Elongational flow of polyvinyl chloride

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ELONGATIONAL FLOW OF POLYVINYL CHLORIDE

by

MOHD. NASIR B. ZAINAL ARIF

A Doctoral Thesis Submitted
in Partial Fulfilment of the
Requirements for the Award of
DOCTOR OF PHILOSOPHY
of the
Loughborough University of Technology

December 1983

Supervisor: Dr. D.E. Marshall,
Institute of Polymer Technology

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Finally but not least, the author would like to thank John Whitehead, the typist, and also all who have in one way or another played a role which made this work possible.
IN THE NAME OF GOD, MOST GRACIOUS, MOST MERCIFUL

They shall not hurt nor destroy
In all My holy mountain:
For all the earth shall be full of the knowledge of the Lord
As the waters cover the sea.

W. MONTGOMERY WATT
This humble contribution of the slave of God is specially dedicated to my beloved family, friends and finally but not least to NIE...
The abbreviations frequently used are as follows:

\[
\begin{align*}
\mu_a(t) & :- \text{ apparent elongational viscosity} \\
\alpha_a(t) & :- \text{ apparent elongational stress} \\
\lambda & :- \text{ true strain} \\
\eta_a & :- \text{ apparent shear viscosity} \\
D_{OE} & :- \text{ chain bending and stretching component of deformation} \\
D_{HE} & :- \text{ high elastic deformation or chain slippage with no slippage} \\
D_{visc} & :- \text{ viscous deformation or chain slippage} \\
T_g & :- \text{ glass transition temperature} \\
DOP & :- \text{ Di-2-ethylhexyl phthalate}
\end{align*}
\]

Other abbreviations used will be explained accordingly.
ABSTRACT

The elongational behaviour of both rigid and plasticised polyvinyl chloride were investigated using the prototype Rutherford Extensional Rheometer. Prior to this, the search for a suitable clamp design and sample shape, the tests on the compatibility of silicon oil as the heating medium for plasticised polyvinyl chloride and the reproducibility of measurements of the rheometer were carried out.

Constant strain rate experiments were carried out over a range of constant strain rates and temperatures. The elongational behaviour at elevated temperatures ranging from 160°C to 190°C, and the effects of plasticiser composition of a particular type, i.e. di-2-ethylhexyl phthalate (DOP) and plasticiser types were studied. An attempt was made to compare the elongational behaviour with shear behaviour under similar conditions and with predicted theoretical values using the Chang and Lodge rubber-like model equation.

Two methods of evaluating shift factors, arising from the increase in temperatures and plasticiser composition were postulated. It was revealed that the shift factors (elongational viscosity) by the first method, at elevated temperatures and plasticiser composition were approximately related to the reciprocal of the absolute temperatures and the weight fraction and the glass transition temperatures of the plasticised PVC, respectively, whereas the shift factors evaluated by the second method were governed by an independent form of the W.L.F. equations.

Changing the plasticiser types, the shift factors using the second method, were found to be in a limited sense related to the molecular weights of the plasticiser. The trend in efficiency and compatibility of the
plasticisers was restrictedly related to those efficiencies obtained by other workers using properties such as elongation at 100% modulus. The difference might be attributed to different states of polyvinyl chloride measured, i.e. melt state (processing) and solid state (finished).

The elongational behaviour of polyvinyl chloride observed might be explained in terms of dominance in various components of a typical tensile deformation, which was dependent on the conditions. By analogy, this might presumably be associated with the nature of polyvinyl chloride, i.e. the degree of crystallinity.

The occurrence of the dual relationship in elongational behaviour of polyvinyl chloride might be attributed to some form of phase transition, say, from predominantly crystalline to predominantly amorphous or the total tensile deformation was mainly made up of bending and stretching of bonds ($D_{OE}$) and chain uncoiling (no slippage), ($D_{HE}$) or chain slippage ($D_{visc}$) and vice-versa.
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CHAPTER 1

FUNDAMENTAL PROPERTIES AND
RHEOLOGY OF POLYVINYL CHLORIDE

1.1 Flow Properties

1.1.1 Introduction

It has been generally accepted and understood\(^1\)\(^-\)\(^3\) that the basic art of polymer processing is mainly concerned with forming polymer compounds into desired shapes and fixing the shapes by such processes as cooling, crosslinking and coacervation. Thus, it does not require much imagination to show that the science concerned with the flow and deformation of matter, known as rheology, is of interest to the polymer processor.

Due to this realisation, both theoreticians and technologists alike have made vast progress in understanding rheology, viz a viz, to understand processing faults and defects and hence to make logical suggestions for adjusting the processing conditions, either minimizing or completely removing the faults, to make a more intelligent selection of the best polymer or polymer compounds to use under a given set of circumstances. Finally, this leads to both qualitative and to some extent quantitative relationships between factors such as output, power consumption, material properties and also operational variables such as temperature and pressure, and to some limited extent provide information on molecular structure. However, most of these established works and theories are primarily associated with simple shear flow.
Not until a few years back, though initial work was pioneered by Trouton\textsuperscript{4} and later by others,\textsuperscript{5-9} there was an increasing recognition that most practical flows such as extrusion and injection moulding include elongational or extensional as well as shear flow. Hence, there seemed to be a relative shift in studies from shear to elongational rheology. In fact to date, there have been several reviews by Petrie\textsuperscript{10}, Dealy\textsuperscript{11} and White\textsuperscript{12} which dealt exclusively with elongational flow of polymer melts and polymer solutions.

Generally and qualitatively, the shear flows of almost all polymer melts and solutions follow a similar pattern. This is not the case for elongational flow where significant differences in character exist for different polymer systems. For example work by a number of workers\textsuperscript{13-28} on polymer melts whose viscosity under simple shear decreased with increasing stress, found that the elongational viscosity might vary depending on stress applied as well as depending on strain and/or time.

Work by Takserman-Krozer\textsuperscript{25} and also Giesekus\textsuperscript{26} showed the differences between shear and elongation and led to the conclusion among other things that phenomena in elongation could not be explained in terms of experiments or theories concerning shear flow. Frank\textsuperscript{27} made a distinction between them which can be summarized as follows.

In shear, if a molecule is extended it is orientated parallel to the streamlines and lies more or less in fluid of uniform velocity and does not affect the motion greatly, whereas in elongation the ends of a molecule are in fluid of increasingly different velocity, so that once the velocity gradient is large enough to surpass the natural tendency of the molecule to coil up, there is a rapid change to the extended form which affects the motion significantly.
The purpose of this work is essentially to study the elongation properties of a commercially rigid and plasticised polyvinyl chloride, with the latter being stressed over a wide range of conditions such as strain rates and temperature. Variation with concentration and types of plasticiser have also been investigated. The bulk of the work has been carried out using the Rutherford Extensional rheometer and for comparison purposes, the shear flow data has been obtained using the Davenport Capillary rheometer.

In order to understand elongational flow, it is appropriate and essential to attain some basic ideas on behaviour and characteristics of materials both Newtonian and non-Newtonian in simple shear flow.

1.2 Rheological Equation of State

If a stress or load is applied to solids, liquids and all intermediate materials, they will deform or strain instantaneously or continuously with time and the mathematical relationships between stress, strain and time are known as rheological equations of state. For polymer melts, they do not necessarily fit the behaviour patterns indicated by these equations, thus in some cases, it is better to use a graphical relationships such as flow curves.

Now, let us look at some rheological equations of state of some of the more important classes of material.

1.2.1 The Ideal (Elastic) Solid

Basically, the ideal elastic solid obeys Hooke’s law and sometimes it is known as Hookean Solid. Here, the stress in it is proportional to the strain.
For tensile strains, it is given by

\[ \sigma = \varepsilon \lambda = \varepsilon \frac{\Delta L}{L} \]  

where \( \sigma \) is the imposed tensile stress; \( \lambda \) is the consequent tensile strain, i.e. increase in length \( \Delta L \) as compared with the original length \( L \); \( \varepsilon \) is the modulus of elasticity, and for shear deformation (refer to Fig. 1.1), then,

\[ \tau = \frac{F}{A} = G \left( \frac{\Delta L}{L_0} \right) = G \dot{\gamma} \]  

where \( \tau \) is the shear stress; \( G \) is known as shear modulus and \( \dot{\gamma} \) is the shear strain.

The behaviour can be manifested by Fig. 1.2.
1.2.2 The Ideal Fluid (Newtonian Fluid)

Refer to Fig. 1.3, here, a shear force, $F$ is applied to the top plate and this moves with a velocity, $V$, then, stress-deformation of a Newtonian fluid obeys the following simple relation.

$$\tau = \eta \left( \frac{V}{F} \right)$$

or

$$\eta \left( \frac{du}{dr} \right)$$

... 1.3.

where $\eta$ is known as coefficient of viscosity.

Fig. 1.3 Shear deformation of an ideal fluid
As with 1.2.1, this can be represented graphically by Fig. 1.4

\[ \tau = \eta \dot{\gamma} \quad \ldots \quad 1.4 \]

which is very similar in form to [1.2].

### 1.3 Classification of Fluids

In section 1.2.2, a brief discussion on the behaviour of an ideal (Newtonian) fluid has been made. However, many real materials, particularly polymer melts and solutions and also suspensions in liquids such as polyvinyl chloride pastes do not exhibit the simple characteristic of a Newtonian fluid.
In general, the behaviour of fluids can be approximately classified into three major categories—time independent, time dependent and elasticoviscous fluids.

1.3.1 **Time Independent Fluids**

These are fluids in which the rates of shear rate at a given point is some function of shearing stress at the particular point and nothing else and hence, a Newtonian fluid can be regarded as the simplest form of this type. Also, time independent fluids can be further subdivided into several groups:

a) **Pseudoplastic** (shear thinning). The viscosity decreases with increasing shear rate.

b) **Dilatant** (shear thickening). As above but viscosity increases.

c) **Viscoplastic**. A finite yield stress is required to initiate flow, also known as Bingham Body.

The above classification can be best summarized by Fig. 1.5 and 1.6, respectively.
Fig. 1.5  Flow curves for time independent fluids

Fig. 1.6  Viscosity/shear curves for time independent fluids
1.3.2 Time Dependent Fluids

The time dependent fluids are those whose flow properties such as apparent viscosity, vary with time and in some cases, reversibly or at least the viscosity reverts to its initial value after a long rest. It is often assumed that polymer melts are time independent but evidence accumulated by Schreiber and Rudin,28 Devine29 and others30-31 has shown that disentanglement of molecules during shear would cause time-dependent effects.

Most time-dependent behaviour studies are associated with reversible effects such as thixotropy and rheopexy.

Thixotropic fluids are those fluids whose apparent viscosity is temporarily reduced by previous deformation. This can easily be achieved for example by flocculation or deflocculation of the disperse phase in a multi-phase system by scission of a long chain of molecules.

Figure 1.7, shows the simplest case of symmetrical thixotropy where the structure of the fluid is broken down under increasing duration of shearing.

![Thixotropic fluid behaviour (symmetrical)](image)

Fig. 1.7 Thixotropic fluid behaviour (symmetrical)
Here on cessation of shearing the structure builds up at the same rate as the break-down process and hence, is symmetrical in this sense. The opposite type of behaviour, namely, a build up of structure under steady shearing motion or where the apparent viscosity is an increasing function of the duration of flow, is known as rheopexy or anti-thixotropy. These two opposite behaviours can be represented by hysteresis curves obtained using a rotary viscometer as shown in Figures 1.8 and 1.9 respectively.

![Hysteresis curve of a thixotropic fluid](Fig. 1.8)

![Hysteresis curve of an anti-thixotropic fluid](Fig. 1.9)
1.3.3 Elasticoviscous Fluids

This type of fluid exhibits properties intermediate to those of classical solids and liquids. The occurrences of such phenomena as die swell, calendar swell, neck in and frozen-in orientation are attributed to this type of behaviour.

In polymer melts, this behaviour is due to long-chain molecules taking up an oriented configuration on application of stress but, on release of the stress, bond rotations cause the molecules to take up a random form.

1.4 Rheological Formulae

1.4.1 Time Independent Fluids

Many rheological formulae have been published, with a view to describing one or more features of non-Newtonian behaviour. Some of them have limited use. Listed below are some of the better known formulae which referred to simple shearing motion.

i) Ostwalde de Waele (power law).

This is often represented by the following formulae:

\[ \tau = k \dot{\gamma}^n \] \hspace{2cm} \ldots 1.5)

or \[ \tau = k \sqrt[1-n]{\dot{\gamma}} \] \hspace{2cm} \ldots 1.6)

For \( n = 1 \), it reverts to the Newtonian expression. For \( n < 1 \) and \( n > 1 \), it is used to describe pseudoplastic and dilatant behaviour
respectively. The dimension of the constant, $k$ depends on the value of $n$ and hence it is not a material property.

ii) Viscoplastic (generalised Bingham model).

This can be represented by:

$$\tau - \tau_y = k \left| \dot{\gamma} \right|^{n-1} \quad \ldots \ 1.7)$$

where $\tau_y$ represents a finite yield stress required to initiate flow. In real material, where the real value is difficult to discern, it often represents the value of $\tau$ as $\dot{\gamma} \to 0$ and may more appropriately be regarded as an apparent value.

iii) Ree-Eyring.

Ree and Eyring\(^2\) adapted the rather general Eyring theory of rate processes to treat the flow of non-Newtonian fluids.

Considering that there are $M$ different flow species within the fluid per unit of shear plane area, each contributing to the stress on the shear plane. The shear stress is then given by

$$\tau = \sum_{N=1}^{N=M} C \sinh^{-1} \beta_N \dot{\gamma} \quad \ldots \ 1.9)$$

where $\beta_N$ is the relaxation time of the rate process of the typical $N$th unit, and $C_N$ may be regarded as $M$ disposable constant.

For a Newtonian fluid the $C_N$ are all zero for $N > 1$ and only one term remains. Also as $\beta, \dot{\gamma} \to 0$, $\sinh^{-1} \beta \dot{\gamma} \to \beta \dot{\gamma}$, hence, the formulae reverts to Newtonian behaviour since $\beta \dot{\gamma}$ would be a very small quantity for simple fluids.
1.4.2 Thixotropic Fluids

The only equation for this type of fluid is that suggested by Harris.\textsuperscript{33} In real materials there is often a lack of symmetry between the breakdown of the structure under constant shear and recovery (if any) on cessation of shearing.

1.4.3 Elasticoviscous Fluids

The simplest example is the Maxwell model, shown below (differential representation).

\[ \tau + \frac{1}{G} \tau = \eta \dot{\gamma} \] \hfill \ldots 1.10.

It can be represented by a mechanical model as shown in Figure 1.10.

Fig. 1.10  Diagram of mechanical analogy to the Maxwell model

The theoretical basis of the Maxwell fluid is based upon the assumption that on application of a stress to the body, some instantaneous deformation occurs, this is being followed by a Newtonian type of viscous deformation. The spring and the dashpot are stipulated to show linear elastic behaviour and Newtonian characteristics respectively.
From (1.10), it can be shown that if the strain is fixed and held constant, then the stress will decay.

i.e. since \( \frac{d\gamma}{dt} = 0 \), from (1.10)

\[
\frac{d\tau}{\tau} = -\frac{G}{\eta} \, dt
\]

Integrating,

\[ \log \tau = (\frac{-G}{\eta})t + C \]

At \( t = 0 \), \( \tau = \tau_0 \), hence \( C = \log \tau_0 \)

Therefore,

\[ \log \tau = \log \tau_0 - (\frac{G}{\eta})t \]

or

\[ \tau = \tau_0 e^{-\frac{Gt}{\eta}} = \tau_0 e^{-t/\theta} \ldots 1.12 \]

where \( \theta \) is known as relaxation time.

For a polymer molecule, \( \Theta \), provides a measure of time taken for molecules to recoil after deformation and also a spectrum of \( \Theta \) can be observed since different molecules and also one molecule at different times will have different \( \Theta \) because of differences in their configuration.

Having discussed the general characteristics and behaviour of Newtonian and non-Newtonian fluids which are based on an ideal situation, it is felt relevant to scrutinise the behaviour of some real materials especially polyvinyl chloride.
1.5 Rheology of Polyvinyl Chloride

Polyvinyl Chloride (PVC) is a thermally unstable polymer of variable crystallinity and as such, it presents formidable problems during rheological studies. Rheology of polyvinyl chloride always refers to the processes of deformation and flow above the glass transition temperature, $T_g$. Thus, discussions always cover the viscous and elastic properties in the range of temperatures from $T_g$ to about $230^\circ C$, where the upper temperature limit depends greatly on its degradation velocity.

G. Pezzin has attributed the anomalies in the rheological behaviour of polyvinyl chloride due to the presence of excessive molecular structures of various types at temperatures below the melting point of some crystallites.

Before discussing the factors such as molecular weight, temperature and also plasticisation which influence the rheological behaviour of polyvinyl chloride, it is useful to review some of the common effects appearing when measurements are carried out with unplasticised polyvinyl chloride.

1.5.1 Particle Flow

Berens and Folt on extensive investigation of flow of pure resins and on studying the fracture surfaces of the extrudate, showed the flow of an original polyvinyl chloride resin in a piston driven capillary rheometer could take place partially through slippage of the original unmelted particles (whose diameter is of the order of $10^3-10^4 \text{ Å}$) past one
another, even at temperatures as high as 210°C. The important features disclosed were:

a) a substantial decrease of the apparent viscosity of the system with particle size.

b) the flow curves were extremely non-Newtonian.

c) the molecular deformation would predominate at low shear rates, whereas particle flow prevailed at high shear rates.

d) the elasticity of the melt, i.e. the die swell, increased with temperature, which was contrary to the behaviour of normal polymer melts. This was interpreted as evidence for progressive fusion of particles and consequently for greater contribution of molecular flow mechanism\(^{38}\) with increasing temperature.

e) the melt elasticity decreased with increasing molecular weight, which was in contrast with the viscoelastic theories.

Therefore, in flow of polyvinyl chloride, particle flow is favoured against the molecular deformation mechanism by high molecular weight, low temperature, large particle size and also high crystallinity of the sample.\(^{35}\)

The evidence of two distinct mechanisms of flow has also been reported by Collins and Krier.\(^{39}\) On thorough study on flow of a stabilised polyvinyl chloride dry-blend for temperatures ranging from 160°C to 230°C, both at constant shear rate and at constant shear stress, they found
two distinct flow activation energies. A schematic representation is given in Figure 1.11.

In the low temperature region, characterised by the predominance of particle flow, a low activation energy at constant strain rate was observed, whereas a higher value was observed at higher temperature due to the predominance in molecular flow. The transition from one flow to the other was due to the melting of crystallites. Similar phenomena were also observed with polyethylene\textsuperscript{40} and polypropylene\textsuperscript{41}. 

**Fig. 1.11** Schematic example of Arrhenius plots showing dual activation energy for PVC flow\textsuperscript{39}
They also observed, the marked influence of molecular weight on the activation energy, whereas addition of a solvating agent did not affect this phase change. The strict connection existing between crystallinity of polyvinyl chloride and particle flow has been further enhanced by investigation on polyvinyl chloride samples of high crystallinity where stereoscanning electron microscopic pictures of fracture surfaces of milled samples showed that elementary particles of crystalline polyvinyl chloride started to melt at a temperature about 40°C higher than that of conventional polyvinyl chloride melts.

1.5.2 **Changes of Flow Properties with Time and Thermal History**

Menges and Klenk, and Gale published work on the combined effects of temperature and shear rate on the fusion of polyvinyl chloride resin which was previously mixed with various additives. While Lee and Purdon, using a miniature Banbury studied the viscosity changes of polyvinyl chloride mixtures with shearing time at constant temperature. The curves obtained often showed a maximum (interpreted as the 'gelation' of the polyvinyl chloride dry-blend) followed by a plateau and finally by an upward inflection which marked the beginning of degradation induced cross-linking.

It has also been reported that by increasing the mutual fusion of the polyvinyl chloride particles prior to measurement, both the viscosity and the elasticity increased. These rheological changes were obviously attributed to melting but often chemical degradation and cross-linking have to be also taken into account, even at a relatively low temperature. The main structural changes occurring during rolling of
polyvinyl chloride resins at low temperatures was the conversion of globular particles into fibrillar ones orientated in the rolling direction.\textsuperscript{51}

As a result of structural changes, it is not quite unreasonable to expect the flow curves of polyvinyl chloride from different sources (or tested on different apparatus) to be rarely reproducible. Also if there is a progressive change of polyvinyl chloride structure with increasing temperature, calculation of activation energies from the shift-factors or from flow curves could give discordant results.\textsuperscript{52}

Other common effects which could appear when measurement of rheological properties of rigid polyvinyl chloride are slip flow and viscous heat generation which are mentioned elsewhere.\textsuperscript{35,52-54}

1.6 \textbf{Factors Affecting Polyvinyl Chloride Flow}

1.6.1 \textbf{Effect of Molecular Weight}

From the above section, it is clear that polyvinyl chloride does not often obey the rules of flow of simple amorphous polymeric melts. In particular, the expected molecular weight dependence of flow properties can be altered or masked by the presence of various effects, as already discussed in the previous section, complicated further by thermal degradation.

Generally, the viscosity of polyvinyl chloride increases with increasing molecular weight. This has been found to be true by Berens and Folt\textsuperscript{37} for emulsion polyvinyl chloride resins. Similar evidence has also been observed for suspension resin,\textsuperscript{53} for previously milled or extruded compounds\textsuperscript{54,55} and also for crystalline polyvinyl chloride compounds.\textsuperscript{52}
At 200°C, Pezzin found that viscosity varied with the third power of weight-average molecular weight, $M_w$. Similar dependence has also been reported by Sieglaff. The high value of the exponent and the strongly non-Newtonian behaviour showed by flow curves was taken as a further indication that polyvinyl chloride has a cross-linked paracrystalline structure.

Thus, molecular weight may have opposite effects on the rheological properties of polyvinyl chloride, depending on the polymer history and the range of temperatures. When particle flow predominates, an increase of weight average molecular weight, $M_w$, decreases the elasticity of the melt, apparently because the fusion of the particles becomes more difficult. However, on the contrary, this is not the case when well-melted compounds are investigated at high temperature. Here the presence of crystallites which bond the polyvinyl chloride macromolecules to form a permanent network, causes greater dependence of viscosity and elasticity on molecular weight.

1.6.2 Effect of Temperature

For polymer melt, the functional relationship between viscosity and temperature can be expressed by the Andrade equation

$$\eta = \text{constant} \exp \frac{E_a}{RT}$$

where $E_a$ is the apparent energy of activation for viscous flow at constant rate, $R$ is the gas constant and $T$ is the absolute temperature.

For polyvinyl chloride, it has been found that the above equation was valid for a limited temperature range.
Work by Munstedt\textsuperscript{58} on the dependence of viscosity and extrudate swell on shear rate and temperature, has reported the existence of a distinct critical temperature below which samples showed a rheological behaviour similar to that of a slightly crosslinked amorphous polymer. Above this, the rheological properties were comparable to those of amorphous polymers. This unusual phenomenon was explained by the assumption of a network structure formed by crystallites in the melt. He also found that this temperature increased with increasing molecular weight. This was similarly observed by Collins and Metzger\textsuperscript{53} and also by Pezzin.\textsuperscript{56}

1.7 **Thermal Degradation of Polyvinyl Chloride**

Although polyvinyl chloride is one of the most widely used and most important technical polymers, it has one great disadvantage, i.e. it has a rather low thermal stability. It is well known that polyvinyl chloride splits off hydrogen chloride at high temperature; during this process polyene sequences are formed and the polymer is discoloured. Several detailed surveys on the degradation of polyvinyl chloride have been published.\textsuperscript{34,59,60,61}

Here, a brief discussion on degradation such as initiation, discolouration and also degradation in the presence of plasticisers is made because of its relevancy to problems encountered in this work.
1.7.1 Initial Sites of Dehydrochlorination

Based on works using low molecular models for polyvinyl chloride such as 2-chloroputane, 2,4-dichloropentene, several possibilities of initiation sites for thermal degradation of polyvinyl chloride have been postulated.

For example, MaColl\textsuperscript{62} using a 2,4,6-trichloroheptene model concluded that random allylic chlorine atoms or branches with tertiary atoms were mainly responsible for the initiation. However, several workers\textsuperscript{63-66} using models of copolymers of vinyl chloride and 2-chloropropene revealed the non-existence of tertiary chlorine atoms, due to the steric nature of polyvinyl chloride. Other alternative sites of initiation postulated were the end groups,\textsuperscript{67,68} the unsaturated groups with allylic chlorine,\textsuperscript{69} hydroperoxide or peroxide groups (formed by oxidation with oxygen or ozone).\textsuperscript{70}

1.7.2 Discolouration During Degradation

Discolouration during thermal degradation of polyvinyl chloride is usually associated with the formation of sequences of conjugated double bonds within the polymer chains. The intensity increased with increasing splitting off of hydrogen chloride.\textsuperscript{71} The length and frequency distribution of the polyene sequences of different length could be obtained by spectroscopy.

From analysis of the spectra, several conclusions regarding discolouration were made:-
a) Geddes\textsuperscript{72} determined the amount of hydrogen chloride split off and the number of polyene sequences by ozonolysis.

b) Stromberg et al\textsuperscript{73} revealed that, besides cross-linking, aromatic structures such as benzene and toluene were formed.

c) Braun and Thallmaier\textsuperscript{71} showed there was a shift of frequency distribution to shorter polyene sequences with increase in temperature (implies for discolouration, degradation) starts on many sites simultaneously.

Finally, d) Onozuka and Asahina\textsuperscript{34} discussed the possibility of charge-transfer complexes as the reason for discolouration of polyvinyl chloride.

1.8 Plasticisation of Polyvinyl Chloride

There have been a lot of reviews or theories of plasticisation, to quote but a few by Luna,\textsuperscript{74} Hoffmann and Choi\textsuperscript{57} and by Doolittle.\textsuperscript{75} In this section, it is thus felt not essential to dwell upon it but to concentrate more on the rheological and thermal findings on plasticised polyvinyl chloride.

