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dwell time effects**

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ABSTRACT

Reliable viscosity data are needed by industry for a number of reasons, as a guide to designing products and choosing appropriate grades of material, to predict how a polymer will flow in commercial processing situations and to provide feedback during processing operations. Capillary rheometry is often used by industry to measure the viscosity of polymers. However, there is uncertainty over how long to leave a sample in the rheometer prior to measuring its viscosity. This has become more of a problem as processing temperatures have been pushed to the limit. The effect of different dwell times on viscosity measurement was examined in the context of the ISO Standard 11443. It was concluded that dwell times of five minutes were insufficient to achieve reliable viscosity measurements, whereas dwell times of thirty minutes were found to be sufficient. No evidence of degradation was observed for dwell times of two hours or less where the testing temperature was within the recommended processing temperature range, however, at higher temperatures a slight (<10%) reduction in viscosity was recorded. The unusual behaviour of filled polypropylene increasing in viscosity, seen previously in rotational rheometry, was not observed in capillary rheometry. This is in agreement with the explanation proposed previously. This work should enable industry to use capillary rheometry to measure viscosity with more confidence in the future.

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by Dr M K Hossain, Head, Division of Materials Metrology

CONTENTS

	Page
1 INTRODUCTION	1
2 EXPERIMENTAL TECHNIQUES	1
2.1 EQUIPMENT	1
2.2 CALCULATION OF VISCOSITY DATA	2
2.3 MATERIALS	2
3 RESULTS	2
4 DISCUSSION	2
5 CONCLUSIONS	3
6 ACKNOWLEDGEMENTS	4
7 REFERENCES	4
APPENDIX 1	5

1 INTRODUCTION

Industry needs reliable viscosity data for three main reasons:-

- a) as a guide to designing products and choosing appropriate grades of material,
- b) to predict how a polymer will flow in commercial processing situations,
- c) to provide feedback during processing operations.

Capillary rheometry is often used by industry to measure the viscosity of polymers. The technique is often chosen because it resembles commercial processing in many respects. In capillary rheometry a polymer sample is heated in a barrel and forced through a capillary at a known rate. The pressure resisting the flow is measured. The strain and flow rates experienced by the polymer can be similar to commercial processes such as extrusion or injection moulding. Hence, viscosity measured by capillary rheometry is considered to be relevant to commercial processing and has the potential to meet all the needs of industry described above. References 1 to 5 describe the technique and its applications in detail.

Industry often wishes to process its polymers as close as possible to their degradation temperature. A high temperature is often chosen to keep the resistance to flow (ie viscosity) as low as possible. Benefits arise from faster production rates or lower pressure during production. There is thus a desire to know the viscosity at relatively high temperatures. This leads to a potential measurement problem for capillary rheometry. In traditional capillary rheometry it is necessary to wait until all of the polymer sample has reached the same temperature as the barrel. How short can this dwell time be in practice? If the operator waits too long then the polymer will start to degrade in the rheometer. Conversely, if the operator does not wait long enough the viscosity value recorded will be too high because the whole of the sample has not yet reached the correct temperature. This report presents an experimental investigation into how different dwell times affect viscosity data.

The work is part of a project entitled "Polymer Moulding Models: the Determination of the Viscosity of Polymers as a function of Cure, Temperature and Pressure" (task 5.2) funded by the Department of Trade and Industry.

2 EXPERIMENTAL TECHNIQUES

2.1 EQUIPMENT

Figure 1 shows a schematic diagram of a capillary rheometer. A polymer sample is heated in a barrel and forced through a capillary at a known rate and the pressure resisting the flow is measured. Two different capillary rheometers were used in this study, an ACER 2000 and a RACER supplied by Polymer Laboratories (now part of the Rheometrics Group). Details of the instruments and the conditions used are shown in the following table.

Instrument	Barrel diameter	Die diameter	Die length	Shear rate	Material measured	Location
ACER	20mm	1mm	20mm	1000 s ⁻¹	MDPE	Rapra
RACER	25mm	2mm	10mm	1000 s ⁻¹	Filled PP	NPL

2.2 CALCULATION OF VISCOSITY DATA

The ISO standard 11443 (1) was followed. The apparent viscosity (η_{ap}) is defined as the ratio of apparent shear stress (τ_{ap}) to apparent shear rate ($\dot{\gamma}_{ap}$):

$$\eta_{ap} = \tau_{ap} / \dot{\gamma}_{ap}$$

The apparent shear rate is given by:

$$\dot{\gamma}_{ap} = 32Q / \pi D^3$$

where Q is the volume flow rate and D is the die diameter. Q is calculated from the piston velocity (v) times the cross sectional area (A) of the piston, ie $Q = A \cdot v$.

