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Review of the need and measurement methods for multi-axial extensional testing of polymer melts

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Review of the need and measurement methods for multi-axial testing of polymer melt rheology

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ABSTRACT

A review of the methods for measuring multi-axial extensional viscosity of polymer melts is presented. The unique rotating clamp multi-axial extensional rheometer developed by Meissner represents the current state of the art in measurement technology, with capability for measurement in various modes of deformation and more recently at elevated temperature for polymer melts. Techniques that approximate to controlled measurements (measurement in which the applied strain rate or stress is constant) include the bubble inflation and the lubricated squeeze flow methods. However, use of these approximate methods is still very limited.

Several factors may influence the need for methods to determine multi-axial data. Firstly, there have been recent significant advances in constitutive modelling that enable the prediction of multi-axial properties with greater confidence. Secondly, there is evidence that indicates that upper and lower bounds to multi-axial extensional viscosity data are given by uniaxial extensional viscosity and simple shear data. Finally, the greatest additional strain hardening is exhibited by uniaxial extensional data and is thus a more suitable property for discriminating differences in materials as necessary, for example, for materials selection of for quality control. Combining these factors the need for experimental methods for determining multi-axial data is considerably reduced, especially considering the difficulty of such measurements.

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CONTENTS

1 INTRODUCTION

Measurement of the multi-axial extensional viscoelastic properties of polymer melts, represented most commonly by equi-biaxial and planar extensional viscoelasticity, is not simple. Such properties affect the processing of polymer melts into a myriad of products although they are predominantly for the packaging sector which, in terms of tonnage of polymer converted, is a very significant sector.

In processing polymers, the melt often undergoes significant extensional deformation. For example in blow moulding, film blowing and vacuum forming the melt undergoes significant multi-axial deformation (due to the complex stress fields in processing, the deformation modes are unlikely to be either planar or biaxial but a complex multi-axial deformation that may vary both spatially and with time). In comparison, in injection moulding the melt undergoes predominantly shear deformation through the thin channels of the mould cavity. Thus to understand and consequently predict how materials behave in processes that involve a large degree of extensional deformation one needs to be able to characterise the extensional flow behaviour of polymers. In those processes in which the material undergoes predominantly multi-axial deformation one can extend the argument to understanding how the material behaves in multi-axial deformation modes. However, and as stated earlier, the measurement of multi-axial flow properties of polymers is not simple, the deformations in processing are not purely biaxial or planar, and the cost/benefit of such measurements in comparison with the benefit of the data available from, for example, uniaxial measurements must be considered. There may be occasions when the measurement of multi-axial properties is essential and then there may be no alternative. However, for many applications it may be that uniaxial data will suffice for the purpose.

Some uses of materials data are for quality control, materials selection and trouble shooting. For such applications comparable data are required, but do not necessarily need not to be quantitatively accurate. Of importance is that the trends in the data are meaningful and therefore qualitative comparisons are sufficient.

An alternative use for materials data is for predicting how the material will behave in processing. Several options exist for predicting how materials will behave in complex extensional flows in processing:

1. Empirical correlation of the material's behaviour in processing with the material's properties, for example melt flow rate, shear viscosity and uniaxial extensional viscosity. Such data are determined using relatively well established and available techniques and are thus more easily and more cheaply available.

2. Modelling how materials will behave in processing based on selected constitutive equations and materials properties data obtained under less demanding flow fields, e.g. shear viscosity, first normal stress difference and/or uniaxial extensional viscosity.

3. Correlation of behaviour in processing with qualitative measures of complex extensional flow behaviour, for example bubble-inflation experiments, lubricated squeeze flow or using small instrumented pilot-lines for film blowing.

4. Through full, accurate quantitative measurement of the multi-axial extensional properties using equipment that imposes well defined and controlled test conditions on the specimen. This approach will still normally require the use of numerical modelling of the process to enable reliable predictions to be made. Also, as deformations are likely to be multi-axial[1] and varying both spatially and with time, rather than always being equi-biaxial or planar for which data could be obtained, then constitutive equations will still need to predict the complex behaviour of the melt.

With respect to the first two options above, there is no a priori reason why knowledge of how the material behaves in shear deformation modes will provide reliable correlation with its behaviour in more complex deformation modes. As far as the third option is concerned, the main issue is that qualitative measurements are often obtained under uncontrolled conditions in which the applied strain rate or stress is not constant, the deformation mode is not always controllable and that often the test conditions are not the same as those achieved in processing. Thus correlation with processing behaviour may or may not work depending of the physical similarity of the test with the process. As in all rheological testing it is desirable to select the characterisation method that mimics as closely as possible the process for which the data are required.

Furthermore, the choice of option is influenced by other factors: not only the availability of the measurement equipment but also of the expertise to measure and apply the data thus generated to practical use, whether through correlation with processing or numerical modelling, and also the availability and reliability of modelling software.

This report addresses the need for multi-axial extensional viscoelastic data and reviews what techniques are available that can supply either quantitative or qualitative data. A summary of papers in the literature along with details of the techniques used is presented in Table 1, and terminology related to extensional flow and properties is presented in the Appendix.

2 NEED FOR MULTI-AXIAL EXTENSIONAL VISCOSITY DATA

A survey of interests carried out at a meeting[2] of industrialists indicated that there was relatively little interest in biaxial extensional viscosity. The two topics related to development of measurement methods for biaxial extensional viscosity scored the lowest of all the topics in its category of measurements for process and product design. Discussion with industrialists suggests that there is interest in extensional viscosity as it is relevant to processes such a blow moulding or film blowing. However, in practice rheological quality control is normally limited to melt flow rate testing, although in practice the amount of even that quality control actually carried out can be minimal. The more complex and expensive (both in terms of capital, time and skill level) capillary extrusion rheometer is used, not normally for routine quality control purposes, but more for trouble shooting and development issues. Furthermore, attempts to obtain a measure of uniaxial extensional viscosity are unusual, except for measurement of the entrance pressure drop. However, the significance of the latter may not always be appreciated to the full. No attempts to measure multi-axial extensional viscosity were identified. Such discussions have led the author to the conclusion that the more immediate need is to encourage

[1] Multi-axial in this respect is a wide range of deformations ranging in nature from near equi-biaxial to planar

[2] NPL Industrial Advisory Group Meeting on Measurement Methods Relating to the Processing of Plastics, Leicester, 11 July 2001.

industry in the use of measures of uniaxial extensional viscosity that are much more easily obtained and may provide sufficiently reliable correlation with process behaviour whether it is predominantly uniaxial or multi-axial in nature. This conclusion is reached also in consideration of the following review of the measurement techniques for multi-axial extensional deformation.

In terms of the need for data, estimates of the conditions occurring in processing indicated that strain rates up to 3.2 s^{-1} and strains of up to 1.6 occur in blow moulding, and strain rates up to 1.6 s^{-1} and strains of up to 2.1 occur in film blowing. Processing temperatures for the stretching phase of blow moulding and film blowing may range from approximately 90 °C to 110 °C for PET, 140 °C to 160 °C for PP, 240 °C for PBT and 240 °C to 280 °C for nylons. Although peak processing temperatures - most often related to the temperature at the exit of the extruder or for the injection moulding of parisons - are likely to exceed these temperatures, it is likely that most of the extensional deformation will occur at these temperatures.

One issue that may influence the need to measure multi-axial extensional viscosity properties is that limits to and trends in such data may be achievable via other rheological properties that are easier to obtain. There is limited experimental data in the literature where a material has been characterised in more than one extensional deformation mode thus making it difficult to make conclusive statements. Nevertheless there is evidence to support the fact that multi-axial data are bound by other rheological functions.