Using X-ray diffraction studies, and by the temperature dependence of mechanical properties, Affrey et al.\textsuperscript{76} and Voskresenki and Orlova\textsuperscript{77} gave ample evidence that crystallinity was still present in plasticised polyvinyl chloride. Para crystalline lamellar structures have also been postulated by Bonart.\textsuperscript{78} He also found that increasing the plasticiser concentration increased their dimensions from 150Å to about
300A°, as revealed by low-angle X-ray diffraction measurements. It was also discovered that at low plasticiser concentration, the degree of ordering of the polymer structure is markedly increased.\textsuperscript{77}

In the useful range of plasticiser concentration, the crystallinity was being maintained up to temperatures of the order of 180-190°C as reported by Pezzin, Ajroldi and Garbuglio.\textsuperscript{35} Work by the same authors and also by Rudin\textsuperscript{79} showed that thermal history significantly influenced the flow curves at 150-170°C. Since the glass transition of plasticised polyvinyl chloride is normally below room temperature, storage of the polymer is expected to cause changes of crystallinity and consequently physical properties\textsuperscript{35} and in fact, density and Young's modulus increase linearly with the logarithm of storing time.\textsuperscript{80,81}

Hence, from various work cited above, as well as other evidence, it seems clear that the viscoelastic behaviour of plasticised polyvinyl chloride is strictly related to the history of the compound. For example, those of milled samples changed markedly with mill temperature.\textsuperscript{82} As a consequence, a specific optimum processing temperature is often required by a given compound in order to achieve its best physical properties.

1.8.1 Rheological Properties of Plasticised Polyvinyl Chloride

The influence of composition and plasticiser nature on flow behaviour have been investigated by Schreiber\textsuperscript{83,84} in the temperature range from 150°C to 190°C. It was suggested that the flow behaviour of highly plasticised polyvinyl chloride could be possibly predicted by knowing the Flory-Huggin parameter, $X$ only, while Pezzin\textsuperscript{56} disapproved this because the melt viscosity was expected to depend, beside polymer-solvent
interactions, on the free volume of the system, i.e. on a complex function of concentration and thermal properties of diluent.

Pezzin et al.\textsuperscript{35} has investigated the molecular weight dependence of loss tangent, stress relaxation modulus and flow curves. Their findings were:-

a) the maximum relaxation curves were found to vary linearly with the eighth power of weight average molecular weight, \( M_w \), instead of 3.4 for other polymers.

b) the shear dependence of viscosity could not be described by theoretical equations such as those given by Bueche and Graesly. This was possibly attributed to the greater stability of some macromolecular network junctions or crystallites.

Several authors\textsuperscript{85-88} postulated that plasticiser interacted only with the amorphous regions of polyvinyl chloride, so the crystallites remain intact.

1.8.2 Thermal Properties of Plasticised Polyvinyl Chloride

Plasticisers are added to polyvinyl chloride primarily to reduce the glass transition temperature, \( T_g \) below room temperature. The efficiency of a plasticiser is usually evaluated by its capacity to lower the glass transition temperature, \( T_g \) and related parameters such as brittle temperature or the dielectric or mechanical loss tangent maximum.

Several empirical equations have been obtained to express the variation of glass transition temperature, \( T_g \) with solvent weight fraction \( w \), or volume fraction \( \varnothing \), to quote but a few are:-
a) Boyer and Spencer suggested

\[ T_{g2} - T_g = kw, \quad \ldots 1.14) \]

where \( T_{g2} \) is the glass transition temperature of the undiluted polymer.

b) Jenckel and Heusch added a quadratic term, obtaining

\[ T_g = w_2 T_{g2} + w_1 T_{g1} + k' w_1 w_2 \quad \ldots 1.15) \]

where \( T_{g1} \) is the solvent glass transition temperature.

c) Kelley and Beuche based on free volume concepts suggested

\[ T_g = \frac{\varphi_2 \alpha_{2T_{g2}} + \varphi_1 \alpha_{1T_{g1}}}{\varphi_2 \alpha_2 + \varphi_1 \alpha_2} \quad \ldots 1.16) \]

where \( \alpha_1 \) and \( \alpha_2 \) are expansion coefficients of solvent and undiluted polymer.

d) Kovacs pointed out that [1.16] could not be used if \( T_c = T_{g2} - f_{g2}/d_2 \) because \( f_2 \) would be negative and he obtained for \( T_g < T_c \), the equation:

\[ T_g = T_{g1} + \frac{f_{g2}}{k} \frac{\varphi_2}{\varphi_1} \quad \ldots 1.17) \]

e) Pezzin, Omacini and Grandi using both [1.16] and [1.17] on polyvinyl chloride-diputylphthalate and polyvinyl chloride-dicyclohexylphthalate, found that both systems had a singular point, \( T_c \) in the \( T_g/\text{composition} \) curves as predicted by Kovacs (refer to Figure 1.12). The findings were in close
agreement with Adams and Gibbs\textsuperscript{93} who used statistical thermodynamic treatment in deriving them.

![Graph showing T\textsubscript{g}/composition curves for PVC-DBP and PVC-dicyclohexylphthalate.](image)

**Fig. 1.12** Schematic plot of T\textsubscript{g}/composition curves for PVC-DBP and PVC-dicyclohexylphthalate. Dotted lines obtained using Kelley-Bueche and Kovacs equations.\textsuperscript{92}

1.8.3 Degradation of Plasticised Polyvinyl Chloride

The thermal stability of plasticised polyvinyl chloride is connected with type and amount of the plasticiser.\textsuperscript{65,66} By simultaneous measurement of the absorbed oxygen and the hydrogen chloride evolution, during heating of polyvinyl chloride, Wolkober\textsuperscript{94} observed that the thermal
stability of plasticised polyvinyl chloride was strongly dependent on the stability of the plasticiser.

Several workers\textsuperscript{95,96} suggested that dehydrochlorination was influenced by the peroxide products from the plasticisers. The rate of discolouration was dependent on the amount of plasticiser, though no linear relationship was obtained between plasticiser content and rate of discolouration.\textsuperscript{97} It was suggested that at lower concentrations the interactions between the polar groups in polyvinyl chloride and the plasticiser molecules were stronger than between polyvinyl chloride chains. Hence the solvation of the polyvinyl chloride chain by the plasticiser molecules could have some stabilising effect.

In the next chapter, some fundamental aspects of elongational flow will be discussed.
CHAPTER 2

ELONGATIONAL FLOWS

2.1 Introduction

In Chapter 1, discussions have been primarily associated with shear flows, however, elongational flows may on some occasions play a significant role in flows which cannot be realistically described as shear flows. For examples, the drawing of a thread of molten polymer to form fibre and the phenomenon of sharkskin, may be recognised as being due to an elongational or stretching flow in the outer edge of the extrudate. In fact, it has already been realised that whenever there are convergent or divergent flows during polymer processing, elongational flow effects are important.

In this chapter, various aspects, such as historical background of elongational flows, both theoretical and experimental works (including methods of measurement and problems commonly encountered during measurement) and also its limitations and finally but not least, the applications will be briefly looked at.

2.1.1 Historical Development of Elongational Flows

It is not adequate to discuss the development of elongational flow without mentioning or giving a brief review of the pioneering work by Trouton\textsuperscript{4} which later formed the basis for understanding the idea of elongational flows.
The work of Trouton involved the determination of the elongational viscosity of pitch and other similarly very viscous substances. By comparison with shear viscosity obtained from torsion experiments, he was able to confirm the theoretical prediction that elongational viscosity was three times the shear viscosity. This finding was later known as Trouton relationship, i.e. $\mu = 3\eta$, where $\mu$ and $\eta$ are the elongational and shear viscosities respectively.

After the initial work by Trouton, it was then followed by a number of workers such as English, Tammann and Jenckel and Lillie, which involved the determination of viscosity of glass. All of them utilised the term 'mobility' which they defined as the rate of elongation of unit length of a glass rod under the action of unit stress and used it in determining the appropriate temperatures for the working and annealing of glass. English in his work, related viscosity (obtained in simple shear) with the reciprocal of mobility (elongational viscosity) but this was later disapproved by Scott due to lack of data available. Other contemporary workers besides those already mentioned were Boow and Turner, Phillipoff and also Van Nieuwenburg.

A few years later, Scott Blair published an extensive review of experimental techniques which included uniaxial extension or compression of bitumen, butter, resin, rubbers and metals and also discussed the problem of maintaining constant stress during a large extension. Based on this review, Andrade made the first attempt by stretching lead wires under the influence of a specially shaped weight immersed in water. This ingenious method (using a suitably shaped cam) was rediscovered by Cogswell and also Leaderman, some 25 years later. Up to this stage,
however, most of the work involved the use of highly viscous type materials, similar to those considered by Trouton.

As a result of lack of interest in these types of material, in the succeeding years relatively little attention was given to the problem. However, this state of affairs was suddenly revamped with the enhancement of interest in studies of polymer solutions and melts, and other non-Newtonian fluids. Among those was Reiner\textsuperscript{103} who made the first study of non-Newtonian fluid (purely theoretical) and led to the formulation of a Reiner Rivlin model. Theoretical investigations of elongational viscosity of viscoelastic fluid were initiated by Yamamoto\textsuperscript{104,105} while Nitschmann and Schrade\textsuperscript{13} were responsible for pioneering the experimental work for polymer fluids.

The present contemporary studies of elongational flow of polymer melt goes back to 1960. Using Trouton's method, Ziabicki\textsuperscript{14} determined the elongational viscosity of Nylon 6 during melt spinning. A similar method was employed by Kase and Matsuo\textsuperscript{15} on polyethylene terephthalate. Both the experiments were highly non isothermal in nature, hence the elongational viscosity being a function of position along the spine line. The basic studies of elongational viscosity as a rheological property were pioneered by workers such as Cogswell,\textsuperscript{17-20} Vinogradov,\textsuperscript{23,106-112} Lodge,\textsuperscript{113-115} Meissner\textsuperscript{21,22} and Ballman,\textsuperscript{16} to name a few, in the mid 1960s. Most of these workers independently proposed careful isothermal techniques for determination of elongational viscosity. These techniques will be briefly discussed in the later section. Before discussing further techniques, we will look at some of the fundamental aspects of elongational flows.
2.1.2 Basic Relationships of Elongational Flows

It is not the aim here, to review any of the mathematical constitutive model equations which have been extensively used by several workers such as the Ward-Jenkins and Bird-Carreau models, Meister and Bogue-White models, but instead to look at equations which are directly relevant to the design and interpretation of experiment.

However, for a more thorough treatment and understanding of these model equations, the reviews by Petrie, where he gave an extensive review of constitutive equations for elongational flows obtained from the physical principles of conservation of mass and of momentum or analysis of Coleman and Noll should be consulted.

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**Fig. 2.1** Extension of a polymer (cylindrical) with initial length $L_0$, with one fixed end.
Referring to Fig. 2.1, where a cylindrical bar of length, $L_0$ and cross-sectional area, $A$, is subjected to a tensile force, $F$. In a uniform uniaxial extensional flow, the velocity distribution is given (cylindrical coordinates) as,

$$U_x = \dot{e} L_0 (e > 0) \quad \ldots 2.1$$

and

$$U_r = \frac{1}{r} \dot{e} r \quad \ldots 2.2$$

where $\dot{e}$ is the strain rate of deformation.

If, furthermore, $\dot{e}$ is constant at a value of $\dot{e}_0$, from $t = 0$ up to some time, $t$ (constant rate). then equation [2.1], can be integrated to give,

$$L(t) = L_0 \exp (\dot{e}_0 t) \quad \ldots 2.3$$

The elongational stress, $\alpha$, in the sample is related to the force and area by

$$\alpha = \frac{F}{A} \quad \ldots 2.3$$

Under constant strain rate experiments, the stress will rise and this can usually be interpreted in terms of a stress-growth function (function of time) defined as;

$$\mu_a (\dot{e}_0, t) = \alpha(t)/\dot{e}_0 \quad \ldots 2.4$$

The quantity measured, $\mu_a (\dot{e}_0, t)$ is the apparent elongational viscosity (varies with time). However, when the stress approaches a constant value, the stress-growth function is equal to the elongational viscosity,
For a Newtonian fluid, this material function approaches to a constant value, equal to three times the zero shear viscosity, while for non-Newtonian fluids, it can be represented by,

\[ \mu(\dot{\varepsilon}) = \frac{\alpha}{\varepsilon_0} \rightarrow 3\eta_0 \]

where \( \eta_0 \) is the zero shear viscosity.

Fig. 2.2 shows a typical example of the above situation, obtained under constant strain rate experiments.

**Fig. 2.2** A schematic log, log. plot of elongational viscosity \( \mu(\varepsilon,t) \) vs time for LDPE (after Meissner").
By analogy with the shear deformation, Cogswell\textsuperscript{20,118} and others\textsuperscript{10,119} predicted the existence of three types of elongational flow behaviour. These can be summarised as follows,

a) The elongational viscosity is independent of elongational strain rate and equal to three times the zero shear rate apparent shear viscosity (given by equation [2.6]). Materials showing this kind of behaviour can be classified as Troutonian.

b) The elongational viscosity increases with strain rate which is analogous to dilatancy in shear regimes. The material is then regarded to be tension stiffening.

c) The elongational viscosity decreases with strain rate. The material may be described as tension thinning (analogous to pseudoplasticity or shear thinning behaviour).

Figure 2.3, shows the variation of elongational viscosity with strain rate for some common polymers. Thus, this confirmed the very existence of the three types of behaviour.

The above classification is based on the constant strain rate mode experiments. However, Cogswell\textsuperscript{20} and several others\textsuperscript{120,121} classified the behaviour of polymer melts under constant stress mode experiments, hence, they used the variation of elongational viscosity with tensile stress. Further discussion on this subject will be made later.
Now, let us consider in qualitative terms, the various components of a typical tensile deformation and also its possible mechanism.

2.2 Components and Mechanism of Elongational Deformation

2.2.1 Components of Deformation

When polymeric materials are subjected to tensile stresses, three components of deformation can be realised.\textsuperscript{118}
a)  Bending and stretching of bonds ($D_{OE}$).

This is (both inter- and intra-molecular) the response of a Hookean solid and the deformation is instantaneous and is usually associated with a high modulus ($G_{OE}$). This response is predominant for rigid materials such as polystyrene at room temperature and can be usually represented by a metal spring model.

b)  Chain uncoiling (no slippage)($D_{HE}$).

This is a response of an ideal rubber (high elastic deformation). It is not quite instantaneous and time to reach equilibrium depends on the ease with which the molecules can coil and uncoil. The high elastic deformation is often represented by a spring and dashpot in parallel (Kelvin and Voigt model).

c)  Chain slippage ($D_{visc}$).

This is the process of flow where segments of polymer chain slide irreversibly past each other. Under a given stress the viscous deformation, $D_{visc}$ continues linearly with time and is often represented by a dashpot.

Now, let us imagine a polymeric material whose total deformation on application of stress is the sum of independent components mentioned above. If at time, $t_0$, it is subjected to a tensile stress, $\sigma$ and then is maintained constant until time $t_1$ (constant stress) at which point it is abruptly released (Figure 2.4a), then, the three components will be as shown in Figures 2.4b, c and d. Hence the sum of the deformations will be as shown in Figure 2.5;
\[ D_{total} = D_{OE} + D_{HE} + D_{visc} \]

Fig. 2.4  

a) a fixed load is imposed between \( t_0 \) and \( t_1 \)

b), c), d) Responses of ordinary elastic, highly elastic and viscous materials respectively.
Fig. 2.5  Deformation - time curves

a) Material, showing substantial ordinary elastic, high elastic and viscous component of deformation.

b) Material in which high elastic deformation predominates.

Although the above model is an over-simplification, at least it provides a useful picture of the influence of the deformation components on the deformation-time pattern of a polymer. Obviously, the predominance of the three factors will differ with materials and also operating conditions. However, if we consider a material in which there is a dominance of each type of deformation, the following observations would be observed when it is subjected to a sudden load.

a) On the instant of application of stress, i.e. before either chain uncoiling or viscous flow has taken place, the deformation
is dominated by the $D_{OE}$ component. In polymer melts it was observed\textsuperscript{118} that if the stress exceeded the value of the order of $10^6 \text{Nm}^{-2}$, then fracture occurred, probably due to the interchain bond being unable to sustain the stresses. Hence, the occurrence of phenomena such as melt fracture and sharkskin may be attributed to polymer melts being subjected to sudden stresses causing fracture before there is time for a viscous or a high elastic response.

b) Within a second or two, and usually in a small fraction of this time, the ordinary elastic deformation ($D_{OE}$) will have been dwarfed by the high elastic deformation ($D_{HE}$), and thus rapidly reaching an equilibrium value.

Now, if we assumed the chain uncoiling as a unimolecular physical reaction where the rate of uncoiling is proportional to the fraction of molecules still uncoiled, then, it can be postulated\textsuperscript{118} that $D_{HE}(t)$, the value of $D_{HE}$ at time $t$ after application of a stress, is related to the equilibrium deformation $D_{HE}(\infty)$ by

$$D_{HE}(t) = D_{HE}(\infty)(1 - e^{-t/\Theta_m})$$ \hspace{1cm} \ldots 2.8

where $\Theta_m$ is the reaction rate constant (average time taken for the molecules to deform $1-\frac{1}{e}$ of their equilibrium value.

Hence, at this stage, the instantaneous modulus of the high elastic deformation is infinite but as the molecules uncoil the modulus falls at a rate governed by equation [2.8].
c) Since the component of viscous deformation \( (D_{\text{visc}}) \) increases linearly with time from the moment of application of stress, it will eventually overtake the high elastic deformation \( (D_{OE}) \) in magnitude, usually within a few seconds.

However, in commercial processes elongational flow occurs for only a few seconds and sometimes for much shorter times, so the dominance of the viscous deformation cannot be assumed.

For constant strain rate experiments, the chain uncoiling process may enhance the rate of stress build-up, hence the component of molecular chain uncoiling \( (D_{HE}) \) is much higher than the viscous counterpart \( (D_{\text{visc}}) \). In this case, the measured elongational viscosity comprises a component due to chain uncoiling elastic effects and therefore becomes a function of time.

This presumably explained some of the pattern observed by those working with a constant strain rate mode of measurements.\(^{16,21,22}\) However, it is worth reiterating, that the situation is very much dependent on the experimental conditions such as temperature and strain rate. For example, at low strain rate, the material may behave like a liquid and thus can be continuously drawn, but at very high strain rate, the stress build-up is very rapid such that the tensile stress of the material is soon exceeded and the sample breaks.

2.2.2 Mechanism of Elongational Deformation

(Instability and Fracture)

The ability of polymer melts to be extended to several hundred percent illustrates remarkable stability. This ability of fibre formation is also
known as spinnability. It has been investigated empirically and reviewed by Pearson, White and Ide, Denn et al and also Ziabicki. 

Basically, it can be presumed, that there are three possible types of failure mechanism in elongational flows; i.e. capillarity, ductile failure and cohesive fracture (refer to Fig. 2.6).

**Fig. 2.6** Mechanism of filament instability

a) Capillarity  b) ductile failure  c) cohesive fracture

The occurrence of these mechanisms is dependent on the precise nature of the flow and its history and on factors which would cause local stress concentration in the filament and hence breakage unexpectedly and prematurely on the basis of the overall extension of the filament and the applied force.

a) Capillarity

Capillarity, according to Ide and White, is the surface tension-induced breakup of filaments into droplets or ligaments. The action of surface tension to propagate disturbances and cause the breakup of a liquid
column was originally proposed by Plateau\textsuperscript{125} and then by Rayleigh\textsuperscript{126} while the capillary instability in viscoelastic fluid jets had been considered by Middleman\textsuperscript{127} and also by Yerushalmi et al.\textsuperscript{128}

b) **Ductile failure**

Ductile failure is one where rapid reduction in cross-section of the filament occurs causing necking in areas of high stress level. This phenomena was first considered by metallurgists investigating the failure of steel and other metals.\textsuperscript{129,130} A careful discussion of necking in solid polymers was made by Vincent.\textsuperscript{131}

However, the analysis of necking for elasticoviscous liquids owed much to Chang and Lodge.\textsuperscript{132} They defined spinnability in terms of the behaviour of the ratio of the areas of two filaments extended by application of the same force. For a Newtonian liquid the ratio of smaller area to larger area ($A_s/A_L$), tends to zero, thus a neck is drawn down proportionately more than the rest of the filament. For rubberlike liquid, this is not the case, where at higher strain rates there is an increasing resistance to elongation.

Recently, Ide and White\textsuperscript{133,134} made a careful study of the mechanism of necking and ductile failure of polymer melts such as that of polyethylene and propylene in uniaxial elongational flow. Using a linear stability analysis on a White-Metzner convected Maxwell model, they suggested that filament stability and elongation to break depended on the Weissenberg number, $\Omega E$, molecular weight and "a" parameter.

c) **Cohesive fracture**

Cohesive fracture can be defined as an instantaneous rupture occurring when the tensile strength of the material is exceeded. General theories of fracture based on critical stresses and energies dated back to
the 19th century. Griffith showed that fracture was generally associated with the presence of microscopic defects. Fracture in metals usually occurred in a developing neck as discussed by Orowan and Nadai, i.e. the ductile failure and fracture mechanisms were combined.

However, when working with polymer melts which are viscoelastic fluids in nature and not solids, they often show very distinct characteristics in response. They may display large deformations when stretched at small rates and fracture occurs only with rapid deformation. Reiner and co-workers viewed this in terms of the energetic theory of strength, and developed a 'dynamical theory of strength' based on it. They proposed that the energy of deformation could be divided into two distinct parts, the dissipative (in viscous flow) and recoverable (elastic) parts; they also suggested that only the latter contributed to failure. More recent findings by Vinogradov et al. however, revealed that things were more complex but obviously the idea stipulated offered a valuable first approximation.

Results obtained by Ide and White showed that high molecular weight low density polyethylene filaments generally exhibited cohesive fracture at high strain rates but could be extended almost indefinitely at low strain rates. By comparison, high-density linear polyethylene melts undergo ductile failure and give rise to poor elongation at break. Ziabicki suggested that cohesive fracture was usually observed for polymer melts at high strain rate. Investigations on the stretching of molten polymers and development of structure during fibre formation have been extensively carried out by Chen et al. and Takaki and Bogue and by the Tennessee Group respectively.
2.3 Measurement of Elongational Behaviour

A variety of experimental procedures have been developed for measuring elongational viscosity where each varies considerably in sophistication and each has its own limitations, notably on the viscosity of the material with which it may be used. Here, following Nazem and Hill\textsuperscript{146} and Walters,\textsuperscript{119} the methods of measurement can be classified into two types, i.e. controllable and non-controllable.

2.3.1 Controllable Experiment

A controllable experiment is one in which the stress, the force or the strain rate, is kept constant and the value of the other is determined (varies with time).

Thus, the controllable types have different modes of measurement such as constant stress, constant strain rate, constant force and also constant velocity. Useful surveys and critical discussions of the various modes and experimental methods have been given by Dealy,\textsuperscript{11} White\textsuperscript{12} and others.\textsuperscript{112,146}

2.3.1 (a) Constant Stress Measurement

Pioneering work on the constant stress measurement of polymer melts was carried out by Cogswell.\textsuperscript{17-20} In this method, a rod-shaped specimen is held at each end by a suitably shaped cam and immersed in an oil bath (to minimise deformation of the material under its own weight). A constant force is applied to the cam, so that the force applied to the specimen is inversely proportional to its length and hence directly
proportional to its area. Design equations for such a cam have been presented by Dealy.\textsuperscript{11} Other workers\textsuperscript{108,121,146} developed Cogswell's design or independently approached the same method for measurement of constant stress.

One advantage of the constant stress type is that the elastic response reaches equilibrium immediately. Hence equation [2.7] becomes

\[ D_{\text{total}} = D_{E} + D_{\text{visc}} \ldots 2.8 \]

where \( D_{E} = D_{OE} + D_{HE} \)

If the time for \( D_{E} \) to reach equilibrium is very small compared to the time-scale of the experiment, i.e. \( D_{E} \ll D_{\text{total}} \) then [2.8] becomes

\[ D(t) = D_{E} + et \quad \ldots [2.9] \]

where \( D(t) \), deformation after time, \( t \).

Equation [2.9] provides a linear relationship between \( D(t) \) and \( t \).

One disadvantage of this type of measurement is, it reaches equilibrium very rapidly, thus providing less information on the transitional behaviour of the polymer melt under investigation.

2.3.1 (b) Constant Strain Rate Measurement

Constant strain rates experiments with end separation were initially used by Ballman\textsuperscript{16,147} and followed by Vinogradov et al.\textsuperscript{23} Meissner,\textsuperscript{21,22} and so on.

Figure 2.6 shows some of the elongational viscosity measurement methods at constant strain rates.
Since the velocity has to be increased in line with the specimen end separation, constant strain rates experiments often take a longer time than constant stress experiments to reach a state of dynamic equilibrium and in most cases such a state does not materialise. However it does provide more information on transitional behaviour of the material investigated.

Other modes of measurement in the controllable experiments are constant force and constant velocity. These methods have been used by Karem and Bellinger, Chen et al, Takaki and Bogue and others.
2.3.2 Non-Controllable Experiments

It has been pinpointed by Acierno et al.\textsuperscript{154} Han and Lamonte,\textsuperscript{155} Walters\textsuperscript{119} and also Chen et al.\textsuperscript{141} that the non-controllable experiments were more attractive than the controllable experiments because they operated under conditions closely resembling a real technological operation and also their ability to measure elongational properties of polymer melts with much lower viscosity. However there are major disadvantages, being non-isothermal in nature and there is a considerable variation in strain rates or stress along the spinline.

2.3.2 (a) Fibre-Spinning Apparatus

This method is an adaptation of the conventional fibre-spinning apparatus and has been used by Metzner\textsuperscript{156,157} Han and co-workers\textsuperscript{155,158} and also Acierno et al.\textsuperscript{154}

The apparatus is shown schematically in Fig. 2.7.

Though this method gives a close similarity to the commercial fibre-spinning it has a few disadvantages, namely the stress varies with the threadline, flow conditions can affect the response of the fluid at a point on the threadline especially for materials with memory: and also it can be beset by other sources of influence such as gravity, surface tension and air drag.

Also this method is only suitable for very viscous material\textsuperscript{156-158} although Hudson et al.\textsuperscript{159} have attempted to adapt the technique to more mobile systems.
2.3.2 (b)  The Open Syphon Method

Basically this method has a similar flow situation to the fibre-spinning apparatus, although Kanel favoured this method because the test fluid in the reservoir region was in its virgin state (absence of complicated shear and elongational flow) before being extruded to form threadline. Again, this method has its own disadvantages such as mentioned in the fibre-spinning apparatus (section 2.3.2 (a)) and also the
difficulty in interpretation of results. The basic technique has been discussed by Pickup, Kanel and Astarita and Nicodemo.

Other non-controllable experiments are the converging-flow technique used by Kizior and Seyer, Marruci and Murch and the triple-jet method introduced by Oliver and Bragg.

Having reviewed some of the methods of measurement of elongational behaviour of polymer melts, one has to be careful not to seek quantitative agreement between results obtained by these methods and as has been suggested by Petrie and also Walters to consider each type of elongational flow experiment separately.

In practice, measurement of elongational flow may be hindered by a variety of problems such as the maintenance of a constant temperature, sample fracture in the grips, difficulties in operating at high elongation rates, the length of time required to make measurements and problems in analysing the deformation pattern.