The apparent shear stress is given by:

$$\tau_{ap} = P \cdot D / 4 L$$

where P is the test pressure and L is the die length. Thus from the measured pressure, piston velocity and geometric parameters the apparent viscosity is calculated.

2.3 MATERIALS

The two materials chosen for this study were a medium density polyethylene "NCPE 6032" made by Neste and kindly supplied by BICC Cables (NPL reference HAD 001) and a calcium carbonate filled polypropylene "Astryne DG176" (NPL reference HAR 004). The filled polypropylene was kindly made and supplied by Himont.

3 RESULTS

Figure 2 shows the results of the measurement of the apparent viscosity of the medium density polyethylene using the ACER capillary rheometer. Measurements were made after dwell times from 5 minutes to two hours at 200, 250 and 300°C. No corrections were made to the data. Figure 3 presents the measurement of the apparent viscosity of the filled polypropylene using the RACER capillary rheometer. In order to measure viscosity at very short dwell times it was necessary to use a second pressure transducer as shown in figure 4. Measurements were made at 180, 230 and 280°C up to dwell times of two hours. A measurement of the change in temperature of the filled polypropylene melt was also made over the first hour at 280°C (figure 5).

Figure 6, from (6), shows two measurements of the complex viscosity of the same batch of filled polypropylene measured by rotational rheometry at Cambridge University. The higher strain rate data (50 rads/second) showed very little change in viscosity with time, whereas the lower strain rate data (1 rads/second) showed a marked increase.

4 DISCUSSION

A rapid reduction in viscosity was found as the dwell time was increased from zero to about ten minutes, figures 2-4. After thirty minutes the viscosity values remained constant except for the highest test temperatures which were deliberately chosen to be above the normal processing temperatures for each material. The ISO Standard (1) recommends a dwell time of at least five minutes and also that a check be made to ensure that any further changes in apparent viscosity are less than $\pm 5\%$. In figure 2 the viscosity value reduces to within 5% of

its equilibrium value after a dwell time of about 7 minutes. In the case of the RACER rheometer this occurs after about 12 minutes (figures 3 and 4). Thus a dwell time of 5 minutes is considered insufficient and the need to repeat viscosity measurements until a constant value is reached is confirmed.

The RACER rheometer seems to require slightly longer dwell times than the ACER. This is not unexpected because of the RACER's larger diameter barrel which means that heat from the barrel wall will take longer to reach the centre of the polymer sample.

At the highest temperatures, some evidence for degradation can be seen. After two hours at 300°C the polyethylene viscosity has dropped by 7% of its value after 30 minutes (figure 2). The filled polypropylene viscosity also fell by 7% after two hours at 280°C (figure 3). In neither case can a plateau region be defined. It appears that degradation has started before the samples have reached thermal equilibrium.

The time taken to reach thermal equilibrium is around 15 minutes in the case of the filled PP at 280°C (figure 5). The initial drop in viscosity has occurred by this time. The rate of change in viscosity does not exactly mirror the rate of change in temperature. This provides a further reason for repeating viscosity measurements until a constant value is reached rather than relying on the less direct temperature measurement.

It is possible to use data such as shown in figure 5 to obtain an estimate of the thermal diffusivity. This can then be used together with a model to predict how long the material will take to equilibrate at other temperatures and in other rheometers (eg with a smaller diameter barrel). Unfortunately, the mathematical solution is not trivial, see Appendix 1.

It is interesting to compare the capillary rheometry of the filled polypropylene (figure 3) with the previous rotational rheometry measurement, see figure 6 (6). This figure shows an increase in viscosity (as measured by rotational rheometry) of nearly two orders of magnitude over a three hour period at 230°C. However, when the measurement strain rate was increased from 1 to 50 rads/second virtually no increase was seen. The explanation given was that filled polypropylene can spontaneously order, which produces a more viscous material. This ordering can, however, be destroyed by testing the samples at high strain rates. This explanation predicts that no increase in viscosity should occur at 230°C when the viscosity is measured by *capillary rheometry* because of the much higher strain rates. Figure 3 indeed confirms that no increase occurs.

