Relationships between PVC plastisol rheology and particle size distribution for filled and unfilled systems

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RELATIONSHIPS BETWEEN PVC PLASTISOL RHEOLOGY
AND PARTICLE SIZE DISTRIBUTION
FOR FILLED AND UNFILLED SYSTEMS

by

JOHN ALAN COOK B.Sc., G.P.R.I.

A Doctoral Thesis submitted in partial fulfilment
of the requirements for the award of
Doctor of Philosophy of the
Loughborough University of Technology


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I would also like to acknowledge my indebtedness to Stephanie for her faith in me and constant support throughout the last three years.
To Stephanie
Key-Words

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Paste Polymer
Particle Size Distribution
Rheology
Filler
Spray Drying
Particle Size Analysis
Mercury Porosimetry
Structure Development
RELATIONSHIP BETWEEN PVC PLASTISOL RHEOLOGY AND PARTICLE SIZE DISTRIBUTION FOR FILLED AND UNFILLED SYSTEMS

by JOHN ALAN COOK

ABSTRACT

To control the rheological properties of PVC plastisols commercial manufacturers take great care to control the particle size (PS) and particle size distribution (PSD) of a polymer latex, as these exert a strong influence over the flow characteristics of an uncompounded plastisol. However, the fundamental mechanisms controlling viscosity are not clearly understood.

Several techniques have been developed to measure the PSD (sedimentation analysis and laser diffraction) and viscosity over an extended shear rate range for plastisols prepared from carefully selected paste polymers. Care has been taken to establish the reliability of these techniques, as previous workers have experienced problems in obtaining reliable correlations from plastisol systems. Many have failed to measure the PSD within the plastisols, incorrectly basing their observations on latex PSD.

By careful selection of emulsion, seeded emulsion and microsuspension paste polymers the combined effects of polymerisation technique, emulsifier type, spray drying, milling and paste preparation on plastisol rheology have been established.

For many applications plastisols contain mineral fillers, which have a similar PS to the paste polymers. Addition of these materials can drastically change plastisol rheology. Until now, it has been assumed that plastisol viscosity rises with filler content and depends on plasticiser absorption characteristics. To elucidate the actual mechanism controlling the response of plastisols to fillers, calcium carbonate (coated and uncoated), titanium dioxide and Spheriglass filled systems have been studied.

To establish a model which will allow paste polymer systems to be designed more accurately, the paste polymers used in the initial part of this study have been spray dried under widely differing conditions. Careful measurement of the rheology and PSD of filled and unfilled plastisols prepared from these materials has highlighted the effect of PS, PSD, paste polymer porosity and filler interaction on plastisol rheology.

It has been clearly demonstrated that the plasticiser absorption characteristics of a filler are not the only factors controlling filled plastisol rheology, as previously thought. I have shown that the response of a plastisol to filler addition also depends on the interaction between filler PS and the paste polymer PSD.
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1.1 INTRODUCTION

A plastisol is a system containing fine particles of poly vinyl chloride (PVC) dispersed in a plasticiser. The main advantage of plastisols over standard PVC is that the moulding or coating of articles can be done at or near room temperature, thereby reducing the operating cost of fabrication. The only high temperature needed is during the relatively short (1-5 mins) heating cycle for fusing the plastisol into a homogeneous film or article. Upon initial application of heat, the PVC particles are swollen by the plasticiser until all the plasticiser is absorbed at about 65 - 100°C. At this point, the material is dry but has virtually no physical strength. This is called the gelled state. With a further increase in temperature, the polymer is dissolved in the plasticiser leading to a homogeneous state of fusion.

The production of a plastisol from PVC resin involves homogenisation of the various ingredients using one of several types of mixers, followed by deaeration to eliminate entrapped air. A typical process is illustrated in Figure 1.1.

FIG.1.1 - TYPICAL PLASTISOL PROCESSING OPERATION. FROM REF.(1).
Plastisols are used in diverse applications by many different processes. This diversity requires different properties not only at room temperature but also in the fused state. In general, the most important plastisol property is the viscosity-shear rate relationship, as shown in Figure 1.2. For example, the spray coating and dip coating processes require different rheological properties.

FIG.1.2 - TYPICAL FLOW BEHAVIOUR OF VINYL PLASTISOLS OVER THE SHEAR RATE RANGE SEEN IN NORMAL PROCESSING. FROM REF.(1).

In order to meet the requirements for each application, the plastisol formulation is changed through fillers, lubricants and the nature and level of plasticiser. A typical plastisol formulation is given in Table 1.1.

Table 1.1 - TYPICAL PLASTISOL FORMULATIONS. FROM REF. (1).

<table>
<thead>
<tr>
<th>Component</th>
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<tr>
<td>PVC dispersion resin</td>
<td>60-100</td>
</tr>
<tr>
<td>PVC blending resin</td>
<td>40-0</td>
</tr>
<tr>
<td>Plasticizers</td>
<td>30-100</td>
</tr>
<tr>
<td>Filler</td>
<td>0-100</td>
</tr>
<tr>
<td>Stabilizer</td>
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<td>Pigments</td>
<td>0-5</td>
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<tr>
<td>Lubricants</td>
<td>0-2</td>
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<td>Solvent</td>
<td>0-10</td>
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<tr>
<td>Other additives</td>
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Resin modifications are used when simple changes in the ingredients are not sufficient to produce the desired properties. Modifications such as using copolymers, changing the particle size (PS) and particle size distribution (PSD) are often employed. While the PSD of resins varies considerably, the resins, to a large extent, can be classified as being unimodal or bimodal. The difference in the PSD stems from the procedure used during polymerisation.

1.2 PREPARATION OF PASTE POLYMERS.

1.2.1 Polymerisation Techniques

1.2.1.1 Conventional Emulsion Polymerisation

The conventional emulsion polymerisation technique involves the dispersion of vinyl chloride monomer in a water phase using emulsifiers and the incorporation of water soluble initiators. Polymerisation normally results in a latex particle size of about 0.01-0.2 μm which, when spray dried, are only suitable for the very highest viscosity plastisols.

The soap system used during polymerisation is usually based on an anionic emulsifier with a concentration of 2 - 3%. At these levels, which are above the critical micelle concentration (CMC), the emulsifier molecules agglomerate into small groups called micelles. Each micelle contains between 50 and 100 soap molecules which are so arranged that their hydrophobic ends gather together at the centre of the micelle, while their hydrophilic ends form the outer surface, interfacing with the water. In the core of some of the soap micelles, small amounts of monomer are solubilised, although the majority is dispersed as relatively large monomer droplets. Harkin was the first to suggest that initiation of polymerisation takes place in the micelle by a free radical generated in the water phase diffusing into the micelle. As the monomer in the micelle is polymerised, more monomer diffuses into it at the expense of the dispersed monomer. This mechanism, as proposed by Gellner, is described schematically in Figure 1.3.
The monomer/polymer particle forming within the micelle continues to grow, until a secondary primary radical is introduced from the water phase, at which point, there is bimolecular termination. A terminated monomer/polymer particle may acquire another free radical and start polymerising again until being terminated by a further radical. The final latex particles are produced when all the available monomer has been consumed.

More recently, it has been postulated\textsuperscript{10} that, in the case of vinyl chloride, initiation might occur outside the micelle and there is some evidence to support this. Ugelstad et al\textsuperscript{11} propose a mechanism involving a rapid desorption and reabsorption of radicals in the latex particles; while Peggion et al\textsuperscript{12} claim that, for emulsion polymerisation of vinyl chloride, the radicals produced in the aqueous phase initiator react with the monomer dissolved in the water.

Whether or not micelles are the sole locus for polymerisation, the concentration and type of emulsifier would be expected to strongly influence the number of latex particles formed. Peggion et al\textsuperscript{12} found that the number of particles formed increases as emulsifier concentration is increased and that for a series of sulphonates, at a given concentration, the number of particles formed increases with
increasing alkyl chain length. These results confirm the importance of micelles on particle formation, since the CMC is expected to fall with increasing alkyl chain length, thus the number of micelles at a given concentration increases.

In a similar way Rangnes and Palmgren'3 found that sodium dodecyl sulphate produced a smaller particle size latex than sodium cetyl sulphate and, as such, the former is useful for the production of high viscosity paste resins.

For the emulsion process, the size of the latex particles grows throughout the polymerisation. The increased surface area requires a corresponding increase in emulsifier to maintain latex stability. The rate of fresh soap addition must, however, be carefully controlled in order to avoid the formation of new particles by generation of new micelles.

1.2.1.2 Seeded Emulsion Polymerisation

In order to produce polymers that form low viscosity pastes, a latex with particle size of about 0.3-2.0 μm is required. To increase the latex particle size of an unmodified emulsion polymerisation, which is typically 0.01-0.2 μm, the technique of seeding is used, whereby preformed seed latex particles are 'grown' to the required size.

When employing the seeding technique in emulsion polymerisation, it is important to carefully control the quantity of seed used and the level of emulsifier to avoid creating a second generation of particles. If insufficient seed is used (i.e. < 3%), the reaction rate will be slow and the available surface area will not be sufficient to prevent fresh nucleation. However, too much seed reduces the potential for increase in latex particle size. The emulsifier level should be controlled between 25-40% of theoretical unimolecular coverage'4 in order to ensure latex stability but prevent fresh micelle formation which would create a second family of particles. As the seeds grow during polymerisation, the surface area increases and so further
additions of emulsifier should be made, either in aliquots or continuously proportioned. ICI has developed sophisticated methods for controlling the rate of emulsifier addition, which include monitoring contraction in batch volume and heat evolution as a measure of the extent of conversion.

Low viscosity plastisols can be prepared from latices having a bimodal size distribution. Such latices may be prepared by various methods, several of which have been disclosed within patents. These include the simple physical mixing of products or the mixing of two or more seed latices of different sizes followed by polymerisation using this mixture of seed latices as the nuclei. A further technique involves the use of a single preformed seed in conjunction with a second emulsifier type used at sufficient quantity to cause the formation of an additional population of smaller size.

1.2.1.3 Microsuspension Polymerisation

Microsuspension is the name given to the process whereby a small particle size PVC latex is produced using a monomer soluble initiator, as in the suspension process. The microsuspension process results in latex particles with diameters in the range 0.1-3.0 μm. This represents a larger and wider PSD than is obtained with an unmodified emulsion polymerisation, thus making the technique more applicable to the production of paste polymers.

The microsuspension process does not rely on the formation of micelles, although high levels of emulsifier (1-2%) are still required to stabilise the droplets. In order to obtain the required PS, the ingredients are usually premixed and then fed, via a homogeniser, to the polymerising reactor. The homogeniser produces the required droplet size by submitting the premix to powerful mechanical forces. The droplets formed are stabilised in the reactor by the emulsifier system and only require gentle agitation during polymerisation. Since the PS of the final latex is substantially that of the initial droplet dispersion, homogenisation conditions can be used to adjust the latex PSD. Rees
considered the theories controlling homogenisation together with the practical aspects relating to high speed pumps. In a patent by ICI\textsuperscript{20}, operating conditions during microsuspension polymerisation have been elaborated.

1.2.2 Effect of Spray Drying Parameters

1.2.2.1 Atomiser Conditions

Polymer isolation from a latex produced by emulsion or microsuspension polymerisation is usually carried out by spray drying\textsuperscript{7,23}. Spray driers usually consist of a large inverted conical shape container into which the latex is introduced as a fine spray. It is then dried by hot air before the particles reach the wall of the drying chamber. There are two types of atomising device in commercial use, the spinning disc where latex is atomised at the periphery of a high speed rotating wheel into which the latex is fed, or nozzles through which the latex is passed at high speed to cause a fine spray. Increased nozzle pressure and increased peripheral speed of a disc atomizer both cause a reduction in particle size.

