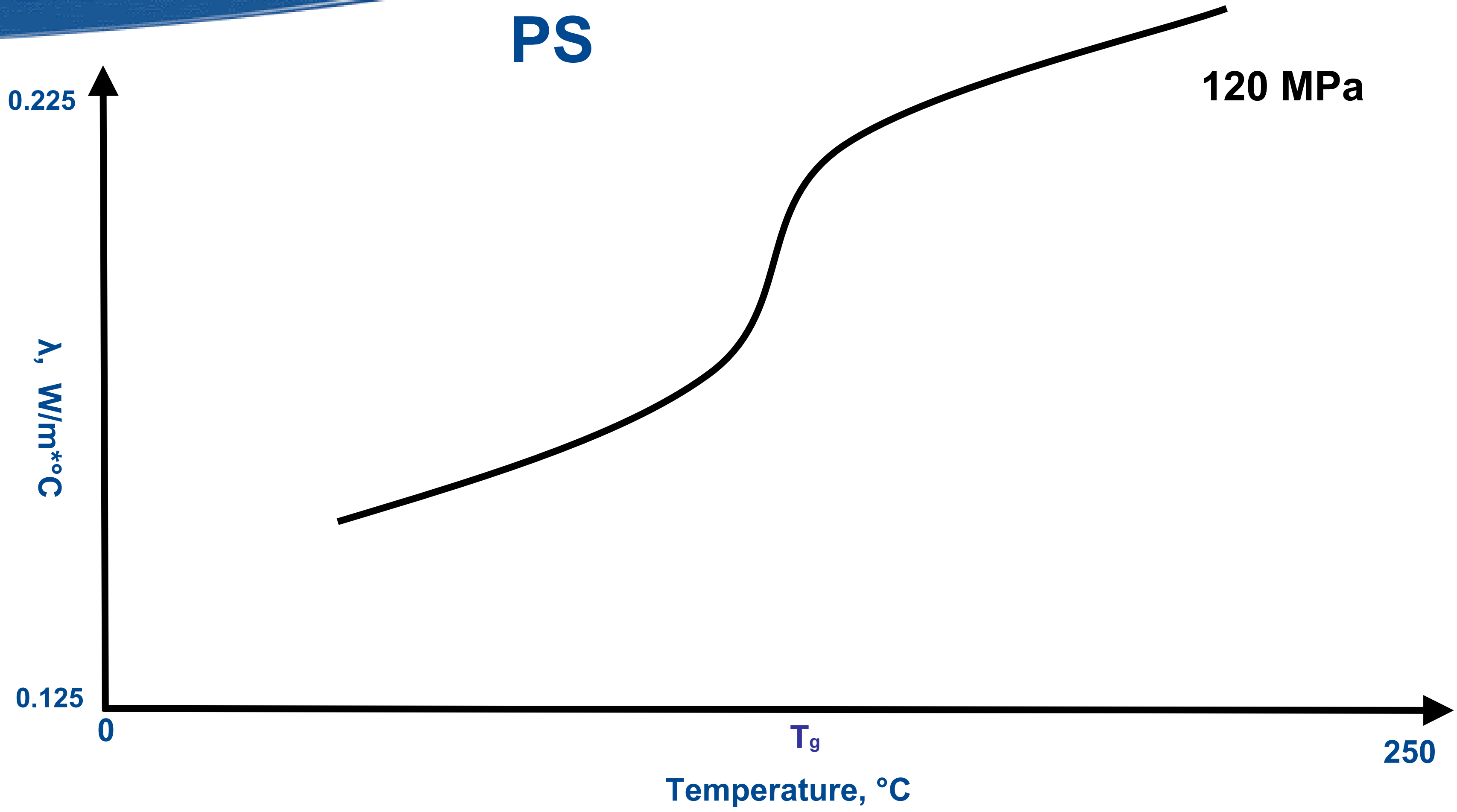


ANTEC'90 p862-865

Line Source Probe

F. OEHMKE and T. WIEGMANN 1990s

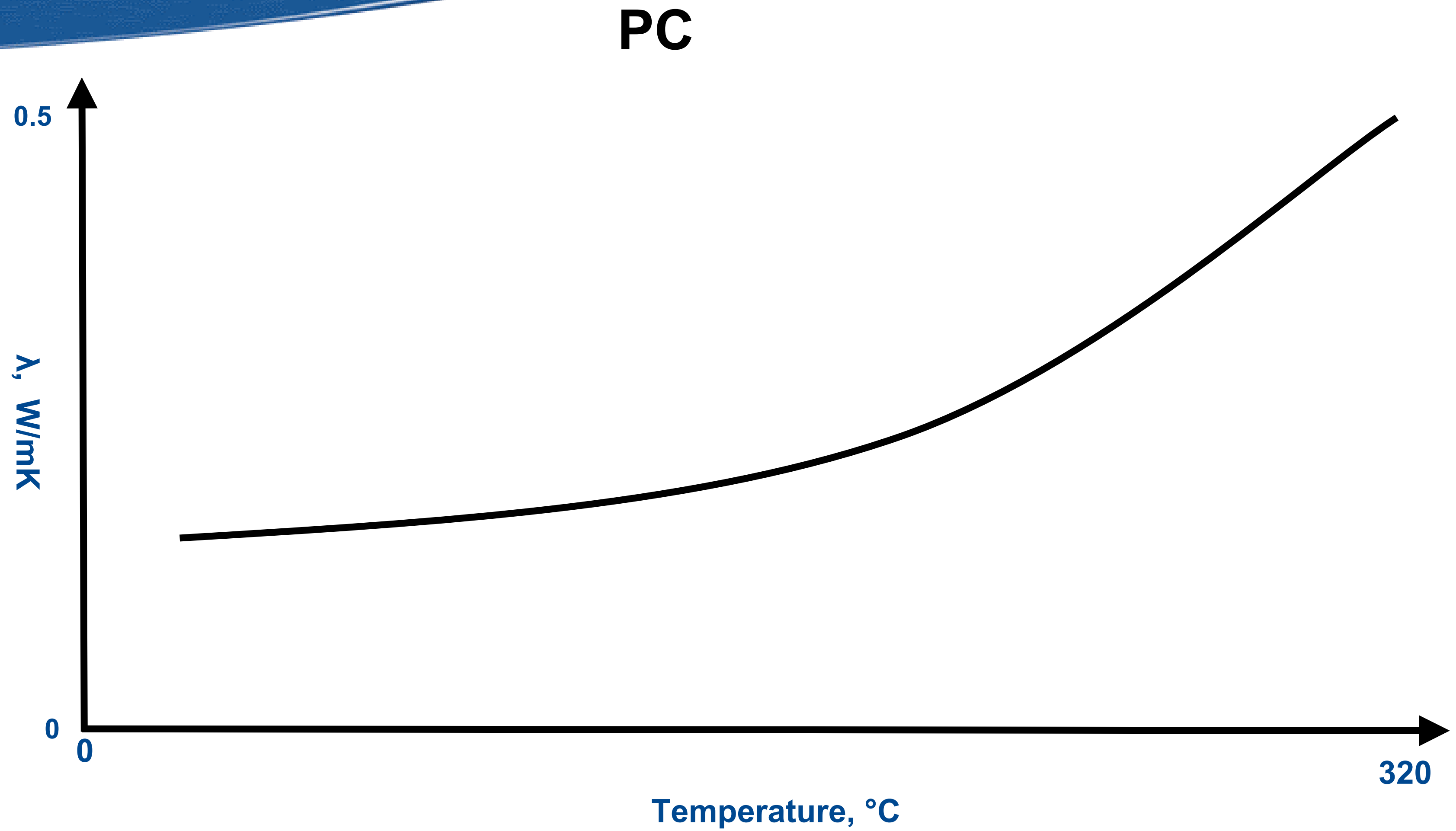
Cooling under pressure



ANTEC ’94, p2240-2242

