

Practical Rheology for Polymer Production and Processing.

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ABSTRACT

The continuous demands of more cost-effective and rapid production of polymer products is leading to increasing demands in knowing about the behaviour of the materials during the production process. Also the fact of increasing demands in thermal and mechanical properties of polymer products makes the materials more complex and still more complicated to process. The purpose of this paper is to highlight the state of art in modern capillary rheometry and the opportunities these instruments give the user to a safe production.

INTRODUCTION

It is a well known fact that practical polymer properties are not depending only on the properties of the raw materials, but also strongly depending on the process conditions. Almost all polymers will be processed in a molten stage under strongly various shear and elongational deformations. The processing behaviour of a polymer melt is affected by its rheological behaviour, i. e. its viscous and elastic flow behaviour. These rheological properties are strongly depending on molecular structure of the polymer.

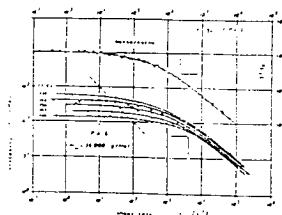
Some of these correlations will be discussed by presenting selected experimental results, as well as the importance of knowing and being able to optimize practical processing. Polymer rheology will be treated by discussing experimental techniques to determine visco-elastic properties in the shear-rates of practical processing.

1. MOLECULAR PARAMETERS OF POLYMERS AND CORRELATIONS TO THE RHEOLOGICAL BEHAVIOUR OF ITS MELTS

Graph 1. shows a typical double logarithmic graph of viscosity versus shear rate, measured on PA-6 at different temperatures. As can be seen the viscosity at low shear rates is independent of the shear rate. This behaviour is well known from low molecular weight materials and is called "Newtonian". Viscosity is highest in this region and is also called "zero shear viscosity".

At higher shear rates viscosity decreases with increasing shear rate, which is called "pseudo-plastic behaviour" or "shear thinning", and is due to an orientation of the macromolecules as they flow, which gives a reduction of the density of entanglements in the melt. Shear thinning, which is characteristic for every polymer melt, is especially interesting for polymer processing.

It means for instance that increasing the extruder pressure by a factor of 2 will increase the output by much more than a factor of 2, depending on the slope of the viscosity curve.



Graph 1: Viscosity Curves of PA 6 at different temperatures and T-invariant mastercurve (acc. to Laun)

1.1 VISCOUS FLOW COMPONENT

In general it can be stated that the narrower the molecular weight distribution is, the less steep is the viscosity drop. The shear thinning part of the viscosity curve is of special interest to everyone who is involved with polymer production and processing and wants to optimize these processes and used processing equipment. Shear thinning occurs for almost all polymer melts in the shear rate range of practical polymer processing. It is clear that it is important to measure viscosity in the shear rate range which is relevant for practical polymer processing. These ranges are shown in Fig 1.

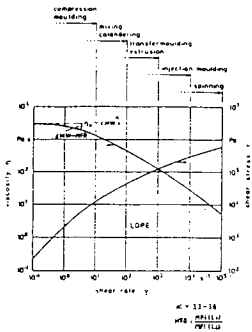
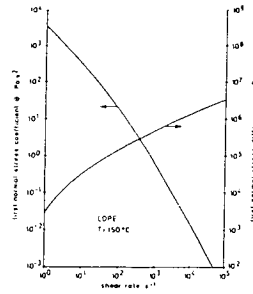


Figure 1: Flow and viscosity curves and shear rate range of some practical processes

1.2 ELASTIC FLOW COMPONENT

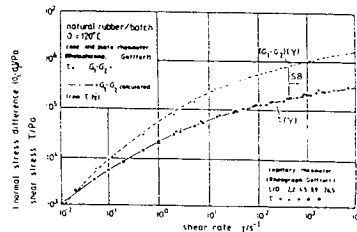
A pure shear deformation gives an orientation of the macromolecules in flow direction. It also generates normal stress differences in the melt due to an elastic flow component. These normal stresses are creating the well known Weissenberg effect and are the cause of unusually high inlet and outlet pressure losses, and of swelling effects at changes in cross sections of flow passages. The elastic flow component is described by first normal stress difference σ and the first normal stress coefficient θ . These elastic parameters are strongly depending on shear rate as can be seen from the double logarithmic graph 2.