In the following section some of the problems and their solutions will be briefly discussed.

2.4 Problems and their Solutions in Measurement of Elongational Flow

Having mentioned the common problems associated with measurement of elongational flow, now let us look at some of them more closely and some of their possible solutions.
2.4.1 **Maintenance of Constant Temperature**

It is obvious that when working with polymer melts, it requires a controlled temperature in the range of 100-300°C. In both methods of measurement (controllable and non-controllable), various ways have been suggested and attempted.

Ballman, Osamu et al, Kamei and Onogi held the sample in a specially designed oven. In the case of Onogi, in order to minimise temperature variation down the sample, the temperatures of the upper and lower parts of the oven were separately controlled.

However, the most widely used technique is to hold the specimen in an oil bath, or in some cases the sample floats on the oil. In the first case, it is usually important to have the densities of the sample and oil closely matched, whereas in the second case special precaution has to be taken to ensure temperature uniformity.

The use of oil baths, besides providing a means of controlling the temperature does provide the extra bonus of rapid heat transfer, partially supporting the weight of the specimen and reducing the problem of sagging.

Ide and White, in their theoretical work on stability of extending liquid filament has included the surface tension effect besides other rheological properties. It was postulated that surface tension could be neglected for highly viscous polymer melts (greater than $10^{-5}$ Nsec m$^{-2}$). Most data on elongational flow published so far has been of this type where the effect of surface tension is insignificant.
2.4.2 Clamp Design (Failure at the Grip)

Generally, measuring systems involving end separation are usually hindered with clamp design and most workers$^{10-12, 119}$ have adopted an individual course of action which may suit a particular or limited range of polymer melts. In order to obtain a reasonably large draw ratio (extension) in a fixed length of a bath, the initial length is usually short. The ends of the samples are firmly held but with care, in order not to generate stress concentration which would lead to preferential drawing and failure at the grip.

Some of the solutions are as follows:-

Ballman$^{16, 147}$ used specimen with thicker end sections, simplifying a requirement for a tedious preforming operation; Cogswell$^{17-20}$ strengthened the ends of the specimen by cooling the clamps, thus requiring a further complication to the apparatus; Vinogradov et al$^{28}$ glued his specimen to a holder, however gave no details of the procedure; Meissner$^{21, 22}$ used a roller system which gripped continually a new piece of polymer; Shaw$^{168}$ used a ring specimen rather than the normal cylindrical specimens which overcome the problem of clamping specimen ends; while the Rutherford equipment used in this work used an oval-shaped specimen (Detailed discussion of the machine has been given by Smoker$^{169}$ and also in Chapter 3).

2.5 Experimental Results for Various Polymer Systems

Table I, shows the results of some common polymers as a function of elongation rate.
Table I  
Results of some common polymer as function of elongation rates

<table>
<thead>
<tr>
<th>Polymer</th>
<th>Structural Unit</th>
<th>Constant Elongation Rate</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. High density polyethylene (HDPE)(^{17-20,170})</td>
<td>({\text{CH}_2\text{CH}_2}_n)</td>
<td>Decrease</td>
</tr>
<tr>
<td>2. Low density polyethylene (LDPE)(^{120,171,172})</td>
<td>({\text{CH}_2\text{CH}_2}_n)</td>
<td>Increase</td>
</tr>
<tr>
<td>3. Polypropylene pp(^{120})</td>
<td>({\text{CH}_2\text{CH}_2\text{CH}_3}_n)</td>
<td>Decrease</td>
</tr>
<tr>
<td>4. Polystyrene ps(^{16})</td>
<td>({\text{CH}_2\text{CH}}_n)</td>
<td>Increase</td>
</tr>
<tr>
<td>5. Polyisobutylene PIB(^{107,173})</td>
<td>({\text{CH}_2\text{CH}(\text{CH}_3)_2}_n)</td>
<td>Constant</td>
</tr>
<tr>
<td>6. Polymethyl Methacrylate PMMA(^{123})</td>
<td>({\text{CH}_2\text{CH}^3\text{COOCH}_3}_n)</td>
<td>Constant</td>
</tr>
<tr>
<td>7. Nylon 6(^{174})</td>
<td>({\text{NH}_2\text{C(CH}_2)_5}_n)</td>
<td>-</td>
</tr>
<tr>
<td>8. Polyvinyl Chloride (^{109,175})</td>
<td>({\text{CH}_2\text{CH.CI}}_n)</td>
<td>-</td>
</tr>
</tbody>
</table>

Since elongational studies on polyvinyl chloride are rather limited, it is felt more essential to give some general comments on the
experimental results obtained on some common polymers which have been widely investigated as summarised in Table I. For more detailed information, reviews by Petrie,\textsuperscript{10} Walters\textsuperscript{119} and others should be consulted.

2.5.1 Polystyrene (PS)

Polystyrene, especially the commercial free-radical polymerised atactic type is the most widely studied polymer melt. The initial study under constant rates conditions was by Ballman\textsuperscript{16} and then followed by Vinagradov et al\textsuperscript{107} with the latter using a broader range (of strain 6.0 sec\textsuperscript{-1}) rate (0.0008 - 6.0s\textsuperscript{-1}).

However, the later work by Everage and Ballman\textsuperscript{147} which gave an easier data presentation will be discussed. Generally, at lower strain rates, the viscosity increased slowly to a steady-state value equal to three times the zero shear viscosity. At higher strain rates, an increasing tendency to unbounded stress build up and failure via the cohesive type mechanism was observed. Similar trends were observed by the Tenessee Group\textsuperscript{141-145} and also by Vinagradov et al.\textsuperscript{107}

Work on constant stress experiments have been carried out by Vinegradov et al\textsuperscript{108} and also by Mundstedt.\textsuperscript{176} Both observed quite distinct behaviours with viscosity increasing and decreasing respectively with stress. Work using the melt spinning method\textsuperscript{148,155} showed the viscosity decreasing with strain rate.

Figure 2.8 shows the result for polystyrene.\textsuperscript{124}
2.5.2 Polyethylene (PE)

Since the nature of polyethylenes is such that they have broad molecular weight distributions, plus possessing varying degrees of long- and short-chain branching and also amounts of comonomer such as 1-hexene, 2-pentene and so on, thus one would expect the respective behaviours will vary considerably.
2.5.2 (a) Low Density Polyethylene (LDPE)

The basic studies of this polymer may be attributed to Meissner,\textsuperscript{21,22} where he investigated the stress build up under constant strain rates conditions. He observed that at low strain rates the stress approached a steady state similar to polystyrene mentioned in section 2.5.1. Also, as with polystyrene, at high strain rates, the unbounded stress growth was noted.

Similar observations were reported by Shaw\textsuperscript{168} and by Ide and White\textsuperscript{134} with the latter observing a greater tendency to unbounded stress growth than was the case for polystyrene, and also suggested that cohesive fracture attributed to failure at high strain rates. A somewhat different behaviour was noticed by Laun and Mundstedt,\textsuperscript{177,178} where the apparent unbounded stress growth led to a high steady state elongational viscosity and also a maximum value was obtained in the steady state elongational viscosity strain rates data. This significant difference might be due to the use of different commercial grades of polymer and also to different equipment used.

In the constant stress experiment, Cogswell\textsuperscript{17-20} observed the elongational viscosity generally increasing with increasing stress levels, and this was attributed to increasing branching in low density polyethylene. A similarity in the results to that of polystyrene is noteworthy.

Figure 2.9, shows the variation of apparent elongational viscosity with time and strain rates as obtained by Ide and White.\textsuperscript{134}
2.5.2 (b) High Density Polyethylene (HPPE)

Investigations in the stress-development of high density polyethylene at constant strain rates can be attributed to the following: Macosko and Lornsten,\textsuperscript{148} Shaw,\textsuperscript{168} Ide and White\textsuperscript{133,134} and Chen et al.\textsuperscript{140} Similar results to low density polyethylene and polystyrene were observed by Macosko and Lornsten, while other data, especially those obtained by Ide and White, observed distinctively different behaviour.

Referring to Fig. 2.10, generally the stress build up is much slower and linearity is never exceeded, the elongational viscosities decreasing with increasing strain rates. Elongational at break is small and failure is attributed to necking as has been suggested by others.\textsuperscript{141,148}
Fig. 2.10  Elongational viscosity as a function of time and strain rate (after Ide and White)\textsuperscript{134}

The anomalies between the results obtained may be due to structure of high density polyethylene.

Work on constant stress,\textsuperscript{122} showed that elongational viscosities were constant at low stress levels but decreasing with increasing stress, while similar results to those obtained at constant strain rates were observed by Han and Lamonte\textsuperscript{155} using the melt spinning method.

Generally, one can say that high density polyethylene is tension thinning while low density polyethylene is tension stiffening.
2.5.3 **Polypropylene (PP)**

The elongational behaviour of polypropylene under constant strain rate has been extensively investigated by Ide and White,\textsuperscript{134} and by Titomanlino et al.\textsuperscript{179} Results showed a similarity to those for high density polyethylene (section 2.5.2 (b)), i.e. the unbounded stress build up was not observed and the viscosity decreasing with strain rates. A similar response was noted by Cogswell\textsuperscript{17,18} working under constant stress condition. Failure was attributed to necking.

While investigations by Ozamu et al.\textsuperscript{166} using the melt spinning method observed that at low strain rate, the viscosity decreasing towards the steady state value obtained under constant strain rate conditions. At higher strain rates, the elongational viscosity remained constant at first, i.e. similar to that of Han and Lamonte\textsuperscript{155} for high density polyethylene, then started to increase with increasing strain rates.

2.5.4 **Polyisobutylene (PIB)**

Investigations for polyisobutylene can be attributed to Vinagradov et al,\textsuperscript{106,107} Peng and Landel\textsuperscript{180,181} and Stevenson\textsuperscript{182} using the constant strain rates mode of measurement. Although stress build up was slow, the Troutonian relationship was achieved. Results under constant stress conditions have been reported by Baily\textsuperscript{183} and Cogswell and Moore\textsuperscript{184} where again the Troutonian relationship was attained though their data appeared to be in the linear viscoelastic region.
2.5.5 Other Polymers

Work on polyvinyl chloride at constant strain rates has been carried out by Vinogradov et al.\textsuperscript{109} and Kazama et al.\textsuperscript{185} Results by Vinogradov et al. showed that the steady state condition was unattainable even at low strain rates. They attributed this to the polyvinyl chloride being in the state of transition from the glassy to the high elastic state. Furthermore, when it was close to the glassy state preceding the failure, intensive processes such as the initiation of microcracks in the bulk of the polymer occurred. At high strain rates, the unbounded stress build up showed a maximum similar to those observed by Meissner\textsuperscript{21} on high density polyethylene. Another noteworthy point obtained was the possibility of the existence of certain optimum ratios between the strain rates and temperatures at which the maximum strength of the filament was attained.

Amongst those working with polymethyl methacrylate (PMMA) under constant stress and constant strain rates experiments were Cogswell\textsuperscript{18} and Ide and White\textsuperscript{134} respectively. Cogswell observed that elongational viscosity was independent of stress whereas Ide and White noticed a contrasting behaviour, similar to the polystyrene already described in section 2.5.1.

The behaviour of cis-1,4-polyisoprene has been studied by Stevenson\textsuperscript{182} and Vinogradov et al.\textsuperscript{138} Stevenson observed that the unbounded stress build up increased with time for the higher strain rate, at 80°C whereas Vinogradov et al. noticed that in the range 0.0001 to 1.0 sec\textsuperscript{-1}, the data was linearly viscoelastic and the Troutonian relationship was fulfilled.
Elongational flow of glass-fibre reinforced Newtonian oils and polymer melts have been reported by Mewis and Metzner\textsuperscript{186} and by Chan et al\textsuperscript{187} respectively. It has been found that for the first case, there is a large increase in elongational viscosity with increasing shear rates. For the latter, the elongational viscosity was very high at low strain rates but fell off rapidly with increasing strain rate. This was found to be true, for particle-reinforced polystyrene, high density polyethylene and polypropylene melts.

Investigating the influence of carbon black on rheological properties of molten polystyrene, Lobe and White\textsuperscript{188} found that at high black loading, approximately 20 volume (\%) led to yield values in both shear and elongational. The elongational viscosity was observed to be a decreasing function of strain rate.

Other polymer systems which have been investigated, but will not be reviewed are for example Epoxy resin\textsuperscript{189} Natural rubber\textsuperscript{190,191} Styrene-butadiene rubber (SBR)\textsuperscript{192,193} and Polybutadiene\textsuperscript{139,194,195}

To conclude this chapter without giving some applications of elongational studies seems inadequate. However, it is well understood that applications to polymer melt processing are numerous. In the next section, a brief review will be attempted.

2.6 Elongational Flows in Polymer Processing

The purpose of this section is just to highlight in quantitative terms, polymer processes in which some aspects of elongational flow might play a significant role.
2.6.1 Melt Spinning

For a polymer to be used as a fibre, one important property besides the properties of fibres is its spinnability. This may be defined according to Ide and White\textsuperscript{134} as the ability of fluids to be stretched out into filaments of small and uniform cross-section without melt fracture occurring. This can only be achieved when both the viscous and high elastic responses can combine rapidly thus avoiding excessive stress build up. One property that can give this indication is elongational viscosity, and this is dependent on the nature of the melt, i.e. whether tension thinning or tension stiffening or Troutonian.

In stretching a molten thread which may contain points of defects or non-uniformities (smaller cross-sectional areas), thus they become high stress concentration areas. If the melt is non-elastic and either Troutonian or tension stiffening such as low density polyethylene (refer to section 2.5.2 (a)), the higher stress or strain rate causes further thinning and in turn greater stress, ultimately the non-uniformity becomes prominent and leads to failure. But if the melt is non-elastic but tension stiffening such as polystyrene (refer to section 2.5.1), the high stress concentration at the points of defect will increase the elongational viscosity to such an extent that it compensates for the excessive stress build up. Thus, the non-uniformity does not increase and the whole system stabilises.

However most fibres are made of crystalline polymers where at high strain rates condition, crystallisation will be enhanced (increase in crystalline melting point, T\textsubscript{m}). This phenomenon is known as strain induced crystallisation. In real spinning operation, this increase in T\textsubscript{m}, in most non-uniform regions can further boost stability.
2.6.2 Extrusion Blow Moulding

In conventional blow moulding processes, a tube known as a "parison" is initially extruded vertically downwards. This tube is then engulfed by two mould halves and inflated to the shape and the size of the mould cavity. Elongational flow may occur during both the parison formation and during inflation.

The extruded parison stretches due to its own weight, a phenomenon known as parison sag. Brydson suggested that the stretching was made up of two components:

a) high elastic deformation, \( D_{HE} \) (complete within a second or two after parison is formed).

b) elongational viscous flow, \( D_{visc} \) (continues with time).

It is reasonable to suppose that the ratio \( (D_{HE}/D_{visc}) \) increases with the following,

a) with increase in average molecular weight.

b) with decrease in temperature.

c) with increase in parison length but constant weight (i.e. reduction in cross-sectional area).

Cogswell has reasoned that the tensile stress, \( \sigma \), was proportional to, i) the parison length \( L \), and the strain rate, \( \dot{\varepsilon} \), ii) the sag velocity, \( v \), divided by the parison length.
Using the above reasoning, he expressed the elongational viscosity in terms of the above parameters and suggested that the total sag was approximately related to parison length and elongational viscosity by

$$\text{total sag} \propto \frac{L^3}{\mu}$$

Using the relationship, he then pointed out that if a parison of length $L$ could be handled by a polymer of viscosity, $\mu$, then to produce a parison of length, $2L$, but with the same sag required a polymer with $2^3$ times the viscosity.

2.6.3 Extrusion Coating

Lamb$^{197}$ used the elongational flow behaviour in explaining the draw resonance phenomenon in extrusion coating. Draw resonance is characterised by alternate thick and thin longitudinal deposits of polymer onto the coated substrate. This effect is predominant with tension thinning materials such as polypropylene but not low density polyethylene, which is tension stiffening. The explanation given is similar to those given in melt spinning (presence of under-sized non-uniformities on the extruded web).

2.6.4 Injection Moulding

Refer to Fig. 2.11, which shows a schematic diagram of a centre-gated disc mould. Here, when a polymer is injection moulded, the melt spreads out in a disc form, i.e. radially (A) and annularly (B). In the radial direction, the flow comprises mainly of shear, whereas in the annular direction, elongational flow increases with the diameter of melt front.
Hence, knowing the elongational behaviour of polymer melts used in the processing, one can approximately prevent or minimise the occurrence of radial shrinkage or annular shrinkage on cooling.

![Fig. 2.11 Centre-gated disc mould](image)

**Fig. 2.11 Centre-gated disc mould**

### 2.6.5 Convergent Flow During Extrusion and Calendering

In a typical tapered die, the flow may be regarded as convergent, hence, the total flow is made up of both shear and elongational components. The ratio of tensile deformation to shear deformation can thus be assumed to increase with increasing the angle of the tapered die.

However, Cogswell\(^{198}\) has pointed out the actual risk of using data based on laboratory scale equipment, for predicting behaviour on full-scale equipment. Hence more thorough work has to be carried out in order to fully understand the problems encountered in real processing.
2.6.6 Film Blowing Extrusion

Tubular film blowing process is the most common method of producing thermoplastic film. Referring to Fig. 2.12, which shows a general view of the process.

Melt from the extruder is turned through a right angle and extruded vertically upwards in the form of a thin tube. This tube is expanded by internal air pressure to form a bubble and then stretched in the direction of flow by means of nip rollers.

Hence, elongational flow forms an important part of the processing which in turn is governed by the melt properties and also temperatures and strain rates. In order to be able to be stretched uniformly, the melt must have good elongational properties.

Fig. 2.12 General view of the film-blowing process
The examples given above show how the studies of elongational flow would perhaps enhance the understanding of many polymer processes, though in its present state its importance is far from adequate. Finally but not least, a thorough investigation is thus needed, before its real applications can be materialised in the near future.
CHAPTER 3

APPARATUS AND EXPERIMENTAL PROCEDURE

3.1 Introduction

The investigation of elongational flow behaviour of commercial grade polyvinyl chloride is part of the work involving the prototype Rutherford Extensional Rheometer. The testing of machine performance and the study of elongational behaviour of linear density polyethylene (LDPE) have been carried out by Smoker 168,199-202

Prior to the investigation, initial work has been carried out to search for a suitable clamp design, the lack of which has been hampering the progress of the work. The use of silicon oil as the heating medium in the instrument has also been a major concern, especially with plasticised polyvinyl chloride, where it was thought to affect the elongational properties. Therefore, investigation into its effect on properties such as the glass transition temperature, tensile strength and so on, were conducted, to justify its further use.

The elongational studies of polyvinyl chloride can be classified into four major areas,

a) to obtain a general elongational flow pattern for polyvinyl chloride.

b) to investigate the dependence of elongational behaviour of polyvinyl chloride on strain rates, and to compare with shear flow data under similar conditions.
c) to investigate the elongational behaviour at elevated temperature.

and  
d) to study the influence of plasticiser composition and types on the elongational behaviour.

3.1.1 Aims of the Present Work

From the above, therefore, the main purpose of the present work can be summarised as follows:- to have an insight into the understanding of the elongational behaviour of polyvinyl chloride and its dependence on the operating conditions (strain rates and temperature) and also on the plasticiser composition and types; to establish some form of relationship (empirical) between the elongational properties and the above parameters.

3.1.2 Instruments Used

Besides the Rutherford Extensional Rheometer, supplementary tests were carried out using,

i) the Davenport Capillary Rheometer (shear flow data).

ii) Du Pont D.T.A. 900 (measurement of glass transition temperature, Tg)

iii) J.J. Extensiometer (tensile strength)

and iv) Wallace Micro Hardness Tester (Hardness)

Brief discussions of the instruments, except ii) and iv), will be made in the following sections.
3.2 The Rutherford Extensional Rheometer

The instrument had been produced as a prototype machine by the Rutherford Laboratory in February 1980. Prior to this, consultations between the non-Newtonian sub-committee of S.R.C. and Dr. D.E. Marshall and Mr. F.N. Cogswell have been made with the aim of producing a universal machine, capable of determining quantitatively, the elongational properties of a wide range of polymer melts.

However, prior to the present state of the equipment, work has been hampered by a number of problems such as temperature control, strain rate control and clamp design, and thus some modifications were needed to rectify the situations.169,199-201

At its present state, it is a developed practical instrument capable of accurate and reproducible measurements of elongational flow behaviour of polymer melts having a viscosity greater than $10^5$ Pa.s. However, minor changes are still possible which will improve the performance further.

In the following section, a general description of the extensional rheometer will be given. This will include its general features and also its operating instructions. A detailed discussion on these aspects has also been reported elsewhere.202

3.2.1 General Features

The general features of the extensional rheometer is illustrated by figures 3.0 a), 3.0 b) and 3.0 c); a simplified plan, front view, rear view and top view respectively.

Figure 3.1 shows the schematic diagram of the extensional rheometer interconnection system. The features numbered 1-24 are:-
Referring to Figure 3.1, signals are passed between the modules and also between the control panel and other units on the rheometer; length potentiometer, tachometer, transducer and motor servo control, to maintain a positive feedback loop system. The same system has been previously employed by others.\textsuperscript{10,11}

The Rutherford Extensional Rheometer has four modes of operation:

i) Constant strain rate

ii) Constant stress

iii) Constant force

iv) Constant velocity

However, only the first mode has been used throughout the work.
Before discussing the operating instructions of the instrument, it is felt relevant to examine other important aspects such as the oil bath, clamp design and not least the sample shape.

3.2.2 Oil Bath

Failure to maintain acceptable temperature variations along the bath and at any one particular point has been one of the main problems associated with the earlier design of the oil bath. It was reported by Smoker\textsuperscript{169,199} that the temperature variations were \( \pm 5 \) along the bath and up to \( 2^\circ C \) at any one point, respectively.

The present oil bath as shown in Figure 3.2 has reduced the temperature variations to, \( \pm 2^\circ C \) along the bath and less than \( \pm 0.5^\circ C \) at any one particular point.\textsuperscript{200} However, due to the larger volume capacity, the heat-up time for the bath to reach the set temperature and to stabilise is extended to approximately 60 minutes. However, this is still acceptable.

3.2.3 Sample Shape

Before the adoption of the present sample shape, various other methods have been attempted but with no success. The methods involved the use of bar shaped samples, similar to those of other workers\textsuperscript{10–12,119} but with different clamp designs.\textsuperscript{199}

Shaw\textsuperscript{168} previously employed O-ring samples for studying the tensile behaviour of polymer melts with a measure of success, while Myers and Wenrick\textsuperscript{203} encouraged the use of oval rings in preference to the O-rings.
The preference may be attributed to oval rings, giving rise to minimum excessive stress formation during the initial stages of deformation (usually associated with the O-ring, where pre-stretching is inevitable.

Fig. 3.3  A Photograph of the Oval Ring Sample

Figure 3.3 shows the dimensions of the oval ring sample. It was prepared by compression moulding in a 4 cavity mould and samples produced were free of defects such as bubbles, voids, sink marks etc., which would be the sources of failure or erroneous results. Besides producing samples free of defects, they were also free of stress and orientation.\textsuperscript{204} Smoker employed a different method of sample preparation.\textsuperscript{202}

Apart from the above criteria, the lower cost and also ease especially in the die making, were the reasons compression moulding was
preferred. While Smoker's criteria was perhaps the faster speed (larger number of samples per mould), he later found that the sample failure rate per mould was high and eventually had to revert to cut samples (from sheet).

3.2.4 Sample Holders

Having decided the suitability and advantages of using oval ring samples, special sample holders were required for the extensional rheometer. Shaw and Myers and Wenrick used a single post on each arm of the sample holders. This gave rise to strong frictional forces at the point of contact between the samples and the holder which caused deviation from an ideal homogeneous deformation.

Here, polyethylene terephthalate 'horseshoe' (Figure 3.4) sample holders were adopted. They were mounted permanently on the carriage arms.

![Schematic plans of 'horseshoe' sample holders](image)

Fig. 3.4 Schematic plans of 'horseshoe' sample holders
This type of sample holder has several advantages. Amongst them are that no moving parts are involved, and the properties of polyethylene terephthalate, i.e. poor heat conduction (cf. with metal counterpart), thus the points of contact between samples and holders is at the same temperature as the bath, and a low coefficient of friction enables a very close approximation to an ideal uniaxial tension to be maintained throughout the length of the sample.

3.2.5 Operating Instructions

The operating instructions of the extensional rheometer have also been described elsewhere.202 Refer to Figure 3.0 a), b), c) and 3.5 a), b).

The operating instructions can be described as follows:

i) Switch on the mains and the heater with the bath lid closed, set the required temperature by adjusting the temperature control panel (Figure 3.5 a). Leave it for approximately 60 minutes to enable the temperature to stabilise.

ii) Once the temperature has stabilised, the control switch is switched on and one of the experimental modes (in this case, constant strain rate) is selected (refer to 3.5 b).

iii) Dimensions of the sample, viz a viz, initial length and diameter are set. The initial length or the effective length, \( L_o \), is shown in Figure 3.3 (Figure 3.5 b).
iv) Select the required strain rate using the gear selector ($10^{-1}$ - $10^{-5}$ s$^{-1}$) and strain rate knob (0.1 - 0.9) (Figure 3.5 b).

v) With the mode knob placed at "SETTING", the moving carriage is positioned approximately to about the sample's length. This can be done manually (for finer adjustment) or automatically (Figure 3.5 b).

vi) Open the lid and insert the sample into the sample holders using a pair of tongs; close back the lid. Leave for about 10-20 minutes depending on material and temperature.

vii) Zero the force reading by adjusting the knob at the rear of the machine.

viii) Revert the Mode knob to "CONSTANT STRAIN RATE MODE". With the length and stress outputs connected to the Phillip Dual Pen Recorder, the test can then be run by pressing the "ON" button (Figure 3.5 b).

ix) Since the "CUT OFF" mechanism is not working, observation on the sample's failure has to be made through the glass on top of the lid. The sample's failure can also be indicated on the recorder by a sudden drop in stress. Press the "OFF" panel to stop the test (Figure 3.5 b).

Figure 3.6 shows a typical output of length and stress versus time at any test conditions. Reproducibility of the results obtained will be discussed in the next chapter.
3.2.6 Data Analysis

The Sharp MZ-80k has been used to aid and speed up the data analysis. The programme written by Smoker\textsuperscript{202} required the stress and length data evaluated from the chart (Figure 3.5) to be fed into the computer, and the viscosities and strains were then obtained.