Wagner [1] noted for an HDPE and LDPE that uniaxial and first planar extensional viscosities exhibited similar degrees of strain hardening whereas equi-biaxial viscosity exhibited less additional strain hardening. For the second planar extensional viscosity some strain softening was exhibited by the HDPE but minimal strain hardening for the LDPE (data were conveniently normalised by constants which rescale the extensional viscosity to the time-dependant zero-shear viscosity at small times, i.e. dividing by 3 for uniaxial extensional viscosity, 6 for equi-biaxial extensional viscosity, 4 for the first planar viscosity and 2 for the second planar viscosity). Wagner [1] noted that the strain hardening was more pronounced for LDPE. Meissner [2, 3] and Berger [4] reported that for a polyisobutylene the first planar extensional viscosities exhibited additional strain hardening but the second planar extensional viscosities exhibited strain thinning.

Khan [5] commented that differences in PS, HDPE and LDPE materials due to branching were most clearly pronounced, in terms of the strain hardening response, in terms of uniaxial extensional viscosity values. In comparison, in terms of biaxial extensional and in step-shear there was a less pronounced difference in behaviour between different materials.

Similarly Takahashi [6] reported that additional strain hardening in biaxial deformation was observed, but was not as pronounced as that exhibited in uniaxial extension, and that it is more apparent for polymers having a broad molecular weight distribution. The additional strain hardening in equi-biaxial viscosity at high strains has also been noted by Laun [7] for PIB, Wagner [1] for HDPE and to a greater extent for LDPE, and by Ebrahimi [8] for PS. Again, the magnitude of the additional strain hardening is less pronounced than that observed in uniaxial extensional viscosity. Also, the additional strain hardening in equi-biaxial data at high strains is predicted by the modified POM-POM model, Verbeeten [9], and provided good agreement with the upturn in the experimental data of Wagner [1].

Laun and Schuch [7] commented that there was evidence that the transient uniaxial extensional viscosity represents an upper limit of strain hardening and the transient simple shear represents

a lower limit of strain softening. The first planar extensional viscosity values (normalised values considered as detailed above) were slightly lower than uniaxial extensional viscosity values but with similar strain hardening characteristics. The equi-biaxial extensional viscosity values were very similar to the limiting zero-shear behaviour (linear viscoelastic behaviour). Finally, the second planar extensional viscosity values were between the limiting zero-shear data and the transient simple shear data. Although this was the case for the polyisobutylene at room temperature, the results presented for LDPE indicated that the second planar extensional viscosity values were lower than the simple shear values but the authors indicated that this may well have been due to scatter in results.

Thus the evidence is indicative that the uniaxial extensional viscosity and simple shear data provide upper and lower bounds respectively to the equi-biaxial, first planar and second planar extensional viscosity values. Furthermore the uniaxial extensional viscosity data, which exhibits the greatest degree of strain hardening, provides the best opportunity to differentiate between materials.

Various authors have compared behaviour in multi-axial processing with uniaxial extensional behaviour and found correlations. Macosko [10] commented that different grades of material which performed differently in blow moulding exhibited differences in uniaxial extension at low rates and high extension times (corresponding to high strains), but not in dynamic or steady shear viscosity. Differences were also apparent in the elasticity as measured by the first normal stress difference using cone and plate geometries (almost a factor of x2 difference), extrudate swell (15% difference) and also in melt strength obtained by fibre spinning measurements. Macosko [10] speculated that biaxial measurements may be useful for characterizing materials for blow moulding purposes but presented no evidence in support of that statement. Swerdlow [11] suggested that the rupture in uniaxial deformation can be used to predict rupture in film bubble blowing of LDPE. Kalyon [12] suggested that the best polymers out of VLDPE, LDPE, LLDPE and HDPE for film blowing stability exhibit the highest uniaxial stresses and no strain hardening, and that there was no correlation with shear flow properties. Thus uniaxial extensional measurements have proved of value for understanding multi-axial processes. However, none of these authors correlated the behaviour with biaxial or other multi-axial extensional properties and thus the comment by Macosko [10], that biaxial measurements may be useful for characterizing materials for blow moulding purposes, remains unchallenged.

3 MEASUREMENT METHODS FOR MULTI-AXIAL FLOW

3.1 MULTI-AXIAL DRAWING

As previously stated, the measurement of the multi-axial flow properties of polymer melts is not easy. This is, in part, reflected by the lack of literature on the topic, and also by what literature is available. Meissner [2, 3, 13-15], Wagner [1] Demarmels [16] Berger [4] have reported results of measurements using the same multiple rotary clamp instrument (no doubt at different stages in its development). Of these only Wagner [1] reported measurements on polymer melts at elevated temperature (150 °C and 190 °C), the remainder reporting measurements on polyisobutylene at approximately 23 °C.

The instrument used by these researchers is basically an array of rotary clamps set in pairs at various angles around the perimeter of the specimen, their positioning depending on the required deformation mode. The pair of rotary clamps, one each side of the specimen's

thickness, are effectively tank tracks that grip the specimen between them. Through control of the track speeds and measurement of the forces through the clamps and the specimen dimensions, the stresses and strains in the specimen can be determined. The imposed strains can also be checked by printing a grid onto the surface of the specimen prior to testing and then optically monitoring the change in the grid during testing. For equi-biaxial extension a circular specimen is clamped using 8 pairs of rotary clamps around its circumference. For planar extension the clamps are arranged around a rectangular specimen in order to obtain the necessary deformation. Cutters are positioned between the clamps to minimise complications and resultant disturbance in the strain rates across the specimen due to edge effects.

Wagner [1] presented results on LDPE, HDPE and PS at 150 °C to 190 °C using the multiple rotary clamp instrument to obtain first planar, second planar and equi-biaxial extensional viscosities. For all deformation modes, strain rates were in the range 0.003 s^{-1} to 0.1 s^{-1}, and strain to failures in the range 1.6 to 5.8. Strains to failure in equi-biaxial extension were up to 3 while in planar extension they were up to 5.8. This instrument is not only the state of the art, in terms of quantitative measurements of multi-axial viscosity, but is the art: no other multi-axial drawing instruments for polymer melts having been identified in the literature.

3.2 BUBBLE INFLATION

In bubble inflation a circular specimen is clamped between two ring plates and is subjected on one side to an elevated pressure that deforms the specimen to create the “bubble” or domed shape. From measurements of the original specimen dimensions, the pressure difference across the bubble and the height of the bubble the stresses and strains in the bubble can be determined, from which the equi-biaxial extensional viscosity of the polymer can be deduced. This approach has been used by Denson [17, 18], De Vries [19], Hoover [20], Joye [21, 22], Maerker [23] and Rhi-Sausi [24]. By using a rectangular geometry, thereby inflating a log-shaped bubble, Denson [18] measured the planar extensional viscosity of an acrylonitrile-butabiene-styrene co-polymer at 138 °C (analysing the mid region of the specimen away from the constrained ends). Dealy [26] commented that this method could be used to measure materials with a viscosity as low as 10^5 Pa.s [22].

Initial work on the bubble inflation method utilised gas [21, 22] as the pressurising medium. However, control of the inflation of the bubble proved to be difficult. Denson [18] commented that the use of a more incompressible fluid rather than a gas permitted better control of the test thereby allowing constant stress or constant strain rate to be more reliably obtained. Subsequently, Rhi-Sausi [24] used an oil to pressurise and control the temperature of the polymer.