Plastisol viscosity is primarily controlled by the PS and PSD of the resin\textsuperscript{21}; studies have shown that the agglomerates (known as secondary particles), created by spray drying, play an important role in plastisol viscosity and viscosity ageing\textsuperscript{22}. Hoffmann et al\textsuperscript{23} undertook a study to determine the effect of drying parameters on resin PSD and the subsequent plastisol viscosity and viscosity ageing. Using a pilot plant nichols/niro spray drier, fitted with centrifugal disc atomisation, they made the following observations;

(1) Resin agglomeration present in the plastisols increases with increasing outlet temperature. The higher outlet temperature is obtained by a reduced latex feed rate to the atomizer. The higher outlet temperature causes two changes, both of which should increase the degree of agglomerate fusion. Firstly, decreasing feed rates to centrifugal disc atomisers produce smaller droplets\textsuperscript{24} which dry faster and should
be more highly fused because of their longer heat history. Secondly, the higher dryer temperature should more thoroughly fuse the agglomerates, which should resist breakdown during plastisol mixing and result in more agglomerates in the plastisol.

(ii) Increasing the atomizer speed increases the agglomeration present in the plastisols, because the higher speeds produce smaller spray droplets. This results in more highly fused agglomerates which resist breakdown during paste preparation.

(iii) The amount of agglomerates present in the plastisols increases with inlet temperature, as higher temperatures fuse the particles more thoroughly.

Hoffmann et al also considered the effect of spray drying parameters on plastisol viscosity and viscosity ageing and arrived at the following conclusions:

1. Viscosity increases with increasing outlet temperature.
2. Viscosity decreases with increasing inlet temperature.
3. There appears to be no relationship between atomizer speed and plastisol viscosity.
4. As dryer temperatures are increased, plastisol viscosity ageing decreases (Section 1.3.3).

1.2.2.2. Nature of Secondary Particles.

The morphology of polymer particles can strongly influence both the plastisol viscosity and its change with time. Boisan and Feldman demonstrated that secondary particles obtained at high outlet temperatures showed resistance to deagglomeration. Primary particles became irreversibly agglomerated so that viscosity ageing is limited. In general, these plastisols (pastes) have a high viscosity and are practically unprocessable. The secondary particles are porous and contain internal cavities caused by the rapid evaporation of water enclosed in the particles during formation.
Spray dried PVC particles have a mean diameter of 40 - 50μm, with some particles up to 100μm. It is often necessary to follow the spray drying process by a grinding or pulverising operation in order to change the PSD and plastisol viscosity. The absence of large particles may be necessary to ensure a good gloss and prevention of surface imperfections, especially when using very thin coatings such as in wall paper manufacture. Although this technique does not achieve complete mechanical deagglomeration, it does accelerate the paste forming process. This is because the fragments of secondary particles will undergo deagglomeration more rapidly when in contact with the plasticiser. 

Butucea et al. found that when spray drying is carried out at high outlet temperatures grinding has a negative effect because fragments of secondary particles with irregular shapes are formed. These are unable to undergo deagglomeration, so that a plastisol with a higher viscosity is obtained. This is because of the retention of a certain amount of plasticiser in their surface, swelling of the internal primary particles and the increase in inter-layer coefficient of friction caused by their angular shape. This is illustrated by comparing test No.1 with test No.3 in Table 1.2.

Table: Table 1.2 - Effect of the Grinding Process on Plastisol Viscosity.

<table>
<thead>
<tr>
<th>Test No.</th>
<th>Type of Latex (Mean dia. µm)</th>
<th>Atomising Conditions</th>
<th>Plastisol Viscosity (cP)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Entry Temp (°C)</td>
<td>Exit Temp (°C)</td>
</tr>
<tr>
<td>1</td>
<td>0.79</td>
<td>155</td>
<td>70-72</td>
</tr>
<tr>
<td>2</td>
<td>0.79</td>
<td>155</td>
<td>52-54</td>
</tr>
<tr>
<td>3</td>
<td>0.79</td>
<td>155</td>
<td>70-72</td>
</tr>
<tr>
<td>4</td>
<td>0.79</td>
<td>155</td>
<td>52-54</td>
</tr>
</tbody>
</table>

* Ground Polymer
Butucea et al. have shown that when spray drying is carried out at lower temperatures (test No.4), grinding has only a minimal effect. This is because the secondary particles consist of superficial aggregates of primary particles which will, in any case, undergo rapid deagglomeration in the plasticiser.

1.2.2.3. Emulsifier Variations.

Merinov et al. have shown that emulsifier type can have a profound effect on particle agglomeration during spray drying. Large quantities of monionic surfactant (such as a monocalkyl ether of polyethylene glycol) or fatty alcohols are capable of increasing the strength of agglomerates. It is proposed that the surfactant acts as a cementing agent for the primary latex particles in the spray drying process. As the melting points of these materials are in the range 30-60°C, cementing of the particles is accomplished through crystallisation of the emulsifier during polymer drying.

1.3 RHEOLOGY

1.3.1 Viscosity of Suspensions

1.3.1.1. Effect of Concentration of the Dispersed Phase on Suspension Rheology

One of the most widely studied variables in plastisol rheology has been the concentration of PVC. It is well known that below a certain concentration of particles in the suspension, the flow obeys the Einstein relationship:

\[ n = n_0 (1 + 2.5\phi) \]

where \( n \) = suspension viscosity and \( n_0 \) = solvent viscosity.

In increasing the concentration (\( \phi \)) the flow deviates more and more from this relationship as shown in Figure 1.4.

-10-
To account for such behaviour, numerous modifications of equation (1.1) have been proposed\(^3\). One of the most important extensions has been made by Vand\(^4\). He assumed that two spheres met, rolled around each other and were separated by the shearing action of the solvent:

\[
n_{\text{rel}} = 1 + 2.5\sigma + 7.35\sigma^2 + \ldots. \quad (1.2)
\]

This is similar to the Einstein equation except that higher-order terms have been added to compensate for the effect of collision. Vand checked his equation by suspending glass spheres in a medium with approximately the same density as glass and obtained a good correlation. Others\(^5\) have checked this equation with glass spheres and found it gives a good approximation, up to 30% volume concentration. However, at higher volume fractions, there is substantial scatter in the results. This indicates that factors other than concentration influence properties of the suspension. As a consequence, this equation does not
hold for commercial PVC plastisols where the concentration range is approximately 54% solids.

Consideration of the size of the particles along with their concentration in the suspension has led to the following equation;

\[ n = A \exp (Bc) \]  \hspace{1cm} (1.3)

where \( c \) is the concentration of the particles by weight. \( A \) has been related to the particle-particle interaction and \( B \) to the size, shape and surface of the particles. This equation is based on similar ones proposed for variations of viscosity with concentration in pigment dispersions\(^{22}\) and for mineral powders in high viscosity asphalts\(^{34}\). Although this equation was found to be valid in the concentration range of 47-60 weight % particles, it was found to be unsatisfactory with certain plasticisers\(^{6}\). In such systems, it was found that the particles may be swollen by the plasticiser\(^{34}\), thus causing a higher than expected rate of increase in viscosity with volume fraction of solids. Unfortunately, the nature of the variation of \( A \) and \( B \) with different particle sizes, distributions and plasticisers is, as yet, unknown.

Other approaches to the problem of concentrated dispersions have been made. Mooney\(^{36}\) considered the addition of spheres to an existing dispersion of spheres of the same size. The added spheres increased the viscosity in two ways; they occupy the liquid left over by the original spheres and also reduce the amount of liquid available for the original spheres. Using a function similar to the Robinson equation\(^{34}\) based on free space, Mooney developed the following;

\[ \ln n_{rel} = \frac{2.5\sigma}{1-K\sigma} \]  \hspace{1cm} (1.4)

where \( K \) is a self-crowding and hydrodynamic interaction factor and \( \sigma \) is the volume fraction of spheres. When \( \sigma \to 0 \) this equation becomes the Einstein equation. Mooney predicted that the most probable value of \( K \) would be 1.35, corresponding to close packing of the spheres, or a volume of 74.1\% spheres. Loose packing or face-centred spheres, where
the spheres were just free to move, would correspond to a $K$ of 1.91 or a volume of 52.4% spheres. A value of $K = 1$ would correspond to 100% spheres - which is impossible unless there was a continuous gradation of particle sizes.

The Mooney equation was applied by Brodnyan to data from five different investigations and the data were approximated by $K = 1.35$ and fell between $K = 1.91$ and 1.00. The variation in $n$ rel with increase in volume fraction is shown in Figure 1.4. The Einstein equation is approached at very low concentrations in the region below 6% solids volume. Above this level, the relative viscosities depart rapidly from the Einstein equation and are approximated by the Mooney equation. Above 10-20% volume concentration, the relative viscosities increase very rapidly and approach a 1000 - fold increase at 60% by volume.

When the plasticiser level in a plastisol is decreased, the viscosity increases. The change in viscosity is small at first, but at a critical concentration there is an abrupt increase in the viscosity, as shown in Figure 1.5 of Figure 1.4 for glass spheres dispersed in a medium of similar density.

FIG.1.5 - EFFECT OF VOLUME OF PARTICLES ON THE VISCOSITY OF PVC PLASTISOLS. FROM REF. (1).
In an attempt to establish a mathematical relationship for such an effect, Johnston and Brower\textsuperscript{37} extended the Mooney equation\textsuperscript{36} for rubber latices to the form,

\[ n \text{ rel} = \frac{(1 + 0.5\omega)^{1.5}}{(\omega - \varepsilon) \exp \left[ 1.25/(1-\varepsilon) \right]} \]  

(1.5)

where \( \omega \) was defined as the volume fraction of resin, at which the viscosity of the dispersion became infinite. Satisfactory agreement was found with experiments using different plasticisers and a monodisperse distribution of particle size. However, it is not clear if the above equation will also hold for poly-disperse particles.

1.3.1.2. Effect of Colloid Forces on Viscosity

There are two basic mechanisms for the stability of colloidal suspensions. The first one is the Derjaguin – Landau – Verwey – Overbeek (DLVO) theory\textsuperscript{40} which considers electrostatic repulsion as the stabilisation mechanism, see Figure. 1.6A

**FIG. 1.6 – NET POTENTIAL ENERGY (V) CURVES AS A FUNCTION OF PARTICLE SURFACE SEPARATION (L) FOR CHARGE STABILISATION (A) AND STERIC STABILISATION (B). FROM REF. (1).**
The second one is the so-called steric stabilisation scheme which considers an absorbed solvated surface layer on the particle as being responsible for colloid stability, as shown in Figure 1.6B. It is proposed by this theory that the interaction parameter, $\chi$, between the surface layer and the suspending medium is the factor that determines stability. Thus, the higher the interaction between the medium and the surface layer (i.e. the lower the value of $\chi$), the higher the stability of the suspension and the lower the tendency for aggregation. This approach is relatively new and has been covered in a review by Osmond and Waite.4

With aqueous polystyrene latices at volume fractions as high as 0.50, Krieger and co-workers42,43 have observed, at high ionic strengths or low surface charge densities, only moderate shear thinning with well-defined Newtonian high and low-shear limits. Krieger and co-workers42,43 found that subsequent reduction in the ionic strength, which extends the range of electrostatic repulsions between particles, dramatically increased viscosities at low shear rates, eventually producing an apparent yield stress or infinite zero-shear viscosity, as shown in Figure 1.7.

FIG.1.7 - EFFECT OF ADDED ELECTROLYTE ON THE RELATIVE VISCOSITY ($\mu/\mu_0$) OF A POLYSTYRENE LATEX SUSPENSION. FROM REF. (44).

<table>
<thead>
<tr>
<th>Electrolyte</th>
<th>Concentration</th>
</tr>
</thead>
<tbody>
<tr>
<td>Deionized</td>
<td>(1.876 \times 10^{-4} \text{M})</td>
</tr>
<tr>
<td>HCl</td>
<td>(1.876 \times 10^{-3} \text{M}), (9.378 \times 10^{-2} \text{M})</td>
</tr>
</tbody>
</table>
With nonaqueous polyvinyl chloride plastisols Willey and Macosko found somewhat different behaviour, as shown in Figure 1.8. For fluids which serve as solvents for dissolved PVC molecules, a volume fraction of suspended spherical particles of 0.20 produced slightly non-Newtonian viscosities. With very good solvents, for which interparticle forces should be repulsive and the suspension stable, the low-shear viscosity was significantly higher but remained finite. The most dramatic effect appeared with poor solvents for which the highly flocculated suspensions were markedly more viscous with an apparent yield stress.

