

Pressure/Volume/Temperature Behaviour Of Polymers During Rapid Cooling

Introduction

Shrinkage and warpage are two common problems in plastic components. The consequences of incorrect mould design leading to excessive shrinkage or warpage are often very expensive in terms of scrap or longer cycle times than necessary. Lack of confidence in the prediction of shrinkage can also lead to reluctance to bid for work requiring tight tolerances. As tolerances get tighter and profit margins come under more pressure the ability to be able to predict confidently the final size and shape of plastic components is becoming more important. Software such as Moldflow or C-Mold seeks to reduce the risk of producing parts with shrinkage or warpage problems by providing quantitative predictions based on reliable data. One of the important input data sets to these software packages is pressure/volume/temperature (PVT) behaviour. Until very recently, PVT data has only been available at, or near, equilibrium conditions. However, in injection moulding, it is important to cool as rapidly as possible to reduce cycle times and maximise equipment utilisation. Thus a method of measuring PVT behaviour of polymers during *rapid* cooling is needed.

NPL has demonstrated a method of measuring PVT behaviour of polymers during rapid cooling (up to 250°C/min) and under high pressure (up to 250 MPa). This document summarises the key features of this work and provides examples of initial results. Companies in the injection moulding industry, or suppliers to the industry, are invited to participate in further work to demonstrate the value of this new PVT measurement method.

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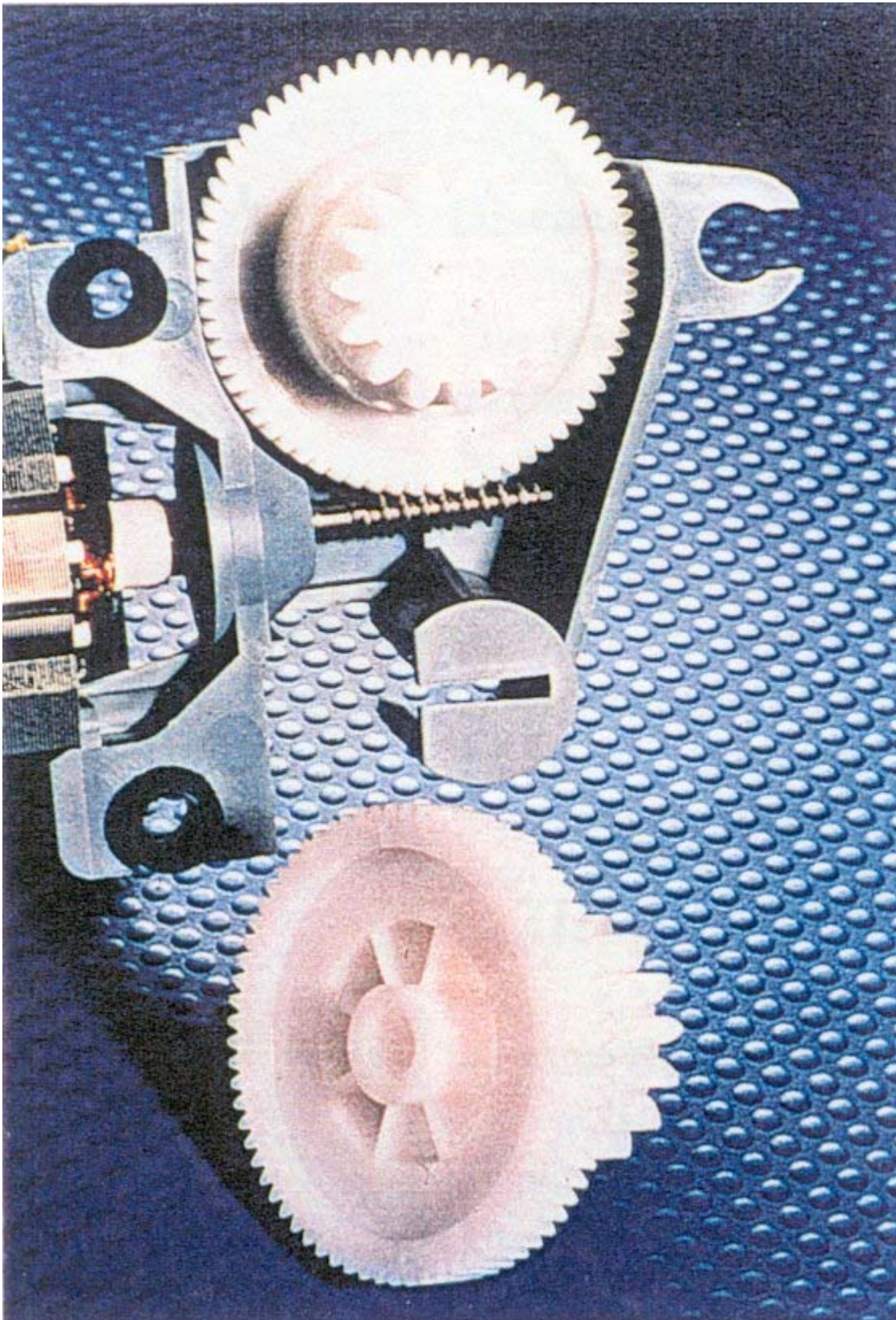