The simplest option for controlling the inflation is to operate under conditions of constant pressure [22]. Constant stress or strain rate are more difficult to obtain, requiring feedback control. However Joye [22] pointed out that the constant pressure results are not easy to interpret. To obtain true measures of the extensional flow behaviour, measurements should be performed under either constant stress or constant strain rate conditions rather than under conditions in which neither of these are constant. Nevertheless Joye [22] reported favourably on the constant pressure method, trying to overcome some of the difficulties in operating under constant stress or strain rate. Significantly for obtaining simple measures, when the pressure and burst time are transformed into viscosity- and strain-like parameters then a good correlation with true equi-biaxial viscosity data was observed. The authors suggested that this

may be fortuitous but nevertheless may prove adequate for quality control purposes.

As well as measuring the extensional flow behaviour on start-up, i.e. increasing stress or strain, Joye [22] reported on measuring the retardation behaviour of the polymer by deliberately bursting the bubble, near its edge, to provide rapid removal of stress within the bubble membrane. By observing the collapse of the bubble the retardation behaviour of the melt could be analysed.

In deforming the bubble under so-called constant strain rate conditions, constant strain rate is actually only obtained in the region near the pole of the bubble (originally the centre of the undeformed specimen). Thus measurement of the height of the bubble will only approximate the "constant" strain rate: detailed measurement of the profile in the region of the pole of the bubble is required to obtain accurate measures of the strain rate.

Initial work using the bubble inflation technique focused on the measurement of polyisobutylene at room temperature, Joye [21, 22], Denson [17] and Maerker [23]. Subsequently, high temperature polymer melts were investigated by De Vries [19], Denson [18] and Rhi-Sausi [24]. The latter commented that the method was limited to strains up to approximately 1.7, except for very low strain rates (the highest strain rate reported was 0.063 s^{-1}). At nominal strains above this value the actual strain rate becomes non-uniform. Rhi-Sausi [24], in the most recent of these publications, commented that to obtain reliable properties at higher strain rates then alternative methods are required.

For polymer melts, De Vries [19] reported strain rates up to 0.22 s^{-1} and Rhi-Sausi [24] reported rates down to 0.008 s^{-1}. In comparison, for PIB at room temperature Joye [22] reported rates as low as 3 x 10^{-6} s^{-1} (or 92 hours to attain a strain of 1) and Maerker [23] reported that constant strain rates had been achieved at values up to 0.8 s^{-1}. Maerker indicated that such high strain rates had been achieved, and that those rates were constant, because in their measurements and analysis only the region near the pole was considered. This resulted in a need for greater experimental complexity in terms of characterising the shape of the bubble. Obviously the very low strain rates are unlikely to be suitable for polymer melts at elevated temperatures due to degradation issues (apart from the obvious economic issues of testing and processing over such timescales) but clearly demonstrate the wide, but still low, range capability of the method.

An alternative to the standard bubble inflation method, but following a similar principle, was that adopted by Laun [7] in which he investigated the use of a blowing instrument that measured the planar extensional viscosity of the material. The measurements involved the stretching of a tube of polymer in the axial direction while keeping the diameter of the specimen constant by pumping oil into the core of the tube-shaped specimen. Planar measurements were reported at strain rates of 0.08 s^{-1} for PIB at room temperature, and 0.05 s^{-1} and 0.01 s^{-1} at 125 °C for LDPE with strains of between 3 and 4 being obtained. The range of strain rates is obviously quite limited and is presumably constrained by the experimental configuration.

3.3 LUBRICATED SQUEEZE FLOW

In lubricated squeeze flow a sample of melt is squeezed between two parallel plates, there being a lubricant e.g. silicone oil, between the specimen and the plates. From measurements

of the force, initial separation and speed of the plates, the strains, strain rates and stresses can be determined. Two initial configurations have been used. In the first the specimen is initially smaller than the diameter of the plates and during squeezing increasingly fills the gap between the plates. In the second, the initial diameter of the specimen is the same as that of the plates and material is extruded out from between the plates. In the latter configuration the test may be influenced by the constraining action of the polymer outside the diameter of the plates [6]. Hsu [25] commented that the use of a specimen of initial diameter smaller than that of the plates is preferable. Chatraei [27] suggested using a rod through the central axis of the specimen and plates to prevent the specimen slipping out of the plates.

Chatraei [27] reported good agreement of data with that obtained from multiple rotary clamp equipment for a PDMS at room temperature. He demonstrated the use a tracer line in the specimen to check the efficiency of the lubricant and to identify that the deformation was equi-biaxial.

Lubricate squeeze flow measurements of polymer melts at elevated temperatures are reported by Soskey [28], Khan [5], Hsu [25, 28], Takahashi [6] and Ebrahimi [8]. The greater number of researchers using this multi-axial technique perhaps reflects the greater ease with which such measurements can be performed. Hsu [29] reported that strains up to 4.5 were achieved, whilst Soskey [28] reported results obtained at strain rates up to 0.5 s^{-1} and strains up to 2.3.

Adequate lubrication of the specimen within the plates was crucial to obtaining accurate data. Starvation of lubricant, in particular at high strains, resulted in an apparent strain hardening of the material as the friction forces between the specimen and plates increased. The effect of too low a lubricant viscosity resulting in lubricant starvation was clearly apparent in results presented by Chatraei [27]. Khan [5] comment that optimal results were obtained when the specimen viscosity was 500 to 1000 times that of the lubricant viscosity, and reported that strains up to 1.4 were obtained with no lubricant loss. Hsu [25] reported that other potential sources of error relate to errors in the measurement of specimen thickness during the test due to the compliance of the instrument, the contribution of edge effects and due to the inertia/acceleration characteristics of the instrument on start-up.

Hsu [25] commented that steady state flow was achieved at lower strain when using constant stress compared with when using constant strain rate. Thus constant stress was preferred when steady state response was of principal interest, and constant strain rate when the transient response was of most interest.

3.4 STAGNATION FLOW

The principle of the method is that material flowing out of two opposing funnel-shaped channels produces, at the centre between the funnels, an extensional flow field. The technique has been used more commonly for polymer solutions, e.g. Cathey [30]. Van Aken [31] investigated the use of opposed jet measurements for a polystyrene melt at elevated temperature (140 °C to 170 °C). Strain rates in the range 0.001 s^{-1} to 1 s^{-1} were achieved. However, to obtain the desired flow kinematics and thus negligible wall friction it was necessary that the flow was lubricated. Silicone oil was successfully used as the lubricant. The authors commented, however, that for the given geometry the maximum strain that could be achieved was limited to approximately 2.4 and so steady state conditions may not be reached.

3.5 USE OF PROCESSING TYPE EQUIPMENT

Han [32] and Sweeney [33] investigated the use of film blowing equipment to obtain measures of the multi-axial extensional flow behaviour of HDPE, LDPE, PP and PS. Han [32] reported that, because of difficulties in control of the bubble, non-uniform biaxial deformation of the material was obtained during all the tests, as was also the case for Sweeney [33]. Furthermore, the strain rates were not constant with position along the bubble and thus interpretation of data is complicated. Han [32] added that by controlling the bubble pressure and other processing conditions it was [theoretically] possible to obtain either uniaxial or biaxial extensional flows. Han [32] reported biaxial strain rates of 0.2 s^{-1} for LDPE and 0.1 s^{-1} for HDPE and PP, obtained under isothermal conditions. Han [32] compared uniaxial extensional data obtained using the blown film method with that obtained from a melt spinning method and commented that the results were encouraging [although results had to be extrapolated as the strain rates from the two methods did not overlap]. Furthermore, it was noted that as both techniques were similar in nature, i.e. drawing down of a fibre or thin cylindrical geometry, the level of agreement was not surprising and should not be taken as an indication of the quantitative accuracy of the method but rather the qualitative agreement between similar methods.