FIG. 1.8 - EFFECT OF SOLVENT QUALITY ON THE RELATIVE VISCOSITY OF PVC PLASTISOLS. FROM REF.(44).

These samples highlight the sensitivity of the rheology of a suspension of sub-μm particles to the nature and strength of the interparticle forces. Unfortunately, a detailed understanding of these relationships remains limited.

In an attempt to identify the colloidal forces controlling plastisol viscosity, Khanna measured the zeta potentials of PVC powders dispersed in di-alphanyl phthalate (DAP), using an electrophoretic method. Generally, the magnitude of the zeta potential (a measure of the electrostatic forces), carried by the PVC particles, was
not high enough to provide sufficient electrostatic charge to stabilise the dispersion Khanna\textsuperscript{46}, therefore, attributed the stability of plastisols to the presence of absorbed solvated layers on the surface of the polymer particles, which maintain stability through the steric mechanisms, see Figure 1.6B.

Further evidence in support of the steric mechanism of stabilisation was provided by Willey\textsuperscript{7} who determined the onset of dilatancy for a plastisol, produced from a unimodal resin, as a function of solvent strength (Section 1.3.2.1 a). As the solvent power was reduced (and hence $\chi$ increased) the forces between particles, as measured by the onset of dilatancy, were reduced as predicted by the steric stabilisation scheme. These observations confirm the work of Khanna, for plastisols which are non-aqueous suspensions with low dielectric strength\textsuperscript{44}, electrostatic forces are of secondary importance and rheology is dominated by the steric mechanism.

1.3.2 Non - Newtonian Flow of Plastisols (see Appendix 14)

1.3.2.1. Dilatant and Discontinuous Flow Behaviour

1.3.2.1.a. Proposed Flow Mechanisms

Dilatant viscosity behaviour, observed in suspensions containing monosized spheres of PVC, is transformed into a discontinuous viscosity behaviour when the volume fraction of solids is raised above 0.50\textsuperscript{46}, as shown in Figure 1.9

Although rheological dilatancy in the flow of suspensions was first recognised in 1938\textsuperscript{47}, quantitative studies concerned with this phenomenon are rare. Metzner and Whitlock\textsuperscript{48} provided one of the first quantitative attempts to examine rheological dilatancy in which they accepted, as part of their theory, Reiner's\textsuperscript{42} concept of layers of spheres gliding over one another. Although the concept is feasible, proof has been lacking. Morgan\textsuperscript{52} concludes from his study of aqueous pigment suspensions, that Metzner and Whitlock's theory is not
applicable to these systems, and favours a theory of shear induced
association or flocculation of particles. Gillespie\textsuperscript{84} suggests a kinetic
process in which bonds are continuously formed and broken to describe
the dilatant viscosity behaviour of suspensions with solids contents
below 50% by volume.

FIG. 1.9 - EFFECT OF VOLUME FRACTION OF 1.25 µm PVC IN DIOCTYL
PHTHALATE UPON VISCOSITY DISCONTINUITY AT 25°C. FROM REF. (48).

In an attempt to understand the mechanisms which lead to the
discontinuity in the apparent viscosity of monodisperse PVC spheres in
dioctyl phthalate (figure 1.9), Hoffman\textsuperscript{48} proposed the following model
for viscometric flow. Forces of attraction and repulsion acting between
particles in the dispersion interact with the forces of the shear field
to cause the formation of surfaces of two dimensional hexagonally packed
spheres, which pass over one another in the direction of flow. As one
increases the relative velocity of these neighbouring surfaces of
spheres, the shear stress transmitted from one surface to the next
through the interstitial fluid is increased. Some critical value of the
shear stress is finally reached at which the shear stress couple on the
surface of hexagonally packed spheres is just sufficient to overcome the
forces between the spheres which hold them in place. When this happens,
sections of the ordered surfaces roll up into eddies and the onset of
disordered flow occurs. The extra energy required by the spheres when
they jam into one another during flow causes the discontinuous jump in
the apparent viscosity at the instability point.

Far above the discontinuity point ordered flow occurs once again. Hoffman\textsuperscript{49} believes, although it is as yet unproven, that eddies occur in
the disordered flow which are broken into successively smaller units as
the shear rate increases. Thus the eddies ultimately become individual
spheres rotating in ordered surfaces of hexagonal packing at high shear
rates. This implies that the surface of ordered particles contain
spheres which do not rotate freely at shear stresses below the critical
shear stress.

Evidence to support the above model is obtained from\textsuperscript{49}: (1) viscosity curves for suspensions containing monosized polyvinyl chloride
spheres at various volume fraction levels; (2) light diffraction from the
ordered and unordered arrays of spheres obtained at various shear rates;
and (3) photographs of the ordered planes of hexagonally packed
spheres.

The discontinuity shear rate goes to zero when the volume fraction
of solids is raised to 0.60. This would be predicted from the model as
planes of hexagonally packed spheres placed over one another have 0.605
volume fraction of solids when the planes just meet.

Hoffman\textsuperscript{49} modified a Weissenburg rheogonimeter (viscometer) so
that light diffraction from the suspension could be measured during
shear in torsional flow. Using this equipment, he was able to prove
that PVC particles were present in hexagonal packing below the
discontinuity point and that an order-disorder transition occurs at the
discontinuity shear rate, followed by a resumption of ordered flow at
higher shear rates. He was also able to photograph the particles at
nominal magnifications of 1,150 and 800 X. These photographs provide
further evidence for the hexagonal packing.
1.3.2.1.b Solvation Effects on Dilatancy

Willey accepted Hoffman's belief that dilatant behaviour corresponds to a breakup of the ordered layers of particles, this breakup being the result of competition between the colloidal repulsion forces which stabilise the layers and the shearing forces. Hoffman developed a phenomenological model to predict the effects of system variables on dilatancy based on the existence of electrostatic repulsions between suspension particles.

PVC plastisols, however, are non-aqueous suspensions with low dielectric strength, where electrostatic forces are thought to be of secondary importance. In such systems, it is believed that stability is achieved through the steric stabilisation mechanism. The sterically stabilised colloid particles have a solvated polymer species strongly bonded to their surfaces. For PVC systems, the stabilising polymer is thought to be a blend of the PVC chains and emulsifier species.

If the suspension continuous phase is a solvent for the polymeric species on the particle surfaces, then the free energy charge associated with closer approach is positive and the particles repel each other. When the suspending medium is a non-solvent for the stabiliser, the free energy charge on close approach is negative and spontaneous flocculation occurs.

Willey prepared concentrated suspensions (0.54 volume fraction of solids) from resins which were ion exchanged to remove excess surfactant. He found that suspensions prepared with the narrow size distribution, 1.2 μm resin, exhibited slight shear thinning, followed by nearly Newtonian behaviour progressing to shear thickening, prior to the abrupt dilatancy. See figure 1.10.
FIG. 1.10 - TYPICAL VISCOSITY VERSUS SHEAR RATE DATA FOR A HIGH VOLUME FRACTION (0.54) PLASTISOL MADE FROM MONODISPERSE (1.2 μm dia.) PVC LATEX. HERE THE DISCONTINUITY OCCURS AT 40 s⁻¹. FROM REF. (47).

The effect of the suspending medium solution properties on dilatancy, according to Willey, are listed in Table 1.3. For the two phthalate ester systems, going from a better solvent (2 - Ethylhexyl phthalate (DOP)) to a poorer solvent (Dimethyl phthalate (DMP)) causes a decrease in the flow strength μrd (proportional to shear rate) required for dilatancy. The same is also true for the mixed solvent / non solvent systems. Increasing the concentration of aliphatic oil reduces the μrd at which dilatant behaviour is observed.

TABLE 1.3 - EFFECT OF SUSPENDING MEDIUM ON DILATANCY SHEAR STRESS. FROM REF. (47).

<table>
<thead>
<tr>
<th>Suspending medium</th>
<th>μμrd (dyn/cm²)</th>
</tr>
</thead>
<tbody>
<tr>
<td>DOP</td>
<td>23.6</td>
</tr>
<tr>
<td>DMP</td>
<td>1.4</td>
</tr>
<tr>
<td>DOP/hydrocarbon (73% DOP)</td>
<td>15.6</td>
</tr>
<tr>
<td>(40% DOP)</td>
<td>1.4</td>
</tr>
<tr>
<td>(34% DOP)</td>
<td>0</td>
</tr>
</tbody>
</table>
The decrease in $\mu_{rd}$ in the mixed solvent systems is nearly linear with DOP concentration as shown in Figure 1.11. In a sterically stabilised system, the interparticle repulsion force should vanish at a composition near the phase separation point for the stabiliser polymer in a dilute mixed solvent system. This was the case, turbidimetric titration of a 0.5% PVC/DOP solution with the aliphatic hydrocarbon gave a PVC limit of 32% (W/W) DOP. In a plastisol with a continuous phase composition of 34% DOP, the suspension became non-flowing and $\mu_{rd}$ reduces to zero as shown in Figure 1.11.

FIG.1.11 - EFFECT OF PLASTISOL COMPOSITION ON THE DISCONTINUITY SHEAR STRESS FOR A BLEND OF DOP WITH ALIPHATIC OIL (1.2 $\mu$m DIAMETER $\sigma = 0.54$). FROM REF. (47).

1.3.2.1.c Prediction of Critical Shear Rates.

In formulating plastisols for use in processes which involve high shear rates, it would be useful if the presence of an unwanted viscosity discontinuity could be predicted. Williams and Bergen sought to
investigate the rheology of concentrated plastisols with particular emphasis on the discontinuous viscosity behaviour (of mono-dispersed systems) as influenced by particle size characteristics of the resin and nature of the plasticiser.

Prior to this investigation, determination of the maximum concentration of resin that could be incorporated in a plastisol had been carried out by extrapolation and/or curve fitting techniques. A new, simpler technique was developed that provided a measure of the maximum volume fraction of resin that would form a just-fluid plastisol, designated $\phi_{\text{mix}}$.

**Fig.1.12 - Effect of Volume Fraction of Resin on the Discontinuity Point:**

$K: 0.585\,\text{VF}$, $L: 0.605\,\text{VF}$, $M: 0.635\,\text{VF}$, $N: 0.644\,\text{VF}$. From Ref. (55).

The dotted line followed by an arrow (.....→) in Figure 1.12 indicates the onset of a discontinuity in viscosity. The graph illustrates the flow curve for plastisols at concentrations ranging from 0.585 - 0.644 volume fraction of resin. When the volume fraction of resin is increased, the viscosity increases and the critical shear rate at which discontinuity occurs ($\dot{\gamma}$) decreases.
In an effort to normalise volume-fraction data to reflect specific volume effects for multiple plasticiser / resin dispersions, a reduced volume fraction $\Phi_R$ was developed by Williams and Bergen\(^5\), as a measure of the deviation from $\Phi_{\text{mix}}$:

$$\Phi_R = \frac{1}{M} \sum_{i=1}^{n} \sum_{j=1}^{m} \frac{x_i y_i}{\Phi_{\text{mix}_{ij}}}$$

(1.6)

where $x_i = \text{volume fraction of the } i\text{th liquid phase}, y_i = \text{volume fraction of the } j\text{th solid phase}, \Phi = \text{total volume fraction of resin (s)}, n = \text{number of plasticisers}, m = \text{number of resins and } \Phi_{\text{mix}_{ij}} = \Phi_{\text{mix}} \text{ of } i\text{th plasticiser with the } j\text{th resin.}$ The reduced volume fraction $\Phi_R$ is a measure of departure from the maximum volume fraction of resin obtainable with the resin(s) / plasticiser(s) system and is a simple mixing algorithm.

In Williams and Bergen's study\(^5\) the viscosity discontinuity was found to vary with the type and concentration of resin and type of plasticiser. A plot of the discontinuity shear rate versus the reciprocal of the reduced volume fraction of all the plastisol formulations used in their study fell on a straight line as shown in Figure 1.13.

