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# Industrial needs for polymer melt elasticity measurements

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**ABSTRACT**

The industrial requirements for elasticity measurements on polymer melts and rubbers are reviewed. The findings presented are based on discussions held with industrialists from the polymer processing industry and supporting industrial sectors. Industrialists are generally aware that the elasticity of plastics melts and rubbers affects processing and the properties of the products formed, particularly in the processes of extrusion, blow moulding and thermoforming. Examples of processing problems that were considered to be due, at least in part, to the elasticity of the melt are given. It is reasonable to comment that in comparison with shear viscosity, the understanding of elasticity and how it affects processing is limited. Nevertheless, it is generally accepted that elasticity is important for the processes listed above. The review has highlighted the importance of elasticity induced by extensional flow on processing behaviour. Industrially relevant testing conditions for elasticity measurements have been specified. An improved understanding of how elasticity affects processing, and improvements in measurement technology are required to aid industry to process plastics more profitably.

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# 1. INTRODUCTION

This review of the industrial needs for elasticity measurements has been carried out as a preliminary stage of the project financed by the Department of Trade and Industry (DTI) entitled "Polymer moulding models: the determination of the elasticity of polymer melts", also referred to as PMP5. The objective of the review was to identify more clearly the needs of industry for elasticity measurements so that the programme of research can be more closely tuned to meet current and future industrial needs, thus enhancing the value of the project to industry.

The review is based primarily on discussions held with industrialists from the polymer processing industry and the supporting industrial sectors of polymer and test equipment suppliers. The survey has focused on the processes of extrusion, blow moulding, film blowing, film drawing and thermoforming. To a lesser extent the issues raised apply to injection moulding and for this reason this industrial sector has been included, albeit to a lesser degree, in the review.

Before proceeding with the findings of the review on industrial needs for elasticity measurements and data it is desirable to clarify what is meant by elasticity. All polymer melts exhibit a viscoelastic response when subjected to a deformation or force. A viscoelastic response comprises a viscous or non-recoverable component, and an elastic or recoverable component. The ISO standard on terminology for plastics (ISO 472) defines *viscoelasticity* as *"The stress response of a material acting as though it were a combination of an elastic solid and a viscous fluid with flow dependent on time, temperature, load, and rate of loading"*. Also, ISO 472 defines *elasticity* as *"The property of recovering original size and shape when deforming forces are removed"*, and *viscosity* as *"The property of resistance to steady flow exhibited within the body of a material"*. In the context of polymer processing it is perhaps misleading to discuss the elasticity of the melt. It is the viscoelastic behaviour, the relative contributions of the elastic and viscous components to the overall flow behaviour that is important. In using the terms elastic behaviour or elasticity herein the terms viscoelastic behaviour or viscoelasticity are implied.

It is emphasised that a polymer melt can respond viscoelastically to a shear deformation, an extensional deformation or to any complex deformation. A statement of the relative importance of these deformation modes in processing is made, though discussion is not restricted to one form of deformation unless otherwise specified.

The phenomena described herein as being elasticity related are generally complex. Their behaviour is governed by the full viscoelastic response of the material to the imposed deformation or force, and to thermal and physical effects. No attempt is made to definitively relate the rheological, thermal and physical properties to the phenomena described.

## 2. THE NEED FOR MELT ELASTICITY MEASUREMENTS

### 2.1 GENERAL

The need for elasticity measurements can be broadly categorized into the three main areas, namely:

materials characterisation;

process design;

product properties.

These three areas obviously have overlap in that materials characterisation is necessary for process design and predicting product properties, and that process design has obvious implications for product properties. However it is desirable to divide the topic of elasticity into these three categories for convenience. Each of these is considered in turn below.

### 2.2 MATERIALS CHARACTERISATION

A primary reason stated for materials characterisation is to enable comparison of materials, either nominally of the same grade, or of different grades or polymer type. The former is for quality control and/or trouble-shooting purposes to check the consistency of materials supply. In trouble-shooting the need is to identify whether it is the material that is causing the production problem, eg increased extrudate swell or melt fracture. In this respect a qualitative technique is required that is sensitive to the variations in the material's properties and can be correlated to the processing behaviour.

The need to compare different grades of the same polymer type or of different types is to meet several requirements expressed by processors and materials suppliers. Comparison of materials is necessary for evaluating the suitability of new or untried materials grades for the particular process in question. It was considered desirable to have a more rapid technique for screening of candidate materials rather than embarking on costly processing trials (small scale or otherwise) and for this purpose a qualitative technique that is sensitive to the relevant materials properties is necessary. The potential benefits that could be obtained through the use of improved screening methods to identify materials of better performance are increased production rates and reduced scrap rates .