Nano Flash Method
S. KNAPPE 2000s

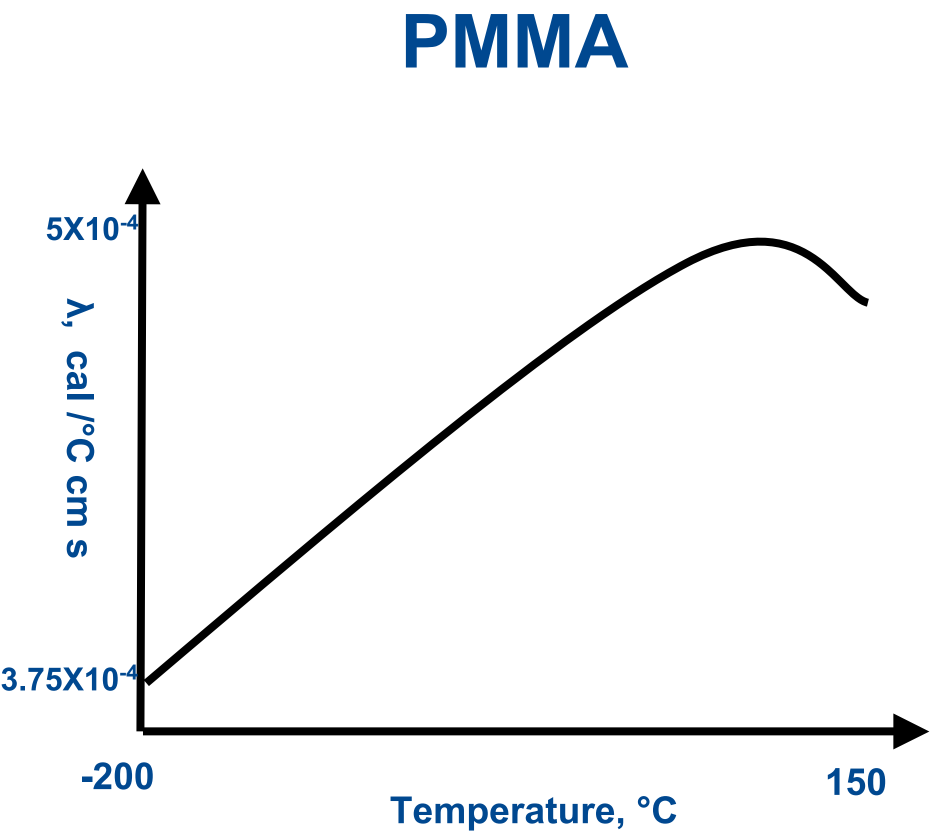
Non-contact

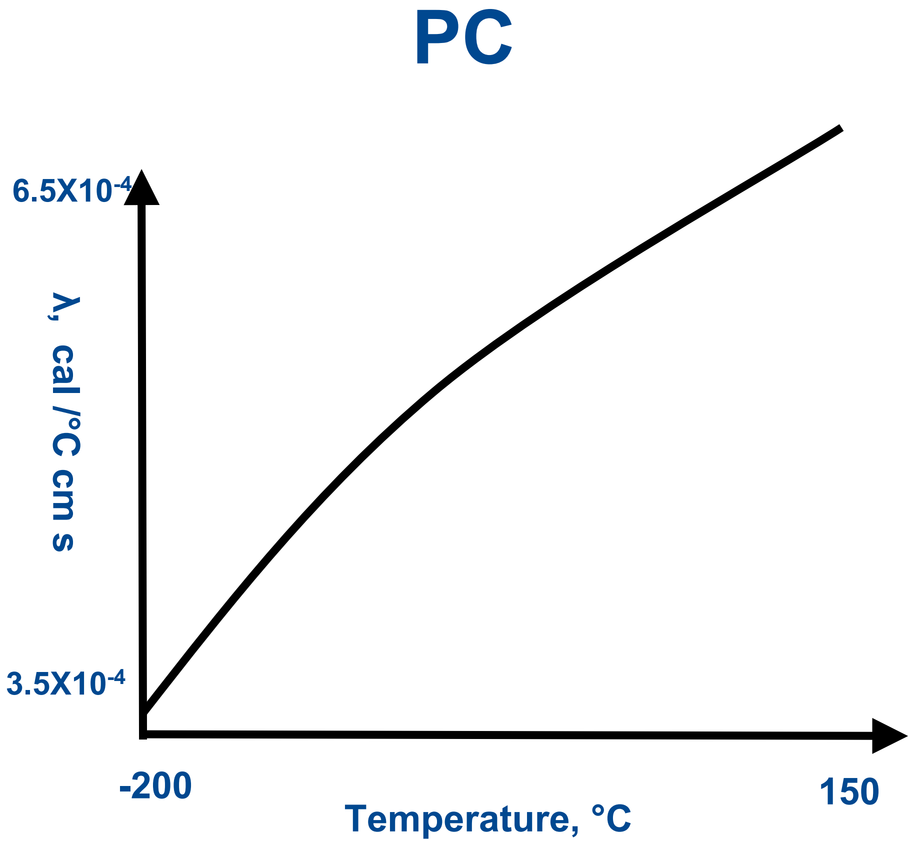


Kunstoffe, 10 (2004) p235-237

Steady State Hot Plate:
K. EIERMANN 1960s

Heating ?