Figure 1: Moulded gears are products which could take advantage of improved PVT data to achieve tighter tolerances (Photograph courtesy of DuPont Engineering Polymers).

Apparatus

The rapid cooling PVT apparatus is shown in Figures 2 and 3. Polymer pellet or powder is placed in the cylindrical cell and a test sample compression moulded in situ usually at 40 MPa. The polymer is heated to the initial test temperature and the chosen pressure applied through a piston. The volume is determined from the diameter and

the piston position which is measured to within 0.001 mm. The sample is then cooled and the changing volume measured at constant pressure. If the cooling fluid (air) is passed through liquid nitrogen, cooling rates of up to 250°C/min can be achieved. Cooling is remarkably linear when liquid nitrogen is used. Linear cooling can also be achieved without liquid nitrogen up to about 35°C/min. The temperature can be measured at four positions; three at the edge of the polymer sample and one in the centre of the polymer. Obviously, with very rapid cooling, large temperature gradients exist within the sample. Currently measurement is limited to 420°C down to room temperature, though measurement at lower temperatures will be available shortly. Once the shrinkage curve at one pressure is obtained the sample is reheated and the shrinkage curve for a second pressure is measured. Normally six pressures from 20 MPa to 250 MPa are recorded on a single sample.

Measurements can also be made with samples of different diameters from 6 mm to 14 mm. For measurement below 250°C a novel PTFE sealing system is used, above 250°C a Vespel sealing system has to be used.