5 CONCLUSIONS

- Dwell times of five minutes were found to be insufficient to achieve reliable viscosity measurements, whereas dwell times of thirty minutes were found to be sufficient.
- No evidence of degradation was observed for dwell times of two hours or less where the testing temperature was within the recommended processing temperature range, however, at higher temperatures a slight (<10%) reduction in viscosity was recorded.
- In general it is recommended that dwell times are increased until a constant viscosity value is reached. However, this procedure may not be valid outside the normal processing temperature range, where degradation can occur before a constant value is reached.

- The unusual behaviour of filled polypropylene increasing in viscosity, seen previously in rotational rheometry, was not observed in capillary rheometry. This confirms the previous conclusion that the effect should not be significant for commercial processing.

6 ACKNOWLEDGEMENTS

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7 REFERENCES

- 1 ISO Standard 11443:1994, *Determination of the fluidity of plastics using capillary and slit die rheometers*.
- 2 Brydson, J.A., *Flow properties of polymer melts*, George Goodwin Ltd, London, 1981 (2nd Edition).
- 3 Walters, K., *Rheometry*, Chapman and Hall, London, 1987.
- 4 Dealy, J.M., *Rheometers for molten plastics. A practical guide to testing and property measurement*, Van Norstrand Reinhold Company, London, 1982.
- 5 Ritchie, P.D., *Physics of plastics*, Van Norstrand Reinhold Company, Princeton New Jersey, 1965.
- 6 Liang, R.F., *Interim technical report on rotational rheometry of unfilled and filled polymers*, Cambridge University report for projects PMP4 and PMP5, March 1994.

APPENDIX 1

Mathematical Model for the temperature rise in a capillary.

The equation for the diffusion of heat in cylindrical coordinates is:

$$\frac{\delta^2 T}{\delta r^2} + \frac{1}{r} \frac{\delta T}{\delta r} = \frac{1}{k} \frac{\delta T}{\delta t} \quad [1]$$

where T = temperature, r = distance from the centre of the capillary, t = time and k = thermal diffusivity.

For the case of a hot capillary rheometer barrel being filled with cold polymer the solution of the differential equation at the centre line is:

$$T_c = T_w - \frac{2T_w}{a} \sum_{n=1}^{\infty} \frac{e^{-k\alpha_n^2 t}}{\alpha_n J_1(a\alpha_n)} \quad [2]$$

where T_c = Temperature at the centre, T_w = Temperature at the wall (assumed constant), a = barrel radius, J_1 is a Bessel function of the first kind and α_n are the roots of the Bessel function $J_1(a\alpha_n) = 0$. (Reference Carslaw and Jaeger, Conduction of Heat, Clarendon Press 1948, p 173).

To determine k from this is not trivial because this would involve fitting [2] to the experimental results (figure 6). Numerical procedures to solve such problems are available, but have not been invoked in this case.