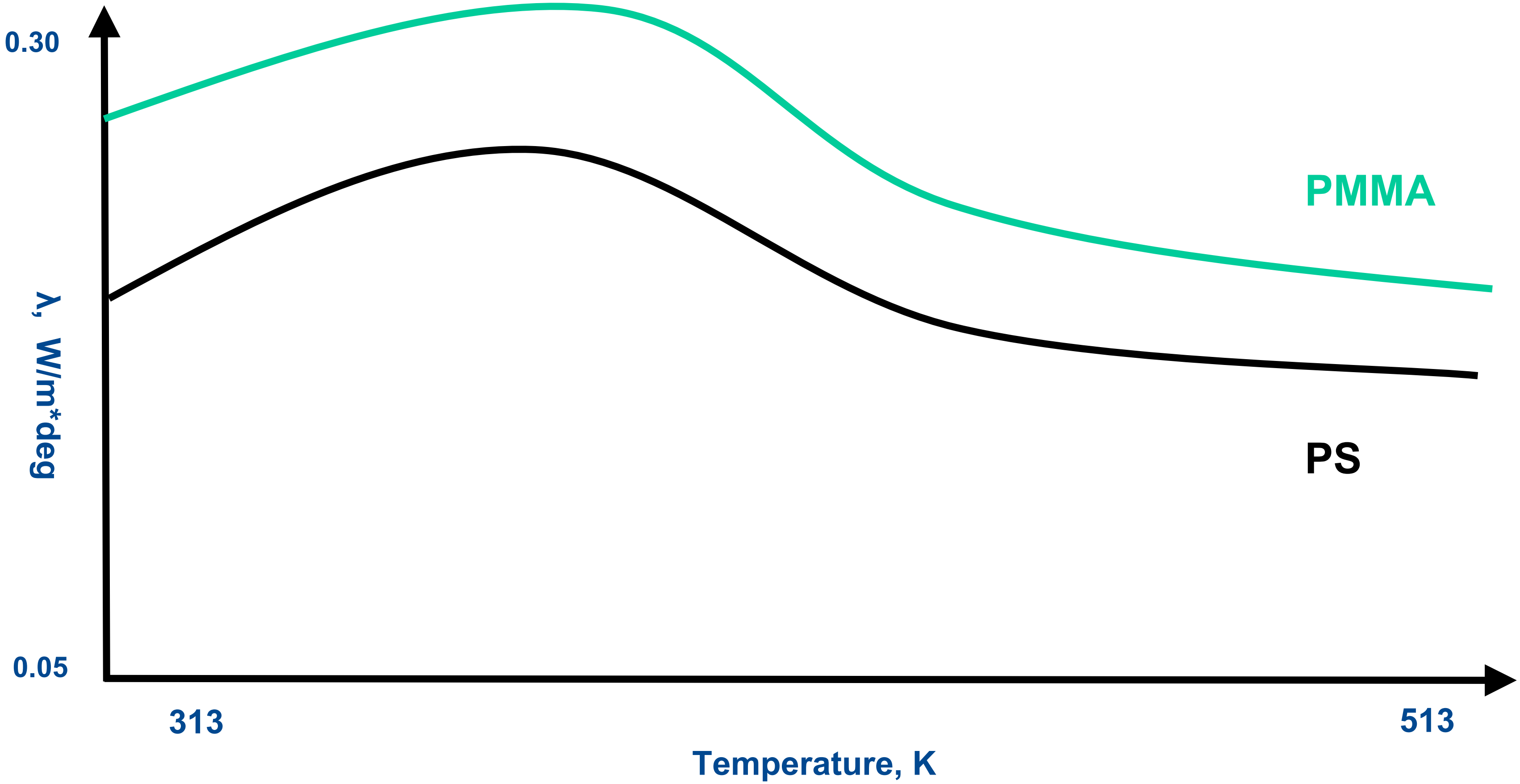




Kunstoffe, 55 (1965), p335-338

Acalorimeter and Bicalorimeter
A BASHIROV et al 1970s

Heating/cooling ?

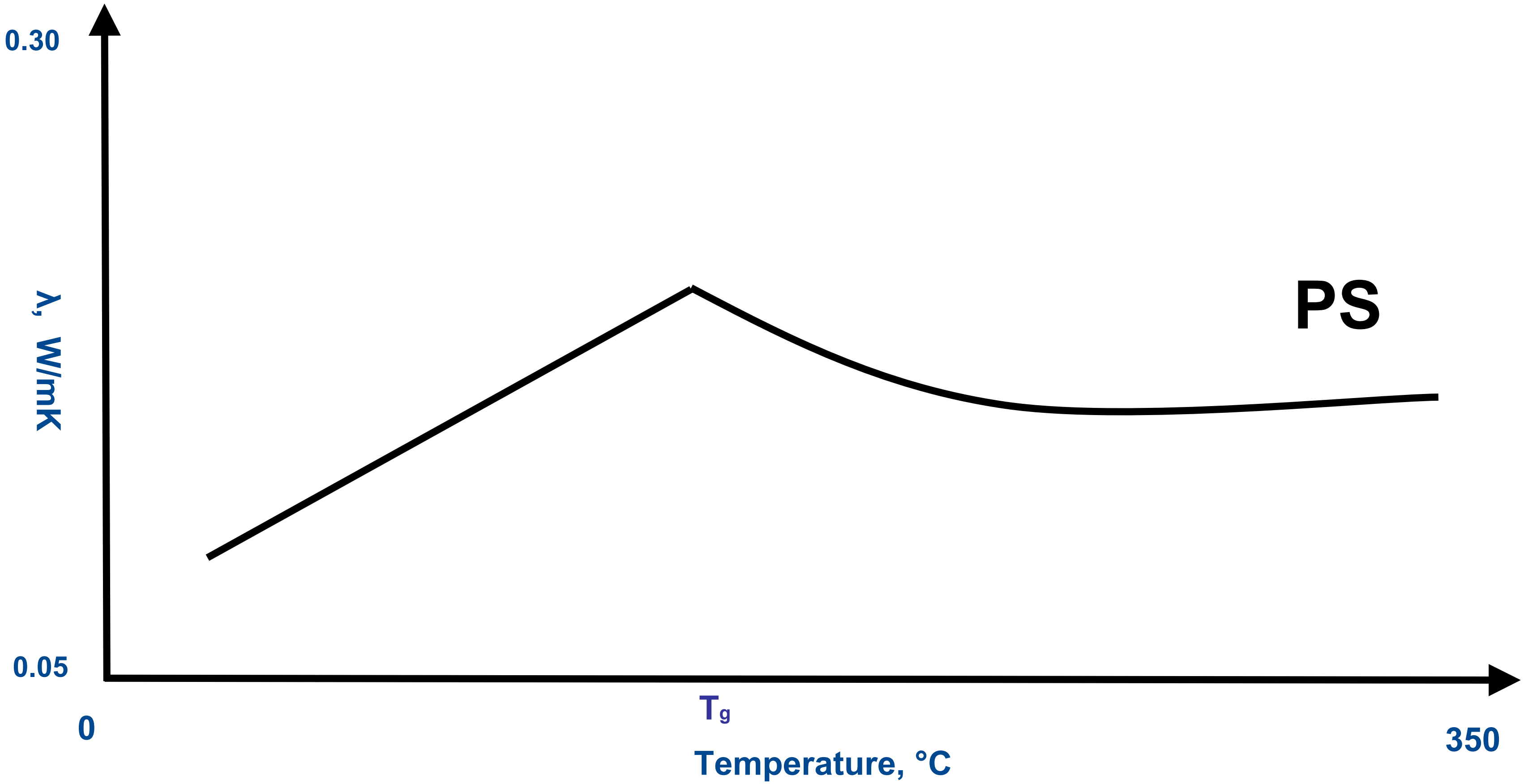


Polymer Mechanics, 3 (1975), p553-555

Lee's Disc Technique

SOMBATSOMPOP and WOOD 1990s

Heating/cooling?