FIG. 1.13 - CORRELATION BETWEEN DISCONTINUITY SHEAR RATE AND REDUCED VOLUME, $\Phi_R$, FROM REF (56).
A least-squares fit is represented by the expression:

\[
\log_{10} \gamma_d = -9.8568 + 10.437 / \sigma R 
\]  

(1.7)

The use of the above equation is very straightforward. One only needs to know \( \sigma \) mix for the particular resin/plasticiser combination to be able to predict \( \gamma_d \) as a function of \( \sigma R \).

1.3.2.2. Pseudoplastic Flow Behaviour.

Study of flow behaviour over a wide range of shear rates indicates pseudoplastic flow at low and high shear rates and shear thickening at intermediate shear rates as shown in Figure 1.2. With increasing concentration of solids, the entire flow curve rises and the intermediate shear thickening becomes more pronounced. Lazor has suggested that the initial pseudoplastic flow is due to aggregate breakdown. As the loosely bound aggregates are broken up, the plasticiser that is immobilised in the aggregates contributes to lowering the viscosity by increasing the quantity of the available liquid phase.

Villey, however, has shown by a freeze fracture replication study of PVC - DOP plastisols, that there is very little aggregation in such systems. The steric stabilisation theory also supports this observation. It is, therefore, difficult to envisage aggregation of the type suggested by Lazor. On the other hand, Villey has shown that at a given volume fraction interparticle forces are constant and that Brownian motion governs the viscosity at low shear rates. Similar dependence of suspension viscosity on the Brownian motion was also shown by Kreiger and Dougherty for suspensions of polystyrene latices. Therefore, the pseudoplastic flow at low shear rates may be explained as a competition between the randomising effects of the Brownian motion and the "orienting" effect of the shear force. At higher shear rates, the Brownian effects become insignificant.
As outlined in Section 1.3.1.1, the first theoretical treatment of
suspension rheology was published by Einstein. This and subsequent
extensions to his equation are based on the assumption that the flow
around suspended particles is described by the hydrodynamic equations
of motion. However, particles in suspension are subject not only to
hydrodynamic forces, but also non-hydrodynamic forces. The latter
consist of thermal (Brownian), electrical and London-Van der Waal's
forces. These are treated in the Derjaguin-Landau-Verwey-Overbeeck
(DLVO) theory of colloid stability. The Brownian forces result from
thermal agitation of the molecules of suspending liquid. This process
is represented by a Diffusion Constant, \( D = kT / R_w \), where \( K \) is the
Boltzman constant, \( T \) the absolute temperature and \( R_w \) a resistance
coefficient. \( R_w \) increases with particle size, relating the motion of the
particle to the force acting on it. This means that the diffusion
constant, \( D \), decreases with increasing particle size and large particles
are affected less by Brownian forces than small ones.

Electrical forces, which arise from charges on particles due to
the surfactant species, may have a limited effect on viscosity, compared
with forces due to steric interactions (Section 1.3.1.2). Such forces
may arise either from the resistance of the charged cloud to deformation
or from repulsion between the particles. As with Brownian effects, such
interactions decrease in importance as the size of the particles
increases. The London-Van der Waal forces are the weak, short range
attractive forces between all particles.

This relationship between particle size and the magnitude of the
forces acting on particles is very important as will be shown in Section
1.5. Pseudoplasticity increases rapidly with a reduction in particle
size (below 0.5 \( \mu \text{m} \)) due to the increasing effects of non-hydrodynamic
forces.
1.3.3 Ageing Characteristics of PVC Plastisols

1.3.3.1. Effect of Time and Temperature

The main problem associated with PVC pastes is their instability with respect to time, i.e., the change in viscosity with time during storage. The initial viscosity of a PVC paste and the speed at which it ages, indicates its suitability for processing and also indicates its shelf life. The practical method of judging the stability of the PVC paste is to determine the change in viscosity after storage for several days at room temperature.

In commercial production of PVC dispersion resin, the particle size ranges from the primary emulsion particles (0.1 - 1.5 μm) to the agglomerates (> 1 μm) formed in the finishing operations (spray drying and grinding). The type and amount of agglomerates have been shown to be important to plastisol ageing through the mechanism of deagglomeration. Such deagglomeration will change the particle size distribution and packing efficiency leading to a change in plastisol viscosity. In addition, more surface area will be exposed to the plasticiser which will increase the amount of bound plasticiser and effectively increase the solids volume loading. This will result in a viscosity increase. The increase in exposed surface area will also increase the rate of polymer swelling, solvation or dissolution which will also lead to rheological changes.

More stable plastisols may be prepared by spray drying the polymer at higher temperatures. Under such conditions, the secondary particles will be highly fused. Such agglomerates will then be more resistant to deagglomeration in the plastisol.

Particle swelling can also influence plastisol viscosities by producing larger particles which in effect increases the effective volume fraction. Such an increase will raise the viscosity of the plastisol. The swelling process also changes the way in which a plastisol will respond to shear through changes in the particle-particle interactions.
Swelling can lead to the development of structure in a plastisol at rest. Such structure requires additional energy to deform and flow, resulting in increased low shear rate viscosities.

The role of polymer dissolution on plastisol viscosity was followed by Willey and Macosko and shown to be an operative mechanism under certain conditions. Molecular weight and molecular weight distribution of the resin, as well as temperature, affect resin solubility in the medium. The dissolved polymer can also contribute to structure development which results in further viscosity increases.

In an attempt to elaborate the ageing phenomenon, Hoffmann and Garcia identified resins with both high and low heat ageing characteristics. One factor known to effect flow behaviour of the vinyl plastisols is particle size and size distribution of the dispersed phase (Section 1.5). Consequently, Hoffmann and Garcia investigated the effect of PS and PSD on the heat ageing process by using a comparison study between low and high heat ageing resins.

Sedigraph particle size analysis indentified differences between the two resins. The high ageing resins tended to have smaller primary particles. On ageing the plastisols, Hoffmann and Garcia observed significant deagglomeration in the high ageing resins. There was a reduction in the concentration of secondary particles and an increase in the level of primary particles. It was proposed that the secondary particles were breaking down to liberate the primary particles. Unfortunately, in this study Hoffmann and Garcia only measured changes in viscosity during ageing, at one shear rate, using a Brookfield Viscometer. It would be interesting to see if changes in PSD on ageing, as a result of the liberation of primary particles, caused a change in the shape of the flow curve. For example, with continued deagglomeration of secondary particles dilatancy may appear as the sharp unimodal distribution of primary particles is regenerated.

To investigate the effect of the solvation process on ageing, different plasticisers with varying plasticising activities were
examined. Hoffmann and Garcia\textsuperscript{61} found that the higher the activity, the more a given resin plastisol heat-ages. The plasticiser - resin interaction was also examined by determining if any polymer was being dissolved by the plasticiser while in the plastisol. Centrifugation of the plastisol followed by precipitation isolated a fraction of dissolved material. The amount of this material was found to be proportional to the heat ageing characteristics of the resin; poor ageing plastisols contained a higher level of the dissolved material. Infrared and C$^{13}$ nmr identified the dissolved fraction as dissolved resin with no identifiable structural differences from the base resin. Gel permeation chromatography (GPC) showed the dissolved polymer fraction to be a slightly lower molecular weight material, approximately 30\% for certain resins. Examination of GPC curves showed a substantial fraction of the base resin with the same molecular weight as the dissolved polymer portion, indicating that there was adequate polymer available for extraction. Micro-colorimetry work by Hoffmann and Garcia\textsuperscript{61} on DOP - PVC systems at 37°C, has shown that an exotherm occurs rapidly after the DOP contacts the resin, thus suggesting a strong interaction between the PVC and DOP, which can lead to polymer dissolution.

1.3.3.2. Effect of Plasticiser Type

Relationships between plasticiser solvent power and the ageing characteristics of PVC plastisols have been largely empirical. Bigg and Hill\textsuperscript{62} have proposed the use of a plasticiser activity parameter ($\alpha$) to represent numerically the solvent power of a plasticiser for PVC:

$$\alpha = \frac{(1 - \chi)}{\text{mw}} \times 10^3$$ \hspace{1cm} (1.8)

where $\chi$ is the Flory - Huggins interaction parameter and mw is the molecular weight of the plasticiser. The Flory - Huggins interaction parameters may be determined by measuring the apparent melting temperature ($T_m$) of individual granules of PVC polymer suspended in an excess of plasticiser. The $\chi$ values are then calculated from $T_m$, according to the procedure of Anagnostopulos et al\textsuperscript{63}:
\[
\frac{1}{T_m} = 0.002226 + 0.1351 \left( 1 - \chi \right) / \nu_1 \quad (1.9)
\]

where \( \nu_1 \) is the molar volume of plasticiser at \( T_m \).

Bigg and Hill\(^2\) evaluated six plasticisers of widely differing activities and structures. The change in viscosity after 7 days of plastisols prepared from each plasticiser are shown in Figure 1.14 as a function of activity. The larger the value of \( \alpha \), the greater the solvent power of the plasticiser for PVC.

FIG.1.14 - EFFECT OF PLASTICISER SOLVENT POWER ON THE AGING OF PVC PLASTISOLS. FROM REF.<62>.

It appears from this limited study that the aged viscosity of PVC plastisols correlated well with the solvent powers of plasticiser, expressed by the activity parameter \( \alpha \).
In a study by Porrvik\textsuperscript{24}, it was found that a plastisol prepared from a phosphate plasticiser was dilatant while a plastisol prepared to the same solids content using DOP (a phthalate plasticiser) was pseudoplastic.

Phosphate plasticisers cause PVC to swell or dissolve. Porrvik thought there were grounds for believing that dilatancy was due to the fact that the PVC particles swell even at room temperature and so increase the percent by volume of polymer, which in turn would increase dilatancy. To test his theory Porrvik prepared two plastisols one using DOP, the other trixylyl phosphate (TXP). He found that the particles within the plastisol prepared from TXP were swollen to three times the diameter of the particles in the phthalate plastisol system. Porrvik, therefore, attributed the change from pseudoplasticity to dilatancy with plasticiser type to the increase in apparent polymer volume.

The paste polymer used in Porrvik's investigation of the transition from pseudoplasticity to dilatancy contained 80% by weight of particles, with diameters of 0.15 µm, which were swollen to approximately 0.45 µm by TXP. Kaltwasser et al.\textsuperscript{31} in a study of relationships between PSD and rheology found that as the size of the primary particles increases, there is a changeover from pseudoplastic to dilatant flow. The transition occurs at approximately 0.4 to 0.5 µm. It seems more likely, therefore, that the change in rheology observed by Porrvik was due to the change in the size of the primary particles rather than the change in apparent volume fraction.

1.4 PARTICLE PACKING CONSIDERATIONS

1.4.1 Packing of Powders

1.4.1.1 Practical Techniques for Determination of Maximum Packing Density

The first practical treatment of particle packing was carried out by Westman and Hugill\textsuperscript{66} in 1923 at the University of Toronto. Since it
is self evident that the packing of large volumes of particles of uniform size and shape is independent of particle size, Westman and Hugill first developed a piece of equipment capable of achieving the same packing density for uniform size particles, irrespective of their particle size.

In their initial experiments, they evaluated the effect of particle size (PS) and specific gravity (SG) on packing density and void content. They found that spherical particles pack to 40% void content, irrespective of PS and SG, which in their study ranged from 80 μm to 4,800 μm and 2.75 to 11.25, respectively. When spheres pack into a regular cubic arrangement, in which each sphere touches six other spheres, the void content is 48%. When piled into close hexagonal formation, in which there are twelve contacts per sphere, the void content is 26%. The observed void content was in fact 40% and so packing was neither cubic nor close hexagonal. When spheres are piled so that packing in the horizontal layer is hexagonal, but cubic in the vertical layer, the calculated void content is 39.5%. Therefore, from the calculated void values it seems likely that the spherical particles of uniform size pack into horizontal hexagonal layers. Indeed, with the larger particles Westman and Hugill did observe such a packing arrangement. These observations are of great importance and support Hoffman's theory that, for uniformly sized 1.0 μm PVC particles suspended in DOP, particles arrange themselves in hexagonally packed layers which lead to dilatancy at a critical shear rate.