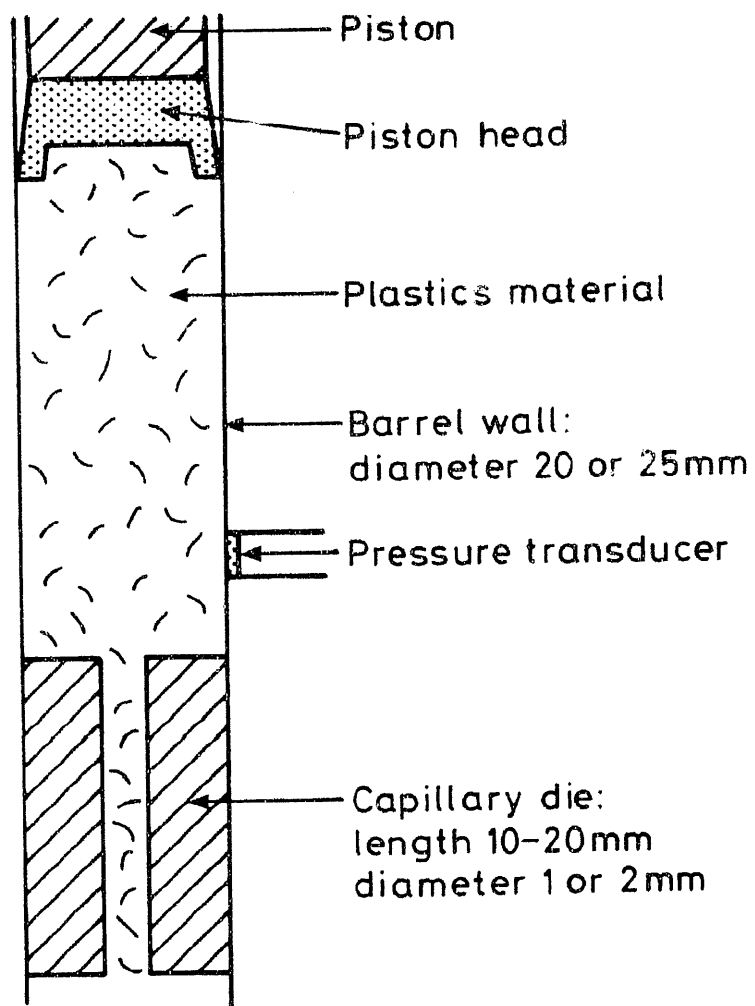


Figure 1 Capillary die extrusion rheometer

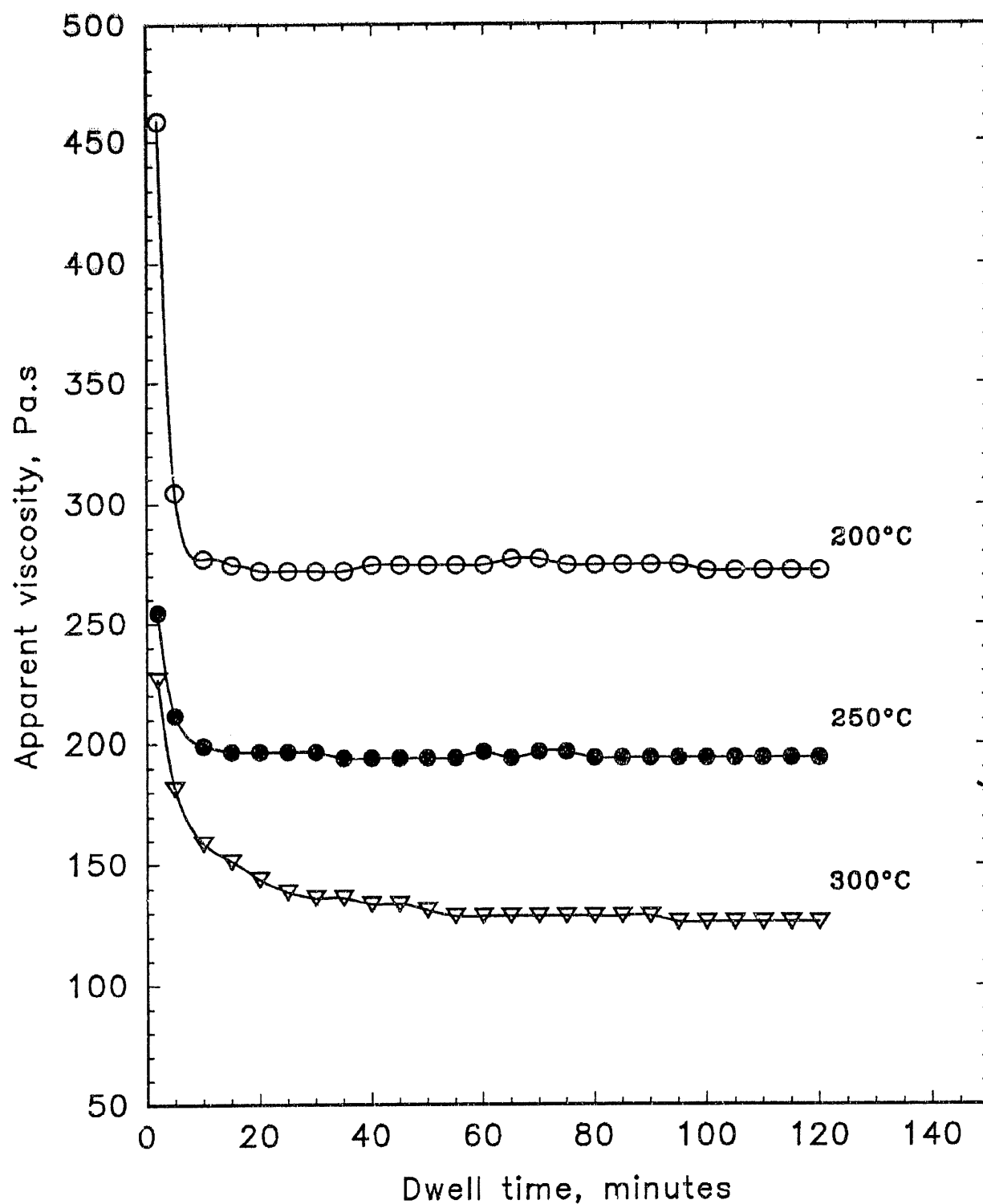


Figure 2. Apparent viscosity of medium density polyethylene, measured with the Acer capillary rheometer, as a function of dwell time.
(Data supplied by Rapra Technology.)

