

**Industrial need for
extensional
viscoelasticity
measurements**

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ABSTRACT

This report presents the findings of a survey of industrial needs for extensional viscoelastic measurements of polymer melts that was carried out as part of the project MMP11: Measurement of extensional viscoelastic properties of polymers. A range of industrially relevant materials and the conditions of temperature, strain and strain rate at which they are processed, for example in film extrusion, film blowing, profile extrusion and blow moulding, were identified. The main applications for an extensional measurement technique were considered to be for materials development and selections purposes.

Maximum process temperatures for these processes and polymers are up to approximately 300 °C although the majority of requirements for extensional viscoelastic measurements are lower, typically below 260 °C. Estimates of Hencky strains and strain rates in processing were typically in the range 0.2 - 2 and 0.3 - 5 s⁻¹ respectively. Significantly lower strain rates are appropriate for characterising the parison sag behaviour of materials.

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MMP11: Measurement of extensional viscoelastic properties of polymers,
a project of the Department of Trade and Industry EAM programme
on measurements related to the processability of materials

Approved on behalf of Managing Director, NPL
by Dr M K Hossain, Director, Centre of Materials Measurement and Technology

CONTENTS

1.	INTRODUCTION.....	1
2.	INDUSTRIAL REQUIREMENTS FOR EXTENSIONAL VISCOELASTICITY MEASUREMENTS	1
3.	CANDIDATE MATERIALS IDENTIFIED FOR INVESTIGATION	5
4.	CONCLUSIONS.....	5
5.	ACKNOWLEDGEMENT	5
6.	REFERENCES.....	6

1. INTRODUCTION

This report presents the findings of a survey of industrial needs that was carried out as part of the project on the measurement of extensional viscoelastic properties of polymers (project reference MMP11, milestone 1). The project addresses the development and assessment of methods for characterising the extensional viscoelastic behaviour of polymer melts. It is one of a number of projects on measurements related to the processability of materials that are funded by the Engineering, Automotive and Metals Division (EAM) of the Department of Trade and Industry. The first two main objectives of this project are:

- To review existing methods for measuring the parameters that describe the viscoelastic behaviour of polymeric materials under stress fields that are predominantly extensional,
- and to develop new methods, as required, that will allow measurements to be made at extensional strain rates comparable with those encountered during industrial processing.

The objective of the first stage of this project (milestone M1) was to determine the requirements of the polymer processing industry for extensional viscoelasticity measurements. This will help establish the specification of the instrument that is to be developed at the National Physical Laboratory (NPL) so that it may most appropriately meet the needs of UK industry. The objectives were, specifically, to choose suitable industrially-relevant materials and to set upper limits on the testing conditions of temperature, strain and strain rate at which properties data for those materials are required. These needs were identified through industrial visits, telephone interviews and through the first industrial advisory group (IAG) meeting held at the NPL on 6 July 1996. The processing techniques that were targeted were blow moulding, extrusion, film blowing, film extrusion and thermoforming. In establishing the specification for the equipment the processes of fibre spinning, wire coating and injection moulding were not considered as the experimental approach of contraction flow analysis is potentially more suited to providing data as it more closely mimics these processes. However, data on these processes are presented for completeness to establish the upper limits of strain and strain rates for use in the assessment of the contraction flow methods that is to be carried out in a separate phase of this project (milestone 2). Milestone 1 has also contributed to an improved understanding and development of the preferred dissemination routes for the work to industry.

2. INDUSTRIAL REQUIREMENTS FOR EXTENSIONAL VISCOELASTICITY MEASUREMENTS

Several general observations were made in telephone conversations and during industrial visits that were carried out as part of the assessment of industrial needs. Convertors tended to rely upon the material producers/suppliers for providing materials of certified quality. In some cases no in-house testing of raw materials was carried out: the emphasis was placed on testing of the manufactured product. Several convertors carried out limited tests on the raw material. Materials suppliers provide processing properties data although this was often limited in scope. Several processors desired more processing properties data than was in some cases available. Materials suppliers were also experiencing increased pressure to provide flow simulation services to users thus demanding increased quantities of processing properties data for their materials. Thus the main emphasis for materials testing is placed upon the materials producers.

The main application for an extensional measurement technique for materials suppliers was

for use in materials development, and for convertors it was for materials selection. In pre-selecting candidate materials using such a test method substantial savings in trial or small-scale production runs could be obtained. In addition, there were requirements for quality control applications as existing methods were considered inadequate in differentiating between batches of material with which processing problems had occurred.