Polymer testing 16 (1997) p203-233

Summary of literature review

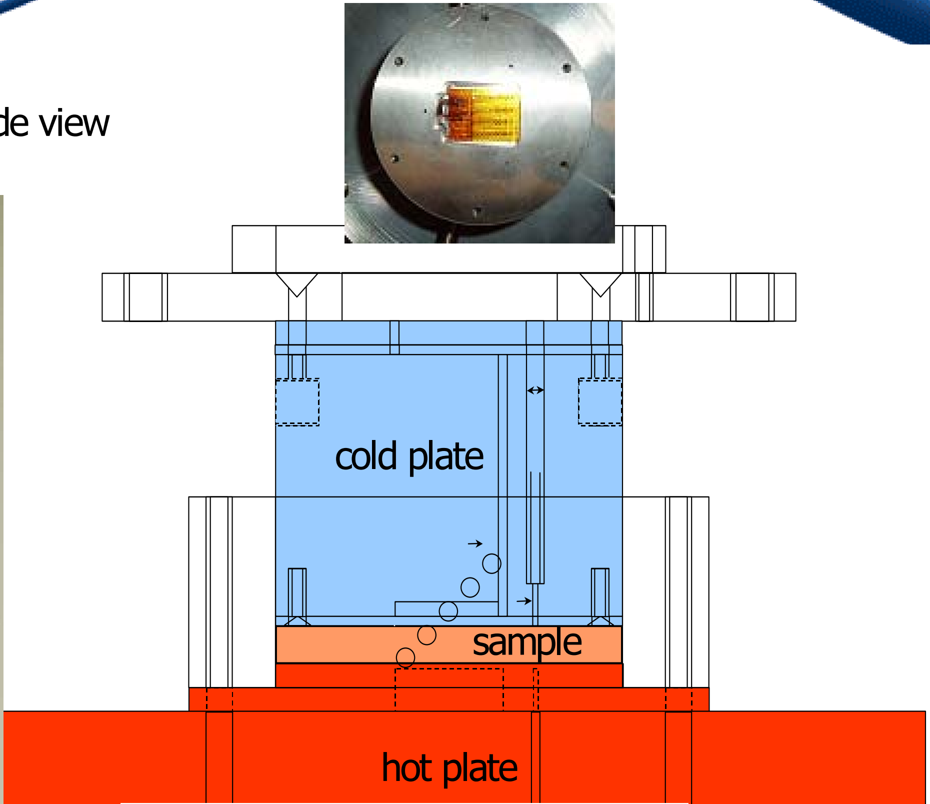
Apparent trend in thermal conductivity data for amorphous polymers measured above glass transition temperature by technique:	
Decrease in thermal conductivity	**Increase in thermal conductivity**
Steady state hot plate	Line Source Technique
Bicalorimetric and Acalorimetric Methods	Nano Flash Method
Lee’s Disc	

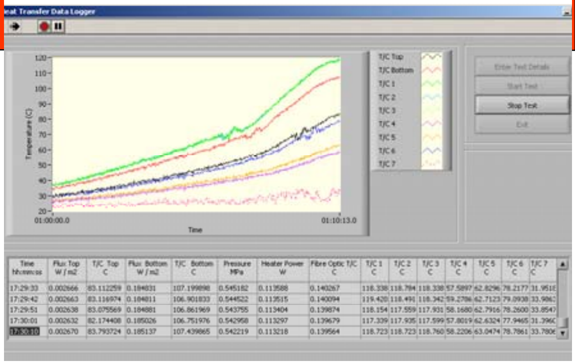
National Physical Laboratory

Development of heat transfer equipment for measurement of thermal conductivity and heat transfer coefficient

Heat transfer apparatus

Side view





Time hh:mm:ss	Flux Top W / m2	T/C Top C	Flux Bottom W / m2	T/C Bottom C	Pressure MPa	Heater Power W	Fibre Optic T/C C	T/C 1 C	T/C 2 C	T/C 3 C	T/C 4 C	T/C 5 C	T/C 6 C	T/C 7 C
17:29:33	0.002666	83.112259	0.184831	107.199898	0.545182	0.113588	0.140267	118.338	118.784	118.338	57.5897	62.8296	78.2177	31.951
17:29:42	0.002663	83.116974	0.184811	106.901833	0.544522	0.113515	0.140094	119.420	118.491	118.342	59.2786	62.7123	79.0938	33.986
17:29:51	0.002638	83.075569	0.184881	106.861969	0.543755	0.113404	0.139874	118.154	117.559	117.931	58.1680	62.7916	78.2600	33.854
17:30:01	0.002632	82.174408	0.185026	106.751976	0.542958	0.113297	0.139679	117.339	117.935	117.599	57.8019	62.6324	77.9465	31.396
17:30:10	0.002670	83.793724	0.185137	107.439865	0.542219	0.113218	0.139564	118.723	118.723	118.760	58.2206	63.0474	78.7861	33.780