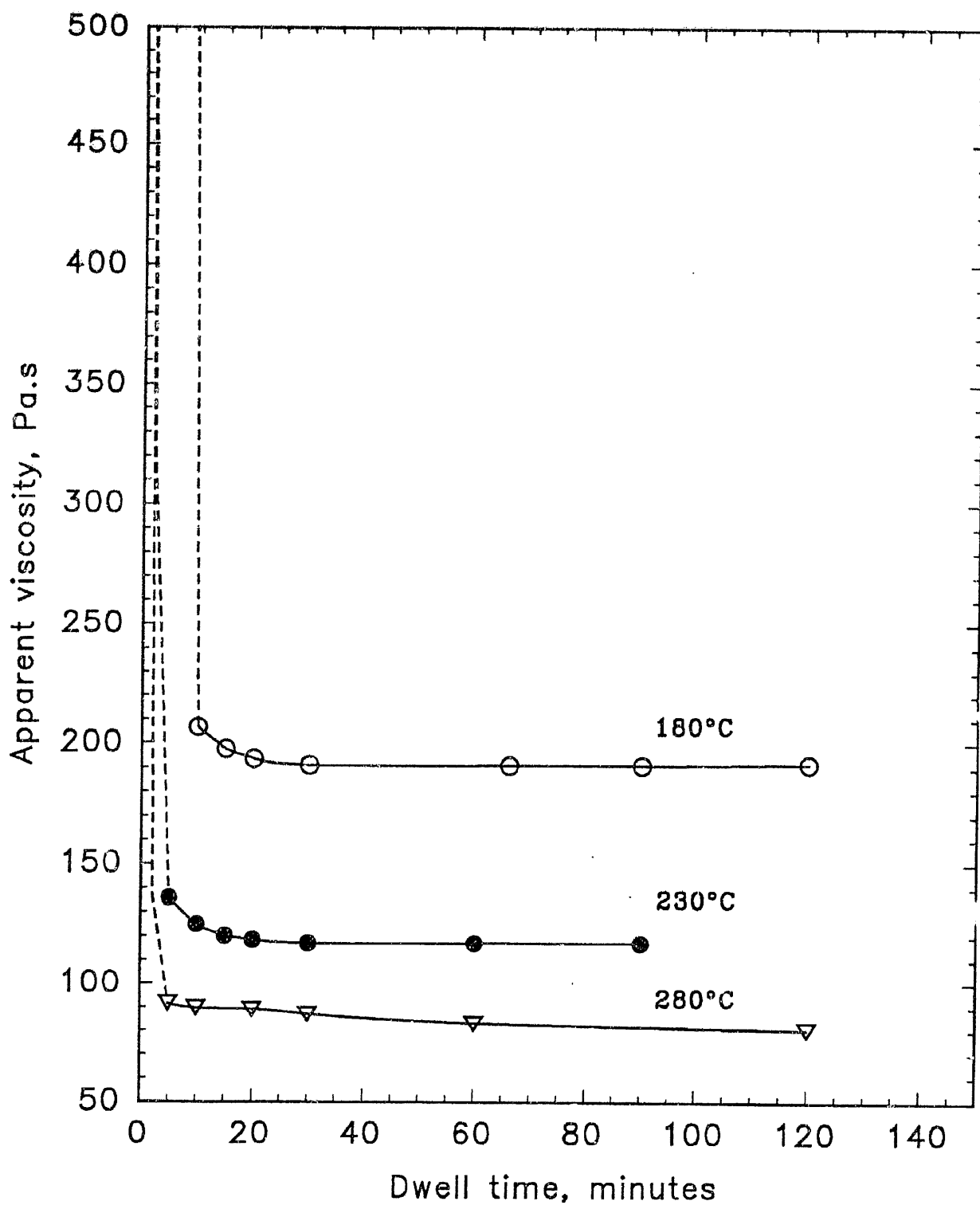


Figure 3. Apparent viscosity of filled polypropylene, measured with the Racer capillary rheometer, as a function of dwell time.

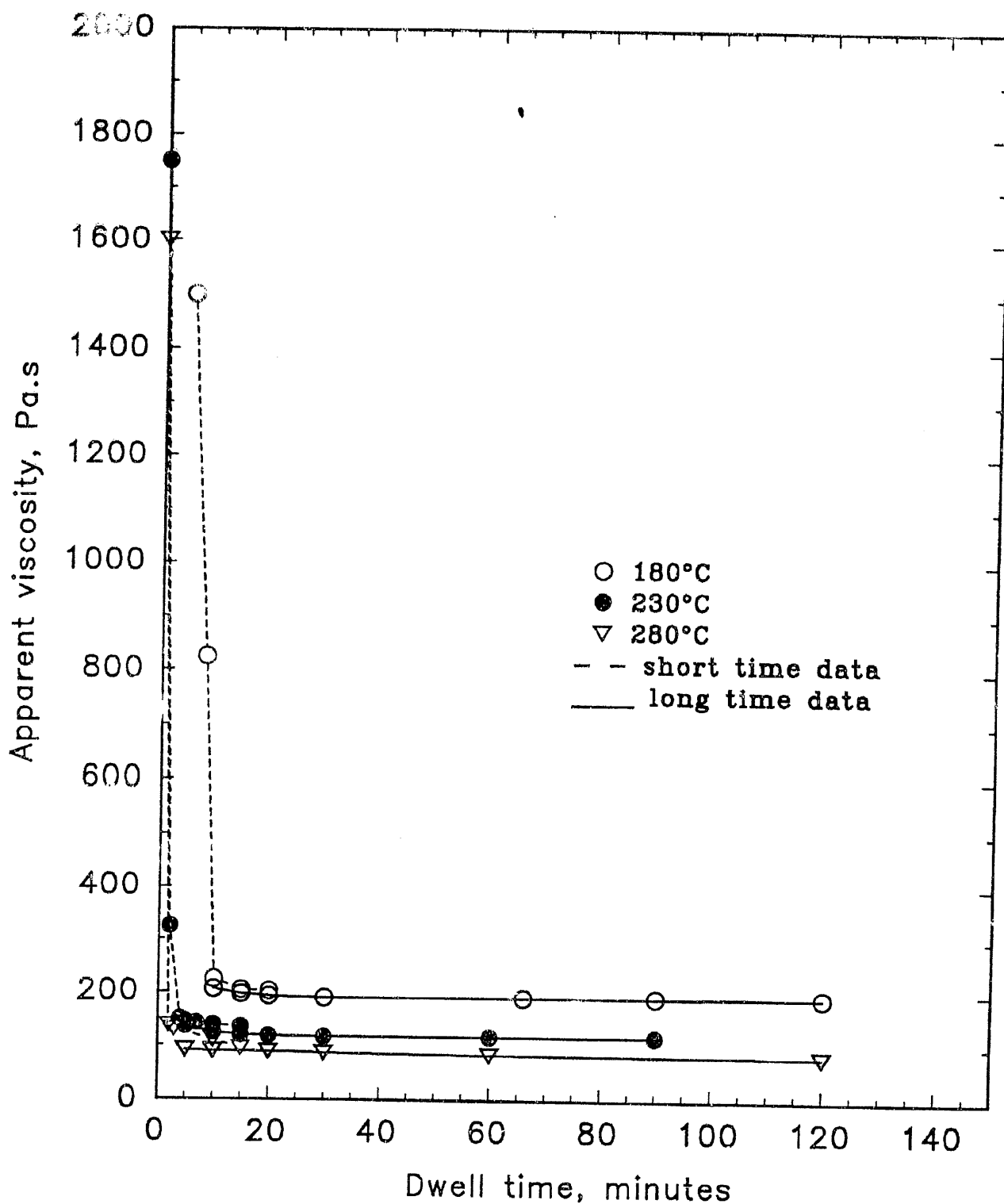


Figure 4. Apparent viscosity of filled polypropylene, measured with the Racer capillary rheometer, as a function of dwell time. Short time data was measured with a 0-1000bar transducer, long time data was measured with a 0-200bar transducer.