Although linear plots of stress versus true or Henky strain were available, here, preference was given to log-log plots of viscosity or stress as a function of time as advocated by many workers.\textsuperscript{10,12,119} The criteria for this preference was the relevance of deformation (viscosity or stress) with time of deformation rather than with a measure of extension (true strain or Henky strain). However, whenever it was necessary, the latter representation could still be used.

The full listing of the above programme is available elsewhere.\textsuperscript{202}

3.3 The Davenport Capillary Rheometer

The Davenport Capillary Rheometer has been used to obtain the flow shear data of polyvinyl chloride. It is shown in Figure 3.7.

This consists of a 22mm diameter ram which is capable of being driven into or out of a controlled heated barrel. The extrusion dies are fitted into the base of the barrel so that the polymer is extruded vertically downwards. Pressure is measured in the barrel by means of a pressure transducer fitted into the bottom end at a point roughly parallel with the top end of the die.
3.4 Du Pont D.T.A. 900

The Du Pont D.T.A. 900 is a versatile instrument capable of giving a wide range of information on a small sample. Here, it has been used primarily to determine the glass transition temperature, \( T_g' \), of polyvinyl chloride, according to ASTM D3418.205

Basically it consists of two cells, one containing the sample under test and the other an inert sample which does not undergo changes in the temperature region of interest. These cells are heated between them at a controlled rate and the temperature difference (\( \Delta T \)) between them is plotted as a function of temperature; a plot of \( \Delta T \) versus temperature is called a thermogram.

When a change (physical or chemical) occurs in the sample, either a positive or negative \( \Delta T \) results. The glass transition temperature, \( T_g' \), is obtained from the thermogram and corrected for the non-linearity of Chromel-Alumel thermocouples using standard tables.

Description of other testing instruments, i.e. the J.J. Tensiometer and the Wallace Micro Hardness Tester will not be given because of their minimal use.

3.5 Materials Used

3.5.1 Polyvinyl Chloride

One commercial grade polyvinyl chloride has been used throughout this work. It is 'Corvic' 857/116, a suspension, low molecular weight homopolymer supplied by ICI Ltd. It has been chosen because it possesses excellent melt flow characteristics and it has also been suggested that with suitably formulated compositions and correct processing conditions,
samples which are free from flow defects, superior physical properties and improved appearance can be obtained.

Due to the excellent melt flow characteristics, Corvic S57/116 has been advocated for use, in critical processes in which polyvinyl chlorides of higher molecular weight may give difficulties in processing because of their higher melt viscosities. In plasticised form, it may also give advantages in some applications, especially with high filler loadings.

Technical data for 'Corvic' S57/116 is as shown in Table II.  

<table>
<thead>
<tr>
<th>Property</th>
<th>Units</th>
<th>Value</th>
<th>Test Method</th>
</tr>
</thead>
<tbody>
<tr>
<td>k value</td>
<td></td>
<td>57</td>
<td>No. 1</td>
</tr>
<tr>
<td>Viscosity number</td>
<td></td>
<td>80</td>
<td>180-R174</td>
</tr>
<tr>
<td>Packing density g/ml</td>
<td></td>
<td>0.62</td>
<td>No. 2</td>
</tr>
<tr>
<td>Apparent density g/ml</td>
<td></td>
<td>0.55</td>
<td>180-R60</td>
</tr>
<tr>
<td>Passing 250µm wt% (60 mesh)</td>
<td></td>
<td>99.9</td>
<td>No. 3</td>
</tr>
<tr>
<td>Passing 7.5µm wt% (200 mesh)</td>
<td></td>
<td>5.0</td>
<td>No. 3</td>
</tr>
<tr>
<td>Volatile content wt%</td>
<td></td>
<td>0.2</td>
<td>No. 4</td>
</tr>
</tbody>
</table>

Test Methods

No. 1:- Calculated from relative viscosity data obtained by 180-R174.

No. 2:- From volume of 20g of polymer dropped 30 times from a height of 51mm.
No. 3:— By sieving dry polymer for 30 mins in humid air using sieves according to BS410:1969.

No. 4:— Weight loss after one hour at 135°C.

3.5.2 Plasticisers

All the plasticisers used are shown in Table III with their typical properties, and have been supplied by Albright & Wilson Ltd.

Table III  Technical specifications of plasticisers for polyvinyl chloride

<table>
<thead>
<tr>
<th>Plasticisers</th>
<th>Molecular wt.</th>
<th>Properties</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Relative density at 25/25°C</td>
</tr>
<tr>
<td>Di-2-ethylhexyl phthalate (DOD)</td>
<td>390</td>
<td>0.985</td>
</tr>
<tr>
<td>Di-iso-octyl phthalate</td>
<td>390</td>
<td>0.984</td>
</tr>
<tr>
<td>Di-n-butyl phthalate</td>
<td>278</td>
<td>1.045</td>
</tr>
<tr>
<td>Di-iso-decyl phthalate (DIDP)</td>
<td>447</td>
<td>0.966</td>
</tr>
<tr>
<td>Dinonyl phthalate (DNP)</td>
<td>418</td>
<td>0.971</td>
</tr>
<tr>
<td>Di-2-ethylhexyl adipate (DOA)</td>
<td>371</td>
<td>0.925</td>
</tr>
<tr>
<td>Tritolyl phosphate (TTP)</td>
<td></td>
<td>1.165</td>
</tr>
</tbody>
</table>
3.5.3 Stabiliser

The stabiliser used is a liquid barium/cadmium/zinc (Irgastab BC 445) supplied by Ciba-Geigy Ltd. Since it is reported as self-lubricating,208 no separate lubricants have been used. It has been chosen because it has been reported to impart a high degree of heat stability and to give good running properties to the polyvinyl chloride. Also it is advocated to give samples with good, but not crystal, clarity.

Liquid stabiliser is selected in preference to the solid counterpart because it is generally easier to store, handle and dose.

Table IV is the technical specifications of Irgastab BC 445.208

<table>
<thead>
<tr>
<th>Stabiliser</th>
<th>Properties</th>
</tr>
</thead>
<tbody>
<tr>
<td>Irgastab BC 445</td>
<td>colour density refractive</td>
</tr>
<tr>
<td>(Liquid Ba/Cd/2n)</td>
<td>Gardner (20°C; g/ml) index</td>
</tr>
<tr>
<td></td>
<td>7 max 1.03 ± 0.01 ND²⁰</td>
</tr>
<tr>
<td></td>
<td></td>
</tr>
</tbody>
</table>

3.6 Formulations of Polyvinyl Chloride

The formulations used throughout this work are summarised in Table V, shown below.
Table V  Formulations of Polyvinyl Chloride, according to Chapters

<table>
<thead>
<tr>
<th>Materials</th>
<th>Grade of Material and Chapters</th>
<th>Parts per hundred (pphr)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. polyvinyl chloride</td>
<td>Corvic S57/116, same, same</td>
<td>100</td>
</tr>
<tr>
<td>2. plasticiser</td>
<td>DOP, DOP, DBP, DOP, DIOP, DIDP, DOA, TTP</td>
<td>0, 30, 50, 30, 50, 0-60</td>
</tr>
<tr>
<td>3. stabiliser</td>
<td>BaCdZn, same, same</td>
<td>4.0</td>
</tr>
</tbody>
</table>

N.B.

a), b) and c) refer to Chapters 4, 5 and 6 respectively.
d) - Chemical names, given in section 3.5.2.

3.7  Preparation of Samples

3.7.1  Blending

Before the polyvinyl chloride compounds can be ready for process, the above ingredients have to be dispersed within the polyvinyl chloride resin. For this purpose, a T.K. Fielder high speed mixer has been utilised to produce a series of powder blends.

Figure 3.8 shows a schematic diagram of the T.K. Fielder. Basically it can be regarded as a combination of a mixing unit and a cooler. The heater mixer is a cylindrical bowl, where steam, oil or water (at pre-
set temperature) can be circulated in its jacket so as to enable the temperature of the mixed material to rise. It is made of stainless steel to prevent excessive sticking of the materials to the walls.

The stationary baffle with an adjustable angle ensures that the materials tumble back into the vortex created by the action of the impeller, thus optimising the mixing action. A sensing thermocouple is incorporated in the blade. The high speed rotation (500 to 4000 rpm) of the propeller, coupled with rotor blades provides a strong impact, shearing and friction effects on the polyvinyl chloride particles, thus a uniform blend is obtained.

Once a certain degree of blending is reached (dependent on rotor speed and time or temperature) the material is dumped into the cooler via the discharge valve. Cooling is essential, to remove the heat from the blend and also to prevent formation of lumps and ensure a free-fibrous powder.

3.7.2 **Dry Blending Conditions**

Katchy\textsuperscript{209} and others\textsuperscript{210,211} using the fielder, have found that the degree of blending, consequently the properties of the dry blends such as bulk density, particle size distribution etc. were dependent on the blending conditions (rotor speed, time or temperature and cooling time). Here, the main aim is to produce a uniform blend with every blending, thus approximately consistent conditions have been maintained during the blending process.

The blending conditions used are shown in Table VI.
Table VI  Blending conditions on the T.K. Fielder

<table>
<thead>
<tr>
<th>Stage</th>
<th>Conditions</th>
</tr>
</thead>
<tbody>
<tr>
<td>i. Mixing</td>
<td>a) Temperature 70 ± 5°C</td>
</tr>
<tr>
<td></td>
<td>b) Time 10 ± 1 mins.</td>
</tr>
<tr>
<td></td>
<td>c) Rotor Speed 3000 rpm</td>
</tr>
<tr>
<td>ii) Cooling</td>
<td>a) Time 7 ± 1 mins.</td>
</tr>
<tr>
<td></td>
<td>b) Rotor Speed 500 rpm</td>
</tr>
</tbody>
</table>

Also, in the additional part of this work, where a small amount of polyvinyl chloride blends were required, a 1 litre, high speed food mixer (Kenwood) was used to simulate the fielder.

3.7.3 Compression Moulding

The oval-ring samples were compression moulded using a 4-cavity mould and electrically heated press (cooling system provided by water circulating through both top and bottom platen). Figure 3.9 shows the simplified plans of the mould.

Fig. 3.9  Simplified plans of the 4-cavity, 2-plate mould.
The surfaces of the plates were chromium plated as highly recommended for polyvinyl chloride.\textsuperscript{212,213}

Generally, the principal stages in the compression moulding process are as follows:

a) raising the temperature of the polyvinyl chloride compounds to a level where application of pressure can cause sufficient flow without thermal decomposition taking place.

b) on application of pressure, the polyvinyl chloride compounds flow to a level and assume the shape of the mould in which they are contained.

and finally

c) cooling to a temperature, at which the mouldings are removed from the mould without distortion taking place.

According to BS2782: Part 9: Method 901A for polyvinyl chloride, the mould charge should preferably be in the form of sheet rather than granules, thus this necessitates the milling process. However, in this work, as a precaution samples of least shearing action and also thermal histories were needed because their existence could presumably have a significant effect on the elongational behaviour of polyvinyl chloride, hence the granular form was chosen.

3.7.4 Moulding Conditions

With the aims, primarily to produce samples free from voids, sinks, ridges etc., as have been discussed earlier (section 3.2.3), or in laymen's terms visibly perfect and acceptable samples, the following conditions were used:-
Moulding temperature = (160–180) °C ± 5%
Pre-heating time = 7.0 ± 0.5 mins.
Cooling time = 10.0 ± 5 mins.
Cooling temperature = 55 ± 5°C.
Pressure = 70 bar pressure

The moulding temperature varied with the polyvinyl chloride formulations used.

3.8 Experimental Methods

3.8.1 Effect of Silicon Oil (Heating Medium) on Polyvinyl Chloride

Silicon oil has been widely used as the heating medium because of its physical properties such as high thermal stability, flash points and melting point, inertness to reactions and chemical changes, etc. Vinogradov et al however, used glycerine in his work on polyvinyl chloride at temperatures less than 150°C. This is not suitable for the work, involving a higher temperature range. Some preliminary tests, simulating the real situation, were performed to investigate its effects on polyvinyl chloride, and consequently would justify its use as the heating medium.

Samples of suitable sizes and shapes, according to test requirements were prepared by compression moulding. They were then placed in conical flasks filled with the silicon oil, and placed in an oven at 100 ± 1°C for 1 hour. Measurements such as their weight, tensile strength, hardness and glass transition temperature, $T_g$ before and after the treatment were measured.
3.8.1 (a) Tensile Strength (BS2782: Part 3: Method 320C)

Test specimens were cut from the 0.5mm compression moulding sheet, and the dimensions (width and thickness) shown in Figure 3.10 were determined. Measurements were obtained using the J.J. Tensile Testing Machine. Three samples were used for each measurement and if any obvious failure occurred, for example a jaw break, the results were discarded.

The tensile strength (TS) of the samples before and after treatment, were then evaluated.

![Tensile Test Specimen](image)

Fig. 3.10 Tensile Test Specimen

3.8.1 (b) Hardness (IRHD) BS2782: Part 0: Method 365D

Button shaped samples were cut from the cylindrical part of the oval-ring test specimen. The hardness determined using the Wallace Micro Hardness Testing machine.
3.8.1 (c) **Glass-Transition Temperature (T_g) ASTM D3418**

The $T_g$ of the samples, before and after treatment, were determined using the Du Pont 900 thermal analyser connected to a Du Pont 941 thermal mechanical analyser. A typical thermogram is as shown in Figure 3.11. Detailed $T_g$ determination will be given in Appendix I.

Besides the above measurements, the weights of samples before and after treatment were obtained, and any weight loss calculated.

\[
i.e. \text{ weight loss (\%) } = \frac{W_o - W_F}{W_o} \times 100
\]

where $W_o$ and $W_F$ are initial and final weights respectively.

Visual observations to discover any discolouration of the silicon oil were made (cf. with a buffer silicon oil).

3.8.2 **Reproducibility of Results Obtained using Rutherford Extensional Rheometer**

About 20 identical oval ring samples were used and tested under similar operating conditions viz a viz strain rate, temperature and also pre-heating and conditioning time using the extensional rheometer. The operating instructions have been given earlier (section 3.2.5).

Plots of apparent elongational viscosity ($\mu_e$) against time/elongational stress versus true strain (log-log plots) and also a statistical treatment were made.
3.8.3 General Elongational Behaviours of Both Rigid and Plasticised Polyvinyl Chloride

Here, samples from both rigid and plasticised polyvinyl chloride were used, and elongational viscosities at various levels of constant strain rates (0.4–0.004 S⁻¹) and at three temperatures (160, 180 and 190 ± 0.5 °C) were similarly determined using the extensional rheometers.

For plasticised polyvinyl chloride, two compositions of di-2-ethyl-hexyl phthalate (DOP) (refer to section 3.6) were utilised. The criterion for preference of DOP is that DOP is the all-round plasticiser, which, although it does not excel in any particular respect, does have the best combination of all properties and like all phthalates also confers good heat stability. Due to this, DOP is one of the most widely used plasticisers, especially amongst the phthalate group. Another criterion is its ease of availability.

For analogy, shear flow data was obtained using the Davenport Capillary Rheometer.

3.8.4 Measurement of Shear Flow Data

Shear viscosities at varying shear rates have been measured using the Davenport Capillary Rheometer (section 3.3)

Approximately 25gm of polyvinyl chloride compounds was packed into the barrel and then compressed by lowering the ram. This was left to thermally equilibrate for 10 minutes to the pre-set temperature. Then, the ram was moved downward at a series of predetermined speeds. Extrudate samples and pressure readings were taken at each of the speeds (using a Phillips recorder).
The shear rate, $\dot{\gamma}$, was determined using the following equation:

$$\dot{\gamma} = \frac{X}{16.5326R^3}$$

where $X$ = piston drive speed (cm/min)
$R$ = die capillary radius (cm)

and the shear stress, $\tau$, was obtained by,

$$\tau = \frac{PR}{2L}$$

where $P$ = pressure recorded (psi or N/m$^2$)
$R$ = die capillary radius (m)
$L$ = die capillary length (m)

To compensate the pressure losses and also end corrections, the Bagley method$^{217}$ (given in Appendix II), was chosen. This was because it is one of the widely accepted methods, virtually without question.

Characterisation was also made by determination of the glass transition temperature of samples after being drawn in the elongational experiments.

3.8.5 Elongational Behaviour of Polyvinyl Chloride at Elevated Temperatures

The dependence of elongational behaviour of plasticised polyvinyl chloride at elevated temperatures was investigated. The main criteria for using plasticised and not rigid polyvinyl chloride were due to ease of samples preparation, and better elongational properties. Further discussion
will be made in Chapter 5. Measurements were obtained using the extensional rheometer.

Here, only two compositions of plasticiser (DOP) (refer to section 3.6) and measurements were conducted at two levels of constant strain rates (0.065\(^{-1}\) and 0.00045\(^{-1}\)). Samples were run at temperatures ranging from 160 ± 0.5°C to 190 ± 0.5°C.

3.8.6 Effect of Plasticiser Composition and Types on Elongational Behaviour of Polyvinyl Chloride

For these purposes, samples were similarly prepared using the formulation given in section 3.6. Elongational tests were conducted at varying conditions. For plasticiser composition, they were at 160 ± 0.5°C (0.0045\(^{-1}\)), 180 ± 0.5°C (0.065\(^{-1}\) and 0.0045\(^{-1}\)) and 190 ± 0.5°C (0.065\(^{-1}\)), whereas, for plasticiser types, they were at 180°C (0.065\(^{-1}\) and 0.0045\(^{-1}\)).

The glass transition temperatures, \(T_g\), of plasticised polyvinyl chloride were determined (section 3.9.1 c).

Using one of the DOP as the reference, an attempt has been made to determine the amount of other plasticisers required to give similar elongational properties as the reference.

Data analysis will be discussed in the following chapters.
Fig. 3.0  a) Extensional Rheometer. Simplified plan: Front view
Fig. 3.0  b) **Extensional Rheometer. Simplified plan: Rear view**
Fig. 3.0  c) **Extensional Rheometer, Simplified Plan: Top view**
Fig. 3.1  Schematic Diagram of the Rutherford Extensional Rheometer
Fig. 3.2 Oil bath. Simplified plan
Fig. 3.5 a) A photograph of the L.H.S. Panel

Fig. 3.5 b) A photograph of the R.H.S. Panel
Fig. 3.6 Typical stress and length recorded as a function of chart speed at a particular condition
Fig. 3.7  Schematic diagram of the Davenport Capillary Rheometer:
Front view

1 - Piston
2 - Capillary
3 - Barrel
4 - Transducer
Fig. 3.8  A schematic representation of the T.K. Fielder
Fig. 3.11: A typical thermogram of polyvinyl chloride sample.
CHAPTER 4

GENERAL FLOW BEHAVIOUR OF POLYVINYL CHLORIDE

4.1 Material Used and Experimental Methods

The materials used and the experimental methods were given in sections 3.6 and 3.8.1 to 3.8.4 respectively.

4.2 Experimental Results

4.2.1 Effects of Silicon Oil on Polyvinyl Chloride

The various properties (before and after treatment) are shown in Table V.

Table V Average values before and after treatment (silicon oil at 100°C and for 1 hour)

<table>
<thead>
<tr>
<th>Measurement</th>
<th>Microhardness (IRHD) + 0.5</th>
<th>Tensile Strength $T_s \pm 0.1\text{kg/cm}^2$</th>
<th>Glass Transition Temperature $T_g \pm 0.5°C$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Initial</td>
<td>77.5</td>
<td>188.7</td>
<td>75.0</td>
</tr>
<tr>
<td>Final</td>
<td>78.5</td>
<td>190.7</td>
<td>76.5</td>
</tr>
<tr>
<td>Percentage loss (%)</td>
<td>1.29</td>
<td>1.06</td>
<td>2.0</td>
</tr>
</tbody>
</table>
It can be seen, the treatment has caused no drastic changes in the properties. The criterion used to justify the use of silicon oil as the heating medium, was that the percentage loss should be less than 5%. In this case, the percentage loss was within the acceptable limit.

Also, the weight loss in the samples was found to be less than 3%, and no visual discolouration was observed (using a buffer solution of silicon oil).

Hence, the use of silicon oil as the heating medium in the extensional rheometer, especially when using plasticised polyvinyl chloride was acceptable. This was enhanced by the fact, that other workers\textsuperscript{10,11} have been using silicon oil without any hesitation. However, it must be mentioned, Vinegradov et al.\textsuperscript{23} used glycerine in his work on polyvinyl chloride, but at much lower temperatures.

4.2.2 Reproducibility of Measurements Obtained by the Rutherford Extensional Rheometer

Since the rheometer is a prototype machine, it was necessary to calibrate and to investigate the reproducibility of the measurements obtained, prior to its further use. This opinion was similarly expressed by Petrie,\textsuperscript{11} regarding any new elongational instruments.

However, the calibration and the testing of the rheometer were thoroughly carried out by the Rutherford Laboratory and by Smoker. The reports have been published elsewhere.\textsuperscript{202}

Thus, the primary purposes of this part of the work were to supplement those findings and also to provide ample information on the reproducibility of all types of elongational properties, such as tensile stress (elongational viscosity), or length (true strain) measured. The second
purpose could presumably form the basis of selecting the preferential usage in presenting the results.

To achieve the above conclusions, a statistical method, which was recommended for testing the variability of the stress-strain diagrams in fibres\textsuperscript{217} was used.

For this purpose, 40 oval ring samples (10 mouldings) were identically prepared and 20 perfect samples were then randomly selected. Elongational properties were then evaluated under similar conditions (refer to section 3.8.2). Statistical analysis of the results was eventually carried out.

4.2.2 (a) Distributions of the Elongational Properties

Table VI shows the mean values of true strain ($\bar{\varepsilon}$), the stress ($\bar{\sigma}$) and the viscosity ($\bar{\mu}_a$) at constant time intervals, except for the mean of the respective final values.

Fig. 4.1 and Fig. 4.2 show the distribution of each independent viscosity as a function of true strain and stress respectively, about the mean values, shown by the solid lines (given in Table VI).

As seen in Figure 4.1, the plots are closely packed together, with the exception of a few. However, all plots seem to merge at the final stages of deformation. Similar distribution is seen in Figure 4.2 and in fact, by close examination, an improved distribution is obtained.

The distribution of the ultimate values about their respective ultimate mean values are shown in Figures 4.3 and 4.4. The shaded areas in both plots are the postulated region of tolerance or acceptability.
Table VI  Mean values of true strain ($\bar{\varepsilon}$), stress ($\bar{\sigma}$) and viscosity ($\bar{\mu}_a$) at 180°C and 0.008 s$^{-1}$

<table>
<thead>
<tr>
<th>No of time interval</th>
<th>True Strain ($\bar{\varepsilon}$)</th>
<th>Stress ($\bar{\sigma}$)$\times 10^{-4}$/Pa</th>
<th>Viscosity ($\bar{\mu}_a$)$\times 10^{-6}$/Pa.s</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>2</td>
<td>0.34</td>
<td>0.69</td>
<td>0.79</td>
</tr>
<tr>
<td>3</td>
<td>0.79</td>
<td>1.79</td>
<td>2.24</td>
</tr>
<tr>
<td>4</td>
<td>1.41</td>
<td>3.31</td>
<td>4.21</td>
</tr>
<tr>
<td>5</td>
<td>2.28</td>
<td>5.43</td>
<td>6.42</td>
</tr>
<tr>
<td>6</td>
<td>3.36</td>
<td>8.00</td>
<td>10.00</td>
</tr>
<tr>
<td>7</td>
<td>4.83</td>
<td>11.70</td>
<td>14.70</td>
</tr>
</tbody>
</table>

Mean Final Values

$\bar{\varepsilon}_F = 6.63 \pm 0.03$
$\bar{\sigma}_F = 1.62 \times 10^5$Pa
$\bar{\mu}_aF = 2.03 \times 10^7$Pa.s

N.B. Mean value, $\bar{x} = \frac{\sum_{i=1}^{N=20} x_i}{N}$

Standard deviation, $S_{n-1} = \sqrt{\frac{\sum_{i=1}^{N=20} (x_i - \bar{x})^2}{N-1}}$

These were derived from the respective standard deviations, i.e. $S_{n-1}$. Take for example, in (Figure 4.4), the new arbitrary axes were drawn through the new origin, i.e. the mean ultimate values of true strains and viscosities ($6.63, 2.03 \times 10^7$). Then the limiting lines were drawn, through the points obtained by $\pm$ the standard deviations, i.e. $\pm 0.38$ and $\pm 0.33 \times 10^7$. Here, the level of acceptance was assumed as $\pm S_{n-1}$ whereas for larger samples population, $\pm 2S_{n-1}$ could be used.

In both figures, the ultimate points fall within the region, showing a satisfactory reproducibility especially for the viscosities and stresses.
Although the distribution about the mean ultimate true strain is still within the acceptance limit, it does, however, show a comparatively poorer distribution.

From the above observations, and within the allowable experimental errors, a few conclusions can be made. These can be summarised as follows:

1) Any sample defects below the level of visually detectable defects, have little or no effect of the results.

2) The measures of viscosity or stress give a better reproducibility than that of true strains, though all are within the acceptable limit used.

In order to ensure a high degree of reproducibility, several precautions are necessary, i.e. the samples must be defect-free, they must not fail at the grips or prematurely, the pre-heating time must be kept constant throughout, and also the temperature of the bath must not fluctuate above the acceptable limit (experience in handling the test) at any time.

Also, it is thus essential for trial runs to be made, prior to the actual measurement, and two or three samples are required for each measurement.

4.2.3 Elongational Behaviour of Rigid Polyvinyl Chloride

Since an attempt would be made to fit the plots, i.e. $\mu_a(t)$ and $\alpha_a(t)$ as a function of time, using the theoretical values obtained using the Chang and Lodge rubber-like model equation,\textsuperscript{113,114,115} it is thus relevant to give a brief account of it, prior to giving the experimental results.
For a growth of uniaxial elongational stress, it has been proposed by Lodge\textsuperscript{115} that the $\alpha(t)$ may be represented by the equation,

$$\alpha(t) = \int_{-\infty}^{t} \mu(t, t') \tau(t, t') dt' \quad \ldots \text{4.1}$$

where $\tau(t, t')$ is the strain tensor and $\mu(t, t')$ is the memory function of the form,

$$\mu(t-t') = \sum_{s=1}^{N} a_s \exp \left(-\frac{(t-t')}{\tau_s}\right) \quad \ldots \text{4.2}$$

where $a_s$ and $\tau_s$ are constants. The elongational viscosity, $\mu(t)$ at the constant strain rate is given by the equation,

$$\mu(t) = \sum_{s=1}^{N} a_s (3-2 \tau_s \nu_s \exp(-a_s t) - \tau_s U_s \exp(-U_s t) U_s^{-1} \nu_s^{-1}) \quad \ldots \text{4.3}$$

where $U_s = \tau_s^{-1} - 2e, \quad \nu_s = \tau_s^{-1} + e$

When the elongational rate is so small that $e$ can be neglected in comparison with all $\tau_s^{-1}$ in the right hand side of [4.3], it follows that

$$\mu(t) = 3 \sum_{s=1}^{N} a_s \tau_s^2 - (1 - e^{-t/\tau_s}) \quad \ldots \text{4.4}$$

Chang and Lodge\textsuperscript{113} compared Meissner's data with the equation [4.4]. In their calculation, the memory function was assumed arbitrarily to have five terms and a five term version of equation [4.4] was used to fit the data. Similar attempts were also made by Ide and White\textsuperscript{123} to fit these data with a similar equation.