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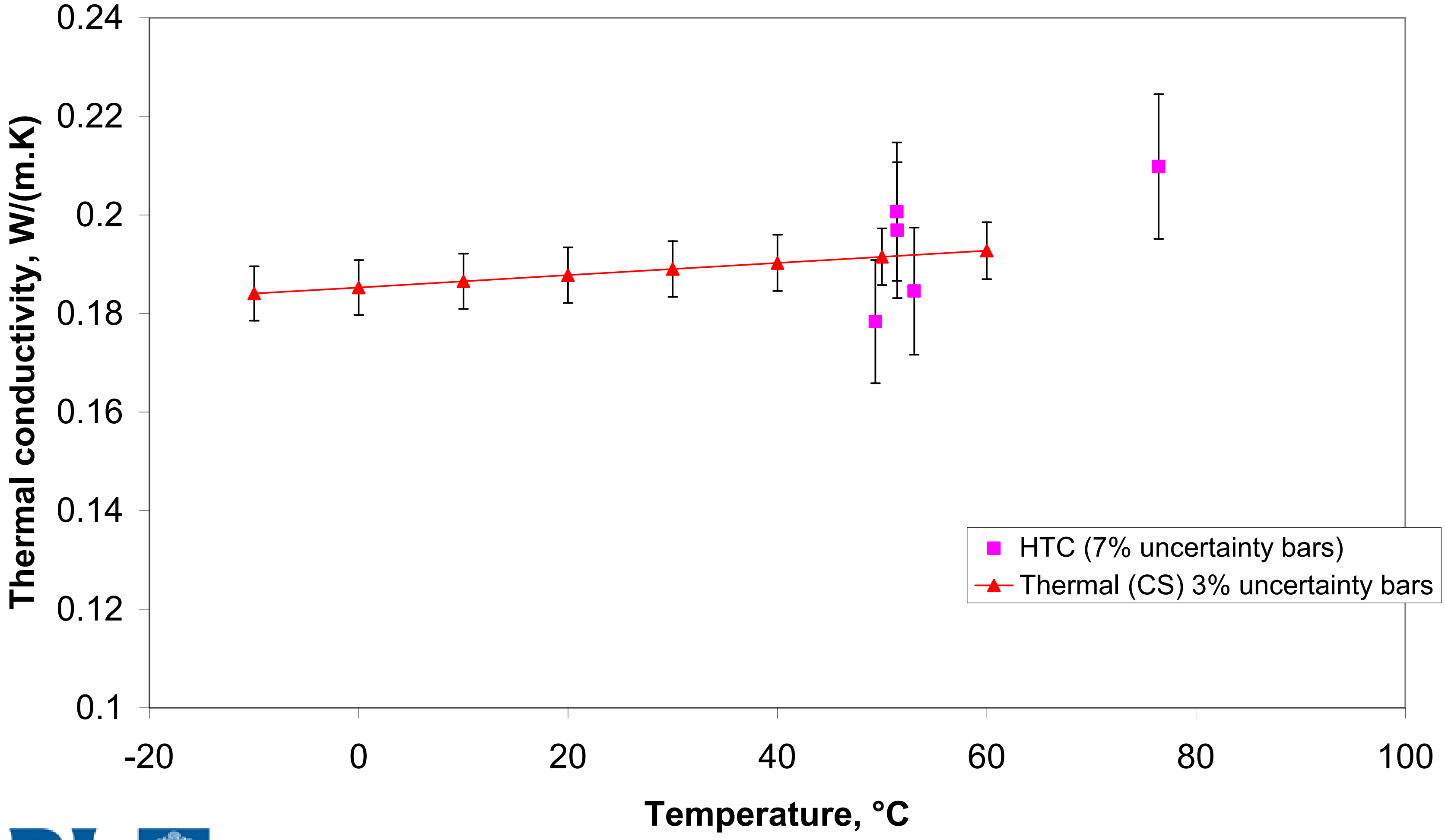
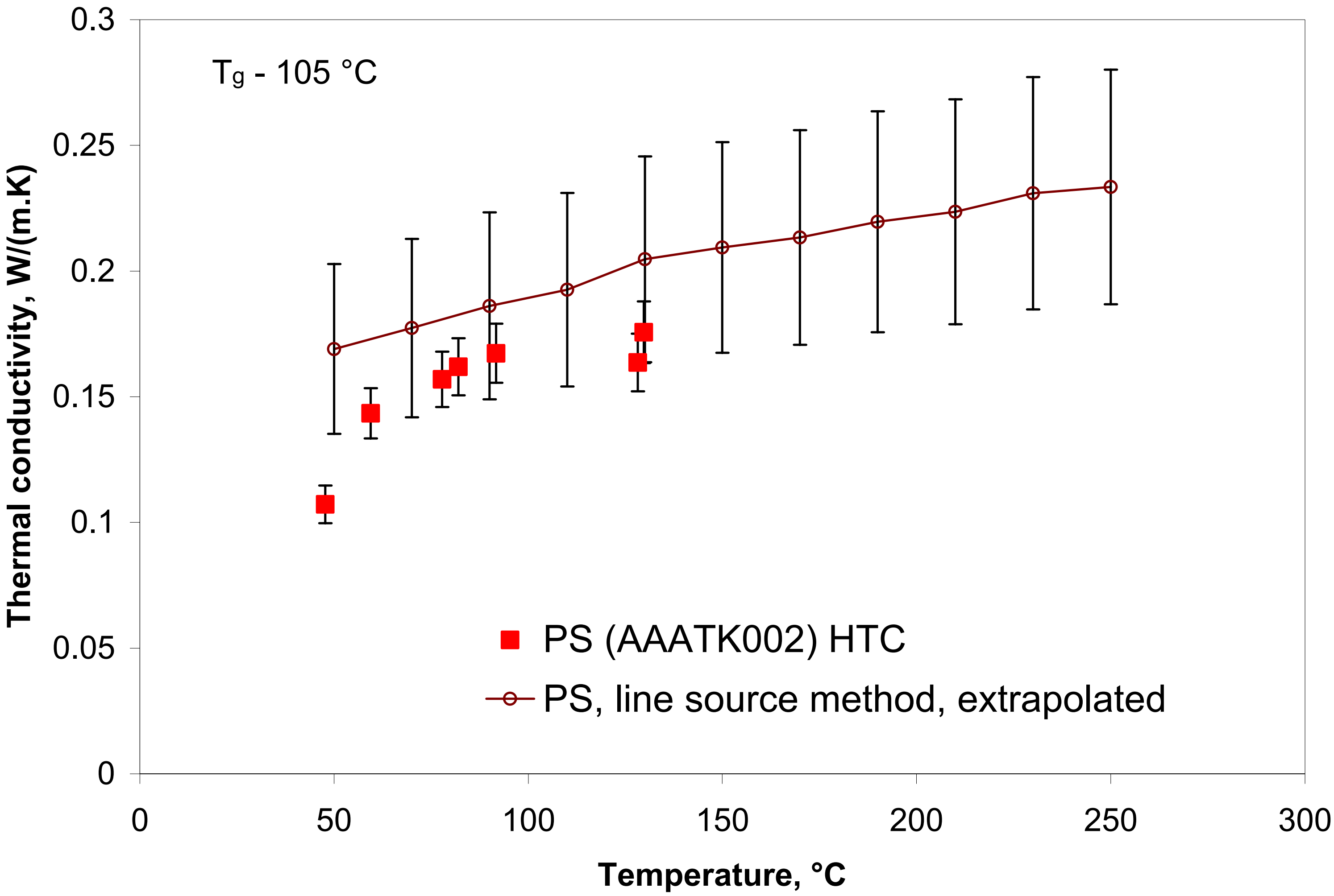
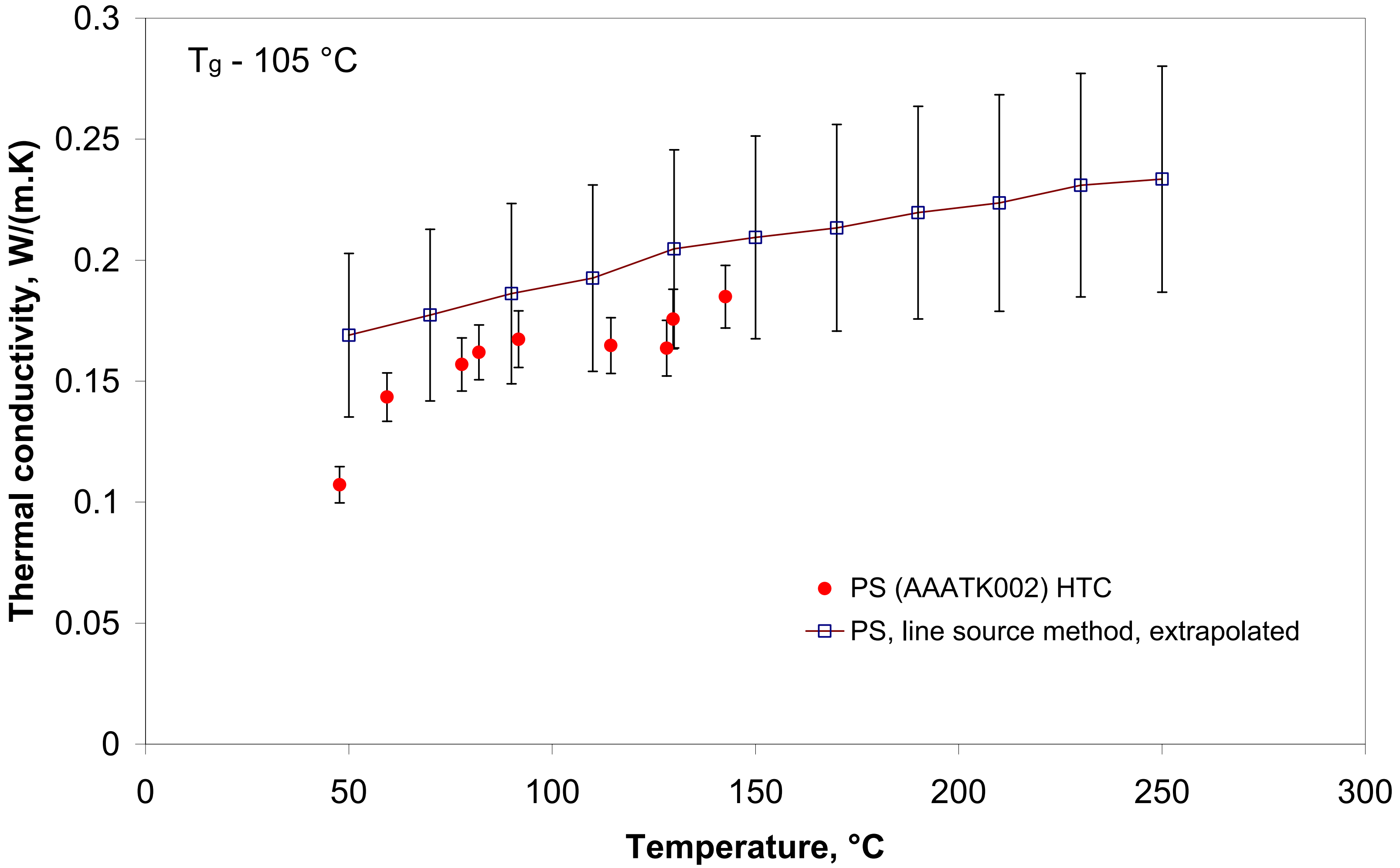
Thermal conductivity of PMMA by HTC