Graph 2: Elastic flow parameters of a LDPE-melt schematically

1.3 COMPARASION OF ELASTIC AND VISCOUS FLOW COMPONENT

A comparison of the elastic and viscous flow components of a NR-batch is shown in graph 3 to demonstrate the importance of knowing both flow components of a polymer melt. The shear stress τ and the first normal stress difference σ are plotted together versus shear rate and it is obvious that these parameters are strongly depending on the shear rate. At very low shear rates the shear stress dominates, but the situation is reversed at high shear rates, where the first normal stress difference is significantly higher. This is demonstrating that the elastic flow component of polymer melts cannot be neglected at high shear rates.



Graph 3: Comparison of measured and calculated normal stress data (acc to Gleissle)

2. EXPERIMENTAL TECHNIQUES TO MEASURE VISCO-ELASTIC DATA OF POLYMER MELTS

In practical rheometry visco-elastic data of polymer melts are measured with rotational

or capillary rheometers. Fig. 2 is showing various design of these devices. Due to frictional heating and edge effects the rotational rheometers are limited to a shear rate region of 10^{-2} to about 10^2 s^{-1} . Capillary rheometers are covering the whole shear rate range of practical processing and with modern design and software are these more easy to handle and operate than the rotational rheometers.

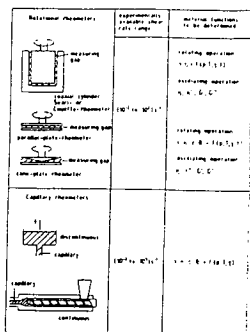


Figure 2: Schematic diagram of types of rheometers suitable for testing polymer melts.

2.1 DETERMINATION OF ELASTIC FLOW COMPONENT FROM VISCOSITY CURVES

Capillary rheometers were in the past useful only for measurements of viscous flow components. Today, however, it exists some empirical equations called "mirror relations" that allow calculation of elastic flow parameters from viscosity curves. These equations have been developed by Prof. Gleissle, Karlsruhe University, Germany, and he found out that there is a mirror relation between a steady state viscosity function and a transient viscosity function at time closed to zero. If time or shear rate are inverted it is possible to convert data from one curve to the other.

Making the same measurement of the first normal stress coefficient θ at different shear rates together with the transient first normal stress coefficient at different shear rates as a function of time there was a "second mirror

relation". By inverting time or shear rate it was possible to convert data from one curve to another - if a "shift-factor" was used. This shift factor is in the range of 2-5 for almost all polymers.

As shown in Fig. 3 the next step was to combine these two empirical mirror relations with some basic equations from theoretical rheology to get an explicit expression to calculate the elastic flow parameters of a polymer melt from its viscosity function.

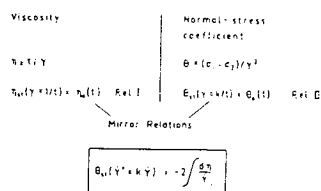


Figure 3: Calculation of 1 normal stress parameters from viscosity measured (acc. to Gleissle).

A comparison between measured and calculated elastic data was also showed earlier in Graph 3. The first normal stress difference measured with a cone plate rheometer in the range available with this instrument are plotted together with calculated from the mirror relations and these values correlate very good. It is evident that calculated data are reasonable to extrapolate into the high shear rate range of practical processing.

One great advantage of these calculations is the use to replace Bagley correction for pressure losses at in- and outlet of the capillary. Measurement with one capillary only is enough and will save much time and work for the operator.

3. CONCLUSION

For a safe polymer production it is important to know the viscous and elastic flow properties in the range of processing. Modern capillary rheometers cover all ranges of polymer production shear rates and are easy to use and operate.