A similar approach was employed here, where a five term version of equation [4.4] has been employed to fit the data obtained. Using
arbitrarily chosen \( I_s \), the constant, \( a_s \) was determined by simultaneous equation at the lowest strain rate, i.e. \( 0.004s^{-1} \), for both 180°C and 190°C.

The programmes for determining \( a_s \) and finding the elongational viscosity, \( \mu(t) \) and elongational stress, \( \alpha(t) \) will be given in Appendix III.

From section 4.2.2 (a), it was shown that the measurements of elongational viscosities, \( \mu_a \) and stresses, \( \alpha_a \) gave a better reproducibility than that of the true strains, \( \lambda \), thus it was preferably chosen to present the data, as \( \mu_a(t) \) and \( \alpha_a(t) \), instead of \( \mu_a(\lambda) \) and \( \alpha_a(\lambda) \), i.e. a function of time, instead of a function of true strain.

However, true strain values would be given to illustrate the measure of extensibility and also to supplement the findings.

4.2.3 (b) Elongational Viscosity, \( \mu_a(t) \)

Figures 4.5 and 4.6 show the log-log plots of the apparent elongational viscosity, \( \mu_a(t) \) as a function of time under various conditions.

Both 180°C and 190°C give an approximately similar trend, with the latter giving a much lower viscosity, \( \mu_a(t)s \). The elongational behaviour at elevated temperatures will be thoroughly explored in the next chapter.

It can be seen that, initially, all plots (0.01s\(^{-1}\), 0.06s\(^{-1}\) and 0.004s\(^{-1}\)) seem to merge together, but the rate increasing with the time, depending on the strain rates (\( \mu_a(e=0.1) > \mu_a(0.06) > \mu_a(0.004) \)). These rapid deviations or increasing tendency to the unbounded stress build-up continue until the samples failed. Another noteworthy point, is the deformation time increasing with the decrease in the strain rate, i.e. \( t_f(0.004) > t_f(0.06) > t_f(0.1) \).
This trend was similarly observed by other workers\textsuperscript{12,113,114} for the various polymers. For polyvinyl chloride, de Vries and Bonnebat\textsuperscript{175} and Vinogradov et al.\textsuperscript{138} have reported similar observations, though at much lower temperatures.

Also, the samples failed cohesively, especially at higher strain rates, but at the lower strain rates, slight necking (ductile failures) was observed.

4.2.3 (c) Elongational Stress, $\alpha_a(t)$

Figures 4.7 and 4.8, show the log-log plots of elongational stress, $\alpha_a(t)$ as a function of time, at 180°C and 190°C respectively. It can be seen that at 0.1s\textsuperscript{-1} and 0.06s\textsuperscript{-1} the stress build-up commences immediately whereas at 0.004s\textsuperscript{-1} it is more slowly and does not start until $t > 12$sec.

The stress-strain curves at 180°C and 190°C are shown in Figures 4.9 and 4.10 respectively. At 180°C, some anomalies are observed. They are as follows:

i) at $\lambda < 0.3$; $\alpha_a(0.004) > \alpha_a(0.06) > \alpha_a(0.1)$

ii) at $0.3 < \lambda < 0.35$; $\alpha_a(0.004) > \alpha_a(0.1) > \alpha_a(0.06)$

iii) at $0.35 < \lambda < 0.55$; $\alpha_a(0.1) > \alpha_a(0.004) > \alpha_a(0.006)$

iv) $\lambda > 0.55$; $\alpha_a(0.06) > \alpha_a(0.004)$

Also, at 180°C, the lowest strain rate, 0.004s\textsuperscript{-1} gives the largest value of true strain.

However, generally, at 180°C samples show poorer extensibility, i.e. lower $\lambda$ when compared with those at 190°C. At 190°C, especially at
0.06s\(^{-1}\), it shows better extensibility, i.e. \( \lambda > 2.0 \) and no anomalies are observed, i.e. \( \alpha_0(0.1) > \alpha_0(0.06) > \alpha_0(0.004) \).

4.2.3 (d) Comparison with Chang and Lodge Equation

Using the plots at 0.004s\(^{-1}\) at 180°C and 190°C, smooth arbitrary curves were drawn through the data points; ordinates values were taken from these curves at \( t=0.1, 1, 10, 100 \) and 1000sec., and the appropriate values for \( a_s \) were evaluated using the five simultaneous equations (N=5, chosen arbitrarily) derived from [4.4]. The values of \( \gamma_s \) used in the calculation were 100, 10, 1, 0.1, and 0.01 sec., following Chang and Lodge. Table VII shows the five corresponding \( a_s \) values at 180°C and 190°C.

Table VII Values of \( a_s \) for polyvinyl chloride at 180°C and 190°C

<table>
<thead>
<tr>
<th>Temperature</th>
<th>( N = 1 )</th>
<th>2</th>
<th>3</th>
<th>4</th>
<th>5</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>( s=100</td>
<td>10</td>
<td>1</td>
<td>0.1</td>
<td>0.01</td>
</tr>
<tr>
<td>180°C</td>
<td>299</td>
<td>931</td>
<td>125 ( \times 10^6 )</td>
<td>-1.55 ( \times 10^7 )</td>
<td>8.17 ( \times 10^9 )</td>
</tr>
<tr>
<td>*190°C</td>
<td>13.6</td>
<td>3189</td>
<td>-2.7 ( \times 10^5 )</td>
<td>3.15 ( \times 10^7 )</td>
<td>-1.7 ( \times 10^9 )</td>
</tr>
</tbody>
</table>

Consequently knowing the \( a_s \), the \( \mu_a(t) \) and \( \alpha_b(t) \) at other immediate values of \( t \) and for other constant strain rate levels could be similarly evaluated. These predicted curves are shown in Figures 4.5, 4.6, 4.7 and 4.8. The quantitative agreement between theory and experimental data appeared to be encouraging, in spite of the fact that there were
marked quantitative differences, particularly at higher values of strain rates. However, at $0.004s^{-1}$, the deviation commenced at $t > 12$ seconds.

Among the significant points from the above comparison are, i) the time where deviation occurred, approximately coincided with the beginning of the unbounded stress growth; ii) it gave some approximate indication of the filament stability and extensibility, and iii) the theory failed to explain the stress build phenomena.

4.2.4 Elongational Behaviour of Plasticised Polyvinyl Chloride (PPVC)

In this section, the general behaviour of the plasticised polyvinyl chloride (30pphr and 50pphr) will be given. However, further detailed discussions will be made in Chapter 6.

4.2.4 (a) Elongational Viscosity, $\mu_a(t)$

Figures 4.11 and 4.12, show the log-log plots of the apparent elongational viscosities, $\mu_a(t)$s versus time at various conditions.

Generally, as expected, much lower viscosities, $\mu_a(t)$s have been obtained, though approximately similar trends still are obtained. The presence of plasticiser enhanced some stability in polyvinyl chloride, thus the unbounded stress build-up occurred at a much slower period. This delay, attributed to the larger true strain, $\lambda$, obtained.

Comparing the true strains between the rigid and the plasticised polyvinyl chloride, under approximately similar conditions (refer to Table VIII), it can be seen that, generally, the plasticised form gives a far better extensibility. However, the values of true strain $\lambda$ were dependent on the conditions.
Table VIII  Comparison of true strain values, \( \dot{\varepsilon} \) between rigid and plasticised polyvinyl chloride at 180°C and 190°C for 0.1s\(^{-1}\), 0.06s\(^{-1}\) and 0.004s\(^{-1}\)

<table>
<thead>
<tr>
<th>( \dot{\varepsilon} )</th>
<th>Rigid (PVC)</th>
<th>Plasticised PVC</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>180°C</td>
<td>190°C</td>
</tr>
<tr>
<td>0.1</td>
<td>0.51</td>
<td>0.87</td>
</tr>
<tr>
<td>0.06</td>
<td>0.60</td>
<td>2.40</td>
</tr>
<tr>
<td>0.004</td>
<td>0.89</td>
<td>1.80</td>
</tr>
</tbody>
</table>

The dependence of true strains, \( \dot{\varepsilon} \), on strain rates for plasticised polyvinyl chloride are shown in Figures 4.13 and 4.14 respectively.

For 30pphr (refer to Figure 4.13) the following observations can be made:

i) At 160°C, \( \dot{\varepsilon} \) decreasing with increasing \( \dot{\varepsilon} \); poor extensibility, showing similarity to the rigid polyvinyl chloride, and failure mostly due to cohesive mechanism, presumably some necking at lower \( \dot{\varepsilon} \).

ii) At 180°C, some stability is imparted to the polyvinyl chloride, thus giving rise to much higher \( \dot{\varepsilon} \). A maximum \( \dot{\varepsilon} \) seems to occur at, 0.003s\(^{-1}\) < \( \dot{\varepsilon} \) < 0.06s\(^{-1}\). Increasing the strain rate further, stability decreases rapidly. Samples failed via ductile mechanism, with predominant necking.
iii) At 190°C, again exhibits a good extensibility, but $\lambda$ decreasing with decreasing $\dot{e}$. Sample failure was due to ductile and necking mechanism, with perhaps slight capillarity.

With 50pphr DOP (refer to Figure 4.14), the pattern changes considerably, where at 160°C, some stability has been imparted to the samples. Higher $\lambda$ was obtained at lower $\dot{e}$ and this decreased with increasing $\dot{e}$, perhaps similar to 180°C for the 30pphr. This stability perhaps, was attributed to the ductile and necking failures mechanism.

At 180°C, an all round stability has been achieved, with optimum obtained in the range of $0.002s^{-1} < \dot{e} < 0.06s^{-1}$ (similar to 190°C for 30pphr).

Finally, at 190°C, samples gave rise to low $\lambda$ (cf. with 180°C), though $\lambda$ increasing with increasing $\dot{e}$. Both 180°C and 190°C samples failed due to ductile and necking, with slight capillarity occurring at 190°C.

4.2.4 (b) Elongational Stress, $\alpha_a(t)$

For this purpose, log-log plots at 0.1s$^{-1}$, 0.06s$^{-1}$ and 0.004s$^{-1}$ at 160°C and 180°C for 30pphr DOP and 50pphr DOP have been used, shown in Figures 4.15, 4.16, 4.17 and 4.18 respectively. The following observations can be made.

a) 30pphr

At 160°C, $\alpha_a(t)$ increasing linearly and slowly initially, showing the attainment of some degree of stability, the stress build-up occurring at
a much slower pace (cf. with rigid polyvinyl chloride). The order w.r.t. time was 

\[ t_f(0.004s^{-1}) > t_f(0.06s^{-1}) > t_f(0.1s^{-1}). \]

This coincided with the order of true strain, i.e. \( \lambda_f(0.004s^{-1}) > \lambda_f(0.06s^{-1}) > \lambda_f(0.1s^{-1}). \)

But, a different trend was observed at 180°C, where the order w.r.t time was 

\[ t_f(0.004s^{-1}) > t_f(0.06s^{-1}) > t_f(0.1s^{-1}) \]

but the order of true strain was \( \lambda_f(0.06s^{-1}) > \lambda_f(0.004s^{-1}) > \lambda_f(0.1s^{-1}). \)

b) 50pphr DOP

At 160°C, as with a), a significant delay in sudden stress growth occurred, i.e. 

\[ t_f(0.004s^{-1}) > t_f(0.06s^{-1}) > t_f(0.1s^{-1}). \]

This showed some stability existing in the sample, hence giving rise to larger values of \( \lambda \), though the order was as follows, \( \lambda_f(0.004s^{-1}) > \lambda_f(0.06s^{-1}) > \lambda_f(0.1s^{-1}). \) As a matter of fact, although \( \lambda \) decreased with \( \dot{\varepsilon} \), as with a), it was at a much slower rate.

A similar pattern was observed at 180°C, with the rapid stress growth, though the order of magnitude of \( \lambda \) differed, \( \lambda_f(0.06s^{-1}) > \lambda_f(0.1s^{-1}) > \lambda_f(0.004s^{-1}). \)

Unfortunately, no comparison can be made with the findings of any other workers, since no data has been reported to date.

4.2.4 (c) Comparison with Chang and Lodge Model Equation

As with section 4.2.3 (b), the five constants, \( a_s \) at various conditions have been evaluated. The constants are shown in Table IX and X.
Table IX  Values of $a_s$ for 30pphr DOP at
160°C, 180°C and 190°C

<table>
<thead>
<tr>
<th>$s(N=5)$</th>
<th>100</th>
<th>10</th>
<th>1</th>
<th>0.1</th>
<th>0.01</th>
</tr>
</thead>
<tbody>
<tr>
<td>$a_s$</td>
<td>$a_1$</td>
<td>$a_2$</td>
<td>$a_3$</td>
<td>$a_4$</td>
<td>$a_5$</td>
</tr>
<tr>
<td>Temperature</td>
<td>160°C</td>
<td>168.6</td>
<td>160.7</td>
<td>57.1</td>
<td>562.7</td>
</tr>
<tr>
<td></td>
<td>562.7</td>
<td>-3.53x10⁴</td>
<td>2.52x10⁶</td>
<td>-1.18x10⁸</td>
<td>5.61x10⁴</td>
</tr>
<tr>
<td>180°C</td>
<td>168.6</td>
<td>-1.37x10⁴</td>
<td>9.99x10⁵</td>
<td>-4.68x10⁷</td>
<td>2.21x10⁹</td>
</tr>
<tr>
<td>190°C</td>
<td>57.1</td>
<td>-3.73x10³</td>
<td>2.69x10⁵</td>
<td>-1.28x10⁷</td>
<td>6.09x10⁸</td>
</tr>
</tbody>
</table>

Table X  Values of $a_s$ for 50pphr DOP at
160°C, 180°C and 190°C

<table>
<thead>
<tr>
<th>$s(N=5)$</th>
<th>100</th>
<th>10</th>
<th>1</th>
<th>0.1</th>
<th>0.01</th>
</tr>
</thead>
<tbody>
<tr>
<td>$a_s$</td>
<td>$a_1$</td>
<td>$a_2$</td>
<td>$a_3$</td>
<td>$a_4$</td>
<td>$a_5$</td>
</tr>
<tr>
<td>Temperature</td>
<td>160°C</td>
<td>168.6</td>
<td>160.7</td>
<td>57.1</td>
<td>562.7</td>
</tr>
<tr>
<td></td>
<td>62.5</td>
<td>-2792</td>
<td>4.16x10⁵</td>
<td>-4.89x10⁷</td>
<td>2.57x10⁹</td>
</tr>
<tr>
<td>180°C</td>
<td>3.5</td>
<td>-153</td>
<td>2.97x10⁴</td>
<td>-3.55x10⁷</td>
<td>1.85x10⁹</td>
</tr>
<tr>
<td>190°C</td>
<td>7.69</td>
<td>-405</td>
<td>7.7x10⁴</td>
<td>-9.18x10⁵</td>
<td>4.83x10⁸</td>
</tr>
</tbody>
</table>

Using these constants, values of $\mu_a(t)$ and $\phi_0(t)$ at intermediate times could be evaluated and fitted into the curves, shown in Figures 4.11, 4.12, 4.15 and 4.18.

As with rigid polyvinyl chloride, initially good superimpositions were obtained but deviation occurred in the later period, with the deviation being larger and happening rapidly at higher strain rates.

Similarly, these deviations would be associated with the rapid build-up in viscosities or stresses. Thus, the theory failed to explain these phenomena.
4.2.4 (d) Comparison with Shear Values

The shear data at 180°C was obtained using the Davenport Capillary Rheometer. Also, Bagley end correction data or something closely resembling it, has been employed.

The plots of viscosities (both elongational and shear) as a function of strain rates are given in Figures 4.19 and 4.20.

Generally, polyvinyl chloride shows a tension thinning behaviour, i.e. viscosity decreasing with strain rate (analogous to the pseudoplasticity or shear thinning behaviour). At very low strain rates, the Troutonian relationships have been obtained, i.e. \( \mu_e \approx 3 \eta \dot{\varepsilon} \).

These findings have been similarly obtained by several workers including Cogswell\(^{18,19,20}\) and Ballman\(^{16}\) working with different polymer systems.

It has also been proved, on shear, following sudden application of shear flow at constant shear rate, \( \dot{\gamma} \) at \( t = 0 \), that

\[
\alpha_s(t)/\dot{\gamma} = \sum_{s=1}^{N} a_s \int_s^2 (1 - e^{-t/S_s})
\]

Equation [4.5] is valid for any value of \( s \) and is identical to equation [4.4], which represents the rubber-like theory of elongational flow at small strain rate, \( \dot{\varepsilon} \), hence

\[
(\alpha_a(t)/\dot{\varepsilon})_{\varepsilon=0} = 3(\alpha_s(t)/\dot{\gamma})_{\varepsilon=0}
\]

This agrees with the above experimental findings. The relationship [4.6] is also known as Troutonian relationship.
4.2.4 (e) Characterisation of Plasticised Polyvinyl Chloride

The glass transition temperatures, $T_g$ of the stretched samples (30pphr) were determined and the schematic thermograms (reduced scale), plus that of the unstretched samples, and are shown in Figure 4.21.

The glass transition temperature, $T_g$ of the stretched sample was slightly greater than that of the unstretched sample, i.e. $66.5 \pm 0.1°C$ and $63.5 \pm 0.1°C$ respectively. This might be attributed to some extent, to the structural changes occurring in the stretched samples.

However, further investigations were not viable due to the difficulty in determining the sample's portion to be taken for the testing, where reproducibility in measurement was poor.

4.3 Discussions

From the evidence amassed so far, some interesting findings have been revealed. However, it was considered essential that the discussions be classified into two major parts, the rigid and plasticised polyvinyl chloride.

4.3.1 Rigid Polyvinyl Chloride

The variation of elongational stress, $\sigma_a(t)$ at 180°C and 190°C, as a function of time, shown in Figures 4.7 and 4.8 respectively, revealed a few interesting points. They are,

i) The steady state flow, i.e. stress reaching a constant value, has not been achieved even at low strain rate, i.e. $0.004s^{-1}$. Hence,
according to Petrie,\textsuperscript{10} the elongational viscosity obtained from the ratio of elongational stress and strain rate could not be regarded as a material property.

However, it was possible to regard the apparent elongational viscosity, $\nu_a(t)$, dependent on time as a material property provided samples were given a long rest before commencing the experiment; this was to ensure that the samples were stress free and without previous deformation histories. The method was originally proposed by Giesus\textsuperscript{26} and then by Meissner.\textsuperscript{21,22}

\begin{itemize}
  \item[ii)] The presence of the unbounded or rapid stress growth (analogous to stress 'overshoot' in shear) for all strain rates measured. This eventually led to the attainment of some critical stress and ultimately the sample failed abruptly. This was somewhat solid-like in nature, though some stability seemed to exist at 190°C, but not sufficient to impart any significant improvement (refer to Table VIII).
  \item[iii)] Samples failed rapidly, corresponding to small deformation time. Take for example, at 190°C (0.004 s\textsuperscript{-1}), samples failed at the deformation time less than 360 s. From visual observation, samples failed through the cohesive fracture mechanism but some necking (associated with stability) was observed at 190°C. This deduction was based on the evidence given by Ziabicki\textsuperscript{14} and also by Ide and White.\textsuperscript{123} These mechanisms are common with polymers having poor spinnability, especially at high strain rates or low temperatures. Visually, samples experienced a rapid reduction in diameter, hence giving rise to poor elongation. However, no qualitative attempt was made on this aspect, besides via visual observation of the samples' failure.
\end{itemize}
Since the viscosities were evaluated from the stresses, Figures 4.5 and 4.6 revealed similar findings to those mentioned above. However, they provided some significant information, not disclosed in Figures 4.7 and 4.8, i.e. the superimposition of various plots at the initial stages, prior to the sudden stress build-up.

The above findings showed the marked difference between polyvinyl chloride and other common polymers such as low density polyethylene, polystyrene etc., reported by other workers,\textsuperscript{12,16,17} especially immediately prior to the failure and the respective dependence of the strain rates.

Figure 4.22 shows the dependence of viscosities for the rigid polyvinyl chloride (derived from Figure 4.7) together with other common polymers (given in Chapter 2).

Thus, the wide variation of viscosity w.r.t strain rates, depending on the nature of the polymers, showed the existence of three types of elongational flow of polymers (already given in Chapter 2). They can be summarised as,

i) Troutonian: \( \mu_a(t) \) is independent of strain rate, e.g. polymethyl methacrylate (PMMA).

ii) Tension stiffening: \( \mu_a(t) \) increasing with strain rate, e.g. polyisobutylene (PIB).

iii) Tension thinning: \( \mu_a(t) \) decreasing with strain rate, e.g. polyvinyl chloride.

It is not uncommon for polymers to show two or more behaviours, depending on the nature of the polymers and the conditions.
The discrepancies between the results obtained here and those reported by de Vries and Bonnebat\textsuperscript{175} might be attributed to the different grades of polyvinyl chloride and the different experimental techniques. Furthermore this was common in the shear measurements, where the flow curves of polyvinyl chloride from the different sources (or tested on different apparatus) gave different results.

The anomalies found in the elongational flow of polyvinyl chloride (cf. with other polymers) might be attributed to the supramolecular structures or heterogenities such as ordered regions of the nematic types, globules and fibrils, and the crystallites,\textsuperscript{35-37,77} i.e. rigid polyvinyl chloride is not a simple amorphous polymer but a slightly crystalline polymer (about 3–10 per cent).

Also, as a consequence of the above mentioned structures and the usually high viscosity in the temperature range measured, a number of anomalous effects were present, hence complicating the measurement. These effects, such as particle flow, change of flow properties with time and thermal history, slip flow, viscous heat generation and also possible degradation.

The behaviour observed could possibly be explained by looking at the components of the tensile deformation.

4.3.2 Components of Tensile Deformation

As has been discussed in Chapter 2, when a polymer is subjected to a tensile stress, three components of deformation might be distinguished, i.e. bending and stretching of bonds (inter and intra-molecular) ($D_{OE}$), chain uncoiling with no slippage ($D_{HE}$) and chain slippage ($D_{vise}$).
If we assumed polyvinyl chloride, whose behaviour on application of stress, may be considered as the sum of these components, then

\[ D_T = D_{OE} + D_{HE} + D_{visc} \]

By changing the conditions such as temperature and stress, the components would vary in their dominance.

At any particular strain rate and temperature, the bending and stretching of bonds (characteristic of a rigid polyvinyl chloride), coupled with the process of chain uncoiling, gave rise to stress build-up greater than could be dissipated by the viscous flow, i.e. \( D_{OE} + D_{HE} \gg D_{visc} \). Hence the measured viscosities were comprised of the two components and were a function of time. These could presumably be characterised by the poor extensibility obtained.

However at \( 190^\circ C \) (0.06s\(^{-1}\)), some stability was imparted, where the chain slippage component might make a small contribution, i.e. \( D_{visc}(190^\circ C) \gg D_{visc}(180^\circ C) \), hence a better extensibility was observed.

4.3.3 Plasticised Polyvinyl Chloride

From the information accumulated so far, the presence of plasticiser has somewhat imparted some flow stability, hence samples could be stretched easily and samples' failure was further delayed (cf. with rigid polyvinyl chloride). However, the effect of the composition and the nature of plasticiser will be further discussed in Chapter 6.

The initial findings in the elongational flow can be summarised as follows:-
i) the stresses and viscosities were very much lower (cf. with rigid polyvinyl chloride) under identical conditions; but the phenomena of sudden stress build-up leading to samples' failure was still present, though it was considerably delayed (refer to Figures 4.11, 4.12, 4.15, 4.16, 4.17 and 4.18).

ii) the extensibilities were enormously improved but still dependent of the conditions such as temperature and strain rates and also composition (refer to Figures 4.13, 4.14). The maximum true strain achieved was, \( \lambda \approx 10 \) (cf. with rigid, \( \lambda \approx 2.0 \)).

iii) the general trend was still preserved, i.e. steady state did not materialise (constant value of stresses), but better fits were obtained using the Chang and Lodge equation, especially at 0.004s\(^{-1}\).

iv) the flow stability seemed to wane for the 50pphr plasticiser, at 190°C, thus giving lower true strain.

In Chapter 1 (section 1.8), the possible molecular structures of the plasticised polyvinyl chloride have been briefly discussed. Thus it would be possible to attempt, using the information available, to explain the observed elongational behaviour of the plasticised polyvinyl chloride.

4.3.3 (a) Relationship Between the Molecular Structures and the Elongational Flow Behaviour

Generally, it has already been shown using the evidence obtained by several workers,\(^ {35,76,77,78} \) the molecular structure of the plasticised polyvinyl chloride is made up to some degree of the ordered regions
(paracrystalline lamellar structures). Also, these regions were known to decrease with increasing amounts of plasticiser.77

This would then explain the delayed occurrence of the sudden stress build-up phenomena and the much improved elongational properties (cf. with rigid polyvinyl chloride). Again, this dominance is dependent on the conditions.

For example at 180°C, and strain rates in the range of 0.004 s⁻¹ to 0.06 s⁻¹, for the 30pphr (refer to Figure 4.11), the viscous component \( \mathcal{D}_{\text{visc}} \) was presumably the dominant component, but at 160°C, the reverse situation occurred, i.e. \( \mathcal{D}_{\text{OE}} \) and \( \mathcal{D}_{\text{HE}} \gg \mathcal{D}_{\text{visc}} \) hence, giving rise to the rapid stress build-up and premature samples' failure.

As for the mechanism of samples' failure, it would be possible to suggest the existence of its close relationships to the molecular structures and also the dominance of each tensile component. Hence at the lower concentration (30pphr), the behaviour of the rigid polyvinyl chloride was still evident but at the higher concentration (50pphr) this was less pronounced. However, it must be stressed, the behaviour was further dependent on the conditions. Further discussions will be made in Chapter 6.