Materials characterisation was identified as an essential part of the development of new materials, in particular to obtain materials of pre-specified behaviour. In this context the characterisation of the material has to be relevant in that one must be able to correlate the data obtained to the behaviour of the material in processing.

The relative contribution of elasticity to the overall flow is related to the temperature at which the material is processed: at higher temperatures the flow is dominated by viscous effects, but at lower temperatures it is dominated by elastic effects. Injection moulding is carried out at temperatures up to 100 °C higher than the melt temperature, whereas blow moulding is carried out at temperatures near the melt temperature. On this basis the flow occurring in blow moulding will be more elasticity dominated than that occurring in injection moulding. Similarly, the degree of elasticity of the flow is related to the rate of flow: a higher rate process exhibits greater elastic effects. Thus in characterising the elastic behaviour of polymers it is necessary that the test conditions are similar to the conditions of processing if the measurements are to be of maximum value.

The most stringent requirement for materials characterisation is for process design for which quantitative data are needed. This will be considered in more detail in the next section.

## 2.3 PROCESS DESIGN, CONTROL AND DEVELOPMENT

One of the primary aims of process design is to get it right first time thereby minimising development and tooling costs and also reducing lead times. A specific aim expressed by one process designer is to minimise processing problems by minimising the maximum shear rates occurring in the process. Also, it is desirable to design the process so that it has as large a processing window as possible while still producing acceptable products. This would, in particular, make the product quality less susceptible to variations in materials supply and processing conditions.

Increased production rates were viewed by industrialist as being desirable, but it was stated that product quality was often a more important factor. Thus there is a balance between production rates and product quality. In many processes the cooling rate is the major limiting factor in production speed. However, a factor related to the elasticity of the melt that limits production output rates is the occurrence of extrusion instabilities, leading in the extreme form to melt fracture.

The relation between the elasticity of the material and product defects was raised by several organisations, the most commonly quoted defects being sharkskin and melt fracture of the extrudate. In extrusion, surface defects and melt fracture of the extrudate can be costly in terms of increased scrap rates and lost production time. Melt fracture and poor surface finish can also occur in blow moulding in the extrusion of the parison where, if tip shut-off is used to cut the parison from the extruder, high shear rates occur. Materials suppliers and processors thought that the understanding of the link between the elasticity of the material and processing phenomena needs to be improved. Through that improved understanding processors will be more able to avoid or minimise processing problems.

## Extrusion

In extrusion processing a key property is the dimensional tolerance of the extrudate, although in extrusion of axisymmetric profiles, ie rod or tube sections, it was commented that this is not a problem where haul-off methods are employed as a means of controlling the dimensions of the extrudate. However, haul-off cannot be used to control independently both the wall thickness and internal diameter, as would be necessary where both dimensions are included in the product specification.

The design of dies for extrusion is carried out often by trial and error procedures based on past experience, and is generally in the hands of a few individuals. A compounder/processor felt that this is an unsatisfactory commercial situation to be in, and that it is desirable to replace the "black art" with modern techniques. It was found that even with experienced die designers metal has to be cut normally two or three times before a suitable, and certainly not optimised, extrudate could be obtained. Modelling of extrudate swell, and thus the prediction of die shapes is viewed as a critical element in improving die design. The benefits would be improvements in die and process design which would result in reduced development lead times and improved product properties.

## Blow moulding

In the extrusion of parisons for blow moulding it is desirable to vary the parison wall thickness to control the wall thickness of the blown article. This requires an ability to predict the extrudate swell of the parison so that the wall thickness can be controlled either by varying the aperture through which the material is extruded (moving core technique), or by varying the flow rate. In addition viscoelasticity data are needed to predict the deformation occurring during the blowing of the parison to form the article and hence to yield its final wall thicknesses.

In blow moulding the occurrence of parison sag, that is the stretching of the extruded parison under gravity, can present processing problems particularly where the rate of sag varies as a consequence of material variability or changes in processing conditions. There is a need to reliably predict and control parison sag in order to optimise processing. The opinion was expressed that a "shop-floor" guide for process operators on the control of parison dimensions is needed.

## Film blowing

In film blowing the elasticity of the material affects the shape of the blown bubble, and thus the dimensions of the product formed. A primary requirement is to avoid bubble fracture and to control bubble shape and stability. To predict the bubble shape relevant elasticity data are required.