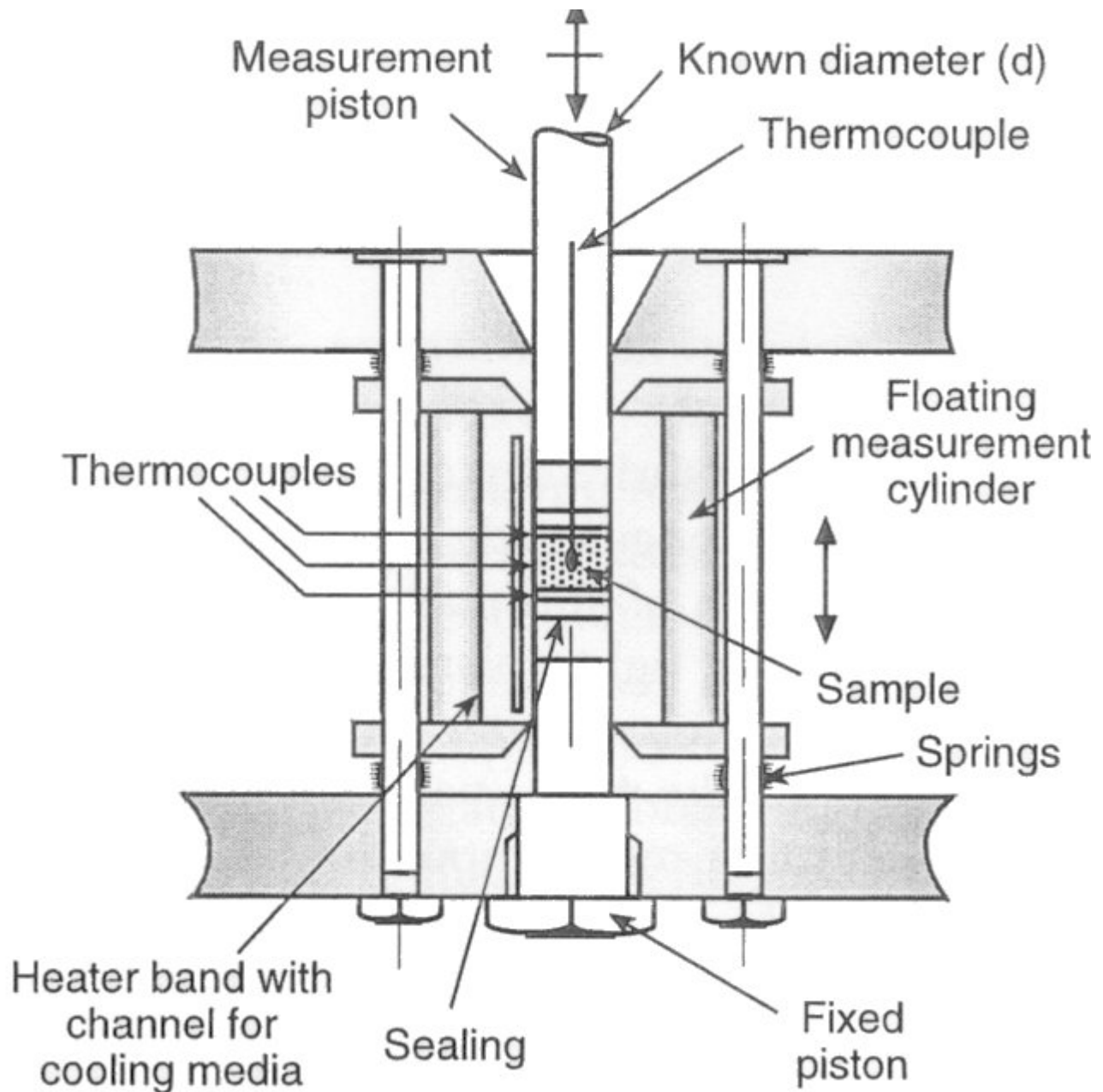


Figure 2: Schematic diagram of apparatus

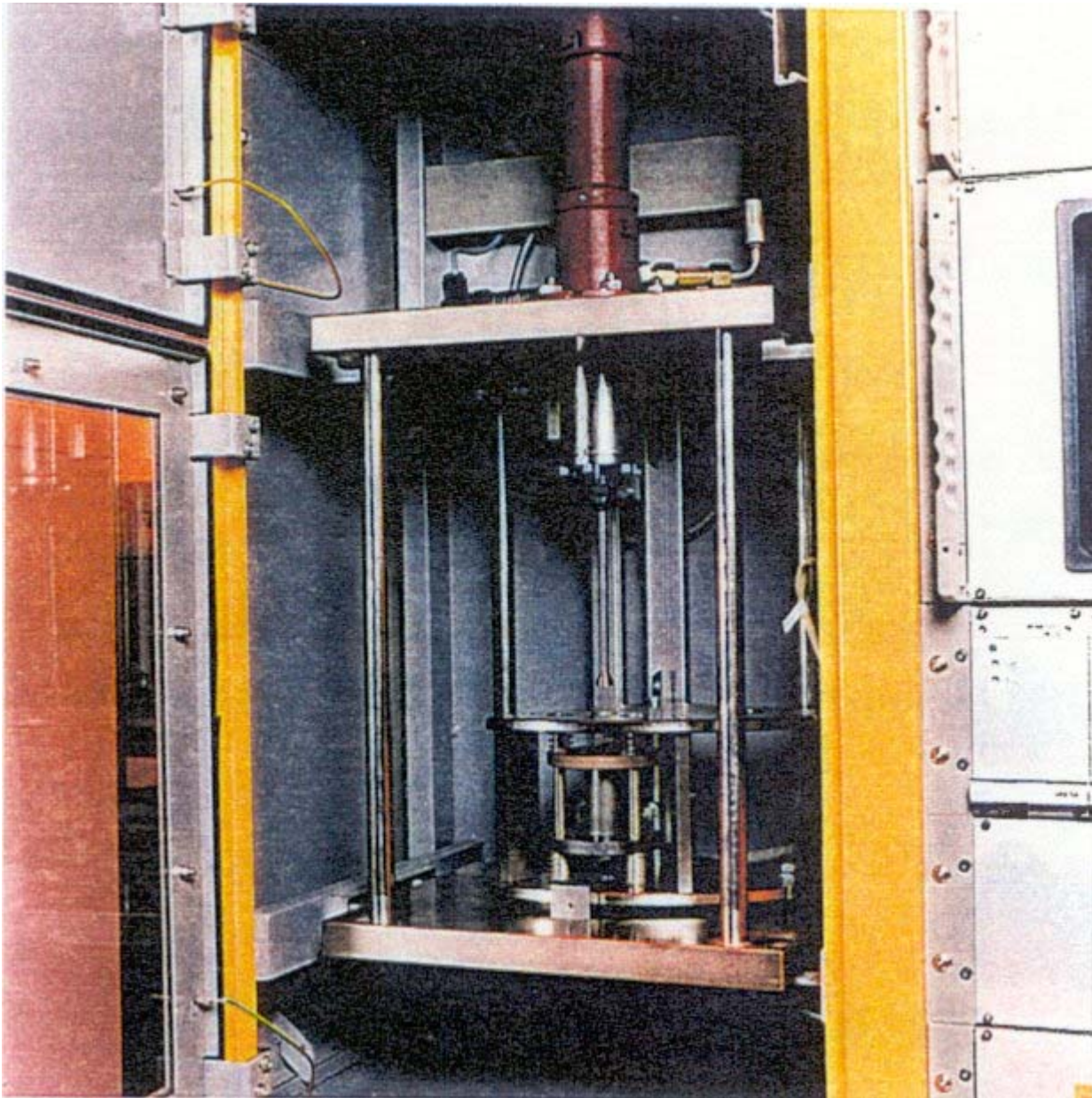


Figure 3: Photograph of apparatus

Results

[Figure 4](#) shows a typical set of PVT curves for polyethylene measured at a cooling rate of $5^{\circ}\text{C}/\text{min}$ (the temperature is measured at the centre of the sample). Initially the change in volume is linear until the start of crystallisation when a sharp reduction in specific volume occurs. Towards the end of crystallisation the curve returns to linear shrinkage. The crystallisation behaviour is strongly dependent on pressure. [Figure 5](#) shows the same material cooled at $214^{\circ}\text{C}/\text{min}$. In this case the PVT behaviour is very different. The curves show a gradual decrease in specific volume as the melt crystallises from the edge of the cell. This results in earlier changes in volume compared with the slower cooling case of [Figure 4](#).