Thermal conductivity of PMMA: HTC c.f. line source data



Thermal conductivity of PMMA: HTC c.f. line source data



Thermal conductivity: summary

Measurements of thermal conductivity of polymers by two different method, yielding reasonable values.

However, need to:

- improve measurement procedures
- address signal noise and improve data analysis procedures
- further validate instruments through intercomparison measurements, and against other methods

Standards for Thermal Properties Measurement of Plastics

Differential scanning calorimetry standards

ISO TC61 SC5 WG8 Thermal Properties

ISO 11357 Plastics - Differential scanning calorimetry (DSC)

- ISO 11357-1: 1997 Part 1: General principles (being revised)
- ISO 11357-2: 1999 Part 2: Determination of glass transition temperature
- ISO 11357-3: 1999 Part 3: Determination of temperature and enthalpy of melting and crystallization
- ISO 11357-4: 2005 Part 4: Determination of specific heat capacity
- ISO 11357-5: 1999 Part 5: Determination of characteristic reaction-curve temperatures and times, enthalpy of reaction and degree of conversion
- ISO 11357-6: 2002 Part 6: Determination of oxidation induction time
- ISO 11357-7: 2002 Part 7: Determination of crystallization kinetics

Plastics thermal conductivity standards

ISO TC61 SC5 WG8 Thermal Properties

ISO 22007 Plastics –
Determination of thermal conductivity and thermal diffusivity

ISO/NWIP 22007-1 Part 1: General principles

ISO/CD 22007-2 Part 2: Transient plane source hot-disc method
(Gustafsson method)

ISO/CD 22007-3 Part 3: Temperature wave analysis method

ISO/CD 22007-4 Part 4: Laser flash method

Plastics thermal conductivity standards

Proposal to develop
Line Source Method for Thermal Conductivity
as part of ISO 22007 series

Method currently standardized as:

- ASTM D 5930-01, Test Method for Thermal Conductivity of Plastics by Means of a Transient Line-Source Technique

However this does not make provision for:

- effect of applying pressure to minimize measurement scatter, and
- effect of pressure on thermal conductivity

ISO TC61 SC5 WG8 Thermal Properties.

Plastics thermal conductivity standards - intercomparison

Proposed intercomparison of thermal conductivity methods (in part, to address differences in literature data)

To be carried out, in support of standardisation activity, including at least:

- Transient plane source hot-disc method (Gustafsson)
- Temperature wave analysis method
- Laser flash method
- Line source probe

To be led by NPL.