4 DETERMINATION OF MULTI-AXIAL EXTENSIONAL FLOW BEHAVIOUR BY MODELLING

The ability of constitutive equations to predict, on the basis of limited data from established test methods, the behaviour of materials in more complex flow fields has been the goal of many researchers for some time. Recent significant advances, notably by McLeish et al [34-36] in the development of the POM-POM model, and by others [9, 37] in developing derivatives of that model have resulted in greater accuracy in predicting the behaviour of polymer melts in flows such as biaxial and planar extension. The POM-POM model has enabled limitations in previous constitutive equations to be overcome, for example the KBK-Z model not fitting planar extensional viscosity well [35, 37, 38]. Inkson [37] commented about the lack of data available in the literature on multi-axial extensional properties, and that this has hindered fuller validation of these models in predicting the behaviour of a wider range of materials. The modified POM-POM model developed by Verbeeten [9] required dynamic shear data and uniaxial extensional data to predict biaxial, first and second planar extensional viscosity behaviour. However, values for additional non-linear parameters were chosen rather than determined. Verbeeten [9] commented that, although the modified POM-POM model fitted the data well there was still room for improvement.

Thus the need for multi-axial measurement methods is likely to decrease as such constitutive models become more reliable, widely accepted and integrated with affordable numerical simulation packages. There is, however, a need to validate the predictions for such constitutive equations and for that reason quantitatively accurate multi-axial measurements as provided by the multiple rotary clamp instrument is likely to be required.

5 DISCUSSION AND CONCLUSIONS

The current availability of methods and organisations able to measure the multi-axial extensional properties of polymer melts is very limited. In terms of well-defined measurement methods, in which the rate or stress of deformation is controlled, then it is limited to the multiple rotary clamp system developed by Meissner. The alternatives are the methods of bubble inflation, squeeze flow and opposed jets that are not so well controlled in terms of their applied constant strain rates or stresses being constant. Furthermore, the method that is potentially the easiest to implement, the lubricated squeeze flow method, is the least similar to the main processes for which such data are required. The use of production type equipment, e.g. film blowing pilot plant, to characterise materials may be satisfactory for comparison of similar materials but is not particularly suited for determining the true rheological properties due, again, to difficulties in controlling the deformation of the melt.

In comparing the methods with the actual requirements for data, the multi-axial rotary clamp device is limited in terms of the maximum strain rate achieved (0.12 s^{-1} [2]) as revealed by the results that have been identified and reported in the literature. The lubricated squeeze flow and bubble inflation methods have achieved higher, albeit still limited, nominal strain rates, although errors in these two methods are likely to increase as the strain rate and strain increase. In terms of the maximum strains achieved, the bubble inflation method is only marginally short on the requirements for data, the other methods having achieved ample strain values. However, it is noted that to fully characterise a material the instrument should be able to measure the material up to its failure strain and in this respect only the multi-axial rotary clamp and lubricated squeeze flow methods have demonstrated their potential suitability. However, although high strains of 4.5 were reported by Hsu [25] using the lubricated squeeze flow method this was more the exception and maximum strains were normally up to 2.5 using this technique: achieving higher strains was made difficult due to lubrication problems. The maximum temperatures at which results have been presented for these methods, at approximately 180 °C or 190 °C, is short of the upper temperature value of 280 °C identified. However, this is an issue that is not considered to be a fundamentally limiting problem with any of these methods.

The limited experimental evidence in the literature indicates that the more difficult to measure multi-axial extensional viscosity functions are bounded by more easily determinable viscosity functions. The greatest degree of strain hardening, and thus the upper limit, is exhibited by transient uniaxial extensional viscosity, and the lower limit of strain softening by transient simple shear viscosity. All other functions, normalised by constants to the linear viscoelastic time-dependant zero shear viscosity, fall between these limits. For quality control purposes the transient uniaxial extensional viscosity would be preferred in that it is more likely to show differences between materials than equi-biaxial and second planar viscosities that exhibit relatively little additional strain hardening (the first planar extensional viscosity exhibits similar strain hardening to uniaxial extensional viscosity).

Combining this with the recent advances in constitutive models for polymer melts, which predict the behaviour significantly better in complex deformations than previous models, results in a reduced need for advanced techniques for measurement of multi-axial extensional viscosity properties. There is likely to remain a need for quantitative multi-axial extensional viscosity data for validation of constitutive modelling but that is likely to remain largely in the domain of academia. However, the need for qualitative measures of multi-axial extensional viscosity is questioned given that a greater ability to compare materials is likely to be had from uniaxial measurements.

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7 REFERENCES

1. Wagner, MH, Bastian, H, Hachmann, P, Meissner, J, Kurzbeck, S, Münstedt, H and Langouche, F, Rheol. Acta (2000) 39: 97-109.
2. Meissner J., Polymer Engineering and Science, 27 No.8, April 1987, pp. 537-546.
3. Meissner J., Die Makromolekulare Chemie Macromolecular Symposia, 68, April 1993, pp. 133-146.
4. Berger L. and Meissner J., Rheological Acta, 31 (1992) pp. 63-74.
5. Khan, SA, Prud'homme, RK and Larson, RG, Rheologica Acta 26 144-151 (1987).
6. Takahashi M., Isaki T., Takigawa T. and Masuda T., Journal of Rheology, 37 (5) Sept/Oct 1993, pp. 827-846.
7. Laun H.M. and Schuch H., Journal of Rheology, 33 (1989) pp.119-175.
8. Ebrahimi N.G., Takahashi M., Araki O. and Masuda T., Journal of Rheology, 39 No.6, Nov/Dec 1995, pp. 1385-1397.
9. Verbeeten, W.M.H, Peters, G.W.M. and Baaijens, F.P.T., Differential constitutive equations for polymer melts: the enhanced pompom models, submitted to J. Rheology, 20 Feb 2000.
10. Macosko C.W. and Lorntson J.M., Society of Plastic Engineers. Technical Paper 19 (1973) pp. 461-467.
11. Swerdlow M., Cogswell F.N. and Krul N., Plastics and Rubber: Processing, March 1980, pp. 11-16.
12. Kalyon D.M. and Czerwonka D.S., Plastics and Rubber Processing and Applications, 14 (1990) pp. 29-33.
13. Meissner J., ANTEC '85, Proceedings of the 43rd Annual Technical Conference, SPE Washington D.C., April 29-May 2 1985, pp. 606-612. 012.
14. Meissner J., Chem. Eng. Commun, 33 (1985) pp. 159-180.
15. Meissner J., Raible T. and Stephenson S.E., Journal of Rheology, 25 part 1 (1981) pp. 1-28.
16. Demarmels A. and Meissner J., Rheological Acta, 24 (1985) pp. 253-259.
17. Denson C.D. and Crady D.L., Journal of Applied Polymer Science, 18 No.6, June 1974, pp. 1611-1617.
18. Denson C.D. and Hylton D.C., Polymer Engineering and Science, 20 No.8, May 1980, pp. 535-539.
19. De Vries, AJ, Bonnebat, C and Beautemps, J, J. Polym Sci.: Polym Symp, 58 pp109-156, (1977).
20. Hoover K.C. and Tock R., Polymer Engineering and Science, 16 No.2, Feb 1976, pp. 82-86.
21. Joye, DD, Poehlein, GW and Denson, CD, Trans. Soc. Rheology 16:3, pp. 421-445 (1972).
22. Joye, DD, Poehlein, GW and Denson, CD, Trans. Soc. Rheology. 17:2, pp. 287-302 (1973).
23. Maerker, JM and Schowalter, WR, Rheologica Acta 13 (1974) pp. 627-638.