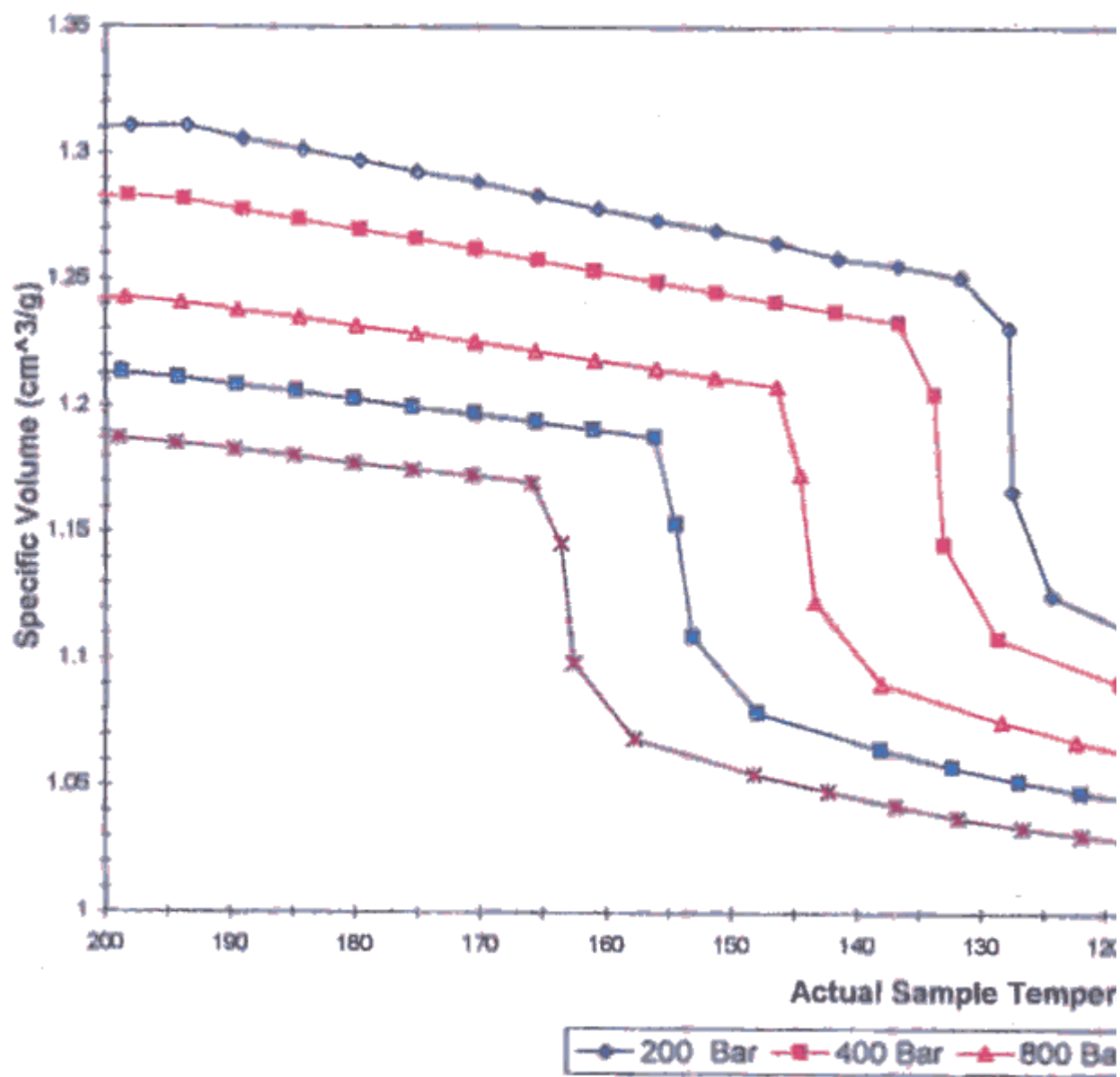


Figure 4: PVT behaviour of polyethylene Rigidex HD5740 at cooling rate of $5^{\circ}\text{C}/\text{min}$