The dissemination of this work should therefore be aimed primarily at the materials supply part of the chain and at convertors for whom material selection was an important part of the production process.

The cost of equipment was considered to be an important factor in the uptake of the technology as companies are under increasing pressure to control or reduce costs on research and development.

In establishing the specific requirements for materials data a feature of the assessment was that a number of contacts had limited understanding of the strains and strain rates that were occurring during processing. Even an examination of the literature revealed little detail about the strains and strain rates. This emphasises the importance of the proposed workshop's educational role but makes precise specification of the requirement for extensional viscoelasticity data more difficult.

Materials and maximum processing temperatures

Materials that predominantly featured in this assessment were PE and PP, Nylon, PET, PC, PVC. Maximum processing temperatures were typically up to 210 °C for PE, 260 °C for PP, 240 °C for Nylon 6, 300 °C for PET and 190 °C for PVC (see Table 1) although temperatures at which stretching of the material occurs can be significantly lower. For example, the upper temperature limit for PET is associated with injection moulding of the parisons for subsequent blow moulding. Injection moulding tends to be dominated by the shear rather than extensional flow behaviour of the material. Thus characterisation of the extensional flow behaviour of PET at 300 °C is of less importance. In comparison, the temperature of the PET parison during inflation in bottle blowing is likely to be of the order of 110 °C. Similarly, for film blowing of PP the maximum temperature of 260 °C is for the polymer exiting the extruder die. Subsequent inflation of the film bubble occurs at approximately 160 °C. However in blow moulding of nylons, PBT and thermoplastic elastomers the inflation temperatures tend to be similar to their extrusion temperatures. In summary, the majority of requirements for extensional properties data would be covered by measurements at temperatures up to 260 °C but often significantly lower than this. The exception to this would be for extrusion and injection moulding of PET in which case it may be up to 300 °C.

Strains and strain rates

There are two types of strains that can be quoted, either Cauchy ε_c or Hencky ε strains (1) and it is important that the difference between these two is clearly identified as their values for the same flow field can differ significantly (for rheological nomenclature see reference 2). In addition to these two terms there is also the commonly used and quoted elongation ratio (ER) that is the ratio of the current length l to the initial length l_0 .

$$ER = l/l_0.$$

The Cauchy strain ε_c is given by the ratio of the change in length δl to initial length l_0 of the sample:

$$\varepsilon_C = \delta l / l_0.$$

and the Hencky strain ε (also referred to as the natural or true strain) by the natural logarithm of the elongation ratio

$$\varepsilon = \ln(l/l_0)$$

The elongation ratio is related to the Cauchy strain by $l/l_0 = 1 + \delta l/l_0$. To illustrate the difference between these values a sample that has been stretched to 10 times its original length has a Cauchy strain of 9 and a Hencky strain of 2.3.

The rate of change of Cauchy strain with time is given by

$$\dot{\varepsilon}_C = 1/l_0 \times \partial l / \partial t.$$

and of Hencky strain by

$$= 1/l \times \partial l / \partial t.$$

In describing and modelling plastics processing the Hencky strain is preferred as the rate of strain of an element of fluid within the flow is independent of its original length and is determined only from the velocity field of that element. It is thus a more suitable characteristic of the flow.

Estimates of uniaxial Hencky strains and strain rates that occur in processing are presented in Table 1. Some of these values were calculated on the basis of process dimensions and velocities and should be taken as broad estimates rather than precise values. In the case of biaxial deformations they were estimated based on velocities in one direction only and are therefore taken to be representative of the flow.

From the values presented in Table 1 it is apparent that the strains and strain rates of processing typically lie in similar ranges for all the processes, with the exception of wire coating and some extrusion processing. Hencky strains were typically in the range 0.3 - 2 (equivalent to elongation ratios of 1.4 - 8) and strain rates in the range 0.03 - 4 s⁻¹ (equivalent to 3 - 400% extension per second). Two organisations suggested that measurements should be available preferably up to 5 and 10 s⁻¹.

In bottle blowing an important criteria was the melt strength of the parison. This property defines its ability to maintain the parison shape under the force of gravity prior to inflation - ie parison sag. Upper limits of Hencky strains for parison sag were estimated to be of the order of 0.2 - 0.4 (25 - 50% extension) occurring at strain rates of less than 0.03 s⁻¹.

Strain rates for wire coating and fibre spinning were significantly higher, possibly up to 1000 s⁻¹. These two processes are more akin to the experimental technique of contraction flow analysis for determining extensional viscosities (3,4,5) rather than stretching techniques and were thus not included for establishing an upper limit to the strains and strain rates for the latter. These techniques are to be assessed in a separate phase of this project.