24. Rhi-Sausi, J and Dealy, JM, Polymer Engineering and Science, March 1981, Vol. 21, No. 4 pp. 227-233.
25. Hsu, TC and Harrison, IR, ANTEC '94, Plastics: Gateway to The Future. Volume II-Materials. Conference Proceedings, SPE San Francisco, CA, 1-5 May 1994, pp.1816-1818. Experimental Factors in Measurement of Elongational Viscosity using lubricated squeezing.
26. Dealy J.M., Journal of Non-Newtonian Fluid Mechanics, 4 (1978) pp. 9-21.
27. Chatraei, SH and Macosko, CW, J. Rheology, 25(4), 433-443 (1981).
28. Soskey, PR and Henning Winter, H, J. Rheology, 29(5), 493-517 (1985).
29. Hsu T.C. and Harrison I.R., Polymer Engineering and Science, 31 No.4, Feb. 1991, pp. 223-230.
30. Cathey C.A. and Fuller G.G., Journal of Non-Newtonian Fluid Mechanics, 30 (1988) pp. 303-316.
31. Van Aken J.A. and Janeschitz-Kriegl H., Rheologica Acta, 20 No.5, Sept/Oct 1981, pp. 419-432.
32. Dae Han C. and Yoo Park J., Journal of Applied Polymer Science, 19 (1975) pp. 3257-3276.
33. Sweeney P.A. and Klewicki J.K., Campbell G.A., Antec 90, Plastics in the Environment: Yesterday, Today & Tomorrow Conference. SPE Dallas, Texas, 7-11 May 1990, pp. 94-97, 012.
34. McLeish T.C.B., Allgaier J., Bick D.K., Bishko G., Biswas P., Blackwell R., Blottière B., Clarke N., Gibbs B., Groves D.J., Hakiki A., Heenan R.K., Johnson J.M., Kant R., Read D.J. and Young R.N., Dynamics of entangled H-polymers: theory, rheology and neutron-scattering, private communication, 28 June 1999, pp. 1-40.
35. Bisko, G. McLeish T.C.B., Harlen O.G. and Larson R.G., Physical Review Letters, 79 no.12, Sept 1997, pp. 2352-2355.
36. McLeish T.C.B. and Milner S.T., Advances in Polymer Science, 143 (1999) pp. 195-256.
37. Inkson N.J, McLeish T.C.B, Harlen O.G. and Groves D.J., Predicting low density polyethylene melt rheology in elongational and shear flows with "pom-pom" constitutive equations, private communication.
38. Vrentas J.S. and Vrentas C.M., Journal of Applied Polymer Science, 49 No.4, 20 July 1993, pp. 733-740.
39. Rheological Techniques, R.W. Whorlow, Ellis Horwood, London, 1992.
40. Gupta, R.K. and Shridar, T., Elongational Rheometers, in Rheological Measurement, Ed. A.A. Collyer and D.W. Collyer, Elsevier Applied Science, London, 1988.
41. Dealy, J.M., Polym. Eng. Sci., 11 (1971) pp.433-445.
42. Dealy, J.M., J. Rheology 39(1) January/February 1995, pp.253-265.
43. Meissner, J., Stephenson, S.E., Demarmels A. and Portman, P., J. Non-Newtonian Fluid Mechanics, 11 (1982) pp.221-237.
44. Rheometry, K. Walters, Chapman and Hall, London, 1975.

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TABLE 1: MULTI-AXIAL MEASUREMENT TECHNIQUES FOR POLYMERIC MATERIALS

Ref.	Principle Author	Year	Method and deformation modes	Material	Temperature	Comments, including strain rates and strains
1	Wagner	2000	Multi-axial multiple rotary clamp Uniaxial, equi-biaxial, first and second planar results	LDPE HDPE PS	150 - 190 °C	Strain rates in the range 0.003 - 0.1 s^{-1} and strains to failure in the range 1.6 – 5.8 were reported. See reference 2.
2	Meissner	1987	Multi-axial multiple rotary clamp Uniaxial, equi-biaxial, first and second planar results	PIB	23 °C	Equi-biaxial measurements at strain rates of 0.0075 s^{-1} to 0.02 s^{-1} up to strains of approximately 2, uniaxial measurements at 0.02 s^{-1} to 0.12 s^{-1} up to strains of approximately 4.5 and planar measurements at 0.007 s^{-1} to 0.08 s^{-1} up to strains of approximately 3 were reported. Homogeneous deformations were reported, with no limit to the maximum strain that could theoretically be achieved using this instrument. A rotary clamp system (tank track style) was used where a number of pairs of clamps around the plate specimen could be positioned to generate any multi-axial extensional flow field in the specimen. Specimens were initially supported on a talc-covered table that was removed when the test commenced. Disk specimens used were 350 mm in diameter and 5 mm thick. It was reported that this equipment was limited to room temperature measurements only.
3	Meissner	1993	Multi-axial multiple rotary clamp First and second planar extension and complex multi-axial results	PIB	Room temperature	See reference 2.
4	Berger	1992	Multi-axial multiple rotary clamp. Uniaxial, first and second planar extension results	PIB	Room temperature	Reported that no correlation of extensional data with shear data could be found thus emphasizing the need for extensional data. Materials of similar molar mass averages but different molar mass distributions had significant differences in uniaxial as well as planar extensions. See reference 2.
13	Meissner	1985	Multi-axial multiple rotary clamp Uniaxial, equi-biaxial	PIB	23 °C	See reference 2.

Ref.	Principle Author	Year	Method and deformation modes	Material	Temperature	Comments, including strain rates and strains
			and first and second planar results			
14	Meissner	1985	Multi-axial multiple rotary clamp Uniaxial, equi-biaxial and first and second planar	PIB	Room temperature	See reference 2.
15	Meissner	1981	Multi-axial multiple rotary clamp Uniaxial and equi-biaxial results	PIB	Room temperature	See reference 2.
16	Demar-mels	1985	Multi-axial multiple rotary clamp Complex multi-axial deformation	PIB	Room temperature	See reference 2.
17	Denson	1974	Bubble inflation: Planar extensional viscosity results	PIB	23 °C	Strain rates in the region of 1 $x10^{-5}$ s^{-1} to 86 $x10^{-5}$ s^{-1}, viscosities of 10^{10} Pa.s to 0.5 x 10^{9} Pa.s respectively, and strains up to 0.7 were reported. A thin rectangular sheet of material was used to determine the planar extensional viscosity, using a gas medium to obtain a constant strain rate at pressures in the range 0 psi to 20 psi pressure range. The rectangular slot used to define the sheet was 2.54 cm x 10.16 cm. Measurement is by injecting gas and then monitoring the creep behaviour of the bubble of polymer: the strain rate was approximately constant at long times. Test durations of 30 minutes reported. Strain measured in the axial direction was 1% of that in the radial direction thus approximating well to the planar deformation assumption. The authors reported that measurements of planar viscosity had not previously been made or reported in the literature.
18	Denson	1980	Bubble inflation. Planar or equi-biaxial	ABS co-polymer	138 °C (22 °C above Tg as representative of vacuum forming)	Planar results at a strain rate of 4.8 x 10^{-4} s^{-1} and at strains up to approximately 1.1 were reported. Measurements could be made under constant stress, constant strain, constant strain rate, oscillatory stress and oscillatory strain conditions. A silicone oil was used as the inflating medium. The authors commented that the use of a gas medium prevents testing at constant strain, constant strain rate or controlled stress conditions. Using a liquid with closed loop control, rather than a gas, overcomes these