As in rigid polyvinyl chloride (section 4.3.2), the behaviour of the plasticised polyvinyl chloride could be explained in terms of the dominance of each component of the tensile deformations. It was possible to assume that the presence of the plasticiser reduced the role played by the bonding and stretching component \( \mathcal{D}_{\text{OE}} \) and chain uncoiling (with no slippage)\( \mathcal{D}_{\text{HE}} \), hence the total tensile deformation was predominantly made up of the chain slippage \( \mathcal{D}_{\text{visc}} \) component.
At 160°C, samples were observed to fail via the cohesive mechanism, whereas at 180°C and 190°C (at higher strain rates), samples failed via the ductile (with enormous necking) mechanisms. For 190°C, at lower strain rates, especially the 50pphr, capillarity mechanisms were observed.

Moreover, the above deductions were made through visual observations, thus no qualitative conclusions could be drawn.

4.3.3 (b) Comparison with Shear Flow Data

Generally, elongational flow measurements gave rise to higher values in the viscosities measured when compared to the shear flow method. This could be explained using the 'match stick' analogy, which was qualitatively proposed by Lodge.115

Fig. 4.23 a) and c):- shear; b) and e):- tension
Consider Figure 4.23 a) and b), a random array of matches, which simulates the amorphous region in the structure of the polymer, i.e., polyvinyl chloride, then both shear and elongational deformation would give rise to very little qualitative response. But considering the same Figure c) and d), the ordered matches, which simulate the ordered region, then it is much easier to shear the matches in the plane in which they are ordered than to stretch.

For the real situation, in this case the plasticised polyvinyl chloride, the molecular structures are a combination of the amorphous and the ordered regions, schematically shown in Figure 4.24.

In shear deformation, the response is generally small because it involves disentanglement of the entangled polymer chain (amorphous region) plus the chain slippage (segments of polymer chains slide irreversibly past each other), hence giving rise to the low viscosity.

In elongational deformation, apart from drawing the entanglement, it is trying to stretch the ordered molecular structures, which in turn offer a tough resistance, hence giving rise to higher viscosity. The situation changes with the amount of plasticiser and conditions (changing the proportion of the structures).

**Fig. 4.24** Schematic representation of the structure of polyvinyl chloride showing both the amorphous and the ordered regions.
4.4 Conclusions

From the above, a number of conclusions can be drawn on the general elongational flow behaviour of polyvinyl chloride (rigid and plasticised). They can be summarised as follows,

i) polyvinyl chloride exhibited a tension thinning behaviour, i.e. viscosity decreasing with strain rates and the plasticised form gave rise to much improved elongational properties.

ii) the optimum elongational properties achieved were dependent on the conditions such as temperatures, strain rates and plasticiser composition. Take for example, for the 30pphr, this was achieved at 190°C and strain rates in the range of 0.035 - 0.06s⁻¹, whereas for the 50pphr, it was at 180°C and strain rates were in the range of 0.02 - 0.004s⁻¹.

iii) A good agreement was obtained between experimental and theoretical predicted values, especially during the initial stages and at lower strain rates. But the Chang and Lodge model failed to explain the sudden stress build-up phenomena.

Finally, based on the above criteria, the plasticised polyvinyl chloride has been preferably chosen for further investigations, outlined in the next chapters.
Plots of $\mu_a$ versus for the polyvinyl chloride samples at $180^\circ \text{C}$ and $0.008 \text{s}^{-1}$

**Fig. 4.1**
Plots of $\mu_a$ versus $\alpha_a$ for the polyvinyl samples at 180°C and 0.008s$^{-1}$

Fig. 4.2
Distribution of the ultimate value about the mean ultimate value.

Fig. 4.3
Distribution of the ultimate values about the mean value

Fig. 4.4

new origin

\[(1.67 \pm 0.38 \times 10^3, 6.63 \pm 0.33)\]
Rigid polyvinyl chloride at $180^\circ$C

**Fig. 4.5**

- Log apparent elongational viscosity $\mu_{el}(t)/\text{Pa.s}$
- Log time, $t/s$
- $\dot{e} = 0.1 \text{s}^{-1}$
- $0.004$
- Chang and Lodge model equation
Rigid polyvinyl chloride at 190°C

Fig. 4.6
Rigid polyvinyl chloride at 180 °C

Fig. 4.7
Rigid polyvinyl chloride at 190°C

![Graph showing the relationship between time and elongational stress for rigid polyvinyl chloride at 190°C. The graph includes data points for different strain rates and a model prediction.](image)

Fig. 4.8
Rigid polyvinyl chloride at 180°C

Fig. 4.9
Rigid polyvinyl chloride at 190°C

![Graph showing the relationship between true strain ($\lambda$) and apparent elongational stress ($\sigma_a(t) / \rho$) for different strain rates ($\dot{\varepsilon}$).]

**Fig. 4.10**
Polyvinyl chloride (30pphr) at 160°C, 180°C and 190°C

\[ \text{Chang and Lodge model equation} \]

Fig. 4.11
Polyvinyl chloride (50pphr) at 160°C, 180°C and 190°C

$e = 0.45^{-1}$

Chang and Lodge model equation

Fig. 4.12
Polyvinyl chloride (50pphr) at 160°C, 180°C and 190°C

Fig. 4.13
Polyvinyl chloride at 160°C, 180°C and 190°C

Fig. 4.14
Polyvinyl chloride (30pphr) at 160°C

Chang and Lodge model equation

Fig. 4.15
Polyvinyl chloride (30pphr) at 180°C

![Graph showing log apparent stress vs. log time]

Chang and Lodge model equation

\[ e = 0.1 \] for 0.06

0.004

Fig. 4.16
Polyvinyl chloride (50pphr) at 160°C

Fig. 4.17
Polyyvinyl chloride (50pphr) at 180°C and 190°C
Polyvinyl chloride (30pphr) at 180°C

Fig. 4.19
Polyvinyl chloride (50pphr) at 180°C
Thermograms (reduced) before and after being stretched for polyvinyl chloride (30pphr)

Fig. 4.21
Comparison between polyvinyl chloride and other common polymers

Fig. 4.22
5.1 Introduction

It is well understood that flow occurs when polymer molecules move past each other; the ease of flow depends on the mobility of the molecular chains and the forces or entanglements holding the molecules together and in general, an increase in temperature reduces the viscosity.

In the case of polyvinyl chloride melt, several workers\textsuperscript{35,36,37} have observed the dual relationship in the plots of $\log \eta$ (shear viscosity) against the reciprocal of the absolute temperature, $1/T$, where they attributed this phenomena to the transition of the polyvinyl chloride from one state (predominantly glassy) to another (predominantly viscous); this has already been discussed in Chapter 1.

In the previous chapter, it has also been shown that the elongational properties of polyvinyl chloride, both plasticised and rigid, were dependent on the temperature (restricted to two or three levels).

Here, the main aim was to investigate the elongational properties further, over a wider range of temperature. However, since plasticised chloride gave better elongational properties such as higher true strain or elongation, coupled with ease of sample preparation and better reproducibility (refer to Chapter 4, section 4.3.3), it was thus preferably chosen.
5.2 Materials Used and Experimental Methods

The material used and the experimental procedure were given in Chapter 3 (section 3.6 and section 3.8.5 respectively).

5.3 Experimental Results

In order to investigate quantitatively and also qualitatively, the effect of temperatures, the results obtained (plots of elongational viscosities/stresses against time) were reduced into mastercurves by two separate methods,

a) Method A

This technique of deriving the mastercurves were similarly used by Shroff et al.,\textsuperscript{120} to investigate the dependence of elongational viscosity of polypropylene on the temperature. The mastercurve at a particular reference temperature (arbitrarily chosen) were obtained by shifting the data of other temperatures at a \(45^\circ\) angle. The temperature dependent of the derived shift factors, \(a_T\), was then obtained.

Further discussion will be given later.

b) Method B

As the above method but, here the mastercurves of a particular reference temperature were evaluated, using a horizontal shift, \(a_T\) instead of the \(45^\circ\) angle shift. The shift factors at other temperatures were obtained using the original William Landel Ferry (W.L.F) equation,\textsuperscript{219} shown below.
\[ a_T = \frac{-8.86 (T - T_r)}{101.6 + (T - T_r)} \quad \ldots 5.1 \]

where \( T_r \) is the reference temperature, arbitrarily selected.

This method has also been used by Onogi and Kamei\textsuperscript{150} and Osamu et al.\textsuperscript{166} in investigating the elongational properties of polystyrene and polypropylene respectively, at elevated temperatures.

5.3.1 Elongational Behaviour of 30pphr DOP

Figures 5.1 and 5.2 show the log-log plots of elongational viscosity as a function of time, at 0.06s\(^{-1}\) and 0.004s\(^{-1}\) respectively over a temperature range (160°C - 190°C).

In both strain rates, as expected the elongational viscosities decreasing with increasing temperature. This can be easily understood, since ease of flow depends on the mobility of the molecular chains and the forces or entanglements holding the molecules together. Increasing the temperature obviously leads to the weakening of the forces or entanglements, i.e. enhancing the chain mobility. Hence, giving rise to the low viscosity.

Several workers\textsuperscript{220,221} have suggested that plasticised polyvinyl chloride can be approximately described by the relation,

\[
\text{crystal + plasticiser} \rightleftharpoons \text{solvated amorphous polymer} \quad \ldots 5.2
\]

Increasing the temperature decreases the crystallinity, and from the law of mass action, equation [5.2] favours the R.H.S. (right hand side). Hence at high temperatures, polyvinyl chloride is liquid-like (or viscous) in nature.
In terms of the components of tensile deformation, we can presume that at low temperatures the total tensile deformation is predominantly made up of the bending and stretching ($D_{OE}$) and the chain uncoiling, with no slippage ($D_{HE}$) components; the viscous component ($D_{visc}$) playing a minor role. This dominance of each component changes with increasing temperature (neglecting the effects of strain rates and plasticiser content).

Comparing the strain rates, i.e. $0.06s^{-1}$ and $0.004s^{-1}$. At $0.06s^{-1}$, the stress build up phenomena occurring immediately and rapidly, i.e. the deformation time, $t$ less than 1 sec., but at $0.004s^{-1}$, this occurring at the deformation time, $t$ greater than $10^2$ sec. and also, between $160^\circ C$ and $180^\circ C$, the rates of rise in the viscosity are approximately similar until the deformation time, $t \approx 2 \times 10^2$ sec., then increasing more rapidly, especially at $160^\circ C$ prior to the failures.

The above pattern is less pronounced at $190^\circ C$; instead an approximately linear relationship is observed. This may be attributed to excessive dominance of the viscous component ($D_{visc}$). Although this increases the ease of flow, it has an adverse effect, i.e. reducing the filament stability and giving rise to premature failure due to capillarity.

5.3.1 (a) Mastercurves Using Method A

Referring to Figures 5.1 and 5.2. A $45^\circ$ line was drawn on each figure (shown). Using the plots of $190^\circ C$ as the reference temperature, which was arbitrarily chosen, the data at other temperatures was shifted downward towards the $190^\circ C$, in a direction parallel to the drawn $45^\circ$ line.

The shifting procedure (refer to Fig. 5.2), taking the $160^\circ C$ plot as a typical example, can be briefly described as follows,
a) A horizontal line, 00', was drawn at the intersecting point between the 45° line and the 190°C plot and a vertical line was drawn from point B (intersection between the 160°C plot and 45° line) and intersecting 00' at point A.

b) Using the 45° similar triangle properties of \( \Delta AOB \), the length BO could be evaluated. The distance BO evaluated was used to determine the shift in the viscosity along the 45° line.

c) Finally, using the distance BO, other points were similarly shifted. Plots of the other temperatures were similarly shifted.

The mastercurves obtained for the 30pphr DOP at 0.06s\(^{-1}\) and 0.004s\(^{-1}\) are shown in Figures 5.3 and 5.4 respectively. It can be seen that the superimposition can be considered satisfactory.

The derived shift factors at various temperatures were plotted against the reciprocal of absolute temperatures and are shown in Fig. 5.5. At 0.004s\(^{-1}\), a linear plot of the Arrhenius type was observed whereas at 0.06s\(^{-1}\) a dual linear relationship was obtained. The relationship can be represented by

\[
a_T = B \exp\left(\frac{E_a}{RT}\right)
\]

where \( a_T \) is the shift in viscosity along the 45° line, \( E_a \) is the activation energy, \( T \) is the absolute temperature, \( R \) is the gas constant and \( B \) is a constant (depending on strain rates and the nature of the polymer).

The activation energies evaluated at 0.004s\(^{-1}\) and 0.06s\(^{-1}\) were 10.18 kcal/mole and 3.97 kcal/mole and 11.92 kcal/mole respectively. The values obtained were reasonable (cf. to 10-20 kcal/mole reported for polyvinyl chloride in shear flow\(^{35,36}\)). Similar observations were made by Munstedt\(^{176}\) and Han and Lamonte\(^{155}\) for polystyrene and low density
polyethylene, with Munstedt observing the dual Arrhenius-type relationship.

The dual relationship might be attributed to transitional changes from a state of predominantly elastic (or glassy), i.e. $D_{OE}$ and $D_{HE}$ to predominantly viscous ($D_{visc}$) or perhaps according to Berens and Folts, transition from particulate to continuum flow in explaining the dual phenomena in shear flow of polyvinyl chloride. However, it must be stressed that in the shear flow, the Arrhenius plots were plots of viscosity and the reciprocal of the absolute temperatures whereas in this case it was the shift in elongational viscosity. This might explain any of the discrepancies observed.

5.3.1 (b) Mastercurves Using Method B

Onogi and co-workers have reported that elongational properties such as viscosity, stress and strain measured as a function of strain rates or time at various temperature ranges can be superimposed on the respective mastercurves by horizontal shifts with the same shift factors for different quantities.

In this case, using equation [5.2], with 190°C plot as the reference (chosen arbitrarily), i.e. $T_r = 190°C$, the shift factors, $a_T$, at other temperatures were evaluated, given in Table XI.

<table>
<thead>
<tr>
<th>Temperatures/°C</th>
<th>$a_T$</th>
</tr>
</thead>
<tbody>
<tr>
<td>160</td>
<td>40.94</td>
</tr>
<tr>
<td>170</td>
<td>8.75</td>
</tr>
<tr>
<td>175</td>
<td>4.63</td>
</tr>
<tr>
<td>180</td>
<td>2.63</td>
</tr>
</tbody>
</table>

Table XI Values of shift factors, $a_T$ at respective temperatures using [5.1]
The mastercurves at 0.06s\(^{-1}\) and 0.004s\(^{-1}\) evaluated are shown in Figures 5.6 and 5.7 respectively. It can be seen, the shifted elongational viscosity increasing monotonically with time. Since identical shift factors were used irrespective of strain rates, it could be used to distinguish their respective behaviours.

At 0.004s\(^{-1}\), a better distribution about the 190°C plot was obtained (cf. 0.06s\(^{-1}\)) showing the validity in selecting the 190°C as the reference. From the mastercurve plots, a few significant points can be made; they are

i) Plots of 175°C and 180°C gave a good superimposition w.r.t to 190°C, whereas plots of 160°C and 170°C gave the least superimposition.

ii) At 0.06s\(^{-1}\), only the 180°C plot gave a reasonable superimposition, thus a poorer distribution was observed.

The above observation can be attributed to the differences in the dominance of components of tensile deformation existing in the sample at a particular temperature. Take for example at 0.004s\(^{-1}\), at 160°C and 170°C, the elastic (D\(_{OE}\)) and the chain slippage, with no slippage (D\(_{HE}\)) were the dominant components whereas at 175°C to 190°C, the viscous component (D\(_{visc}\)) was dominant. Similarly at 0.06s\(^{-1}\), but with the transition from one state to another was more pronounced (gave rise to the dual relationship, given in section 5.3.1 (a)).

An attempt was made to fit the mastercurves using the Chang and Lodge rubber-like equation [4.4]. Two methods were tried.

The first method was based on the work by Osamu et al.\(^{166}\)
where they proposed that the temperature effect can be included in the time constant, $\tau$ in equation [4.4] by the equation,

$$\tau = a_T \tau^o \quad \ldots 5.4)$$

where $a_T$ is the shift factor, given in Table XI and $\tau^o$ is the time constant at the reference temperature.

Using equation [5.4], the $\tau$ at various temperatures were evaluated. Then using the known values of $\tau^o$ and the respective $a_T$, the elongational viscosities at various temperatures were evaluated similarly to those shown in the previous chapter (section 4.2.3 (d)).

Another method employed was to neglect equation [5.4], but using the original Chang and Lodge equation in obtaining the viscosities at various temperatures and eventually the horizontal shifts were carried out.

Both the theoretical plots evaluated are shown in Figures 5.6 and 5.7. It can be seen that the method suggested by Osamu et al.\textsuperscript{166} gives higher predicted values while the second method compared much more favourably with the experimental data especially along the initial stages of the plots.

However, Osamu's method does show a slight indication of the stress build up phenomena, whereas the second gives a constant viscosity. However, no real conclusion can be made since an attempt to fit the 50pphr DOP failed considerably using the first method.

It must be mentioned that they used log-log plots of viscosity against time rather than against the reduced time. Also, they found the method failed to explain the stress overshoot phenomena observed with the experimental data.
5.3.2    Elongational Behaviour of 50pphr DOP

Figures 5.8 and 5.9, show the log-log plots of the elongational viscosity against time at various temperatures for $0.06 s^{-1}$ and $0.004 s^{-1}$ respectively.

As with the 30pphr DOP, the elongational viscosity decreasing with increasing temperature; the rates at $0.06 s^{-1}$ are greater than at $0.004 s^{-1}$. However, at high temperature, especially at $190^\circ C$, although the ease of flow was enhanced, characterised by the low viscosity, samples were observed to fail prematurely. Premature failures were significant at $0.004 s^{-1}$, and might be attributed to both necking and capillarity.

The log-log plots of elongational stress against true strain at $0.06 s^{-1}$ and $0.004 s^{-1}$ are given in Figures 5.10 and 5.11 respectively. It can be seen that no significant trend is observed. Higher values of true strain were obtained at $170^\circ C - 180^\circ C$ (cf. $160^\circ C$ and $190^\circ C$). Also, no attempt was made to use the true strain measurements extensively due to poorer reliability and reproducibility (refer to section 4.2.2).

5.3.2 (a)   Mastercurves Using Method A

The mastercurves at $0.06 s^{-1}$ and $0.004 s^{-1}$ derived, are given in Figures 5.12 and 5.13 respectively. As with the 30pphr DOP, the reference temperature was $190^\circ C$. It can be clearly seen that the superimposition can be considered satisfactory, in fact much better than the 30pphr DOP. Arrhenius-type plots were obtained, shown in Figure 5.14. Here, both strain rates give rise to the dual Arrhenius relationship.

At $0.06 s^{-1}$ and $0.004 s^{-1}$ respectively, the activation energies evaluated are as follows,
a) For \( T < 170^\circ C \), the activation energy, \( E_a \) is 10.63 kcal/mole, whereas at \( T > 170^\circ C \), it is 11.25 kcal/mole.

b) For \( T < 172^\circ C \), \( E_a = 10.01 \) kcal/mole; 

at \( T > 172^\circ C \), \( E_a = 17.0 \) kcal/mole.

This pattern differs from the 30pphr DOP but it somewhat similar to the dual phenomena observed in shear, where the activation energy at low temperature is greater than at high temperature. One possible explanation is that, at high plasticiser content (50pphr), the polyvinyl chloride structure being dominantly amorphous, hence the elongational response is closer to the shear response. Also, the increasing amount of plasticiser, presumably, enhances the transition from one state to another.

5.3.2 (b) Mastercurves Using Method B

Using the shift factors in Table XI, the mastercurves at 0.06s\(^{-1}\) and 0.004s\(^{-1}\) were obtained, and are shown in Figures 5.15 and 5.16 respectively. It can be seen that both superimpositions can be considered satisfactory. As with the 30pphr, the shifted viscosity increases monotonically with time, but the slope at 0.06s\(^{-1}\) is greater than at 0.004s\(^{-1}\).

The theoretical plots (neglecting \( \tau_s = a_s \tau_s^0 \)) compare favourably with the experimental data, especially at the initial stages prior to deviation at the deformation time, \( t \) greater than 10.2sec.

Figures 5.17 and 5.18, show the mastercurves derived from the plots of the elongational stress against true strain, i.e Figures 5.10 and 5.11. Again, the superimpositions are satisfactory as with elongational
viscosity and similarly the shifting stress increased slowly with true strain. Also the slope at $0.06s^{-1}$ is slightly greater than at $0.004s^{-1}$.

5.4 Discussions

From previous sections, it was possible to derive the mastercurves from the log-log plots of elongational viscosity/stress against time/true strain and in fact in most cases, the superimpositions were satisfactory. However, both techniques used seemed to provide differing information on the effect of temperatures on the elongational behaviour of polyvinyl chloride; it is, therefore, appropriate to discuss the results accordingly.

5.4.1 Mastercurves Using Method A

One obvious piece of information derived from this method, was the correlation between the shift factors (elongational viscosity) and the absolute temperatures. Here, most cases except for 30pphr DOP at $0.004s^{-1}$, gave rise to the dual Arrhenius type of relationship. Hence, the activation energies for polyvinyl chloride at various conditions can be evaluated. These values can be summarised and are given in the Table below.

Table XII  Values of the activation energies for polyvinyl chloride
30/50pphr at $0.06s^{-1}$ and $0.004s^{-1}$

<table>
<thead>
<tr>
<th>STRAIN RATES/ε/s⁻¹</th>
<th>Activation Energy/kcal/mole plasticiser/pphr</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>30</td>
</tr>
<tr>
<td></td>
<td>50</td>
</tr>
<tr>
<td>1.</td>
<td>0.06</td>
</tr>
<tr>
<td></td>
<td>11.92</td>
</tr>
<tr>
<td></td>
<td>3.92</td>
</tr>
<tr>
<td></td>
<td>10.63</td>
</tr>
<tr>
<td></td>
<td>11.25</td>
</tr>
<tr>
<td>2.</td>
<td>0.004</td>
</tr>
<tr>
<td></td>
<td>10.18</td>
</tr>
<tr>
<td></td>
<td>10.61</td>
</tr>
<tr>
<td></td>
<td>17.00</td>
</tr>
</tbody>
</table>
The dual activation energy phenomena is quite common for polymer melts under shear flow. For elongational flows, Munstedt, working with polystyrene in the range of 120°C - 260°C observed similar behaviour whereas Shroff et al., working with several polymers such as low/high density polyethylene, polystyrene and polypropylene, and also using similar techniques of obtaining mastercurves at various temperature ranges, obtained a single type of Arrhenius relationship. However they used a log-log plot of elongational viscosities as a function of strain rates instead of a function of time as was being done here.

Also, work by Han and Lamonte, Shroff et al. and Mendelson observed approximately identical activation energies between elongational and shear flow. However, no attempt was being made here, to find the activation energy of polyvinyl chloride under shear flow. However, comparing with those obtained by Collins and Kriers, i.e. in the region of 20 kcal/mole, it is generally of the same order.

The observed dual type of relationship might be attributed to some form of transition occurring in polyvinyl chloride during elongational flow (similar to shear flow). The transition temperature is dependent on the strain rates and the nature of the polyvinyl chloride. Taking 30pphr DOP at 0.06s⁻¹ as an example, this phenomenon occurred at approximately 170°C, whereas at 0.004s⁻¹ this was not observed. The reason might be attributed to the transition occurring at a slower pace and smoothly with no drastic changes, or perhaps because of experimental errors.

The above phenomena can also be explained in terms of the dominance of each component of a tensile deformation. Again taking 30pphr DOP as an example, the following can presumably be realised.
i) At low temperatures the total tensile deformation was dominated by the chain bending and stretching (\(D_{OE}\)) and also the chain uncoiling, with no slippage (\(D_{HE}\)) components but with less viscous component (\(D_{visc}\)) to compensate. Hence this can be represented by, 
\[
D_{TOTAL} = D_{OE} + D_{HE}
\]
This was characterised by high viscosity, low true strain and premature failure.

ii) At high temperature, the situation was reversed, i.e. \(D_{visc}\) was the dominating component, hence giving low viscosity, high true strain and delayed failure.

iii) However the dominance of each component is very much dependent on the conditions and also the nature of the polyvinyl chloride. For example, for 30pphr DOP, the optimum condition was achieved at about 175°C to 180°C.

and iv) The dual phenomena would be observed only when the changes between the two extreme states taking place abruptly as at 0.06s\(^{-1}\) but not at 0.004s\(^{-1}\).

5.4.2 Mastercurves Using Method B

The most evident advantage of this method in investigating the elongational behaviour at elevated temperatures of polyvinyl chloride is that similar shift factors, \(a_T\) derived from equation [5.1] have been used throughout and they are only dependent on the reference temperature, i.e.190°C. However, it can be seen that 190°C chosen was quite satisfactory except for 30pphr DOP where the scatter about the reference plot was fairly large.
This can easily be overcome or improved by selecting the other temperatures as the reference temperature. For example, for 30pphr DOP either 170°C or 180°C could be used instead of 190°C, i.e. 170°C for the lower temperature range and 180°C for the upper temperature range (associated with the dual relationship).

Figures 5.19 and 5.20 are the new mastercurves derived for 30pphr DOP using 180°C as the reference temperature. It can be seen that the situation is very much improved (cf. to Figs 5.6 and 5.7).

Since identical shift factors have been used throughout, irrespective of the conditions and nature of the polyvinyl chloride, hence, the mastercurves derived showed the different effects affecting the elongational behaviour at elevated temperatures. These applications can be summarised as follows,

5.15 to

i) Figure 5.20, shows the mastercurves for 30pphr and 50pphr and at 0.06s\(^{-1}\) and 0.004s\(^{-1}\). It can be seen that the shifted elongational viscosity increasing linearly at the beginning, but then surging upward, i.e. the stress build up occurs especially for the 0.06s\(^{-1}\). Also, as in the previous situation (Chapter 4), i.e. the effect of strain rates under isothermal conditions, both mastercurves merging prior to the stress build up.

ii) Taking mastercurves at 0.06s\(^{-1}\) and 0.004s\(^{-1}\) as examples, the effect of plasticiser composition can be realised, given in Figures 5.22 and 5.23 respectively. Generally, the elongational viscosity decreasing with increasing plasticiser. Further discussion will be made in the next chapter.

In fact, Onogi and co-workers\textsuperscript{150,222,223} have used this method extensively in investigating the effects of branching and molecular weight
distribution on the elongational properties of polystyrene at elevated
temperatures.

5.4.3 Comparison Between Experimental and Theoretical Data

The validity of the theoretical prediction using the Chang and
Lodge rubber-like equation [4.4] and the use of shift factors, $a_T$, derived
by W.L.F. equation$^{219}$ has been demonstrated experimentally (refer to
sections 3.5.1 (b) and 3.5.2 (b)).