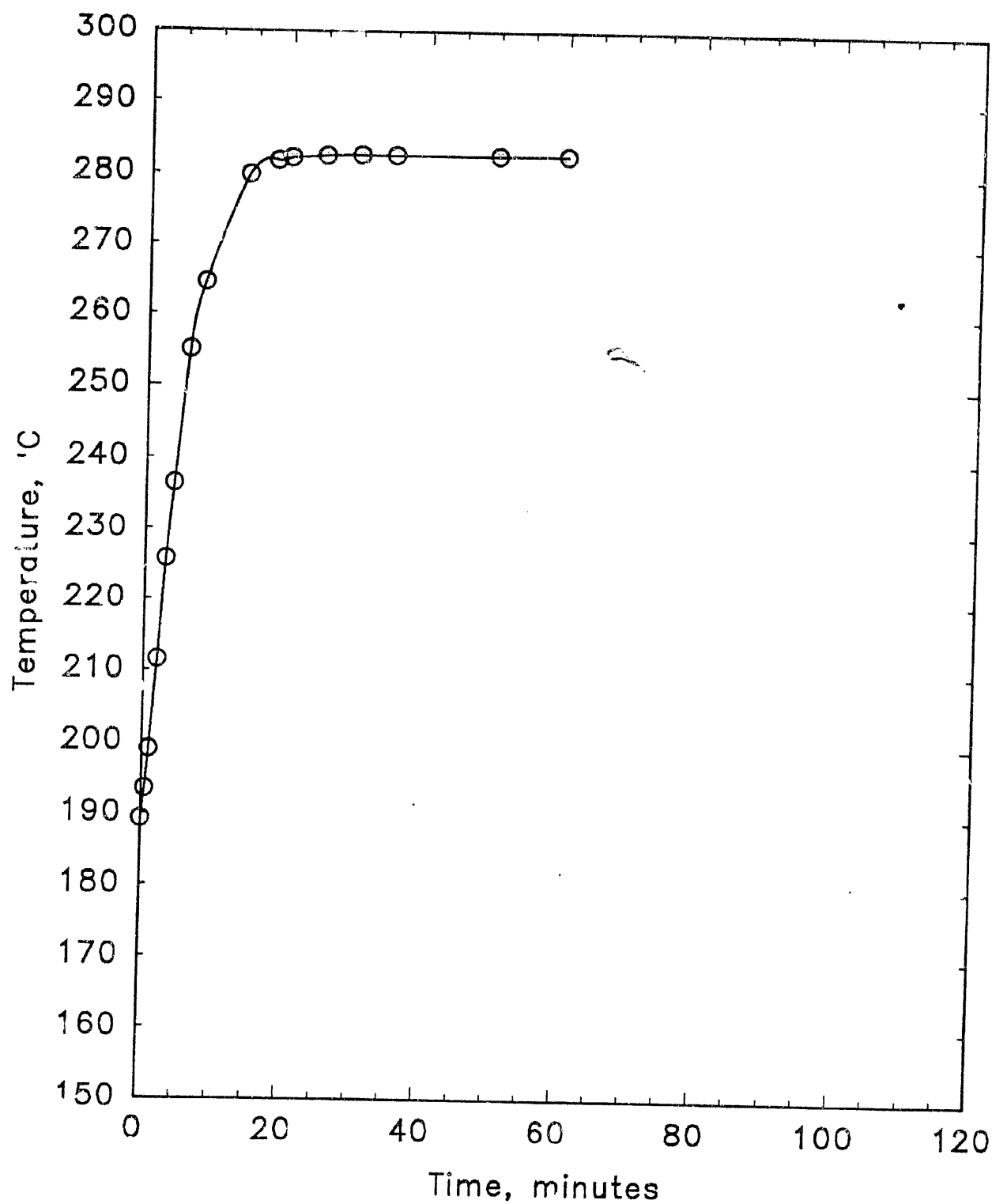


Figure 5. Temperature gradient of filled polypropylene, measured with the Racer capillary rheometer, as a function of dwell time.