Ref.	Principle Author	Year	Method and deformation modes	Material	Temperature	Comments, including strain rates and strains
						problems and also permits dynamic measurements to be superimposed on constant stress or constant strain rate measurements thereby demonstrating the predominantly elastic response of the material.
19	DeVries	1977	Bubble inflation. Equi-biaxial. Uniaxial results also presented	PS PET	110 – 130 °C (above Tg for PS) 88 to 110 °C	Strain rates reported in range 0.02 s^{-1} to 0.22 s^{-1}. Strains up to 1.8 obtained. Constant strain rates were achieved by controlling the gas pressure inside the bubble. The authors reported that near-equi-biaxial deformation exist at the specimen's pole. Strains and strain rates were determined from a grid drawn on the specimen before the test commenced. Specimens were 150 mm in diameter and approximately 1 mm thick. The materials exhibited a rubber-like behaviour as strains were completely recoverable on removal of the applied stress.
20	Hoover	1976	Bubble inflation, Equi-biaxial	PP at (unoriented, biaxially oriented PPs and a polyethylene-polypropylene co-polymer	25 °C (i.e cold drawing)	Strain rates in the range 10^{-5} to 10^{-2} s^{-1} were used, and viscosities were in the range 10^{13} to 10^{9} Pa.s, respectively, were measured. Strains up to 0.5 were reported. A gas inflating medium was used to obtain constant strain rates. Thin film samples 0.076 mm and 0.038 mm thick were used. Biaxial extensional viscosity was determined in the region over which the strain rate and stress was constant, thus deriving steady state properties. The biaxially oriented polymer had a significantly higher viscosity compared with the unoriented polymer. The uniaxially oriented polymer split under pressure before forming an adequate bubble.
21	Joye	1972	Bubble inflation Equi-biaxial	PIB	23 °C	Strain rates in the range 5 x10^{-5} s^{-1} to 5 x 10^{-3} s^{-1} and strains up to 1.1 were reported. A gas inflation medium (N_2) was used to produce a constant stress test. Detailed discussion of the analysis and sources of error was presented. The largest sources of error were due to clamping the sample (soft at room temperature) and control of the gas flow. The authors emphasized the difficulties in obtaining constant strain rate, which was limited to the region near the pole of the bubble.
22	Joye	1973	Bubble inflation Equi-biaxial	PIB	23 °C	Strain rates in the range 3x10^{-6} s^{-1} to 4x10^{-3} s^{-1} and strains up to 1.2 were reported. A gas inflation medium was used to produce a constant pressure test. Test times ranged from 30 s to 60 hours. Also measurements of retardation behaviour on bursting of the bubble were made. The authors reported that fundamental viscosity data could not be determined from the constant pressure method, but when the pressure and burst time are transformed into a viscosity- and strain-like parameters good correlation with true viscosity data was observed. The authors commented that this may be a suitable approach to quality control as it is simpler to carry out than constant stress measurements.

Ref.	Principle Author	Year	Method and deformation modes	Material	Temperature	Comments, including strain rates and strains
23	Maerker	1974	Bubble inflation Equi-biaxial	PIB	23 °C	Strain rates in the range 0.01 s^{-1} to 1 s^{-1} and strains up to 1.4 reported. A gas inflation medium was used to produce constant stress or constant strain rate tests. Deformation was at constant strain rate only at the pole: quantified as being within approximately 25° of the pole for extension ratios less than 4. The author commented that for angles less than 22° curvature corrections were not necessary, thereby simplifying the analysis. The contribution of surface tension was estimated to be less than 0.1% for steady state measurements. It was reported that the strain rates were not linear on start up. An estimate of standard error for viscosity measurement was quoted as 12%.
24	Rhi-Sausi	1981	Bubble inflation Equi-biaxial	LDPE PS	130 °C 160 °C	Strain rates were in the range 0.008 s^{-1} to 0.063 s^{-1}, and strains were limited to 1.7. Bubble inflation was achieved using an oil as the medium to obtain constant strain rate. Strain rates become non-uniform at strains above 1.3 to 1.7, except for very low strain rates. The authors suggested that to reliably measure at higher strain rates then an alternative technique is required.
7	Laun	1989	Tubular film blowing. First and second planar extension	PIB LDPE	23 °C 125 °C	Strain rates used were 0.08 s^{-1} at 23 °C for PIB, and 0.05 s^{-1} and 0.01 s^{-1} at 125 °C for LDPE with strains between approximately 3 and 4 achieved. Planar extensional viscosities were measured using a tube of polymer stretched along its axis while the diameter of the tube was maintained by pumping oil into its core. An exponential increase in the separation of the end of the specimen was necessary to maintain constant strain rate. The tube started off 11 mm in diameter and 20 mm or 40 mm in length with a wall thickness of 1.5 mm. A correlation between minimum thickness in planar tests with Rheotens measured maximum draw down speed was observed. The authors concluded that uniaxial draw-down can be used to infer multi-axial behaviour. A principal difficulty with the method was to obtain the necessary shape of the specimen during deformation by filling with oil. It was reported that testing was non-isothermal and non-homogeneous.
5	Khan	1987	Lubricated squeeze flow. Step biaxial extension (relaxation) Uniaxial results also presented	PS HDPE LDPE	150 - 161 °C	A Rheometrics System Four rheometer was used for biaxial extension relaxation measurements. Hencky strains up to 1.4 were reported with no loss of lubricant. It was reported that differences in the properties of the melts were shown most pronounced in uniaxial extensional viscosity and least in biaxial extensional viscosity. In uniaxial testing the LDPE showed significant strain hardening whereas in biaxial its behaviour was similar to the other materials. Optimal results were obtained when the viscosity of the melt was 500 to 1000 times that of the lubricant (1 Pa.s – 2 Pa.s). The lubricant thickness was 0.05 mm to 0.09 mm. Samples