Both the experimental and theoretical data compared favourably
for the linear parts of the master elongational viscosity/time curves (refer
to Figures 5.6, 5.7, 5.15 and 5.16). The prediction gave a relatively good
interpretation of the experimental data.

However, the theoretical plots failed, either being too low or
approaching a constant, to explain the non-linear parts of the
mastercurves, which were associated with the stress build up or stress
overshoot phenomena.

Fig. 5.24, is a typical trace of the mastercurve of elongational
viscosity against time at elevated temperatures. The part from O-A is one
of relatively rapid change in the elongational viscosity. This is followed by
a longer period of slow change from A-B. Up to point B, the curve is
independent of strain rates, i.e. a common curve to all strain rates which
has a linear viscoelastic behaviour. The rapid rise of elongational viscosity
which is a non-linear effect commences at B, a point approximately
independent of temperature. However accurate assessment of point B is
difficult.
5.5 Mechanism of Sample Failure

There has been extensive discussion by Ide and White\textsuperscript{12,133,134} and Chang and Lodge\textsuperscript{132} on the mechanism of failure in molten polymer filaments when subjected to elongational flow. A brief discussion has been made in Chapter 2. Generally, polymer melts respond in different ways, some stretching out indefinitely and others failing by a cohesive fracture mechanism. Other materials develop necking and eventually fail by propagation of the necks (ductile failure). Also, the response of a particular polymer melt may vary depending upon the strain rates, as has been discussed in the previous chapter (refer to section 4.3). Discussions also have been made on the possible relationships between mechanisms of failure and components of tensile deformation.

From the results gathered so far on the effect of temperatures on the elongational properties, it is possible to suggest that apart from the strain rates, the mechanism of failure is perhaps dependent on the temperature. For example, at low temperature, sample failure might be attributed to fracture and ductile failure, usually characterised by the high elongational viscosity and the low true strain.\textsuperscript{132,134} At high temperature, though ease of stretching is greatly enhanced, the low viscosity often leads to sample failure through necking and perhaps, to some small extent, due to capillarity. Thus, in order to achieve some degree of stability and spinnability, which are important in different processing operations such as melt spinning and film extrusions, the operating conditions such as temperature and strain rates inevitably play a major role.
5.6 Conclusions

From the above, a few conclusions on the temperature dependence of elongational properties can be made. They can be summarised as follows:

i) A dual Arrhenius type of relationship between shift factors (elongational viscosity) and the reciprocal of absolute temperatures were obtained; except for the 30pphr DOP at 0.004s$^{-1}$.

ii) The validity of the two methods of deriving mastercurves has been shown. Both have their own respective uses and limitations to assist the understanding of elongational behaviour of polyvinyl chloride at elevated temperatures.

iii) The Chang and Lodge rubber-like equation has been used to compare the experimental and theoretical data at various temperatures. Generally the comparison was fairly acceptable especially at the linear viscoelastic parts but showed significant discrepancies in the non-linear parts.
Polyvinyl chloride (30pphr) at $0.06 \text{s}^{-1}$

![Graph showing log apparent elongational viscosity vs. log time](image)

Fig. 5.1
Polyvinyl chloride (30pphr) at 0.004s$^{-1}$

![Graph showing the log apparent elongational viscosity, $\mu_a(t)/\text{Pa.s}$, versus log time, $t/\text{sec}$, for various temperatures: 160°C, 170°C, 175°C, 180°C, and 190°C. The graph includes a 45° Superimposition line.](image-url)
Mastercurve of polyvinyl chloride at $0.06s^{-1}$ using method A

---

**Fig. 5.3**

- Symbols:
  - $\Delta$ 160°C
  - O 170°C
  - X 175°C
  - ⊗ 180°C

- Log apparent elongational viscosity
- Log time, t/s

- $T_r = 190°C$
- 45° Superimposition line
Mastercurve of polyvinyl chloride at 0.004s\(^{-1}\)
using method A

Fig. 5.4
Plot of shift factor against $\frac{1}{T}$

for polyvinyl chloride (30pphr) DOP

Fig. 5.5
Mastercurve of polyvinyl chloride (30pphr) at 0.06s\(^{-1}\) using method B

Fig. 5.6
Mastercurve of polyvinyl chloride (30pphr) at 0.004s⁻¹ using method B
Polyvinyl chloride (50pphr) at 0.06 s\(^{-1}\)

![Graph showing log apparent elongational viscosity vs. log time at different temperatures.](image-url)

**Fig. 5.8**
Polyvinyl chloride (50pphr) at 0.004^{-1}

![Graph showing log apparent elongational viscosity vs. log time at 160°C, 170°C, 175°C, 180°C, 190°C with a 45° Superimposition line.](image)

**Fig. 5.9**
Polyvinyl chloride (50pphr) at 0.06 s$^{-1}$

![Graph showing the relationship between log apparent elongational stress, $\sigma_a(t)/\text{Pa.}$, and log true strain $\lambda$.](image)

**Fig. 5.10**
Polyvinyl chloride (50pphr) at 0.004s$^{-1}$
Mastercurve derived using method A of polyvinyl chloride (50pphr) at $0.065 \text{s}^{-1}$.

![Graph showing log apparent elongational viscosity vs. log time for different temperatures.](image-url)

**Fig. 5.12**
Mastercurve derived using method A for polyvinyl chloride (50pphr) at 0.004s$^{-1}$.
Arrhenius plots of polyvinyl chloride (50pphr) DOP

Fig. 5.14
Mastercurve derived using method B for polyvinyl chloride (50pphr) at 0.06s⁻¹

Fig. 5.15
Mastercurves derived using method B for polyvinyl chloride (50pphr) at 0.004s⁻¹

Symbols:

- Δ 160°C
- O 170°C
- + 175°C
- Θ 180°C

Log apparent elongational viscosity, μ₉(t)/Pa.s.

Fig. 5.16
Mastercurve derived using method B for polyvinyl chloride (50pphr) at 0.08s\(^{-1}\)

![Graph showing log apparent elongational stress, \(\sigma_a(t)/Pa\), against log strain rate, \(\dot{\varepsilon}\), with symbols indicating different temperatures: 160°C, 170°C, 175°C, and 180°C. The temperature transition point is labeled \(T_r = 190°C\).]

**Fig. 5.17**
Mastercurve derived using method B for polyvinyl chloride (50pphr) at 0.004s$^{-1}$

Fig. 5.18
Mastercurve derived using method B
for polyvinyl chloride (30pphr) at 0.06s\(^{-1}\)

Fig. 5.19
Mastercurve derived using method B for polyvinyl chloride (30pphr) at 0.004s\(^{-1}\)

Fig. 5.20
Master curves for polyvinyl chloride
showing the effect of strain rates

Fig. 5.21
Mastercurves of polyvinyl chloride at 0.06s$^{-1}$

Fig. 5.22
Mastercurves of polyvinyl chloride at 0.004s$^{-1}$

Fig. 5.23
Typical mastercurve of polyvinyl chloride

Fig. 5.24

log apparent elongational viscosity, $\mu_a(t)/\text{Pa.s}$

$\log \mu_a(t)$

$10^7$

$10^6$

$10^5$

$10^4$

$10^3$

$10^2$

$10^1$

$10^0$

$\log \dot{a}_T/\text{sec}$

Experimental

Theoretical
CHAPTER 6

DEPENDENCE OF ELONGATIONAL PROPERTIES ON COMPOSITION AND NATURE OF PLASTICISER

6.1 Composition of Plasticiser

6.1.1 Introduction

In the previous chapter, the elongational properties of plasticised polyvinyl chloride (PVC) at varying strain rates and at elevated temperatures were investigated. It has been shown that plasticised polyvinyl chloride gives much improved elongational properties when compared to the rigid polyvinyl chloride, i.e. a larger true strain, lower viscosity etc. (section 4.2.3); also it has been shown that the shifts in elongational viscosity (45°) at elevated temperature are related to the absolute temperatures using method A (section 5.4.1) and using method B, the shifts in elongational viscosity along the horizontal axis about the reference temperature, chosen arbitrarily, are governed by some form of William Landel Ferry (W.L.F) equation (section 5.4.2). Here, the effects of composition and plasticiser on the elongational properties were investigated.

Alfrey and Wiederburn,225 working on the effect of composition of plasticiser on the rheological properties of plasticised polyvinyl chloride, have concluded that increasing plasticiser resulted in a vertical, as well as a horizontal, displacement of the curves, i.e. in a similar pattern to the effect of temperature. These findings were later confirmed by Shreiber,83,84 where he used shift factors to reduce the widely different...
melt viscosity/shear rate or time in shear flow of plasticised polyvinyl chloride compounds to well-defined mastercurves. Also, he found that the shift factors were dependent on melt temperature and plasticiser volume fraction.

Based on this information, a similar attempt was made to reduce the elongational viscosities/time data of varying plasticiser compositions at specified temperatures and strain rates into well defined mastercurves. Both methods (refer to Chapter 5, sections 5.3.1 (a) and (b)) were used. For the method A, a relationship between elongational viscosity shifts (45°) and composition and also the glass transition temperatures were investigated.

6.1.2 Material Used and Experimental Methods

The materials used and the experimental methods have already been described in sections 3.6 and 3.8.6 respectively.

6.1.3 Mastercurves Using Method A

Figures 6.1, 6.2, 6.3 and 6.4, show the log-log plots of apparent elongational viscosity/time of varying plasticiser composition at different conditions, i.e. 160°C (0.004s⁻¹), 180°C (0.004s⁻¹ and 0.06s⁻¹) and 190°C (0.06s⁻¹) respectively. However, for 160°C and 190°C, measurements were made using one specific value of strain rate, i.e., at 0.004s⁻¹ and 0.06s⁻¹ respectively. These conditions were used because as shown previously (section 4.2.4), some degree of stability was achieved at low and high strain rates for 160°C and 190°C respectively.

Generally, the elongational viscosity decreases with increasing amount of plasticisers. This is expected since plasticiser has been known
to impart some form of solvation action to the polymer chain; in simple terms, the action of the plasticiser can be described by the relation [5.2],

\[
\text{crystal (PVC) + plasticiser} \rightleftharpoons \text{solvated amorphous polymer}
\]

Thus, an increase in the plasticiser content must result in a decrease in the quantity of crystalline material, corresponding to a reduction in elongational viscosity. Further discussion of this point will be made later.

Although the plots are approximately similar, there are some noteworthy points observed. They can be briefly summarised as follows:

a) The variation of elongational viscosities is dependent on the temperatures and the strain rates. For example, comparing plots at different temperatures (160°C, 180°C and 190°C) and at 180°C but with different strain rates (0.004s⁻¹ and 0.06s⁻¹)
b) Larger shifts in viscosity are observed at 160°C than, say at 190°C.

The mastercurves at various conditions are shown in Figures 6.5, 6.6, 6.7 and 6.8. The superimposition can be considered satisfactory. The large scatter especially at 160°C and at 180°C (0.06s⁻¹) might be attributed, apart from experimental errors, due to each plasticiser composition being made up of a different proportion of components of tensile deformation. For example, for 160°C, at 0pphr DOP, the total deformation is presumably made up of a purely highly elastic component \( (D_{HE}) \) and also a bending and stretching \( (D_{OE}) \) component, with no visible viscous component \( (D_{visc}) \), but this pattern differs with increases in the plasticiser content.

Also, this can be explained in terms of the molecular structure of plasticised polyvinyl chloride, i.e. with the proportion of the crystalline
portion decreasing with increasing plasticiser. However, for 180°C, especially at 0.06s⁻¹, a similar pattern might exist for plasticiser content less than 30pphr. Increasing the plasticiser further, the differences become less pronounced.

At 190°C, the pattern is similar to that at 180°C, but to a greater extent, hence deviation is not clearly observed, i.e., presumably the viscous component of deformation (D_visc) prevails excessively.

6.1.4 Relationships Between Shift Factors (Elongational Viscosity) and Plasticiser Composition

From the respective shift factors in elongational viscosities along the 45° angle evaluated, (log-linear) plots were drawn against the plasticiser composition as shown in Figures 6.9, 6.10, 6.11 and 6.12.

As with the temperature dependence of plasticised polyvinyl chloride, given in Chapter 5, dual linear relationship between the shift factors in elongational viscosity and plasticiser composition were obtained. From the plots the following observations can be made,

a) Under all conditions, except at 180°C/0.06s⁻¹ dual linear relationships were found. This might give some indication of some form of phase transition or changes in the dominance of each component of tensile deformation with changes in plasticiser composition in any particular conditions.

b) Using the plot at 60pphr DOP as reference, smaller reductions in shifts occurring from 30pphr onwards, especially between 50 - 60pphr, showing that increasing the plasticiser beyond, say, 50pphr gave less drastic changes in elongational viscosity or presumably, under any
particular conditions there was a limit in which the amount of plasticiser could be added to bring about any significant drop in elongational viscosity. This fact coupled with the premature failure especially at 190°C for 50pphr and beyond might prove this point, i.e. the presence of some optimum limit in plasticiser composition (dependent on temperature and strain rates).

6.1.5 **Relationship Between Shift Factors (Elongational Viscosity) and Glass Transition Temperature**

The relationships between the shift factors (elongational viscosity) and the glass transition temperature for the plasticised polyvinyl chloride, at various conditions are shown in Figures 6.13, 6.14, 6.15 and 6.16.

As with the plasticiser composition (section 6.1.4) dual linear relationships were obtained, with a transition of some specific glass transition temperature, again, dependent on the conditions. For example, at 160°C and 0.004s⁻¹, the transition occurred at the glass transition temperature, \( T_g \approx 64°C \), whereas at 190°C and 0.06s⁻¹, it occurred at \( T_g \approx 58°C \). Similarly at 180°C, for both 0.06s⁻¹ and 0.004s⁻¹, the transitions taking place at \( T_g \approx 61°C \) and \( T_g \approx 64°C \) respectively.

The effect of plasticiser on the glass transition temperatures, and the empirical relations have been proposed by several workers. For instance, Boyer and Spencer\(^87\) suggested.

\[
\frac{T_{g2} - T_g}{T_{g2} - T_g} = kw
\]

... 6.1)

where \( T_g \) and \( T_{g2} \) are the glass transition temperatures of plasticised and rigid polyvinyl chloride respectively, and \( w \), is the solvent weight fraction, \( k \) is a constant.
Other empirical equations have been given in Chapter 1 (section 1.8.2).

Since increasing the plasticiser composition generally lowers the glass transition temperatures, hence the relationships of shift factors (elongational viscosity) with plasticiser composition and the glass transition temperature show an opposing trend. Perhaps, the transition in shift factors occurs at one particular plasticiser composition, corresponding approximately with its glass transition temperatures.

Another important point is the slopes of the plot. A typical example is at 180°C, where at 0.06s⁻¹, the slopes are tan⁻¹1.7 and tan⁻¹0.7, while at 0.004s⁻¹, they are tan⁻¹1.3 and tan⁻¹0.3, i.e. the rates in the shifts decreasing with decreasing strain rates.

6.1.6 Mastercurves Using Method B

From the original W.L.F equation, given in the earlier section (5.3.1 (b)), a modified version of the W.L.F equation is postulated, given by

$$\log a_T = -8.81(T_g - T_{g_2}) / (101.6 + (T - T_g)) \quad \ldots 6.2$$

where $T_g$ and $T_{g_2}$ are the glass transition temperatures of rigid and plasticised polyvinyl chloride respectively.

Schreiber used a different form of W.L.F equation, to obtain the shift factors in his investigation into the effect of plasticiser composition and interaction parameter on the rheological properties of plasticised polyvinyl chloride.

Using equation (6.2) and the values of the glass transition
temperatures, $T_g$, the shift factors of plasticised polyvinyl chloride were evaluated and are given in Table XIII.

Table XIII  Values of shift factors evaluated equation [6.3]

<table>
<thead>
<tr>
<th>w/pphr</th>
<th>$T_g + 0.5 \degree C$ (reference)</th>
<th>log $a_T$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1.</td>
<td>10</td>
<td>71.5</td>
</tr>
<tr>
<td>2.</td>
<td>20</td>
<td>67.5</td>
</tr>
<tr>
<td>3.</td>
<td>30</td>
<td>63.5</td>
</tr>
<tr>
<td>4.</td>
<td>40</td>
<td>60.5</td>
</tr>
<tr>
<td>5.</td>
<td>50</td>
<td>56.0</td>
</tr>
<tr>
<td>6.</td>
<td>60</td>
<td>52.5</td>
</tr>
</tbody>
</table>

Mastercurves were obtained by shifting the plots of plasticised polyvinyl chloride to the rigid polyvinyl chloride (the referent plot), shown in Figures 6.17, 6.18, 6.19 and 6.20. Plots are of log of the shift factor, $a_T$ against log of the reduced time ($t/a_T$).

Fairly good superimpositions are obtained especially at $190 \degree C/0.06s^{-1}$. At $180 \degree C$, for both $0.06s^{-1}$ and $0.004s^{-1}$, satisfactory superimpositions are obtained initially for all plots but deviation occurs at larger reduced times (referring to plasticiser composition greater than 30pphr). However, at $160 \degree C$, superimposition failed considerably.

The deviations or the large scatter in the mastercurves especially at $160 \degree C$ might be attributed to the existence of distinct structural
differences between rigid polyvinyl chloride and plasticised polyvinyl chloride or in terms of the tensile component of deformation, there is a wide difference in dominance, say, between the rigid polyvinyl chloride and the 10pphr, or between the 10pphr and the 50pphr and so on (similar to section 6.1.3).

However, at 190°C the pattern changes drastically, as can be seen where all plots are superimposed onto the reference plot. This might be attributed to the existence of approximately similar structures or similar components of tensile deformation at the various compositions.

6.2 Discussions

6.2.1 Components of Tensile Deformation

As has been discussed in previous chapters, the possibility of the three types of components of tensile deformation in a typical tensile deformation; also the dominance of each component is dependent on conditions such as strain rates and temperatures. From the above results, it might be presumed that in any particular conditions, the dominance of tensile deformation is perhaps also governed by the plasticiser concentration.

For example at 160°C/0.004s⁻¹, the total tensile deformation is probably comprised of the bending and stretching (D_{OE}) and the chain uncoiling (D_{HE}) components. However, this dominance of each component varies with increasing plasticiser, hence each composition differs from the rest. This might explain the failure to obtain satisfactory mastercurves using both the methods, especially at 160°C.
However, at 190°C/0.06s⁻¹, the pattern is somewhat different, although the prevailing situation still exists, i.e. components of tensile deformation still dependent on the amount of plasticiser but to a lesser degree on the temperature, hence a well-defined mastercurve is obtained (Figure 6.14); while at 180°C, the effect of strain rate comes into play, i.e. with identical temperature and plasticiser composition but different strain rates.

6.2.2 Relationship Between Shift Factors and Plasticiser Composition and Glass Transition Temperatures

From the results given in above sections (Figures 6.9 to 6.12), shows that the log of the shift factors (elongational viscosities) evaluated are related linearly but with two distinct slopes to the plasticiser composition and their respective glass transition temperatures in the opposing manner, i.e. large \( T_g \) corresponds to small \( w \), and vice-versa.

This is expected since it has been shown by several workers that increasing the plasticiser content leads to an approximately proportional reduction in the glass transition temperature and in fact, many empirical equations have been reported.

The existence of dual linear relationship could be attributed to the occurrence of some form of phase transition and this seems to be dependent on conditions, i.e. changes with temperature and strain rate.

Also, from the plots (Figures 6.9 to 6.12), empirical equations can be obtained between the shift factors (elongational viscosity) and plasticiser composition \( (w) \) and the glass transition temperatures \( (T_g) \). They are as follows,
\[
\log a_T = c w + a \quad \ldots \ldots 6.3)
\]
and
\[
\log a_T = \beta T_g + b \quad \ldots \ldots 6.4)
\]

where \( c, \beta, a, b \) are constants depending on the temperatures and the strain rates, and also the nature of plasticiser.

It must be stressed here, though, the above empirical relationship is presumably an oversimplification, it does, however, provide a useful picture on the influence of plasticiser composition on the elongational viscosity of polyvinyl chloride. In order to give a qualitative relationship between them, other factors such as polymer-solvent interaction factor, solubility parameter etc.; temperature, strain rates must be taken into account since they are aptly interdependent.

6.2.3 Relationship Between Plasticiser Composition and Structure of Plasticised Polyvinyl Chloride

Pezzin,35 Schreiber33,84 and others3,45,76-77 have stated that plasticised polyvinyl chloride is still made up of large portions of microcrystalline structures (crystallites). In fact, at 50 per cent plasticiser, polyvinyl chloride was found to be incompletely amorphous.77

Also, it has been found that the crystalline portion or the concentration of crystallites in plasticised polyvinyl chloride was a decreasing function of temperature. It has been suggested that the effect of increasing the plasticiser composition was probably similar to the effect of increasing the temperature.226

According to Aiken et al.,220 when plasticiser was added to polyvinyl chloride, it served to solvate or shield points of contact (leading to the formation of crystals) along the chain and solvation of such points
will, therefore, rupture the crystallites. From equation [5.2], and by the law of mass action, an increase in the plasticiser content must result in a decrease in the quantity of the crystalline portions or segments (crystallites) in the polyvinyl chloride.

Using the above idea as an assumption, then one can perhaps approximately explain the effect of plasticiser composition on the elongational behaviour of polyvinyl chloride. Take for example at $160^\circ$C/0.004s$^{-1}$, where a well-defined mastercurve (Fig. 6.13) was not observed. This might be attributed to a large variation in the distribution between the crystalline and the amorphous portions in any two plasticiser compositions, say, between the 0 and the 10pphr or between the 10 and the 20pphr and so on. While at higher temperature, the differences were less pronounced, hence, smoother curves were obtainable.

Similarly, the dependence of shift factors (elongational viscosity) with either the plasticiser composition or the glass transition temperature can be explained using the above analogy. The dual relationships might be attributed to a transition from, say, a dominance in crystalline state to an amorphous state. Hence, it can also be presumed that this phenomena was dependent on the conditions and also the nature of the plasticiser.

6.3 Types of Plasticiser

6.3.1 Introduction

In this section, an attempt is made to explain the effect of different types of plasticiser on the elongational behaviour of polyvinyl chloride. For this purpose, several types of plasticiser were used, given in section 3.6 in Chapter 3. Two plasticiser compositions, i.e. 30pphr and
50pphr were used and similar sample preparations were employed. Samples were tested at 180°C and at two levels of constant strain rates (0.06s\(^{-1}\) and 0.004s\(^{-1}\)) (section 3.8.6).

The above conditions were preferably chosen based upon the previous work. For example, the temperature tested was 180°C, instead of either 160°C or 190°C. This was because at 160°C, the sample would fail prematurely and anomalies (already mentioned) would arise, whereas at 190°C, the effect of strain rates would be less pronounced, and also at very low strain rate, say, 0.004s\(^{-1}\), samples especially at 50pphr might experience thermal degradation due to longer deformation time. Hence, 180°C was the temperature chosen since presumably it would give an ideal situation for the purpose of investigating the effect of types of plasticiser on the elongational behaviour of polyvinyl chloride.

6.3.1 (a) **Dependence of Elongational Properties on Types of Plasticisers**

The log-log plots of elongational viscosity, as a function of the deformation times for 30pphr and 50pphr plasticiser at 180°C (0.06s\(^{-1}\) and 0.004s\(^{-1}\)) are shown in Figures 6.21, 6.22, 6.23 and 6.24 respectively.

6.3.2 **Mastercurves Obtained Using Method A**

From the plots, using method A (refer to section 5.3.1), various master plots were obtained, given in Figures 6.25, 6.26, 6.27 and 6.28. It can be seen that the superimpositions are satisfactory. The reference plots used were that of tritolyl phosphate (TTP) in all the mastercurves. This
was attributed to tritolyl phosphate (TTP) being the lowest plots (refer to Figures 6.21 to 6.24).

6.3.3 Relationship Between Shift Factors (Elongational Viscosities and the Molecular Weights)

The shift factors (elongational viscosities) evaluated for 30pphr and 50pphr plasticiser content at various conditions are shown in Table XIV.

Table XIV. Shift factors for various plasticisers (30pphr and 50pphr) at 180°C (0.06s⁻¹ and 0.004s⁻¹)

<table>
<thead>
<tr>
<th>Types of Plasticiser</th>
<th>30pphr</th>
<th>50pphr</th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>0.06s⁻¹</td>
<td>0.004s⁻¹</td>
<td>0.06s⁻¹</td>
<td>0.004s⁻¹</td>
</tr>
<tr>
<td>1. Di-iso-decyl phthalate</td>
<td>5.89 x 10⁰</td>
<td>5.26 x 10⁰</td>
<td>3.16 x 10⁰</td>
<td>2.76 x 10⁰</td>
</tr>
<tr>
<td>(DIDP)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>2. Di-nonyl phthalate</td>
<td>3.58 x 10⁰</td>
<td>4.21 x 10⁰</td>
<td>2.52 x 10⁰</td>
<td>2.21 x 10⁰</td>
</tr>
<tr>
<td>(DNP)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>3. Di-iso-octyl phthalate</td>
<td>2.63 x 10⁰</td>
<td>2.1 x 10⁰</td>
<td>2.22 x 10⁰</td>
<td>1.68 x 10⁰</td>
</tr>
<tr>
<td>(DOIP)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>4. Di-2-ethylhexyl phthalate</td>
<td>1.89 x 10⁰</td>
<td>2.63 x 10⁰</td>
<td>2.1 x 10⁰</td>
<td>7.3 x 10⁻¹</td>
</tr>
<tr>
<td>(DOP)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>5. Di-2-ethylhexyl adipate</td>
<td>1.05 x 10⁰</td>
<td>1.15 x 10⁻¹</td>
<td>5.0 x 10⁻¹</td>
<td>8.4 x 10⁰</td>
</tr>
<tr>
<td>(DOA)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>6. Di-n-butyl phthalate</td>
<td>2.95 x 10⁰</td>
<td>4.42 x 10⁰</td>
<td>2.84 x 10⁰</td>
<td>1.89 x 10⁻¹</td>
</tr>
<tr>
<td>(DBP)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

The relationship between the shift factors and the respective molecular weights of the various types of plasticiser are shown in Figures 6.29, 6.30, 6.31 and 6.32.

Although Di-iso-octyl phthalate (DIOP) and Di-2-ethylhexyl phthalate (DOP) have similar molecular weights, they differ in the
molecular configuration. The latter might have been attributed to the difference in the shift factors observed.

One important aspect that can obviously be seen from the plots is that the relationship between the shift factors and the molecular weights of the plasticisers is very much dependent on the plasticiser content and also the strain rates.