## Film extrusion

In comparison with film blowing the role of elasticity in film extrusion was considered to be of less importance as the film extrudate thickness is controlled by haul-off drums. However, elasticity plays a role in the Stenter film stretching process. The effect is more on the development of structure, orientation and frozen-in stress rather than on product dimensions which are physically controlled by the process. In both film blowing and film extrusion elasticity can affect surface finish which is an important aspect of product quality.

## Thermoforming

In thermoforming of sheet film the sheets can distort on heating prior to forming due to frozen-in elastic stresses. The prediction of product thickness requires a knowledge of how the sheet is deformed, and hence the viscoelastic behaviour of the material. Sag of the material prior to the forming operation is undesirable and needs to be minimised. As thermoforming is carried out below the melt temperature elasticity plays a significant part in processing and consequently has a significant influence on the product properties, particularly of dimensional stability. In the thermoforming of multi-layer films stress incompatibilities at the interfaces will be generated if the layers exhibit different stress responses (the deformations being the same in layers at adjacent points) and might result in possible interlaminar failure.

## Injection moulding

Elasticity is thought to play a more minor role in injection moulding compared with the above mentioned processes. Nevertheless it is considered to contribute to the jetting of melt into the mould, flow front behaviour, interface distortion in co-injection moulding and in the generation of frozen-in stresses at the melt-solidification boundary layer. Also, elasticity is likely to have an effect in regions of extensional (or stretching) flow, for example in flows into and from gates. One point of interest raised was on the apparent correlation between extrudate swell behaviour and the surface appearance of injection mouldings with long flow paths. This is possibly due to flow front fracture. Elasticity in the form of bulk modulus of the melt was considered to be important in the packing phase. Both underpacking and overpacking of the melt can results in poor product quality, in particular with respect to dimensional accuracy.

## Polymer processing flow simulation models

There are a number of polymer flow simulation packages that are commercially available that can be used for process design. They cover a range of applications and are of varying complexity. For example, Polyflow (1) can be used to model extrusion, blow moulding and film blowing using a range of viscoelastic constitutive equations to describe the fluid's behaviour. It is based on programs developed at the University of Louvain in Belgium. Polyflow is perhaps one of the more advanced flow simulation packages and is used and being evaluated by some of the more major companies. The data needed for use with Polyflow can be obtained from oscillatory, continuous shear, normal stress and step-strain measurements performed using rotational rheometers and from capillary rheometry measurements.

Other commercially available flow simulation packages with capability to model viscoelastic behaviour include C-PITA (2) and POLYCAD (3). C-PITA is used for simulating thermoforming and film blowing. It is based on programs developed by General Electric. Elasticity is incorporated into the package using the Ogden-Rivlin and Rivlin-Mooney elasticity models. The elasticity data are determined from measurements of film blowing.

POLYCAD (3), which was originally developed at McMasters University in Canada, can be used to model extrusion, injection moulding, blow moulding, wire coating, thermoforming, calendering and mixing. In publicity literature on POLYCAD it is claimed that correlations for normal stress (elasticity) and elongational viscosity data are used with some degree of success. In modelling the thermoforming process elasticity is incorporated either using an Ogden model for elasticity, or the KBKZ viscoelastic model incorporating a Wagner damping function.

The more commonly known polymer flow simulation packages, eg Fillcalc (4) and Moldflow (5), do not have commercially available viscoelastic models, primarily as they appear to have focused on the market of injection moulding for which viscoelasticity is perceived to be of less importance than, for example, in extrusion.

It can thus be seen that the flow simulation models that are commercially available require the full spectrum of rheological data, from the purely viscous models through the range of viscoelastic models to the purely elastic models. Comment is made in publicity literature for POLYCAD that "Needless to say that without good material property data we cannot solve practical problems in polymer processing." This statement highlights one of the primary problems with flow modelling for design purposes: that the data, where available, are of questionable validity for the application.

Comments that are applicable to numerical simulation packages in general are that expert staff are required to run the packages to achieve the best results most efficiently, and that the packages are expensive for SMEs to purchase. The user friendliness of such packages has improved in recent years, though it can still present difficulties particularly when the use of the software is intermittent.

## 2.4 PRODUCT PROPERTIES

Although this review is a part of a project on polymer melts it is necessary to consider the impact that elastic stresses have on product performance. Elastic stresses are generated in the melt during processing and are then subsequently frozen into the product on cooling. For example, in film manufacture the rolls of film produced are often kept in storage before distribution, at significant expense, to allow relaxation of the frozen-in stresses to occur.