Ref.	Principle Author	Year	Method and deformation modes	Material	Temperature	Comments, including strain rates and strains
						were the same diameter as the plates (8 mm or 25 mm) and of initial thickness approximately 5mm. A 2 kg force transducer was used.
6	Takahashi	1993	Lubricated squeeze flow. Equi-biaxial Uniaxial results also presented.	PS PP	145 - 160 °C 180 °C	Strain rates used were in the range 0.01 s^{-1} to 0.1 s^{-1} (constant strain rate). The method used 70 mm diameter test discs with 20 mm initial diameter specimens of 5mm thickness. Exponentially increasing speed of the plates was used to achieve a constant strain rate. The silicone oil lubricants used on the plates limited the upper working temperature to 200 °C, although the oven could be used up to 300 °C. The effect of lubrication was demonstrated to be significant. However there are potential problems with loss of lubricant at high strains. Lubricants of viscosity 5000 cSt to 10000 cSt were optimal to produce the desired deformation, as assessed by inspection of the specimens after testing. Scatter in data was in the range ± 8% to ± 15%.
8	Ebrahimi	1995	Lubricated squeeze flow. Equi-biaxial	PS	160 °C	Strain rates were in the range 0.00034 s^{-1} to 0.085 s^{-1} and strains up to 1.5 were reported. Upturns in equi-biaxial data were reported to be true material behaviour rather than due to experimental problems associated with lubrication. Values for normalized equi-biaxial extensional viscosity both above and below the linear viscoelastic value were observed and were dependant on the strain rate. See also ref 6 for method.
25	Hsu	1994	Lubricated squeeze flow. Equi-biaxial	PS LDPE	130 - 150 °C	Strain rates were in the range 0.001 s^{-1} to 2 s^{-1} and strains up to 2 were reported. Controlled stress, controlled strain and constant load modes were described. The authors commented that the method was simple and versatile, with no clamping problems. However loss of lubricant can be a problem for this method at high strains resulting in apparent strain hardening of the material. Other potential errors are in measurement of sample thickness due to the instrument compliance, edge effects and in start up of the test due to the instrument inertia characteristics. The authors commented that the parallel plate approach in which the specimen is initially smaller than the compressing plates is preferable, in comparison with the method in which the specimen is initially the same diameter as the plates.
27	Chatraei	1981	Lubricated squeeze flow. Equi-biaxial	PDMS	29 °C	Strain rates were in the range 0.003 s^{-1} to 1 s^{-1} and strains up to 2.5 were reported. A constant load mode was used. A centrally located thin rod to provide alignment and sample slippage was used. Plate and initial specimen diameters were either 57.2 mm or 127 mm. The specimen was of initial thickness of 25 mm. Results clearly showed the effect of lubricant viscosity on behaviour, possibly due to the thickness of the applied film of lubricant. The highest viscosity lubricant gave the best quality data (viscosity ratio 60000) whereas the lower viscosity lubricants gave the poorer quality data. Slip velocity profiles were checked by use of tracer line in the specimen that remained straight if slip occurred. It

Ref.	Principle Author	Year	Method and deformation modes	Material	Temperature	Comments, including strain rates and strains
						was reported that there was good agreement with data from sheet stretching measurements on the same material. The authors commented that most bubble inflation is in range 0.0001 to 0.01 s^{-1}, although Maerker (23) had reached 1 s^{-1}. Experimental problems are related to obtaining and controlling constant stress, i.e. bubble burst before steady state is achieved, non-uniformity of bubble thickness, and non-uniform deformation except near the pole.
28	Soskey	1984	Lubricated squeeze flow. Step biaxial extension	PS LDPE	180 °C 150 °C	Strain rates were in the range 0.01 s^{-1} to 0.5 s^{-1}, and strains up to 1.6 were achieved. A Rheometrics RDS-LA instrument was used to obtain constant equi-biaxial strain rates. Step strain times of less than 20 ms were achieved for strains up to 2.3. The authors commented that sheet inflation, stagnation flow and sheet stretching instruments are very sophisticated items of equipment that require large samples that are carefully prepared, are limited to certain temperature ranges and either constant stress and/or constant strain rate modes. Step strain measurements enable the determination of the strain dependent relaxation modulus. The nitial diameter of the specimens was smaller than that of the plates.
29	Hsu	1991	Lubricated squeeze flow Equi-biaxial	PS	160 °C	Strain rates in the range 0.025 s^{-1} to 0.085 s^{-1} were reported, and strains up to 4.5 were achieved under constant strain rate conditions. Controlled stress and controlled strain rate methods were both used. Reportedly, steady state was achieved in controlled stress at strains typically of 1. The authors commented that steady state was achieved at a lower strain in a constant stress test compared with a constant strain rate test, and thus constant stress methods are to be preferred when steady state flow is of primary interest, and otherwise when transient behaviour is of interest. Good agreement of steady state values was obtained between controlled stress and controlled strain methods. Compression moulded samples of 1.27 mm to 3.8 mm diameter and 1.27 mm thickness were used, and were the same diameter as the plates. An alignment hole was used to prevent specimen slippage. Telfon and silicone oil were both used to improve lubrication of the specimen and the plates were immersed in a silicone oil bath. It was reported that the ratio of viscosities of the lubricant to specimen should be of the order of 10^7 and a lubricant thickness of 0.1 mm to 1 mm should be used. The authors emphasized the importance of effective lubrication. They commented that strain rate hardening can be either a real material behaviour or due to experimental difficulties in achieving steady flow, e.g. loss of lubricant resulting. A 44 N load cell was used. The authors commented that the non-linear behaviour of polymers makes it difficult, if not impossible, to predict the extensional behaviour of polymers using shear flow properties

Ref.	Principle Author	Year	Method and deformation modes	Material	Temperature	Comments, including strain rates and strains
						only.
30	Cathey	1988	Opposed jet Equi-biaxial	Semi-dilute and dilute solutions of collagen	Not specified – presumed room temperature	High strain rates up to 600 s^{-1} for low viscosity solutions only were achieved..
31	Van Aken	1981	Orthogonal stagnation flow measurement. Equi-biaxial	PS	140 - 170 °C	Strain rates were in the range 0.001 s^{-1} to 1 s^{-1}. The maximum strain that could be achieved was limited to 2.4 and so steady state conditions may not be reached. Lubrication was needed to obtain the desired flow kinematics in the profiled channel.
32	Han	1975	Film blowing. Uniaxial and non-uniform biaxial stretching	HDPE LDPE PP	160 – 220 °C	Biaxial stretching rates up to 0.2 s^{-1} for LDPE and 0.1 s^{-1} for HDPE and PP were reported. Also uniaxial elongation rates of up to 0.2 s^{-1} were noted for LDPE and up to 0.05 s^{-1} for HDPE and PP. A technique to measure uniaxial and biaxial extensional viscosity using a film blowing line, each deformation being obtained, in theory, by careful control of the pressure inside the bubble. However, it was reported that only non-uniform biaxial deformation was obtained in the tests due to lack of control of the film thickness and radius. It was comment that the bubble shape was extremely sensitive to the internal air pressure. The method was not of constant elongation rate. Equilibrium extensional viscosities were presented but without reference to the strain level. Reasonable agreement of uniaxial data from fibre spinning and film blowing was inferred (extrapolation required).
33	Sweeney	1990	Film blowing line. Complex deformation	PS	Complex thermal and deformation history	Non-isothermal, varying strain rate and non equi-biaxial. Strain rates up to approximately 1 s^{-1} and strains up to 4 were reported. However problems existed in interpretation of the data obtained due to the varying strain, strain rate and temperature of the material as it progressed along the bubble.

APPENDIX A: DEFINITIONS OF EXTENSIONAL VISCOSITY

A.1 Definitions of strain, strain rate, stress and material properties functions in tensile (simple) extension

The following definitions are given by Whorlow [34] for strains and strain rates. Further descriptions are also given by, for example, Gupta et al [40] and Dealy [41, 26].

A.1.1 Elongation ratio

The *Elongation ratio (ER)* is the ratio of the current length ℓ to the initial length ℓ_o of the specimen:

$$ER = \ell / \ell_o \qquad \text{(A1.1)}$$

A.1.2 Cauchy ε_c and Hencky ε strains

The *Cauchy strain* ε_c is given by the ratio of the change in length $\delta\ell$ to the initial length ℓ_o of the specimen:

$$\varepsilon_c = \delta\ell / \ell_o. \qquad \text{(A1.2)}$$

The *Hencky strain* ε (also referred to as the natural or true strain) is given by the natural logarithm of the elongation ratio:

$$\varepsilon = \ln(\ell / \ell_o) \qquad \text{(A1.3)}$$

Thus the elongation ratio is related to the Cauchy strain by

$$ER = 1 + \varepsilon_c \qquad \text{(A1.4)}$$

i.e. $$\ell / \ell_o = 1 + \delta\ell / \ell_o. \qquad \text{(A1.5)}$$

To illustrate the difference between these measures of strain a specimen that was stretched to 10 times its original length has an elongation ratio of 10, a Cauchy strain of 9 and a Hencky strain of 2.3.