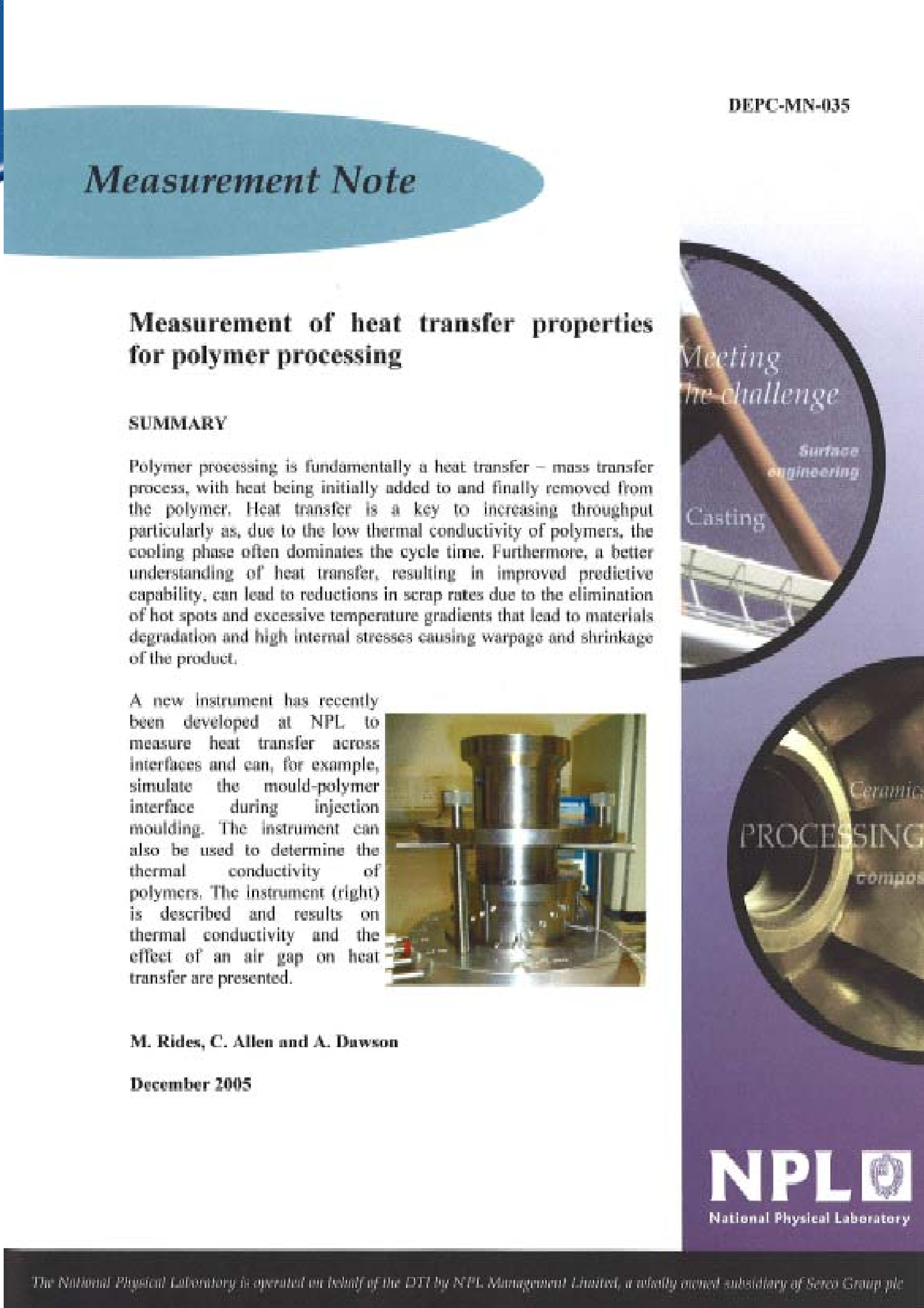
Your input of materials, participating in intercomparison, …

Heat Transfer Activities

Heat transfer

Effect of air gap on thermal resistance modelled and quantified:

air gap equivalent to polymer of 10 x thickness



DEPC-MN-035

Measurement Note

Measurement of heat transfer properties for polymer processing

SUMMARY

Polymer processing is fundamentally a heat transfer – mass transfer process, with heat being initially added to and finally removed from the polymer. Heat transfer is a key to increasing throughput particularly as, due to the low thermal conductivity of polymers, the cooling phase often dominates the cycle time. Furthermore, a better understanding of heat transfer, resulting in improved predictive capability, can lead to reductions in scrap rates due to the elimination of hot spots and excessive temperature gradients that lead to materials degradation and high internal stresses causing warpage and shrinkage of the product.

A new instrument has recently been developed at NPL to measure heat transfer across interfaces and can, for example, simulate the mould-polymer interface during injection moulding. The instrument can also be used to determine the thermal conductivity of polymers. The instrument (right) is described and results on thermal conductivity and the effect of an air gap on heat transfer are presented.

M. Rides, C. Allen and A. Dawson

December 2005

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Heat transfer project H1
2005-08

H1: Measurement methods for heat transfer properties data for application to polymers

Objectives:

- Development of the method for the measurement of heat transfer properties across surfaces (particular interest has been expressed in the effect of the solid/air interface)
- Industrial **case study** to demonstrate the value of reliable heat transfer data
- Support development of **standards** for measurement of thermal properties of plastics, including an intercomparison of thermal conductivity methods that are being proposed for standardisation
- Assessment of **uncertainties in heat transfer data** and effect on modelling predictions
- Development of a new user-friendly **web-enabled modelling** facility, to facilitate industrial adoption of the above

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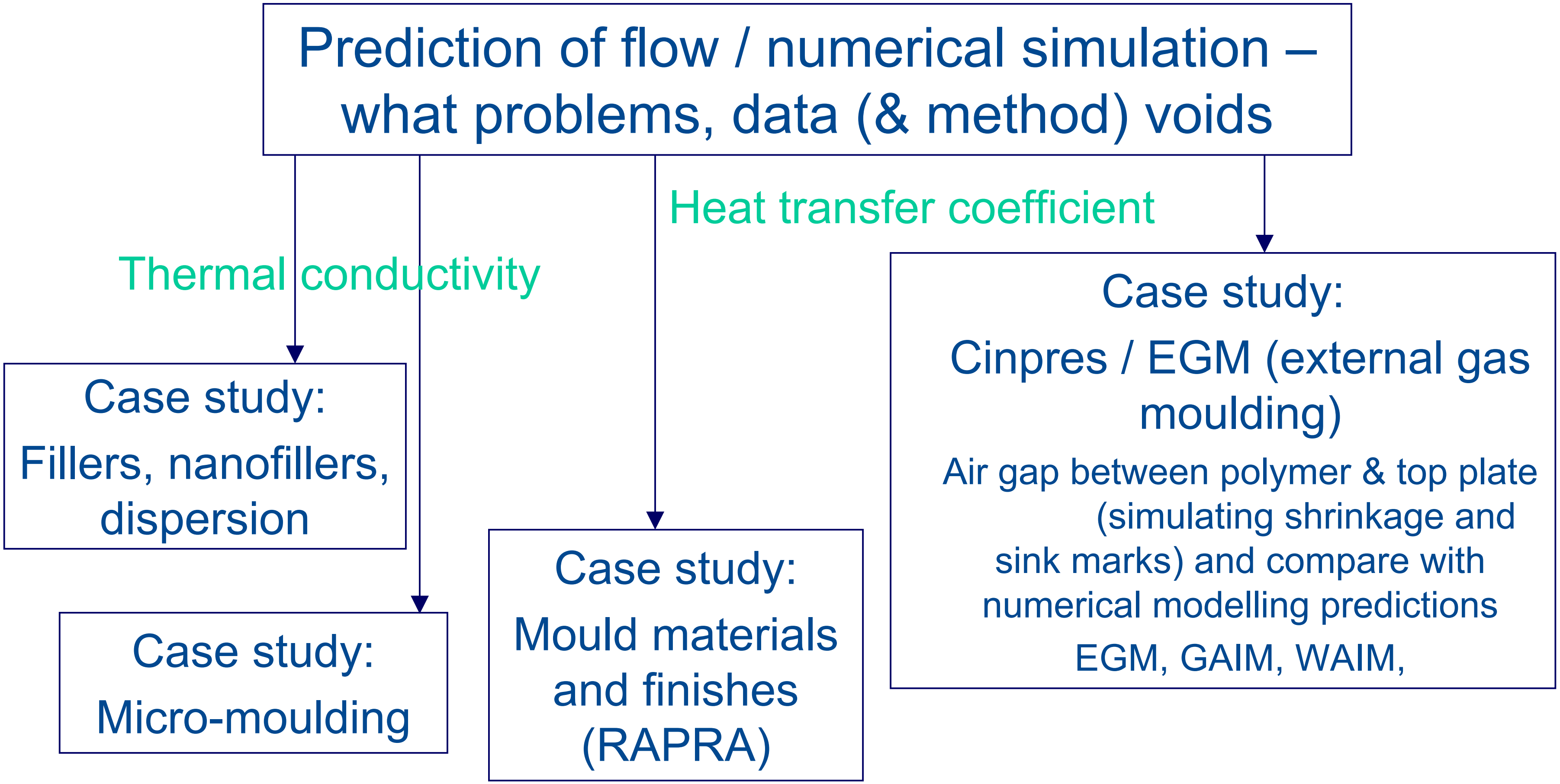
Heat transfer H1