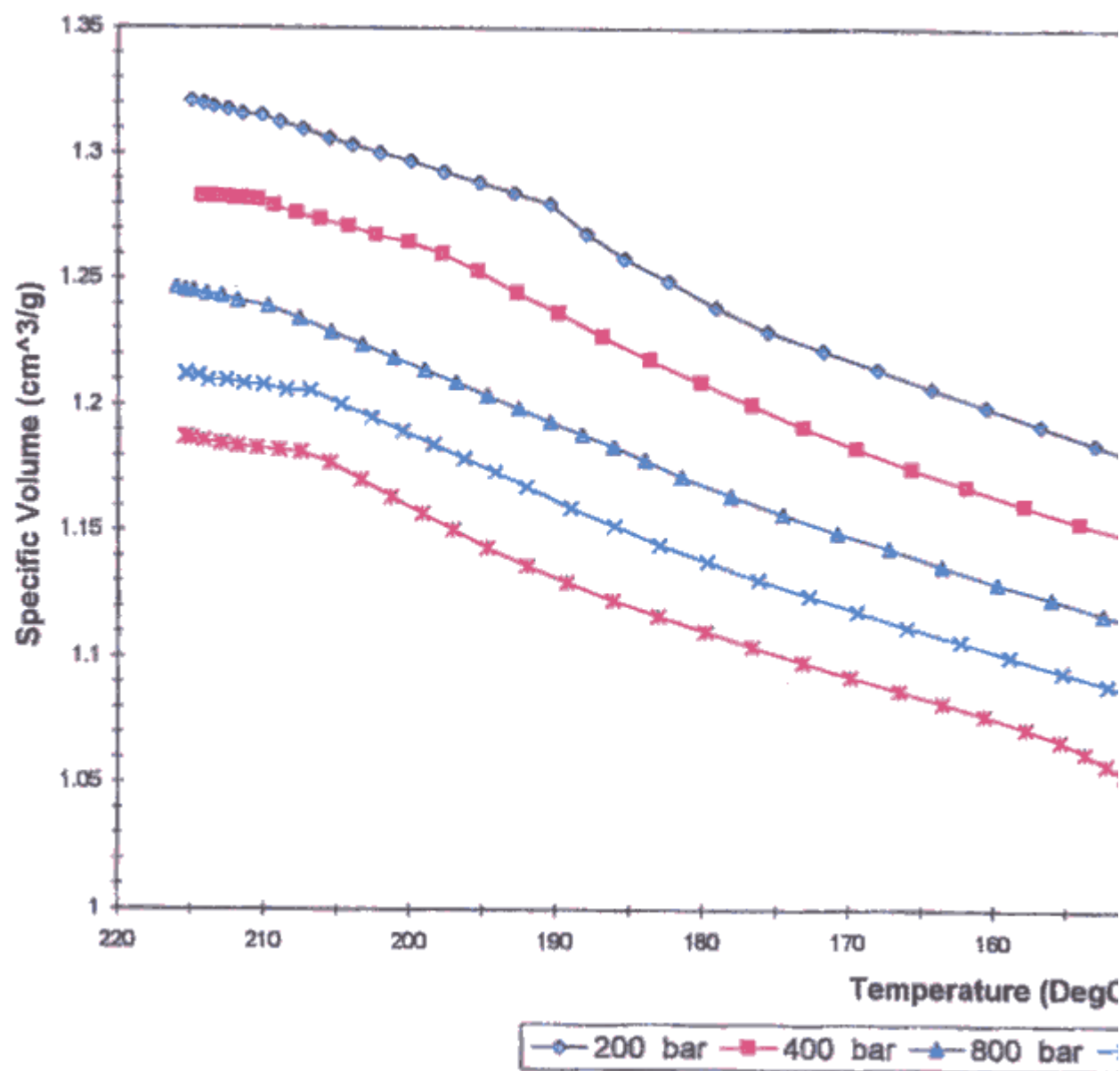


Figure 5: PVT behaviour of polyethylene Rigidex HD5740 at cooling rate of 214°C/min

Discussion

The type of behaviour shown in [Figure 5](#) is thought to be more typical of industrial injection moulding than the traditional slow cooling PVT curves such as those shown in [Figure 4](#). In order to make use of this improved PVT data to predict shrinkage and warpage more accurately, suitable process simulation software is required. Software is commercially available which currently makes use of slow-cooling PVT data. Discussions have been held with leading software suppliers about the opportunity this new measurement method presents and it is expected that future versions of injection moulding simulation software will take advantage of high cooling rate PVT data to further improve their ability to predict shrinkage and warpage.

Acknowledgements

This research was supported by the DTI *Materials Measurement* programme. The PVT equipment described in this report was supplied by SWO.

Further Information

A full report on the PVT behaviour of polymers during rapid cooling will be available in 1999. This report will present further details of the new measurement method, comparisons with more traditional methods and a discussion of the influence sample dimensions have on their PVT behaviour during rapid cooling. The technique has been used to characterise amorphous polymers, thermosets and rubbers as well as thermoplastics. Examples of PVT behaviour of these materials will also be presented.

Further information is also available on other topics relating to the measurement aspects of polymer processing including:

- extensional viscoelastic properties of polymer melts
- measurement of reactive polymer systems
- industrial assessment of techniques to measure rheological properties of polymers during processing
- the effects of thermal conductivity and heat transfer coefficients on polymer processing

NPL also hosts an industrial group on "measurement methods relating to the processing of plastics" which meets three times a year at Teddington. For further information on these topics or for a copy of the full report contact:

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