A.1.3 Cauchy $\dot{\varepsilon}_c$ and Hencky $\dot{\varepsilon}$ strain rates

The *Cauchy strain rate* is given by

$$\dot{\varepsilon}_c = 1/\ell_o \times \partial\ell/\partial t \qquad \text{(A1.6)}$$

and the *Hencky strain rate* by

$$\dot{\varepsilon} = 1/\ell \times \partial\ell/\partial t \qquad \text{(A1.7)}$$

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.

A.1.4 Extensional flows: velocity fields

Terminology and definitions for materials functions describing the response of viscoelastic fluids to various shearing and extensional deformations are presented by Dealy [42]. Mathematical descriptions of extensional flows were presented, for example, by Meissner et al [43] and Walters [44].

For *tensile (simple or uniaxial) extension* where $\dot{\varepsilon}$ is the true strain rate and ε is the true strain, defined as

$$\varepsilon = \ln(\ell / \ell_o) \tag{A1.8}$$

then in rectangular coordinates:

$$v_1 = \dot{\varepsilon}\, x_1 \tag{A1.9}$$

$$v_2 = -\tfrac{1}{2}\, \dot{\varepsilon}\, x_2 \tag{A1.10}$$

$$v_3 = -\tfrac{1}{2}\, \dot{\varepsilon}\, x_3 \tag{A1.11}$$

where $\dot{\varepsilon} \geq 0$.

Alternatively, in cylindrical coordinates:

$$v_z = \dot{\varepsilon}\, z \tag{A1.12}$$

$$v_r = -\tfrac{1}{2}\, \dot{\varepsilon}\, r \tag{A1.13}$$

where $\dot{\varepsilon} \geq 0$.

A.1.5 Material properties

Following the notation presented by Dealy [42], and prepared by the Nomenclature Committee of the Society of Rheology, for start-up flow in tensile (simple) extension at constant (Hencky) strain rate $\dot{\varepsilon}$ the following definitions are given. Equivalent expressions for cessation of steady tensile extension, tensile creep, tensile recoil and tensile step strain are presented by Dealy [42].

A.1.5.1 Net tensile stress

The *net tensile stress* σ_E is defined by

$$\sigma_E = \sigma_{11} - \sigma_{22} = \sigma_{11} - \sigma_{33} = \sigma_{zz} - \sigma_{rr} \tag{A1.14}$$

where σ_{ii} is a stress tensor in either rectangular or axisymmetric co-ordinates. The tensile stress growth function is indicated by σ_E^+ where the + indicates start-up rather than cessation of flow.

A.1.5.2 Tensile stress growth coefficient

The *tensile stress growth coefficient* η_E^+ is defined by:

$$\eta_E^+(t, \dot{\varepsilon}) = \sigma_E / \dot{\varepsilon} \tag{A1.15}$$

where t is time.

A.1.5.3 Tensile viscosity

The *tensile viscosity* η_E is defined by:

$$\eta_E(t, \dot{\varepsilon}) = \lim_{t \to \infty} [\eta_E^+(t, \dot{\varepsilon})] \tag{A1.16}$$

It defines the limiting extensional viscosity and as such represents an equilibrium extensional viscosity if a steady value is achieved.

A.2 Biaxial extensional flow

A.2.1 Extensional flows: velocity fields

The velocity field, in rectangular co-ordinates is given by

$$v_1 = \dot{\varepsilon}_B \; x_1 \tag{A1.17}$$

$$v_2 = \dot{\varepsilon}_B \; x_2 \tag{A1.18}$$

$$v_3 = -\,2\;\dot{\varepsilon}_B \; x_3 \tag{A1.19}$$

A.2.2 Net stretching stress

The *net stretching stress* σ_B is defined by

$$\sigma_B = \sigma_{11} - \sigma_{33} = \sigma_{22} - \sigma_{33} = \sigma_{rr} - \sigma_{zz} \tag{A1.20}$$

where σ_{ii} is a stress tensor in either rectangular or axisymmetric co-ordinates. The tensile stress growth function is indicated by σ_B^+ where the + indicates start-up rather than cessation of flow.

A.2.3 Biaxial stress growth coefficient

The *biaxial stress growth coefficient* η_B^+ is defined by:

$$\eta_B^+(t,\; \dot{\varepsilon}_B) = \sigma_B / \dot{\varepsilon}_B \tag{A1.21}$$

where t is time.

A.2.4 Biaxial extensional viscosity

The biaxial extensional *viscosity* η_B is defined by:

$$\eta_B(t,\; \dot{\varepsilon}_B) = \lim_{t \to \infty} [\eta_B^+(t,\; \dot{\varepsilon}_B)] \tag{A1.22}$$

It defines the limiting extensional viscosity and as such represents an equilibrium extensional viscosity if a steady value is achieved.

A.3 Planar extensional flow

A.3.1 Extensional flows: velocity fields

The velocity field, in rectangular co-ordinates is given by

$$v_1 = \dot{\varepsilon}_P \; x_1 \tag{A1.23}$$

$$v_2 = 0 \tag{A1.23}$$

$$v_3 = - \dot{\varepsilon}_P \; x_3 \qquad \text{(A1.25)}$$

A.3.2 Net stretching stress

The *net stretching stress* σ_P is defined by

$$\sigma_{P1} = \sigma_{11} - \sigma_{22} \qquad \text{(A1.26)}$$

or

$$\sigma_{P2} = \sigma_{22} - \sigma_{33} \qquad \text{(A1.27)}$$

where σ_{ii} is a stress tensor in either rectangular or axisymmetric co-ordinates and σ_{P1} or σ_{P2} is used for the first or second planar values respectively. The tensile stress growth function is indicated by σ_P^+ where the + indicates start-up rather than cessation of flow.

A.3.3 Planar stress growth coefficient

The *planar stress growth coefficient* η_P^+ is defined by:

$$\eta_P^+(t, \dot{\varepsilon}_P) = \sigma_P / \dot{\varepsilon}_P \qquad \text{(A1.28)}$$

where t is time.

A.3.4 Planar extensional viscosity

The planar extensional *viscosity* η_P is defined by:

$$\eta_P(t, \dot{\varepsilon}_P) = \lim_{t \to \infty} [\eta_P^+(t, \dot{\varepsilon}_P)] \qquad \text{(A1.29)}$$

It defines the limiting extensional viscosity and as such represents an equilibrium extensional viscosity if a steady value is achieved.

A.4 Generalised extensional flow

The components of the rate of deformation tensor for extensional flows is reported [Dealy] to be given by

$$\dot{\varepsilon} \begin{bmatrix} 1 & 0 & 0 \\ 0 & m & 0 \\ 0 & 0 & -(1+m) \end{bmatrix} \qquad \text{(A1.30)}$$

A value of m = 0.5 corresponds to uniaxial extension, a value of m =1 to biaxial extension and m = 0 to planar extension.

A suitable method for comparing uniaxial and multiaxial data is to normalise the data, to yield what approached the time-dependant zero-shear viscosity at short times, i.e. uniaxial data would be divided by a factor of 3, equi-biaxial by 6 and planar by 4 or 2 depending on the orientation (first or second planar respectively).