Having established a reliable technique for evaluating packing density and void content, Westman and Hugill carried out experiments with mixtures of two sizes. They found that, as the size ratio of large particles to small particles was increased, more efficient packing was observed, as shown by a higher packing density and lower void content. The improvement in packing density with increasing particle diameter ratio levelled off at around 10:1. The best results (lowest void content) were achieved with 30% small particles with a PS ratio of at least 10:1.
This work was extended to 3 component systems. Limiting cases in which the particle size ratio between the large and medium particles; and the medium and small particles was very large (> 15:1) were considered. They created a solid model in which the mixture of the three sizes, which would confer the highest packing density and lowest void content, could be calculated. Assuming the coarse, medium and fine particles by themselves had the same packing density and the size ratio was very large, optimum packing could be achieved by packing coarse, medium and fine particles in the proportion:

66% coarse; 25% medium; and 9% fine.

Such proportions were calculated as follows, using the solid model due to Westman and Hugill as shown in Figure 1.15.

**FIG. 1.15 - PACKING IN THREE-SIZE SYSTEMS: CALCULATED APPARENT VOLUME (Va) SURFACE FOR VERY LARGE DIAMETER RATIOS. FROM REF (66).**

Since it is difficult to work with solid models, several analytical expressions have been derived to describe the planes shown in Figure 1.15. The composition of a three component system has been described by Westman and Hugill in terms of $x$, $y$ and $z$ where $x+y+z=1$. The three planes which form the minimum $Va$ surface were labelled C, M and F in correspondence to the points through which they pass. These equations are given by:
V_c = ax \hspace{1cm} (1.10)
V_m = x + by \hspace{1cm} (1.11)
V_f = x + y + cz \hspace{1cm} (1.12)

where \( V_c, V_m \) and \( V_f \) are the ordinates of points on the C, M and F planes respectively. \( a, b \text{ and } c \) are the heights at points C, M and F respectively.

The minimum value of \( v \) which is obtained at the junction of the three planes C, M and F is given by:

\[
v = \frac{abc}{ab + bc + ca - (a + b + c) + 1} \hspace{1cm} (1.13)
\]

If the coarse, medium and fine particles by themselves have the same value of \( V_a \) (a measure of void content), then \( a = b = c \) and the minimum apparent volume is given by:

\[
v = \frac{a^3}{(1-a)^3 + a^3} \hspace{1cm} (1.14)
\]

In our example, all three components have the same void content of 37.7 which corresponds to an apparent volume of 1.605. Therefore:

\[
v = \frac{1.605^3}{(1-1.605)^3 + 1.605^3} = 1.057 \hspace{1cm} (1.15)
\]

The proportion of fine, medium and coarse may be calculated as follows:

From (1.10)

proportion of coarse material \((x) = \frac{V_c}{a} = \frac{1.057}{1.605} = 0.66\)

From (1.11)

proportion of medium material \((y) = \frac{V_m - x}{b} = \frac{1.057 - 0.66}{1.605} = \frac{1.397}{1.605} = 0.25\)
From (1.12)

proportion of fine material (z)

\[ z = \frac{V_f - x - y}{c} = \frac{1.057 - 0.66 - 0.25}{1.605} = 0.09 \]

McGeary (1961) extended the research initiated by Westman and Hugill in the 1930's. He confirmed the earlier conclusions that, for a one component system of spheres, the packing density was independent of PS and SG. By considering the possible arrangements of spheres in a packing tube, he proved that such particles pack in horizontal hexagonal planes, as proposed by Westman and Hugill. Such evidence reinforces Hoffman's belief that particles in a unimodal suspension arrange themselves in hexagonally packed layers.

It was found that both the size and shape of the container used for packing influenced the type and density of packing. However, from a practical point of view, the maximum density can be obtained if the container diameter is at least an order of magnitude larger than the sphere diameter.

As in the previous work, McGeary carried out several experiments using binary mixtures of particles and found that the smaller the diameter of the fine particles, the greater the density of the packing. Qualitatively, this behaviour is expected since finer particles would be more able to fill the interstices between the larger particles. McGeary was only able to make such observations using one experimental technique. He vibrated the coarse component until the minimum value was achieved; vibration was stopped. He then added the second component and continued vibration until a minimum volume was achieved. Inferior and lower density packing resulted when the components were blended, poured into the container and vibrated.

McGeary found that packing efficiency decreased rapidly when the ratio of large to small spheres fell below 7 to 1. This value corresponds closely to the triangular pore path formed by any three
close-packed spheres of equal size. For a size ratio of 7 to 1, the small particles can just fit through the triangular pores created by three closely packed large spheres. As such, the small spheres can percolate through the bed of large spheres and thus lead to a minimum void volume. For a size ratio of less than 7 to 1, the small particles are too large to pass through the triangular pore between the large particles and so efficient packing is inhibited.

For ternary packings, the work of Westman and Hugill was confirmed. McGeary achieved maximum density at volume percentages of 66: 25: 10 for coarse, medium and fine components with size ratios of 77: 7: 1 compared with 66: 25: 9 predicted by Westman and Hugill.

1.4.1.2. Theoretical Design for Optimum Packing

In 1931, Furnas developed a mathematical model for predicting the size and volume ratio's of particles necessary to achieve maximum packing. He showed that maximum packing was determined by two factors.

1. The voids in a bed of normally packed material, and
2. The ratio of the size limits in the system

Like Westman, Hugill and McGeary, Furnas worked with ideal systems in which the solid particles of different sizes had the same shape (so that the voids in a bed of sized material were the same for each constituent). He also made the assumption that in a system of many component sizes the ratio between the diameter of particles of successive sizes must be the same for the entire system.

According to Furnas, for a two component system the proportion by absolute volume of the large size ($Z$) may be related to the fraction of voids in a bed of sized material ($V$) as follows:

$$Z = \frac{1}{1+V} \quad (1.16)$$

where the absolute volume of both large and small spheres is unity.
If the diameter of the large particles is \( d_1 \), then the amount of fine material of diameter \( d_2 \) which will exactly fill the interstices of \( d_1 \) is \( 1 - Z \), provided the small particles act as if they are infinitely small. Furnas assumed such an argument and extended it for further sizes to derive the following equation:

\[
\frac{d_1 \cdot d_2 \cdot d_3}{1 + V} = 1 + V + V^2 + V^3 + \ldots \quad (1.17)
\]

Each successive term in the numerator describes the amount of material of successively smaller size necessary to maintain maximum density, assuming that the voids in a bed of sized material are the same for each component size.

This equation can be compared with the solid model due to Westman and Hugill\(^{14}\), as shown in Figure 1.15. For three components each having 37.7% voids, they showed that the following properties would yield maximum density: 0.66 : 25 : 9. Using equation 1.17 the properties necessary to achieve maximum density are as follows:

Coarse (\( d_1 \)) = \[\frac{1}{1 + 0.377}\] = 0.726 \quad (1.18)

Medium (\( d_2 \)) = \[\frac{0.377}{1 + 0.377}\] = 0.274 \quad (1.19)

Fine (\( d_3 \)) = \[\frac{0.377^2}{1 + 0.377}\] = 0.103 \quad (1.20)

\[
\begin{align*}
\% (d_1) &= \frac{0.726}{0.726 + 0.274 + 0.103} = 66% \\
\% (d_2) &= \frac{0.274}{0.726 + 0.274 + 0.103} = 25% \\
\% (d_3) &= \frac{0.103}{0.726 + 0.274 + 0.103} = 9%
\end{align*}
\]
As clearly shown the technique developed by Furnas agrees with the model proposed by Westman and Hugill.

Furnas envisaged a system of broken solids with a certain limiting ratio between the smallest and largest size. He then tried to find the number of intermediate sizes between the smallest and the largest which would yield the maximum possible density for the system. After a series of complicated mathematical derivations and proofs, the following simplified equation was derived:

\[
\frac{\ln V}{(1-V)} = \frac{(2.62 K^\frac{1}{n} - 3.24 K^2/n) \ln K}{(1-0.2-2.62 K^\frac{1}{n} + 1.62 K^2/n) n^2} \quad (1.21)
\]

where \( n \) = one less than the total number of sizes for a system of maximum density

\( K \) = ratio of smallest to largest size

\( V \) = fraction of voids in a bed of sized material

Furnas could find no means of solving this equation directly but was able, via a complicated trial and error method, to plot a series of curves. Each related the limiting size ratio (\( K \)) to the number of size components (\( n+1 \)) in the system which would give maximum density, assuming various void contents, as shown in Figure 1.16.

The use of Furnas's mathematical treatment is best described by considering the following example. For a particular system, assuming an average void content of 0.39, if the minimum PS is 0.01 and the maximum 10, then the size ratio is 0.001. From Figure 1.16, the number of component sizes for maximum density is 2.85.
For an ideal three component system the size of the medium diameter particles would be given by:

\[ d_2 = \sqrt{d_1 \cdot d_3} = \sqrt{0.01 \times 10} = 0.032 \quad (1.22) \]

The proportions of each component may be determined by the following equation as described earlier:

\[ \frac{d_1 \cdot d_2 \cdot d_3}{\text{Total Volume}} = \frac{1 + V + V^2}{1 + V} \quad \text{where} \quad V = 0.39 \quad (1.23) \]

However, in this example the number of components for maximum density is 2.85 and not 3. Therefore, the quantity of the smaller size \((d_3)\) should be reduced to 0.85 of the value obtained by equation 1.23 and the logarithm of the size ratio of the last two terms should be larger than for an even number of component sizes, using the equation:

\[ \log_{10} \frac{d_1}{d_2} = \frac{1}{0.85} \log_{10} \frac{d_1}{d_2} \quad (1.24) \]
Thus the dimension of the fine material \( (d_0) \) will be changed from 0.032 to 0.024.

1.4.2 Packing of Particles Within Suspensions

1.4.2.1. Effect of Bimodal Distributions

The solids concentration for monodispersed suspensions at which the relative viscosity tends to become infinite \((\infty)\) has been studied by many workers. Eilers\(^6\) measured viscosities of concentrated bitumen suspensions with a tube flow viscometer and found that \(\infty\) was approximately 0.74 corresponding to rhombohedral packing. Ting and Luebbers\(^7\) used a Brookfield viscometer to measure viscosities of suspensions of sized glass beads and found that the maximum solids concentration was approximately 0.52 corresponding to a cubic packing. Maron and Krieger\(^8\) investigated both natural and synthetic latices and reported several different values for the maximum solids concentration. For the case of natural latex suspensions, \(\infty\) was approximately 0.74, indicating the densest packing of spheres. However, in the case of Neoprene latex, it ranged from 0.55 to 0.61, indicating any type of packing between cubic and orthorhombic. The disagreement among the reported \(\infty\) may be caused partly by particle size variation, since much of the reported data were not obtained with truly monodispersed systems and also by particle rigidity variations.

To accurately determine \(\infty\) for monodispersed suspensions of rigid particles, Chong et al\(^\text{9}\) measured relative viscosity as a function of solids volume fraction for monodispersed glass beads in low molecular weight polyisobutylene (PIB), using an orifice viscometer. The results of their investigation show that, for such model systems, \(\infty\) is about 0.605, indicating an orthorhombic type of packing which is independent of particle size. Above this concentration, suspensions displayed hysteresis behaviour even at low shear rates, possibly due to volume dilatancy.
Having characterised monodispersed suspensions, Chong et al. investigated the effect of bimodal distributions on relative viscosity as a function of solids content (54 - 74% by volume) using glass beads in PIB. The particle size ratio's in this work were chosen to permit packing of the small spheres in the interstices between the large spheres. The large glass beads had a diameter of 236 μm, the small spheres a diameter of 112.5, 73.8 and 33.0 μm. This led to a diameter ratio of small to large of 0.477, 0.33 and 0.138 respectively. The 112.5 μm particles were too large to fit into the square holes created by the large spheres, while the 33.0 μm spheres could easily thread through the labyrinth of large spheres. In this study, each bimodal suspension had 25% by volume of the total solids as small spheres, since changes in the concentration of small spheres can have a profound effect on viscosity, as shown in Figure 1.17.