In addition, extensional flow measurements were also considered relevant to extrusion of polystyrene foams where the bubble growth is controlled, in part, by the extensional flow behaviour of the resin.

Melt fracture

Of significant importance, particularly in the film extrusion and fibre spinning is that the melt

should not fracture as this then requires costly re-setting up of the production process, excessive waste and lost production. Maximum production output rates and efficiency is often a balance between minimising film thickness and avoiding melt fracture. The ability of a technique to characterise the fracture characteristics of melts in extension is therefore seen as being highly desirable. Melt fracture is also undesirable in other processes, for example blow moulding and thermoforming. Establishing a method and procedure based on the proposed technique for characterising melt fracture would improve materials development and selection procedures.

Table 1 **Various estimates of processing conditions.**

Process	Materials	Process temperatures, °C (temperature of stretching process in brackets)	Elongation ratio	Hencky strain	Hencky strain rate, 1/s
Blow moulding	PA6	240	5	1.6	3.2
	PA66	280	5	1.6	3.2
	PBT	240	5	1.6	3.2
	PET	270-290 (90-110)	5	1.6	-
	thermoplastic elastomer	220	5	1.6	3.2
Film blowing	PE	170-260	-	-	-
	PET	270-290 (90-110)	5	1.6	1
	PP	240 (160)	8	2.1	1.6
	PP	230	1.4	0.34	up to 10 s ⁻¹ preferred
	PP	-	4	1.4	1
	PP	240 (140-150)	6.5	1.9	1.1
Film extrusion	PP	255	-	-	-
	PET	300	1.4	0.34	up to 10 s ⁻¹ preferred
	PET	270-290 (90-110)	5	1.6	1.6
	PET	270-290 (100-120)	4.5 - 5	1.4	1.2 s ⁻¹ , up to 5 s ⁻¹ preferred
Extrusion	PE	200	4.7	1.5	0.03
	PE	210 (105)	4	1.4	0.05
	PE	200	8	2.1	1
	PP	230 (130)	4	1.4	0.05
	PVC	160-210	-	4	5.5
Wire coating	EVA	150-160	35	3.6	<1000
	PE	190-210	35	3.6	<1000

3. CANDIDATE MATERIALS IDENTIFIED FOR INVESTIGATION

A further objective was to identify specific materials of interest that may be used for evaluation of the technique, case studies and for the international intercomparison. A range of potential materials were identified and offered by materials producers (BP, DuPont ICI, Montell UK) and convertors (BICC Cables, Kobe Steel Europe Ltd, Linpac Plastics, Netlon, Stewart & Lloyds Plastics, UCB Films, Van Leer (UK) Ltd) for evaluation by the NPL. These materials principally cover PE, PP, Nylons, PET for use in film extrusion, film blowing, profile extrusion, blow moulding and wire coating. Some of these material have been assessed, or are being assessed, through in-house or external research and development work. Interchange of information related to these materials is likely to occur thereby benefitting this project and the companies and other research organisations involved. Offers of further materials for evaluation of the technique, case studies or for the intercomparison will be considered.

4. CONCLUSIONS

The needs of industry for extensional viscoelastic measurements have been assessed. A range of industrially relevant materials and the conditions of temperature, strain and strain rate at which they are processed, for example in film extrusion, film blowing, profile extrusion and blow moulding, have been identified.

The main applications for an extensional measurement technique were considered to be for materials development and selections purposes and also for trouble-shooting where processing difficulties thought to be due to materials problems were encountered.

Maximum process temperatures for these processes and polymers are up to approximately 300 °C although the majority of requirements for extensional viscoelastic measurements is lower, typically below 260 °C. The upper process temperature of 300 °C corresponds to the extrusion or injection moulding of PET for which characterisation of the extensional flow properties is of less importance.

Estimates of Hencky strains and strain rates in processing were typically in the range 0.2 - 2 and 0.3 - 5 s⁻¹ respectively, excluding the processes of fibre spinning and wire coating. Significantly lower strain rates are relevant to characterising parison sag behaviour.

5. ACKNOWLEDGEMENT

The work reported in this paper was carried out as part of a project on measurement of the extensional viscoelastic properties of polymers (MMP11, milestone 1). This project is part of programme of underpinning research financed by the Engineering, Automotive and Metals Division (EAM) of the Department of Trade and Industry on measurements related to the processability of materials.

The NPL would like to thank all the companies that participated in this study.

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