Energy reduction, efficient design, in-situ monitoring



Prediction of flow / numerical simulation – what problems, data (& method) voids

Thermal conductivity

Heat transfer coefficient

Case study:

Fillers, nanofillers, dispersion

Case study:

Micro-moulding

Case study:

Mould materials and finishes (RAPRA)

Case study:

Cinpres / EGM (external gas moulding)

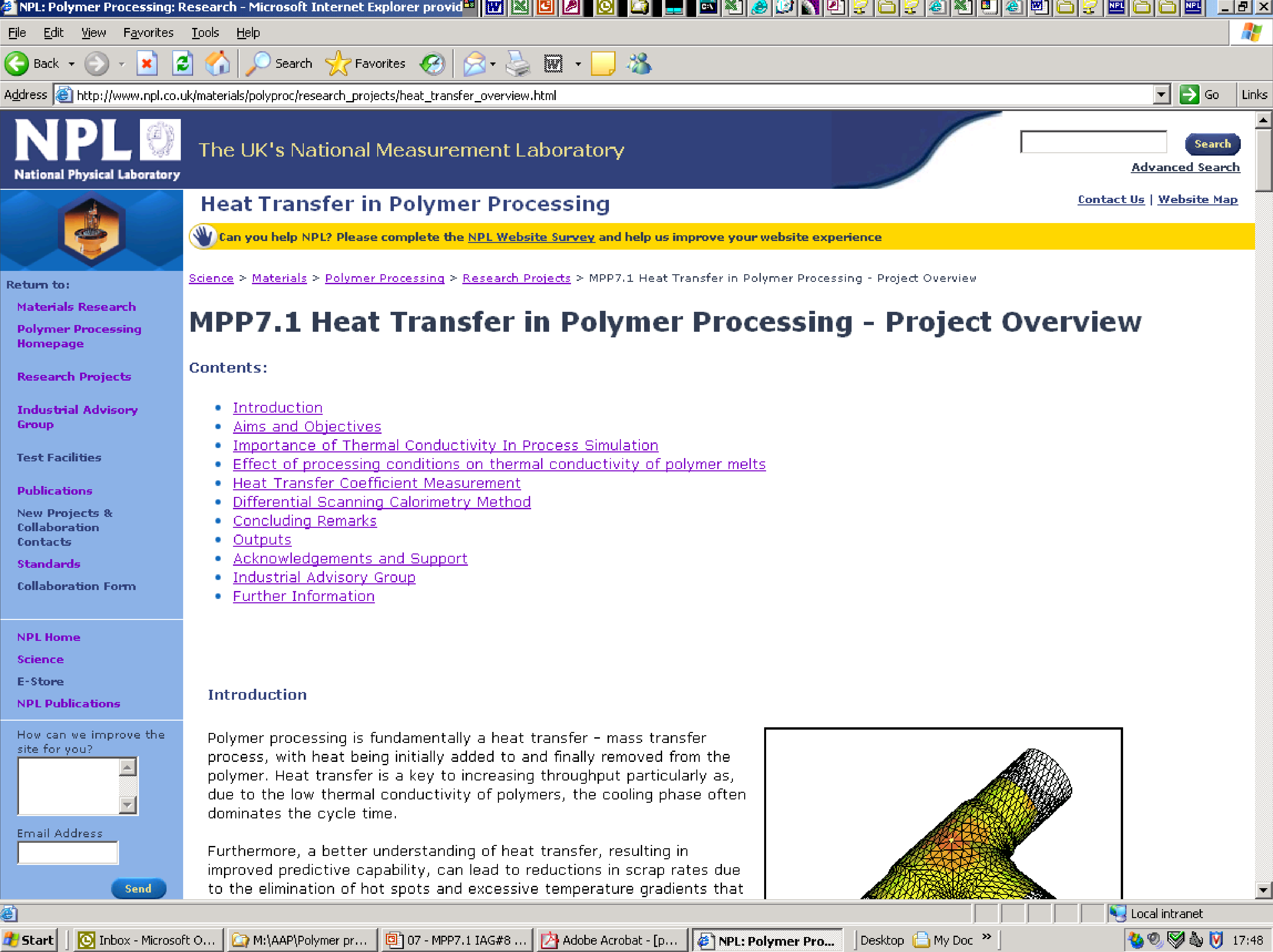
Air gap between polymer & top plate (simulating shrinkage and sink marks) and compare with numerical modelling predictions

EGM, GAIM, WAIM,

Your input to steer the project

The next 12 months

- Investigate discrepancies in data in literature
- Initiate NWIP for standard for line source method
- Initiate thermal conductivity intercomparison
- Carry out industrial case study/studies
- Disseminate thermal conductivity and heat transfer coefficient measurement work



Heat Transfer in Polymer Processing

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MPP7.1 Heat Transfer in Polymer Processing - Project Overview

Contents:

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Acknowledgements

DTI

Crispin Allen, Simon Roberts, Chris Brown