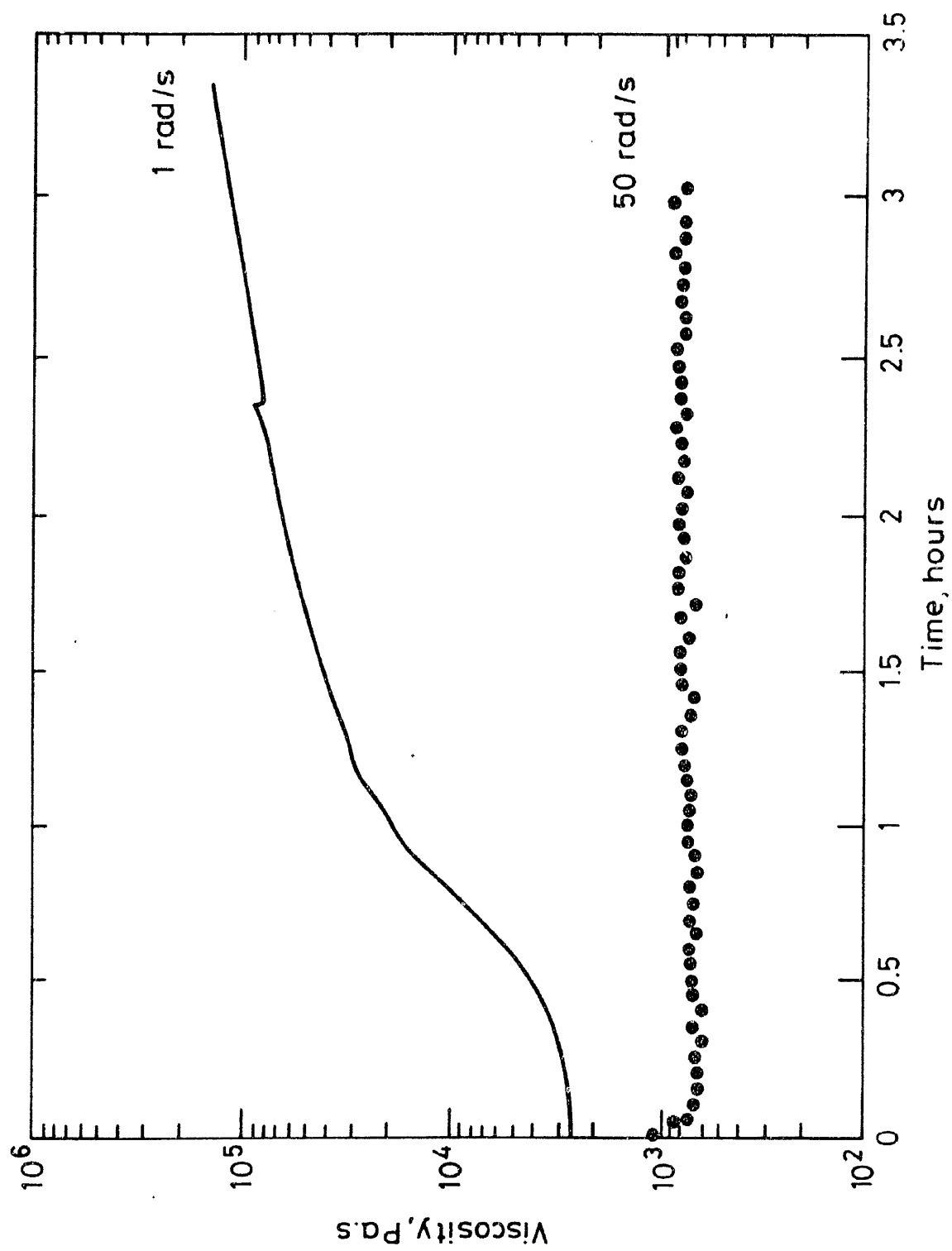


Figure 6 Rotational rheometry of filled pp at 230°C showing an increase in viscosity only when measured at low strain rate (1 rad/s), after reference (6)