**FIG. 1.17 - EFFECT OF PARTICLE SIZE DISTRIBUTION ON THE LOW SHEAR RATE VISCOSITY OF GLASS SPHERES IN PIB. FROM REF. (72)**
Figure 1.18 shows the relative viscosity (at low shear rate) of several bimodal suspensions as a function of solids concentration for several particle size ratios.

**FIG.1.18 - DEPENDENCE OF RELATIVE VISCOSITIES ON SOLIDS CONCENTRATIONS AND PARTICLE SIZE DISTRIBUTIONS. VOLUME FRACTION OF SMALL PARTICLES FIXED AT 25% OF SOLIDS. FROM REF (72)**

![Graph showing relative viscosity as a function of solids concentration for different particle size ratios.](image)

where $\alpha_\text{s} = \text{volume fraction of small particles}$

Chong et al have shown that the relative viscosity ($n_\text{r}$) of a suspension decreases markedly as the PS ratio decreases. For the same solids content, a bimodal distribution of sizes confer a lower viscosity to a suspension than a unimodal distribution. For a bimodal system, $\alpha_\text{s}$ is significantly higher than for a monomodal system and increases with a decrease in the ratio of small to large particles. Surprisingly, Chong et al\textsuperscript{72} found that if the $n_\text{r}$ of unimodal as well as bimodal systems were plotted as a function of reduced solids volume, defined as $\phi/\alpha_\text{s}$, all the data obtained in their work (see Figure 1.18) fell on a single curve, as shown in Figure 1.19.
φ is the volume fraction of dispersed phase and φ₀, determined by extrapolation, is the volume fraction of dispersed phase at which the nᵣ of the dispersion approaches infinity asymptotically. It was found that for even less concentrated suspensions, using data in the literature for pertinent systems, nᵣ as a function of relative solids volume fell on the same master curve. The solid line in Figure 1.19 is represented by the following empirical equation:

\[
\frac{n}{n_0} = \left[ 1 + 0.75 \frac{\phi}{\phi_\infty} \right]^{-a} \quad (1.25)
\]

Such a correlation indicates that the relative viscosity of suspensions of spherical particles is independent of PS and PSD and is only a function of the reduced volume concentration. It is doubtful if such a correlation would be valid for plastisols, since the rheology of suspensions prepared from colloidal size particles (< 1 μm) is influenced by the PS and PSD of the particles, see Section 1.5.
1.4.2.2. Prediction of Viscosity of Multimodal Suspensions.

In the literature there are references\(^ {72,73} \) indicating that the finer particles in a bimodal suspension behave essentially as a fluid toward the coarse particles. The most illustrative work was performed by Fidleris and Whitmore\(^ {73} \) who investigated the settling velocity of a large sphere in a 20% suspension of uniformly sized small spheres. Providing the size ratio, \( R_{s2} \) (small to large) was 1/10 or less, then the large sphere encountered the same resistance to motion when passing through a suspension of smaller spheres as when it passed through a pure liquid of the same viscosity and density as the suspension.

Using this concept, Farris\(^ {74} \) showed that the viscosity of a multimodal suspension of particles can be calculated from the unimodal viscosity data of each size, as long as the relative sizes in question are sufficient to have this condition of zero interaction between coarse and fine. Under such conditions, the behaviour of each size is completely independent of the other.

Farris considered the two parts of the volume making up a suspension of fine particles. The volume concentration of fine filler in the liquid is:

\[
\phi^* = \frac{V_f}{(V_f + V_l)} \quad (1.26)
\]

where \( V_l \) = volume of liquid and \( V_f \) = volume of fine particles.

\( H \ (\phi_f) \) was defined as the relative viscosity of a unimodal system to that of the liquid alone

ie. \( H \ (\phi_f) = \frac{n_f}{n_0} = n_r \quad (1.27) \)

where \( n_0 \) = viscosity of liquid; \( n_f \) = viscosity when filled with fines.
As clearly shown in Figure 1.20, \( H(\omega_f) \) for monodispersed systems is independent of PS. When coarse particles are added to the suspension of fines, assuming zero interaction, the coarse particles can be considered simply as stiffening this already stiffened fluid by an additional factor of \( H(\omega_c) \). This additional factor is the ratio of the new viscosity with coarse and fine particles, \( n_c \), to that of the fluid containing only the fine particles, \( n_f \).

\[
H(\omega_c) = \frac{n_c}{n_f} = \frac{(n_c/n_o).(n_o/n_f)}{[1/H(\omega_c)]} = \frac{n_c}{n_f} \cdot \frac{1}{H(\omega_c)}
\]

\[
(1.28)
\]

where \( n_c/n_o \) becomes the relative viscosity of this bimodal suspension. Hence:

\[
n_o = H(\omega_f) \cdot H(\omega_c)
\]

(1.29)

Farris applied this line of reasoning again and again to obtain:

\[
n_o = H(\omega_1) \cdot H(\omega_2) \cdot H(\omega_3) \cdots H(\omega_n) = \prod_{i=1}^{N} H(\omega_i)
\]

(1.30)

where \( \prod \) denotes product and \( \omega \) is concentration of each size in the apparent liquid. In this system of notation, the sizes are always ordered from smallest to largest as \( i \) goes from 1 to \( N \).
Figure 1.21 illustrates the agreement between the calculated and measured relative viscosity data for a binodal system of near zero size ratio (i.e., one filler fraction has very coarse particles compared to the other, or $R_{12} = 0$) where this assumption of no interaction should be well justified. The calculated relative viscosity data in Figure 1.21 represented by the triangles was derived from the $H_1(\omega_1)$ and $H_2(\omega_2)$ values obtained from Figure 20 using equation 1.30. Also illustrated in this figure are the measured viscosity data for four other size ratio's.

**Figure 1.21 - Effect of PSD on Suspension Viscosity, From Ref. (74)**

The data in Figure 1.21 corresponds to a blend ratio of 25% fine spheres. According to Farris\textsuperscript{74}, using a bimodal blend of $R_{12} = 0$, lines corresponding to $R_{12} = 0.477$ or the other non-zero size ratios in figure 1.21 can be calculated, but the corresponding blend ratios (i.e., the concentration of large to small particles) will be different. In fact, the line for $R_{12} = 0.477$ can be calculated two ways still assuming no interaction. First by having a system of almost all fines or second by having a system of almost all coarse. Similarly, the curves for $R_{12} = 0.313$ and $R_{12} = 0.138$ can be calculated assuming no interaction by selecting more optimized blends, but again the corresponding blend ratio's will be different. From this discussion it appears that all
possible lines between monomodal and best bimodal can be calculated assuming no interaction just by changing the blend ratios. Figure 1.22 illustrates the relationships between the viscosities of bimodal suspensions of zero size ratio for different blend ratios.

FIG. 1.22 - EFFECT OF BLEND RATIO ON SUSPENSION VISCOSITY. FROM REF. (74)

According to Farris, in a bimodal system one obtains the same viscosity regardless of whether \( \sigma_1 \) and \( \sigma_2 \) are interchanged at any concentration of the two sizes. There are two blend ratios that will result in the same viscosity - the second being the reciprocal of the first. When the concentration of large particles equals that of the small particles, \( \sigma_1/\sigma_2 = 1 \) and the suspension viscosity is at a minimum.

Farris's results must be called into question. For bimodal systems, it is important whether a system contains 70% large and 30% small particles, or, 30% large and 70% small particles. In Section 1.4.1, Westman and Hugill\(^{56} \), McGear\(^{67} \) and Furnas\(^{48} \) have all individually shown, by different methods, that the optimum packing of bimodal
systems requires approximately 25% of the dispersion to be present as small particles and not 50%, as suggested by Farris. For bimodal suspensions, Chong et al.\(^7\) have shown that the minimum viscosity is achieved when approximately 25% of the dispersion is present as small particles. Farris also contradicts himself in his paper when he suggests that the change in viscosity of bimodal suspensions, with differing blend ratios, is symmetrical around 50% substitution, as suggested by Figure 1.22. Later in his report he clearly shows that the minimum viscosity for a bimodal system is achieved by 25% substitution of small particles.

1.5. PLASTISOL DESIGN

1.5.1 Effect of Particle Morphology and Particle Size

1.5.1.1. Unimodal Systems

The flow behaviour of a plastisol is determined primarily by the PSD present in the plastisol, the strength of the interaction of the particles between themselves and with the plasticiser, as well as the amount of free plasticiser.

To elucidate the effects of PSD on plastisol viscosity Kaltwasser et al.\(^6\) considered the cases where complete disintegration of secondary structures occurred. Since drying of the latex was carried out at room temperature, the PSD within the plastisol was practically identical to that obtained during polymerisation. For unimodal systems, a reduction in PS from 0.54 to 0.35 \(\mu\text{m}\) was accompanied by an increase in plastisol viscosity as shown in Figure 1.23.

This PS effect confirms the findings of previous workers\(^6,38,1\). For plastisols which are colloidal suspensions (PS < 1\(\mu\text{m}\)) the viscosity does depend not only on volume fraction (as in the case for dilute suspensions of non-colloidal particles, Section 1.3.1) but also on PS, a reduction of which causes a rise in viscosity. This increase is found to be much more pronounced at low shear rates, indicating a contribution
from Brownian and other short range forces. The overall increase in viscosity can be explained as follows: Since the surface area of small particles is greater, the hydrodynamic effect increases with a reduction of PS. In addition, the structural contribution to viscosity depends upon the square of the number of particles, so this contribution rises rapidly with the increasing number of particles per cubic centimetre.

FIG. 1.23 - EFFECT OF PS ON PLASTISOL VISCOSITY. FROM REF.(65)

\[ \text{PS (µm)} \]

- 0.35
- 0.420
- 0.540
- 0.720/0.180
- 0.720/0.150

To date, Kaltwasser et al. have been the only workers to show the transition from structure viscous (pseudoplastic) to dilatant flow with increasing PS, see Figure 1.24a.

As clearly shown, for unimodal systems containing particles smaller than 0.45 µm, pseudoplasticity at low shear rates occurs. For larger particle systems, the flow behaviour becomes dilatant and the particles probably flow in the hexagonal planes proposed by Hoffman. As the shear rate is increased, the time for co-operative movement decreased and eventually flow instabilities occur which lead to dilatancy.
When treating the effect of PS and its distribution on viscosity, it is important to consider the drying and grinding processes during commercial manufacture. If the process is mild, so that the primary latex particles are only loosely bound together, the secondary particles may break down completely to the original primary particles during plastisol preparation. However, when the drying conditions have been severe, sintering of the primary particles may be sufficient to retard or inhibit breakdown and so the suspended particles tend to be the secondary particles. The extent of breakdown may depend on the severity of the shearing conditions during mixing and the interaction with the plasticiser.

The work of Shtarkman and Varonkova° highlights the problems of relating PSD to viscosity. These workers prepared resins of approximately the same PSD but different particle morphology. They spray dried an 0.2 μm PS latex under different conditions using a "Niro"
spray drier. The PSD of these spray dried resins is shown in Figure 1.25.

**FIG. 1.25 - PSD OF 0.2 μm LATEX SPRAY DRIED UNDER VARIOUS CONDITIONS. FROM REF. (76)**

Resin No.1 was composed of highly fused secondary particles which should absorb only small quantities of plasticiser, while resin No.2 was composed of lightly fused particles which have a loose structure and should absorb higher quantities of plasticiser. The rheology of plastisols prepared from these resins is illustrated in Figure 1.26. Resin No.1 produced a highly dilatant plastisol as would be expected from a 4.5 μm unimodal system. Resin No. 2 produced a pseudoplastic material. It seems likely, therefore, that the secondary particles have been broken down, liberating the small primary particles which are responsible for the pseudoplastic flow. If the porous loosely fused secondary particles had remained intact, then the plastisol prepared from resin No.2 would have a higher viscosity and greater degree of dilatancy compared with a plastisol from resin No.1, due to the higher internal porosity of these 7.0 μm particles. It is therefore of paramount importance that plastisol rheology is related to the PSD present in the plastisol at the time of viscosity measurement and not the PSD of the dry paste polymer.
a) Rheological curves for plastisols from resins differing in morphology: 1) fused particles; 2) particles of loose structure;

b) plastisols made from mixtures of resins 1 and 2 in various weight ratios: 90:10 (1); 80:20 (2); 70:30 (3); 60:40 (4); 50:50 (5); 40:60 (6); 30:70 (7); 20:80 (8); 10:90 (9).