The presence of frozen-in stresses in a moulded product can be made apparent by reheating that product: this can be dramatically demonstrated in the case of thermoformed products where processing occurs at relatively low temperatures resulting in a predominantly elastic rather than viscous deformation. Thermoformed products on reheating can almost return to their pre-formed shape, ie a very significant heat distortion. By careful selection of materials and processing conditions the elastic stresses frozen into a moulding could be minimised thereby improving the product quality and performance. Alternatively, control of flow-induced elastic stresses might be desirable where the molecular orientation results in higher values of material properties eg modulus in specified directions.

A further example of the effect of frozen in stresses is in processing of rubbers in which the elastic shrinkage of extruded tread sections can result in complications in cutting of treads to accurate length for tyre lay-up. A tread must be cut to length to allow for subsequent relaxation shrinkage. Variations in the material affecting its swell behaviour will affect both the extent and rate of shrinkage thereby potentially causing production problems. Variations in the compounding of rubbers and therefore in their properties is a particular problem which is related to the lack of control on the specification of the ingredients of the rubber compound, in particular the specification of the base polymer and the carbon black. A similar problem in wire coating is that the insulating sheath can shrink along the length of the conductor. For accurate prediction of orientation effects in all polymer processes a knowledge of the viscoelastic behaviour is critical.

In multi-layer products, for example in films and blown bottles, the different elastic behaviours of the component polymers are thought to cause interfacial problems and distortion, presumably due to the incompatibility of stresses at the interface. To design processes to minimise the stress imbalances generated at interfaces in multi-layer products viscoelasticity data are needed.

## 2.5 TECHNIQUES CURRENTLY USED

The most commonly used technique by those surveyed for characterising the elasticity of polymer melts is by measurement of the extrudate swell, despite there being reported many complications in using this technique and the poor reproducibility of results obtained (the term 'die swell' is also used). As an example, one company that had used the method in the past has stopped using it due to the poor repeatability of results, for as yet unknown reasons. Nevertheless, the comment was made by that company that they would prefer to carry out extrudate swell measurements as the method possesses considerable advantages over other techniques. Extrudate swell measurements can be made at flow rates similar to those occurring in processing. Also, it is a measure of the shear and extensional viscoelastic effects. A second company commented that they want a standardised method for measuring swell behaviour. It was commented that there was poor correlation of extrudate swell measurements with other techniques. None of the companies commented that they carried out interpretation of the raw data in terms of elasticity parameters.

A specific point raised by the rubber industry was the need for measurements of the elastic modulus of uncured rubber in both the tensile and shear modes, ie the elasticity of low modulus materials.

Oscillatory and rotational rheometry, rheo-optics, flow birefringence, bubble growth/stability and fibre spinning are used by one research based organisation to characterise polymer melt elasticity: this kind of effort was not visible within production environments. One major processing company commented that they could not justify having in-house normal stress measurements using a rotational rheometer unless it was demonstrated that there was a strong correlation of normal stress data with processing behaviour. Such rheometers are expensive and would represent a major investment for small and medium sized companies.

A capillary rheometer has been used by one company to measure the relaxation of the bulk compressibility (or bulk modulus) of the polymer, although comparison of the behaviour of different materials is complex as the relaxation rate as measured is also a function of the shear and extensional viscosities of the material. The compressibility of polymer melts is of importance for extruder output stability. Entrance pressure drop data, also obtained from capillary rheometry measurements, have been used to determine the elasticity of melts. However the validity of this approach is questioned.

Parison sag measurements are made by one organisation to characterise the viscoelasticity of melts used for extrusion blow moulding. This technique has the potential benefit over other techniques in that it characterises the viscoelastic behaviour in extension rather than in shear and is thus more akin to the deformation mode occurring in blow moulding.

## 2.6 SPECIFIC MEASUREMENT REQUIREMENTS

In this section the aim is to specify the conditions of temperature, shear rate and strain rate over which elasticity data are required. In extrusion and injection moulding the materials are processed in the melt phase, whereas in film blowing, film drawing, blow moulding and thermoforming they are processed at lower temperatures covering the range from below the melt temperature to above the melt temperature. Thus the temperatures at which elasticity data are required cover a wide range, from below the melt temperature to approximately 100 °C above the melt temperature. However at the higher melt temperatures, for example in injection moulding, elasticity effects are considered to be relatively unimportant as the flow behaviour is dominated by viscous forces.

The processes of film blowing, film drawing, blow moulding and thermoforming are dominated by extensional deformations, whereas injection moulding is dominated by shearing deformations. However it is not possible to generalise in this way about the process of extrusion as the dominant mechanism will depend on the geometry and the processing conditions used.