6.3.4 Effectivity or Efficiency Quantity of Plasticiser

The efficiency quantity can be defined as the quantity which gives specific modulus value at a certain elongation, e.g. a modulus of 1000psi at 100% elongation. Penn has suggested that the concept of effectivity or efficiency quantity could be extended to almost any property. It could be based on the quantity of plasticiser to give, say, a specific softness, elongation, brittle point and so on. Although, some marked differences in the efficiency between plasticisers might be obtained, it is still worth while.

From the efficiency quantity evaluated, the efficiency factor can be determined, i.e. the efficiency quantity of the plasticiser concerned divided by the efficiency quantity of a common plasticiser.

Here, the property used to evaluate the efficiency quantity and then the efficiency factor is the shift factor (elongational viscosity) obtained earlier. The reference plasticiser used is Di-2-ethylhexyl phthalate (DOP). Table XV shows the efficiency quantities and efficiency factors of the various plasticisers evaluated at various strain rates.
Table XV  Efficiency proportions and efficiency factors for various plasticisers

<table>
<thead>
<tr>
<th>Types of Plasticiser</th>
<th>Efficiency Proportion (pphr to give similar shifts as DOP) (%)</th>
<th>Efficiency Factor (DOP = 30%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>0.06s&lt;sup&gt;-1&lt;/sup&gt;</td>
<td>0.004s&lt;sup&gt;-1&lt;/sup&gt;</td>
</tr>
<tr>
<td>1. Di-iso-decyl phthalate (DIDP)</td>
<td>93.5</td>
<td>60.0</td>
</tr>
<tr>
<td>2. Di-nonyl phthalate (DNP)</td>
<td>56.8</td>
<td>48.1</td>
</tr>
<tr>
<td>3. Di-iso-octyl phthalate (DIOP)</td>
<td>41.7</td>
<td>23.9</td>
</tr>
<tr>
<td>4. Di-2-ethylhexyl adipate (DOA)</td>
<td>16.7</td>
<td>13.2</td>
</tr>
<tr>
<td>5. Di-n-butyl phthalate</td>
<td>46.8</td>
<td>50.4</td>
</tr>
</tbody>
</table>

However, it must be stressed that the above values are not absolute, although they do provide some order of difference between the plasticising efficiency of plasticisers. For example, at 0.06s<sup>-1</sup> and 0.004s<sup>-1</sup> the most efficient is DOA but differs on the efficiency factors, i.e. 0.56 and 0.44 respectively and the least efficient is DIDP. Hence, it means that far more DIDP is needed to give the same shift factor.

Based on the efficiency proportions obtained (0.06s<sup>-1</sup>), samples were then prepared. However, as small amounts were required, a Kenwood high speed mixer was used for the blending. Samples were then tested at 180°C, and at 0.06s<sup>-1</sup> and 0.004s<sup>-1</sup>.

Figures 6.33 and 6.34 show the plots of log elongational viscosity ($\mu_a(t)$) versus time at 0.06s<sup>-1</sup> and 0.004s<sup>-1</sup>. It can be seen that a fair reproducibility is obtained at 0.06s<sup>-1</sup> but failed at 0.004s<sup>-1</sup>. This might be attributed to the efficiency proportions being used, i.e. 0.06s<sup>-1</sup>. However
the slight discrepancies at 0.06s\(^{-1}\) might be attributed to the use of the Kenwood mixer.

The shift factors (along 45°) using the tritolyl phosphate as reference were replotted in Figures 6.25 and 6.26.

### 6.4 Discussions

#### 6.4.1 Effect of Different Plasticisers on Structure of Polyvinyl Chloride

There has been previous discussion concerning the possibility of a typical plasticised polyvinyl chloride to exist in two separate dispersed regions, namely, the crystalline regions (only polyvinyl chloride segments) and regions containing amorphous polyvinyl chloride and plasticiser.

As a crude analogy, this system may be assumed to be identical to the one consisting of a saturated solution in the presence of undissolved solute. On the basis of this molecular interpretation of the structure of plasticised vinylite films, it is now possible to consider the effect of different plasticisers on this structure. This may be done by drawing analogies with systems containing small molecules. However, admittedly this is poor if quantitative results are desired, but for a qualitative discussion it is reasonable.

If solutions of the same volume having the same concentration of a low molecular weight solute are evaporated to a volume such that crystals of the solute are deposited from each, then it is possible to make the following statements:

1. In general, the crystals obtained from the poorer solvent will be smaller than those obtained from the better solvents.
2. The total quantity of crystals obtained from the poorer solvent will generally be greater than that obtained from the better solvent.

Then, by analogy, it is possible to suggest that the mode of various plasticisers lies in the solvent power for polyvinyl chloride. For example, when a poor solvent is used as a plasticiser, there will be a larger total quantity of crystalline material than when a better solvent is used. It has also been reported that the dimensions of the crystallites will also be affected.35,77

6.4.2 Solubility Parameter of Different Plasticisers

The knowledge of the solubility parameter of a plasticiser and a polymer is known to be important in predicting the compatibility of the plasticiser. Various methods have been suggested to evaluate the solubility parameter of polymer and plasticiser. Gee227 and Mangaraj et al's methods,228 are the easiest which are based on the swelling of the lightly cross-linked polymer in different solvents. Polyvinyl chloride has been found to have a solubility parameter of about 9.7 (depending on grade).

For plasticisers, Small's estimation229 of the solubility parameter is widely accepted, where he suggested that,

\[
(solubility \text{ parameter}) = \frac{\sum F}{V} \quad \ldots [6.4]
\]

where \(F\) is the molar attraction constants and \(V\) is the molar volume.

Figure 6.35, shows the plots of plasticiser absorbed (using 50pphr DOP) and solubility for some common plasticisers obtained by Hecker and
They used the Small's method to cover a wider range of plasticisers.

![Graph showing plasticiser absorption by plasticised polyvinyl chloride at room temperature](image)

**Fig. 6.35** Plasticiser absorption by plasticised polyvinyl chloride at room temperature

(Data from Hecker and Perry)

However, it must be stressed that in their method, the compatibility was associated with polyvinyl chloride pregelled with DOP and was at room temperature compatibility whereas, here, it involved processing at 180°C. Also, the solubility parameter is known to decrease with increasing temperature.
6.4.3 Dependence of Elongational Viscosity on Different Plasticisers

Using the approximate analogy, between the structure of plasticised polyvinyl chloride and the solubility parameters (sections 6.4.1 and 6.4.2), it might be possible to then explain the elongational behaviour of the different plasticisers used.

From the shift factors (45°) in elongational viscosity obtained, it can be seen that the order of shifts is very much dependent on the conditions. They can be briefly summarised as follows.

i) For 30pphr plasticisers at 0.06s\(^{-1}\) and 0.004s\(^{-1}\), the orders are DIDP > DNP > DBP > DIOP > DOP > DOA > TTP and DIDP > DNP > DBP > DOP > DIOP > DOA > TTP respectively.

ii) For 50pphr plasticisers at 0.06s\(^{-1}\) and 0.004s\(^{-1}\), the orders are DIDP > DBP > DNP > DIOP > DOP > DOA > TTP and DIDP > DNP > DBP > DIOP > DOA > DOP > TTP.

Using the solubility parameter obtained by Hecker and Perry (only DOA, DBP, DOP, DIOP, and DIDP are available) the order of magnitude is DBP > DOP > DIOP > DIDP > DOA (compare with polyvinyl chloride, about 9.7). Hence DBP is the highest compatibility and DOA the least. The trend of their respective molecular weights is DIDP > DNP > DIOP > DOP > DOA > DBP.

Hence, it can be suggested that not only limited relationship between the above trends, i.e. between the elongational viscosity and solubility parameter and also the molecular weight, is observed.

This might be attributed to the tests being carried out under different conditions, thus other factors such as volatility, structural configuration, flash points and so on, would possibly affect the behaviour.
Take DBP for example. Although it has a good compatibility with polyvinyl chloride it is known to have a low flash point (about 170–180°C) and thus is very volatile (about 18.3%), which is undesirable at high temperature. This might explain the larger shift when compared to, say, DOA (200–230, 5–6% respectively).

6.4.4 Components of Tensile Deformation

Since it is approximately possible to relate the quantity of crystallites in plasticised polyvinyl chloride, to different plasticisers, thus, it would be quite reasonable to conjecture their relationship with the components of tensile deformation. Hence, plasticiser which gives rise to a small quantity of crystallites (smaller shift factors, e.g. TTP, DOA), then the total tensile components of deformation are predominantly made up of the viscous component ($D_{\text{visc}}$) and vice-versa.

This relationship is also dependent on the conditions (previously discussed in Chapters 4 and 5).

6.4.5 Efficiency Factors of Different Plasticisers

The knowledge of the efficiency factor, obtained using the shift factors (section 6.3.4), helps in distinguishing the different effects of various plasticisers and assists the compounding, when ease of processing is required. However, the efficiency obtained is based on the processing stages (in melt stage) and this might differ from those based on the finished stage (e.g. 100% elongation). The advantage of the latter is that it gives the ultimate property of the finished product, whereas the first gives the property at the transitional stages.
Conclusions

From the results obtained on the dependence of elongational behaviour of plasticised polyvinyl chloride on the plasticiser composition and types of plasticiser, the following conclusions can be drawn.

i) Increasing the content of the plasticiser decreases the elongational viscosity of the plasticised polyvinyl chloride.

ii) The shift factors (45°) using method A, give rise to dual-linear relationship with the plasticiser content and also the respective glass transition temperatures, $T_g$.

iii) Using method B, shows the relationship between reduction in elongational viscosity with increasing the plasticiser content and the glass transition temperature is governed by some form of W.L.F equation.

iv) The dependence of elongational viscosity on different plasticisers is limitedly related to the molecular weight of the plasticisers and also on the solubility parameter.

v) Using method A, to obtain shift factors (45°), the efficiency proportions, hence the efficiency factors of various plasticisers (based on DOP) are evaluated. However, they differ from those obtained using other properties, e.g. 100% elongation.
Polyvinyl chloride at various compositions (DOP) at 160°C and 0.0045 s$^{-1}$

Fig. 6.1
Polyvinyl chloride at various compositions (DOP) at 180°C and 0.06s⁻¹

Fig. 6.2
Polyvinyl chloride at various compositions at $180^\circ$C and $0.004\text{s}^{-1}$

Fig. 6.3
Polyvinyl chloride at various compositions
at 190°C and 0.06 s\(^{-1}\)

Fig. 6.4
Mastercurve derived using method A at 160°C and 0.0045 s⁻¹

Fig. 6.5
Mastercurve derived using method A at 180°C and 0.0045 s⁻¹

Fig. 6.6
Mastercurve derived using method A
at 180°C and 0.0045 s⁻¹

Fig. 6.7
Mastercurve derived using method A at 190°C and 0.065 s⁻¹

Fig. 6.8

Symbols:

- ○ 0
- □ 10
- △ 20
- ▽ 30
- ■ 40
- + 50
Relationship between shift factor and plasticiser composition at 160°C and 0.004s\(^{-1}\)

![Graph showing the relationship between shift factor and plasticiser composition at 160°C and 0.004s\(^{-1}\). The graph plots log shift factor (elongational viscosity) vs. plasticiser composition (w/pphr). The data points form a downward-curving line, indicating a logarithmic decrease in elongational viscosity with increasing plasticiser composition.]
Polyvinyl chloride at 180°C and 0.06s⁻¹

Fig. 6.10
Polyvinyl chloride at 180°C and 0.004 s⁻¹
Polyvinyl chloride at 190°C/0.06s⁻¹

Fig. 6.12
Relationship between the shift factor and $T_g$ at $180^\circ C$ and $0.004 s^{-1}$

Fig. 6.13
Polyvinyl chloride at 180°C and 0.06s⁻¹

Fig. 6.14
Polyvinyl chloride at 180°C and 0.004s⁻¹

Fig. 6.15
Polyvinyl chloride at 190°C/0.06s⁻¹

![Graph showing a linear relationship between the log shift factor (elongational viscosity), μₘₜ, and the glass transition temperature, Tₙ, in °C. The graph is labeled as Fig. 6.16.](image-url)
Relationship between the shift factor and the reduced time at 160°C and 0.004s⁻¹
Polyvinyl chloride at $180^\circ$C and $0.06\text{s}^{-1}$

Fig. 6.18
Polyvinyl chloride at 180°C and 0.004 s⁻¹

Fig. 6.19
Polyvinyl Chloride at 190°C and 0.06s⁻¹

Fig. 6.20

Symbols:

- 0
- 10
- 20
- 30
- 40
- 50
- 60

Graph showing log shift factor, $a_T$ vs. log time, $t/s_T$.
Polyvinyl chloride (30pphr) at 180°C and 0.06 s⁻¹

Fig. 6.21
Polyvinyl chloride at $0.004s^{-1}/180^\circ C$

![Graph showing log apparent elongational viscosity versus log time](image)

**Fig. 6.22**
Polyvinyl chloride (50pphr) at 180°C and 0.06s⁻¹

Fig. 6.23
Polyvinyl chloride (50pphr) at 180°C and 0.004 s⁻¹
Mastercurve for polyvinyl chloride (30pphr)
at 180°C and 0.06s⁻¹

Fig. 6.25
Mastercurve for polyvinyl chloride (30pphr) at 180°C and 0.004s⁻¹

Symbols:
- Δ DIDP
- + DNP
- ● DBP
- □ DIOP
- ○ DOP
- ▲ DOA
- ◇ TTP

Fig. 6.26
Mastercurve for polyvinyl chloride (50pphr) at 180°C and 0.06s⁻¹

Fig. 6.27
Mastercurve for polyvinyl chloride (50pphr) at 180°C and 0.004s⁻¹

Fig. 6.28

Symbols:

- DIDP
- DNP
- DBP
- DIOP
- DOP
- DOA
- TTP
Relationship between shift factor and molecular weight for polyvinyl chloride (30pphr) at 180°C and 0.065 s\(^{-1}\)

**Fig. 6.29**
Polyvinyl chloride at 180°C and 0.004 s⁻¹

Fig. 6.30
Polyvinyl chloride (50pphr) at 180°C and 0.06s⁻¹
Polyvinyl chloride (50pphr) at 180°C and 0.004s⁻¹

Fig. 6.32
Polyvinyl chloride at 180°C and 0.06s⁻¹

Fig. 6.33
Polyvinyl chloride at $180^\circ$C and 0.004s$^{-1}$
(using efficiency proportion from $180^\circ$C/0.06s$^{-1}$)

**Fig. 6.34**

- **Symbols:**
  - DIDP: △
  - DNP: ×
  - DBP: ●
  - DIOP: □
  - DOP: ○
  - DOA: ▲
  - TTP: ○

Log apparent elongational viscosity, $\mu_a(t)/$P.a.s.

Log time, t/sec
CHAPTER 7
CONCLUSIONS AND SUGGESTED AREAS
FOR FURTHER RESEARCH

7.1 Conclusions

The Rutherford Extensional Rheometer in its present state is an instrument capable of giving fairly accurate and reproducible measurements of elongational properties of polymer melts, whose viscosity is greater than $10^5$ CP. However, it is still restricted to temperatures below 200°C, thus an alternative heating medium has to be found in order to give a much improved versatility and range.

Polyvinyl chloride, both rigid and plasticised, is a tension thinning material, i.e. elongational viscosity decreasing with increasing strain rates and thus, analogous to shear thinning or pseudoplasticity. Plasticised polyvinyl chloride gave rise to better all round properties than the rigid counterpart. Thus, it could be presumed, the presence of plasticiser imparted some stability.

At elevated temperatures, it was found that increasing the temperature decreased the elongational viscosity. The shift factors were evaluated by two independent methods and mastercurves were obtained. The shift factors (elongational viscosity) obtained by the first method were found to exhibit dual linear relationships with the reciprocal of the absolute temperatures. The transition temperatures were dependent on conditions, such as strain rates and plasticiser compositions.

The shift factors derived by the second method were governed by a form of the W.L.F. equation.
Influences of plasticiser composition (di-2-ethylhexyl phthalate) and plasticiser types were investigated. The shift factors derived by the first method, similarly showed the dual linear relationships to the weight fractions and their respective glass transition temperatures. However, for plasticiser types, no such relationships to their molecular weights were obtained. This presumably gave an indication that other factors such as solvent-polymer interaction parameter, or nature of solvents might be involved.

For plasticiser composition, the shift factors derived by the second method were governed by a form of the W.L.F. equation. The superimpositions were satisfactory at 180°C and 190°C, but failed at 160°C. This might be attributed to significant differences in the nature of polyvinyl chloride, say, between 0pphr and 10pphr, 10pphr and 40pphr and so on.

The elongational behaviour of polyvinyl chloride observed, could presumably be explained in terms of dominance in various components of a typical tensile deformation. By analogy, this might be associated with the nature of polyvinyl chloride, i.e. the degree of crystallinity.

Then, the occurrence of the dual phenomena might be due to some form of phase transition, say, from a state of predominantly crystalline to predominantly amorphous or the total tensile deformation being made up of the bending and stretching of bonds (DOE) and chain uncoiling (with no slippage) (DHE) or chain slippage (Dvisc) components or vice-versa. The dominance of each component is dependent on conditions, i.e. strain rates, temperatures and plasticiser composition or types.

Comparison with shear flow data, showed that Troutonian relationship was attainable at very low strain rates. Some validity was
achieved in comparing the experimental results with the theoretical values, predicted using the Chang and Lodge rubber-like model equation. However, it was similarly restricted to low strain rates and at the initial stages, but failed considerably to explain the stress build up phenomena.

The mechanism of failures, i.e. cohesive, ductile (with necking) were visually observed, and this was presumed to be related to the nature of the polyvinyl chloride samples, i.e. dependent on conditions.

7.2 Suggested Areas for Further Research

Although the Rutherford Extensional Rheometer can now be regarded as a versatile piece of equipment, especially with the capability of measuring elongational properties in different modes, it is felt that there is still room for improvement. Hence, the suggestions can be broadly classified into two major areas, i.e. the instrument, and the experimental parts.

a) Instrument.

1. Finding an alternative heating medium, capable of much higher temperatures, having the necessary properties such as being chemically inert, high flash point, etc. This facility is necessary if the newer engineering plastics are to be investigated where high processing temperatures are often involved.

2. A uniform method of sample preparation has to be adopted, regardless of the polymer system. At present, a few methods have been utilised; for example, direct compression moulding (this work), 'cut sample' from compression moulded sheet and injection moulding (though beset by faults).
3. The problem of maintaining constant temperature (uniform) plus long stabilising time, about 50 minutes. Some suggestion on having a stirrer (circulating system, which was abandoned due to high cost) should now be looked at again.

4. Data output can be further improved, say by interfacing with a computer or data plotter. This would facilitate data handling which at present is laborious.

5. A more sensitive linear displacement transducer would facilitate the measurements of properties of polymer melts, whose viscosity is less than $10^5$ CP.

Another possible improvement is the reincorporation of a scissor mechanism.

b) Experimental Work.

1. The obvious areas that can be investigated are the effect of polymer types (grades and molecular weights distribution) of a wider range of conditions. Elaborate characterisation work plus effects of sample preparations, orientations coupled with birefrigence and microscopic techniques, with the hope of looking into the structures of polymers investigated are worth investigating.

2. To enhance any findings on the instrument, collaboration with other elongational instruments available elsewhere ought to be attempted. Comparison with shear measurement may be carried out under more rigorous and over a wider range of conditions.
3. Investigation into the possible use of more accurate model equations, especially as the Chang and Lodge system failed to explain the sudden stress build up phenomena. Also, a qualitative look at the possible failure mechanism and the possible relationship between elongational properties and components of tensile deformations.

4. Preliminary studies showed that polyvinyl chloride is a tension thinning material, i.e. viscosity decreasing with strain rate. Further work has to be conducted using a wider range of conditions.

5. The dual relationships between the shift factors on elongational viscosity with the reciprocal of absolute temperature and also the composition of polyvinyl chloride has to be looked into further, possibly using a wider range of conditions plus different grades and plasticisers. Hopefully this would quantify or validate the above observations.

6. The relationship between elongational properties of polyvinyl chloride and the mechanism of plasticisation and also the properties of various plasticisers are worth looking into in more detail.

7. Finally but not least, to look at its possible applications to explain phenomena or problems associated with real processing situations, where elongational flows are imminent. The aim should be to look at them quantitatively as well as qualitatively.
REFERENCES


46. C. Menges and P. Klenck, Konstoffe, 57 (1967), 598.


56. C.L. Sieglaff, SPE Trans. 4 (1964), 129.


111. G.V. Vinagradov, Polymer, 18 (1977), 1275.


166. J. Osamu, D. Ishizuka and K. Koyama, Polymer, **21** (1980), 164.


205. ASTM D3418.

206. CORVIC S57/116 Tech. Information Sheet, ICI Ltd., U.K.

207. Tech. Information Sheet, Albright and Sons Ltd., U.K.

208. Tech. Information Sheet, Ceiba-Geigy Ltd., U.K.


212. BS2782: Part 9: Method 901A.

213. ASTM D3810.

214. BS2782: Part 3: Method 320C.

215. BS2782: Part 0: Method 365D.


APPENDIX I

DETERMINATION OF THE GLASS TRANSITION TEMPERATURE
(ASTM D3418)

The experimental methods in determining the glass transition temperature, are as follows,

i) 10 to 20mg sample weight of the specimen is usually used. Perform and record a preliminary thermal cycle in nitrogen up to a temperature high enough to erase previous thermal history, heating at a rate of 20°C/min.

ii) Hold temperature for 10 min. and then quench cool to 50°C below the transition temperature of interest, and hold the temperatures for 10 min.

iii) Repeat heating at a rate of 20°C/min and record the heating curve until the desired transition has been completed.

iv) From the thermogram, corrected glass transition temperature, $T_g$ can be evaluated (refer to Fig.1).

![Fig. 1 The glass transition temperature of polyvinyl chloride](image.png)
APPENDIX II

END CORRECTIONS IN SHEAR FLOW MEASUREMENT

For this purpose, the method of Cogswell and Lamb, i.e. a special case of the Bagley's method, has been employed.

Here two dies are used, one of substantial $\frac{L}{R}$ ratio and the other a knife-edged die of zero length, and two assumptions have been made,

i) the pressure obtained $P_o$ with the $\frac{L}{R} = 0$ embraces both entrance and exit corrections.

ii) entrance length errors are ignored.

Then, the true wall shear stress is given by

$$\tau_w = \frac{(P - P_o)}{2L.R}$$

The preference in using this method instead of the original Bagley's method is that it has been advocated for use in elongational flow studies.\textsuperscript{118}
APPENDIX III

DETERMINATION OF CHANG AND LODGE’S CONSTANTS
and the predicted theoretical viscosity and the elongational stress (refer to section 4.2.3)

Below are the programmes written for the above purposes (using the Commodore 64 microcomputer).

A) Programme to Evaluate the Constants, a
of Chang and Lodge Equation [4.4]

```
10 PRINT "SIMULTANEOUS EQUATIONS"
20 PRINT
29 REM - LIMIT A() TO A(R+1) WHERE R=MAXIMUM NUMBER OF EQUATIONS
30 DIM A(15,10)
40 PRINT "NUMBER OF EQUATIONS";
50 INPUT R
60 PRINT "COEFFICIENT MATRIX:"
70 FOR J=1 TO R
80 PRINT 85 PRINT "EQUATION";J
90 FOR I=1 TO R+1
100 IF I=R+1 THEN 130
110 PRINT "COEFFICIENT";I;
120 GOTO 140
130 PRINT "CONSTANT";
140 INPUT A(J,I)
150 NEXT I
160 NEXT J
170 FOR J=1 TO R
178 REM - STATEMENTS 180 TO 220 FIND THE FIRST EQUATION WITH
179 REM - A NON-ZERO COEFFICIENT FOR THE CURRENT COLUMN
180 FOR I=J TO R
190 IF A(I,J)<>0 THEN 230
200 NEXT I
210 PRINT "NO UNIQUE SOLUTION"
220 GOTO 440
229 REM - STATEMENTS 230 TO 270 MOVE THAT EQUATION UP TO THE CURRENT
230 REM - COLUMN OF THE CURRENT ROW
230 FOR K=1 TO R+1
240 X=A(J,K)
250 A(J,K)=A(I,K)
260 A(I,K)=X
270 NEXT K
278 REM - STATEMENTS 280 TO 310 GENERATE A VALUE OF ONE IN THE FIRST
279 REM - COLUMN OF THE CURRENT ROW
280 Y=1/A(J,J)
290 FOR K=1 TO R+1
300 A(J,K)=Y*A(J,K)
310 NEXT K
319 REM - STATEMENTS 320 TO 360 SUBTRACT CURRENT EQUATION FROM THE OTHER
320 REM - THIS PROCESS IS REPEATED FOR ALL EQUATIONS
330 FOR I=1 TO R
340 IF I=J THEN 390
340 X=1/A(I,J)
350 FOR K=1 TO R+1
360 A(I,K)=A(I,K)+X*A(J,K)
370 NEXT K
380 NEXT I
389 REM - THIS PROCESS IS REPEATED FOR ALL EQUATIONS
390 NEXT J
400 PRINT
409 REM - PRINT SOLUTIONS
410 FOR I=1 TO R
420 PRINT "X";I;"=";INT(A(I,R+1)*1000+.5)/1000
430 NEXT I
440 END
```
B) **Programme to Evaluate the Theoretical Elongational Viscosity and Stress at Various Time Intervals**

```plaintext
20 REM USING CHANG & LODGE EQUATION
25 DIM A(5), B(5)
35 PRINT "5 PAIRS OF CONSTANTS DERIVED FROM"
37 PRINT "STRESS & TIME PLOT AT LOW STRAIN RATE."
41 FOR L=1 TO 5: INPUT A(L), B(L): NEXT L: PRINT
46 PRINT "NUMBER OF DEFORMATION TIME ?": INPUT J: PRINT
50 INPUT E
74 FOR K=1 TO J
75 R=0
76 PRINT "VALUE OF DEFORMATION TIME ?": PRINT: INPUT T: PRINT
90 FOR L=1 TO 5
100 D=A(L)*B(L)*2*(1-EXP(-T/B(L)))
110 R=R+D: NEXT L
130 U=R3*P: S=E+U
140 PRINT "NUMBER", "TIME", "VISCOITY", "STRESS": PRINT: PRINT
160 PRINT R, T, U, S: NEXT K
165 PRINT "DO YOU NEED TO CHANG THE STRAIN RATES "&"I PRINT"
162 PRINT "OR FINISH (Y/N/F) ?"
166 INPUT H$167 IF H$="Y" THEN GOTO 400
168 IF H$="N" THEN GOTO 74
170 END
400 PRINT "NEW VALUE OF STRAIN RATE"
420 GOTO 66
```
APPENDIX IV

A front view of the Rutherford Extensional Rheometer