1.5.1.2 Bimodal Systems

Referring back to the work of Kaltwasser et al. (see figure 1.23) plastisols consisting of bimodal distributions had much lower viscosities than plastisols containing unimodal distributions. This is achieved mainly by the alteration of void spaces. When spherical particles are suspended in a liquid, the void spaces must be filled;
excess liquid then separates the particles enabling the system to flow.
For spheres of uniform size which are packed as closely as possible
(hexagonal close packing), the void volume is 26%. However, with a
polydisperse system there is less void volume because the smaller
particles fit in the intersices of the larger ones. Therefore, there is
more plasticiser available as the dispersing medium and so for the same
total concentration of plasticiser, the viscosity of a polydisperse
system will be lower.

For bimodal systems, an increase in the amount of fine particles
generally causes the low shear viscosity to decrease at first, pass
through a minimum and then increase, as shown in Figure 1.17, whereas
the high shear viscosity continually falls with addition of fine
particles. Broadening the size distribution by the addition of fines
would cause a drop in viscosity at both low and high shear ratios; but
as the amount of fines is increased, the effect of Brownian forces
becomes more prominent. When the latter effect becomes more significant
than the effect of broadening the size distribution, the low shear
viscosity increases. At high shear rates, the effect of Brownian forces
is negligible and, hence, the viscosity falls continuously. On the other
hand, when the coarse fraction is increased the viscosity at high and
low shear rates falls continuously.

Kaltwasser et al. mixed latices of different PSD and then
prepared plastisols from resins prepared by spray drying these mixed
latices. Unfortunately, their results are a little confusing; for one
bimodal system, increasing the concentration of the smaller PS latex
reduces the plastisol viscosity, while, for another system increasing the
concentration of the smaller PS latex increases plastisol viscosity.
Such results emphasise the importance of characterising latex PS and PSD
and measuring the PSD present within the plastisols. As Kaltwasser et
al did not measure such parameters it is not possible to draw valid
conclusions from their observations. In fact, such results were
presented in order to indicate the complexity of predicting plastisol
rheology from PSD's.
In the previous section, as shown in figure 1.25, Shtarkman and Voronkova found that the plastisol prepared from the highly fused secondary particles was unstable. The plasticiser separated out of the dispersion. However, when 5% of the resin forming the dilatant plastisol was replaced by an equivalent amount of the pseudoplastic paste polymer, separation of the plasticiser was prevented. This showed that the kinetically unstable dilatant system could be supported by a spatial structure of the pseudoplastic type permeating it.

1.5.2 Suppression of Dilatancy.

1.5.2.1. Effect of Particle Size Distribution

Hoffmann reported a discontinuous viscosity rise in monodispersed suspensions of 1.0 μm diameter particles. The work of Kaltwasser et al., Collins and Hoffmann showed that such behaviour can be suppressed.

Kaltwasser et al. highlighted the importance of controlling the width of the latex PSD during microsuspension polymerisation. Normally, plastisols prepared from microsuspension paste polymers display dilatancy due to the narrow unimodal size distribution, typical of such paste polymers. However, Kaltwasser et al. were able to show that a change from dilatant to pseudoplastic flow could be achieved with microsuspension polymers (consisting of particles of comparable diameter), by increasing the width of the distribution, as shown in Figure 1.27.

These results were for room-temperature dried latices where complete disintegration of secondary particles during paste preparation ensued that the PSD within the latex and plastisol were comparable.

For paste polymers dried under more severe conditions, breakdown of the secondary particles may be limited. In such systems, plastisol rheology is controlled by both the primary and secondary particles. Having prepared PVC particle fractions by air classification, Collins and
Hoffmann were able to suppress plastisol dilatancy by broadening the PSD. They found that addition of coarse particles not only had the most pronounced effect in reducing high shear dilatancy, but also reduced the viscosity at low shear rates.

FIG.1.27 - EFFECT OF MICROSPERSION LATEX PSD ON THE TRANSITION FROM DILATANT TO PSEUDOPLASTIC FLOW. FROM REF.(65)

A, INCREASE IN PSD WIDTH

B, SUPPRESSION OF DILATANCY

The flow curve of PVC plastisols can therefore be modified by careful control of the PSD within the plastisol, through changes in polymerisation techniques, spray drying conditions and milling severity.
1.5.2.2. Effect of Plasticisers and Surfactants.

To produce plastisols with certain rheological characteristics, commercial manufacturers carefully control the particle morphology, PS and PSD of their systems. Unfortunately, the type of plasticiser used to disperse their paste polymers can seriously affect rheology by changing the PS and PSD. For example, particle swelling, dissolution and breakdown to liberate primary particles may be accelerated by more active plasticisers. For example, particle swelling, dissolution and breakdown to liberate primary particles may be accelerated by more active plasticisers. Porväröhöö showed that swelling of particles by more active plasticisers can raise the solids volume fraction and increase PS (of an 0.15 µm paste polymer) above 0.45 µm. Under certain conditions, these effects can impart dilatancy. It is therefore, advisable to use low activity plasticisers if suppression of dilatancy is essential.

Variation of the residual emulsifier content on the PVC can also effect viscosity by two distinct mechanisms:

1) According to Collins and Hoffmann, interaction between the surfactant and the polymer / plasticiser interface can lead to interparticle repulsion, resulting in high viscosities at low shear rates. Hoffman has suggested that electrical forces (due to the surfactant) and Van der Waals forces act to keep the particles in layers. When the shear stress overcomes these forces, the layer like structure is destroyed and dilatancy results. If the interparticle repulsion due to the surfactant is large enough, dilatancy may be suppressed by the emulsifier as the particles are held in hexagonal planes.

2) Kaltwasser et al have shown that for a large coating thickness, macromolecular dispersants become sterically active. Agglomerates of primary particles, therefore, remain completely intact within the plastisol due to the strongly solvated shell of DOP around the PVC. As a result of the reduced breakdown of agglomerates during plastisol preparation, such plastisols had a broad PSD and were pseudoplastic. With a smaller coating layer, Kaltwasser et al found that secondary particle breakdown occurred generating a narrower
unimodal distribution of small particles which conferred dilatancy to the plastisol.

For systems where secondary particle breakdown leads to dilatancy, a high residual emulsifier content may limit secondary particle breakdown and, therefore, reduce dilatancy.

1.5.3 Design for Certain Applications

Commercially, paste polymer resins may be described as being high, medium or low viscosity resins. Underdal et al. measured the rheology and the PSD of plastisols prepared from these materials in an attempt to characterise the systems.

The high viscosity resins had a narrow monodisperse primary PSD. The mean diameters of two typical resins were 0.23 and 0.46 \( \mu \text{m} \). The 0.23 \( \mu \text{m} \) resin gave a higher viscosity, especially at low shear rates. For these systems, the 7.0 \( \mu \text{m} \) secondary particles accounted for approximately 28% of the distribution by weight and were considered to be of little significance, the paste viscosity being determined by the small primary particles.

The medium viscosity resins all had broad polydisperse primary PSD's with a median in the range 0.8 - 1.5 \( \mu \text{m} \) and a wide distribution of secondary particle sizes. Low Brookfield viscosities were attributed to the primary PSD. The polydispersity, however, was not sufficient to avoid dilatancy at high shear rates.

Low viscosity resins had a broad primary PSD which was bimodal in some cases. The size and concentration of secondary particles was usually larger than for the high and medium viscosity resins. Both secondary and primary particle sizes were considered important in avoiding dilatancy.
1.6 ADDITIVES

1.6.1 Viscosity Depressants and Modifiers.

1.6.1.1. Adhesion Modifiers (Epoxy-phenolic resins)

Protective coatings may be obtained from paint materials containing polyvinyl chloride as a binder. The use of such macromolecular binders for production of paint has made it possible to include plastisol materials, which give coatings of high resistance to aggressive chemicals. There are two methods which may be used to promote the adhesion of these coatings. The two coat process is based on the use of an interlayer to the substrate and then application of the plastisol material. In the one coat process, modifiers are added to the plastisol material and in this way coatings with suitable adhesion to the substrate are obtained. Of the two methods, the one coat process is technologically more economical. However, care must be taken due to the adverse influence of modifiers on plastisol viscosity.

Makarewicz considered the effects of incorporating an epoxy-phenolic resin into a plastisol. The viscosity rose sharply with modifier incorporation; Makarewicz attributed this to the formation of three dimensional gel structures and the relatively high viscosity of the epoxy-phenolic resin which caused thickening of the plastisol. He did not characterise the PSD of the plastisols and made no attempt to relate modifier performance to changes in the PSD of the plastisol.

1.6.1.2. Viscosity Depressants.

1.6.1.2.a Glycol Ethers.

Plastisol viscosity may be lowered by the addition of a surface active agent. Polyethylene glycol derivatives and other surfactants are known to be effective. Depending on formulation, 0.5 to 1.5 phr of a surfactant will generally lower the viscosity by 30-40%.
Ponizil sought to explain the action of depressants and viscosity controllers. He selected as an example, comparatively simple systems from a group of glycolethers, as shown in figure 1.28.

FIG. 1.28 - COMPOUNDS USED AS VISCOSITY CONTROLLERS. FROM REF.(79).

<table>
<thead>
<tr>
<th>File No.</th>
<th>Compound (abbreviated form)</th>
<th>Density at 25°C</th>
<th>μm Viscosity at 20°C</th>
<th>Boiling point [°C]</th>
<th>Manufacturer</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Ethylene glycol-monoethyl ether (EM)</td>
<td>0.963</td>
<td>1.4021</td>
<td>1.72</td>
<td>124.5</td>
</tr>
<tr>
<td>2</td>
<td>Ethylene glycol-dimethyl ether (ED)</td>
<td>0.928</td>
<td>1.4076</td>
<td>2.05</td>
<td>155.1</td>
</tr>
<tr>
<td>3</td>
<td>Propylene glycol-monoethyl ether Dowanol PM</td>
<td>0.919</td>
<td>1.4036</td>
<td>1.73</td>
<td>120.6</td>
</tr>
<tr>
<td>4</td>
<td>Dicapryl glycol-dimethyl ether Dowanol DPM</td>
<td>0.951</td>
<td>1.4190</td>
<td>3.33</td>
<td>190.0</td>
</tr>
<tr>
<td>5</td>
<td>Tripropylene glycol-monoethyl ether Dowanol TPM</td>
<td>0.965</td>
<td>1.4320</td>
<td>6.16</td>
<td>243.0</td>
</tr>
<tr>
<td>6</td>
<td>Addition product of 1 mol butanol, 3 mols PO and 4 mols EO (BPCO)</td>
<td>1.4402 (25°C)</td>
<td>19.8</td>
<td></td>
<td></td>
</tr>
<tr>
<td>7</td>
<td>Addition product of 1 mol palmitic acid and 3 mols PO (KPCO)</td>
<td>1.4472</td>
<td>42.1</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

He chose a PVC paste polymer characterised by coarse secondary particles and the absence of independent primary particles. This material did not form a plastisol immediately after mixing with DOP, but a dispersion of sand-like character. Only after several hours did the dispersion assume the character of a plastisol.

Measurement of plastisol viscosity as a function of time allowed stability to be investigated. Plastisol viscosity initially fell but then increased gradually with time, as shown in figure 1.29. Ponizil attributed the behaviour of the plastisol to the resistance of the secondary particle skin to failure. This conclusion was later confirmed by sedimentation, refractometric and solvation measurements.

After paste preparation swelling of the secondary particles occurs, depending on the strength of the surface skin. As a consequence of the swelling pressure the surface skin bursts and the agglomerates...
split up into small primary particles. For Ponizil's plastisols, such a change in PSD improved the packing efficiency of the system resulting in a fall in viscosity.

FIG. 1.29 - TIME DEPENDENCE OF PLASTISOL VISCOSITY. FROM REF.<79>.