Estimates of the maximum shear rates occurring in the processes described are:

film extrusion: up to approximately 400 $s^{-1}$
parison extrusion for blow moulding: normally up to 600 $s^{-1}$
wire coating: up to 10000 $s^{-1}$ in the die tool, but possibly higher
rubber extrusion: up to 1000 $s^{-1}$
rubber injection: up to 10000 $s^{-1}$
rubber milling: up to 100 $s^{-1}$

Estimates of the maximum strain rates in the processes are not so easy to make. In the various extrusion processes the maximum strain rates are considered to be less than the maximum shear rates but certainly within an order of magnitude of those values. In blowing moulding the strain rates related to parison sag will be very low (<0.1 $s^{-1}$), while the strain rates in the blowing process and in thermoforming will be several decades higher. It is likely that the highest strain rates occur in the process of extrusion. For extrusion wire coating the maximum strain rates were estimated to be approximately 500 $s^{-1}$. Thus there is a need to characterise the viscoelastic behaviour of polymer melts in shear at rates up to 10,000 $s^{-1}$ and in extension at rates up to 500 $s^{-1}$.

There is generally no lower limit to the shear and strain rates for which data are required in modelling as in many processes there will be regions where the shear or strain rates will be zero. However in some of the processes a sensible lower limit will be one that defines the limits of acceptable deformation within the time scale of the process or phenomena under investigation. For example, in predicting parison sag it is possible to define a maximum extension of the parison and the maximum time scale over which that extension is permitted to occur, from which a maximum permitted strain rate could be calculated. For example a permitted extension of 10% over a period of 2 second (from the end of parison extrusion to parison inflation) equates to a strain rate of 0.05 $s^{-1}$.

## 3. DISCUSSION

It is reasonable to comment that the relative contribution of elasticity to flow behaviour in polymer processing is poorly understood. However, it is accepted that elasticity is important and that an improved understanding is necessary to facilitate improvements in processing. This was summed up by the comment made by one company in that they needed to understand the relevance of elasticity to processing. To achieve this the measurement capability needs to be improved.

Extrusion, blow moulding, thermoforming and film blowing are processes in which phenomena occur that are attributable largely to elasticity effects. Numerous examples of processing phenomena related to elasticity have been presented. Perhaps with the exception of extrusion, these processes are predominantly extensional flow dominated. The relative contributions to the processing behaviour due to elasticity induced by shear flow and extensional flow is poorly understood. It is pertinent to note that all the established techniques for measurement of elasticity characterise the fluid in shear deformation, with the exception perhaps of extrudate swell measurements which characterise the polymer in a complex flow comprising of both shear and extensional components. The use of the capillary rheometer for measuring extrudate swell was considered to be a suitable and preferred technique for characterising the elasticity of polymer melts. However, it was commented by industrialist that there is need to improve this measurement method, particularly with respect to the poor repeatability of results. Other techniques used by industry include measuring parison sag and rotational rheometry although both are limited in their measurement ranges.

The relative contribution of elasticity to the overall flow is related to the temperature at which the material is processed: at higher temperatures the flow tends to be dominated by viscous effects, but at lower temperatures it is dominated by elasticity. Similarly, the degree of elasticity of the flow is related to the rate of flow: a higher rate process exhibits greater elastic effects. The maximum shear and strain rates occurring in the polymer processes of interest are estimated to be up to approximately 10000 $s^{-1}$ and 500 $s^{-1}$ respectively. At the other extreme there are no lower limits to the shear and strain rates which are required for modelling purposes as rates tending to zero occur in all processes. Viscoelasticity data are needed for the above specified shear and strain rate ranges at temperatures ranging from below the melt temperature up to approximately 100 °C above the melt temperature. However the required combination of test conditions of shear rate, strain rate and temperature is defined by the requirements of the particular process. In generally, the higher rate processes tend to be those that occur at higher temperatures.

## 4. CONCLUSIONS

A large number of phenomena which cause problems or complications in polymer processing are thought to be due, at least in part, to the elastic behaviour of the polymer melt. The relative importance to processing behaviour of elasticity effects induced by shear and extensional flows needs to be clarified.

A significant proportion of the research work on the development of measurement techniques should be on the measurement of elasticity that is induced by extensional deformation rather than by shear deformation if the work is to be of maximum industrial relevance.

The viscoelastic behaviour of polymer melts needs to be characterised at strain rates up to 500 $s^{-1}$ and at shear rates up to 10000 $s^{-1}$ and at temperatures from below the melt temperature to approximately 100 °C above.

In particular there is need to establish a repeatable and reproducible procedure for carrying out die swell measurements as a means of characterising the viscoelastic behaviour of polymer melts.

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