![Time Dependence of Plastisol Viscosity](image)

- a. 0% EM
- b. 0.5% EM
- c. 1% EM
- d. 1.5% EM

The presence of EM seemed to cause an increase in the decomposition rate of secondary agglomerates, this was shown by a shift in the viscosity minimum to lower shear rates as shown in Figure 1.29. Thus, the lowering of viscosity was again being caused by a change in the size distribution of particles, which progresses faster, the more EM is present in the plastisol. However, the primary particles freed from the agglomerates were swelling very quickly, which led to a faster rise in viscosity at extended times. Ponizil expanded his work to consider the compounds listed in Figure 1.28 and found that they all influenced particle breakdown. This family of viscosity controllers may be used to accelerate the breakdown of secondary particles during paste preparation to correct dispersion problems. Under these conditions, paste rheology would probably be controlled by the primary PSD, although viscosity ageing would be accelerated.
1.6.1.2.b Cetyl Alcohol and Sytol AF.

Khanna studied the ageing behaviour of PVC pastes. Like Ponizil he was interested in the effect of additives on the ageing stability of PVC plastisols. He found that plastisols prepared from modified PVC latices exhibited lower initial viscosities and higher ageing stability. Examination of plastisols prepared from cetyl alcohol and Sytol AF modified latices by optical microscopy revealed significant breakdown of secondary particles compared with the unmodified system, confirming the work of Porrvik.

1.6.2 Fillers.

The amount of literature regarding the effect of filler incorporation on plastisol rheology is extremely limited. To date, all investigations of which I am aware, have been concerned with the rise in viscosity, at fixed shear rates, achieved by incorporation of fillers. The effect on the flow curve has not been considered nor have particle packing considerations. At the present time it is therefore impossible to predict changes in rheology due to the combined effects of filler plasticiser absorption, PS and PSD. None of the research workers have characterised the PS and PSD of the paste polymers used in their studies and, therefore, I have exercised caution in the conclusions I have drawn from their work.

Within the plastisol industry it is generally believed that plastisol viscosity increases with filler content and the plasticiser absorption of the filler. Wypych devised a mathematical relationship between filler plasticiser absorption and plastisol viscosity as shown in Figure 1.30.

Many fillers of different PN, PS, PSD and chemical composition were tested. Wypych believed that viscosity depends directly on the PN of the filler as suggested by the high correlation coefficient (r). The PS and PSD of both filler and paste polymer were not considered important. Wypych's equation suggests that plastisol viscosity always
increases with filler incorporation. Farris\textsuperscript{74} has shown conclusively, by experimentation and mathematical modelling, that suspension viscosity may fall dramatically when a second family of particles is added to a dispersion. Although the volume fraction of the system rises, viscosity may fall due to one family of particles packing into the interstices between the larger particles.

FIG. 1.30 - RELATIONSHIP BETWEEN PLASTICISER NUMBER (PN) AND VISCOSITY OF PLASTISOLS CONTAINING 10 PARTS OF FILLER. FROM REF. (80).

![Graph showing the relationship between plasticiser number (PN) and viscosity of plastisols containing 10 parts of filler. The equation is given as $n_{10\,\text{percent}} = 0.02545\,\text{PN} + 3.348\,\text{N}_m^{-2}, r = 0.944$.]

Skalski et al\textsuperscript{1} have shown that no general relationship exists between the plasticiser uptake of fillers and their mean PS. However, a correlation was established between these two factors for individual groups of fillers with the same chemical composition and thus the same kind of structure, as shown in Figure 1.31.
Skalski et al believe that plasticiser absorption is a function of filler PS, PSD, shape, structure formation and surface characteristics. It is therefore possible for two fillers to have similar plasticiser absorption characteristics but a different average particle size. According to Wypych when such fillers are incorporated into a plastisol they should behave in a similar way; this is unlikely. As demonstrated in previous sections of this literature search, suspension rheology is closely related to the PS and PSD of the suspension.

A reduction in filler PS increases the surface area of filler exposed to the plasticiser. It would therefore be expected that plasticiser demand should rise continuously with a reduction of filler PS. Shashkova et al have shown that plastisol viscosity does rise as expected. However, there is an optimum size below which plastisol viscosity starts to fall, as shown in Figure 1.32.
FIG. 1.32 - EFFECTS OF FILLER PS ON PLASTISOL VISCOSITY. FROM REF. (93).

![Graph showing reduction in particle size vs. IR transmittance.]

Such behaviour has been attributed to problems in dispersing the chalk filler. Below a critical size, it becomes difficult to completely wet out the filler surface due to particle agglomeration. Plasticiser demand is therefore reduced and viscosity falls. Examination of the IR adsorption spectra of plastisol samples revealed the presence of a hydrogen bond detected at 3600 cm⁻¹, the intensity of which varied with plastisol viscosity. It was therefore suggested by Shashkova et al. that the magnitude of the IR peak was a measure of the SA of the filler which was in contact with the plasticiser. The adsorption was at a maximum when plastisol viscosity was at its peak, as shown in Figure 1.32.

1.6.3. Rheology Modifiers

1.6.3.1. Improvement of Ageing Stability

Ageing stability may be influenced by the emulsifier system used to stabilise the latex during polymerisation. Anionic surfactants are the most commonly used; with alkali metal or ammonium salts of long chain fatty acids; sulphonates and sulphates or salts of dialkyl sulphosuccinates being most frequently mentioned in the patent literature²²,²³. Cosurfactants are also often mentioned, usually consisting of long chain normal aliphatic acids, alcohols or non-ionic
The formulation of emulsifier systems is still largely an art based on experimental experience although obviously many helpful relationships have been developed.

According to a U.S. patent, due to Joyce, the increase in plastisol viscosity with time may be suppressed by the addition of 0.5 - 10.0 parts per hundred of monohydric aliphatic alcohols having 4 - 14 carbon atoms. Shtarkman et al have found that improved plastisol stability may be achieved when the PVC is covered with ionogenic emulsifiers. It was proposed that stability is due to a strongly solvated shell of DOP around the PVC, resulting from the higher polarity of the absorbed emulsifier. Particular care must be taken when selecting sulphonate emulsifiers if ageing stability is of paramount importance. Berger and Brown did not recommend the use of alkyl sulphonates as emulsifiers for the production of paste forming PVC because they induced a higher rate of plasticiser absorption compared with alkyl amyl sulphonates.

While the effect additives have on plastisol viscosity has been studied, the mechanism concerning the viscosity change is not well understood. Many questions remain unanswered. For example, is it necessary to invoke an electrical phenomenon in explaining the effect on viscosity? Collins and Hoffmann wondered whether these phenomenon can be explained by the change in degree of swelling. Since the volume fraction of solids in a plastisol is so high, one is on a very steep portion of the viscosity - volume fraction curve, Figure 1.5. Small changes in volume fraction (by swelling and deswelling) may have a considerable effect on viscosity. Since alcohols and soaps are non solvents for PVC, it is possible that they may act at the particle surface by affecting the extent of swelling. Collins and Hoffmann suggest that light scattering techniques may be used to investigate the effect of additives on particle swelling behaviour.
1.6.3.2. Control of Pseudoplasticity

In certain instances emulsifiers are post added to a polymerised PVC latex prior to spray drying purely to modify subsequent paste viscosity characteristics. Collins and Hoffmann\(^{39}\) have clearly shown that a paste polymer coated with a linear sodium alkyl sulphate emulsifier imparts a higher low shear viscosity to a plastisol than a branched sodium alkyl sulphate. Using an 0.73 \(\mu\)m monodispersed latex produced without using a surface active agent\(^{39}\) Underdal et al\(^{39}\) have demonstrated the dependence of low shear viscosity on emulsifier content. Part of this latex was spray dried without adding emulsifier, to the two other parts sodium dodecyl sulphate, SDS, and sodium dodecyl ether sulphate with 6 ethoxy groups, SDES (2.8 mols/Kg polymer) were added. Measurements of the viscosity of plastisols prepared from these materials have demonstrated the dramatic effect of emulsifier type, as shown in Figure 1.33.

FIG. 1.33 - EFFECT OF EMULSIFIER (70 phr DOP). FROM REF. (90).

Using the same paste polymer it is, therefore, possible to control pseudoplasticity as required by blending the two emulsifiers.

Underdal et al\(^{39}\) have also demonstrated the effect of humidity on plastisol viscosity. They prepared plastisols from paste polymers which
had been stored at different humidities, plastisol viscosity appeared to fall with increasing moisture content. This is in stark contrast to a Russian paper in which Merinov et al.\(^1\) claim that viscosity at low shear rates rises with increasing moisture content. The rise in viscosity is attributed to a reduction in zeta potential caused by the higher moisture content. Such observations not only conflict with Underdal et al.'s work on moisture content but also Collins et al.\(^\text{**}\) who have demonstrated that a decrease in interparticle repulsion (measured by a fall in zeta potential) causes low shear viscosity to fall, not rise.

1.7. PARTICLE SIZE MEASUREMENTS.

When considering the task of particle size analysis of PVC resins it soon becomes apparent that no one currently available technique can be successfully used for all types of product, as no single technique can quantify a PS range of 0.01 to 1,000\(\mu\). Indeed, when faced with the problem of obtaining a full PSD on a single sample of paste forming polymer it is usually recognised that a combination of techniques, with its attendant difficulties, is required. An indication of the particle sizes involved is given in Table 1.4.

**TABLE 1.4 - PVC PARTICLE SIZE MEASURABLE BY VARIOUS TECHNIQUES. FROM REF.(7).**

<table>
<thead>
<tr>
<th>Product type</th>
<th>Unseeded emulsion latex</th>
<th>Microsuspension latex</th>
<th>Paste polymer</th>
<th>Suspension mass</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>10(^{-2})</td>
<td>10(^{-1})</td>
<td>-10</td>
<td>10(^2)</td>
</tr>
<tr>
<td>Technique</td>
<td>Microscopy</td>
<td>Sieving</td>
<td>Sedimentation (gravimetric)</td>
<td>Sedimentation (centrifugal)</td>
</tr>
</tbody>
</table>

- 67 -
In a review by Clark, the various particle size characterisation techniques are considered with special reference to PVC resins. I do not propose to duplicate this review here, but will give a brief outline of the various techniques available. The special problems encountered when attempting to characterise the PSD within a plastisol will be discussed in section 3.1.2.

1.7.1 Microscopy

The use of a microscope is the most direct method of measuring PS. The direct observation of particles may be advantageous, although subjective assessment of particle size may be necessary for non-spherical particles. The unrefined technique is very time consuming and laborious as at least 100 particles need to be individually sized in order to obtain an accurate result. Many more particles may need to be measured for systems with a wide PSD. The range of particle sizes that may be measured is almost unlimited, for emulsion latex particles (<0.01 - 0.2 µm diameter) electron microscopy is required to achieve the necessary resolution. Although many simple devices have been designed to assist measurement and counting of particles in a photomicrograph, the task remains laborious unless image analysis can be employed.

1.7.2 Sieving

Sieving is the most widely used and probably the easiest method of determining the particle size of PVC powder. Techniques used include hand shaking, mechanical shaking, air-jet apparatus and wet sieving. The major problem encountered with sieving PVC is that of static electricity build-up on particles which causes them to agglomerate, thus giving a false result. The use of an antistatic agent, usually alumina, or the wet sieving technique are used to overcome this problem.
1.7.3 Sedimentation Techniques

The use of sedimentation techniques for particle size analysis is based on the fact that particles falling through a viscous medium quickly attain a terminal velocity and settle at this constant rate for the remainder of their descent. For spherical particles falling singly in an infinite sea of fluid, the relationship between particle diameter and the properties of the system is given by Stokes' equation:

\[
d = 10^4 \frac{18nh}{(\rho-\rho_o)gt}
\]

(1.3.1)

where \(d\) is the particle diameter (micrometers), \(n\) is the fluid viscosity (poise), \(h\) is full height (cm), \(t\) is time (secs) and \(\rho\) and \(\rho_o\) are the densities of the solid and liquid respectively (g/cm\(^3\)).

Many different techniques exist for determining PSD from sedimentation velocity. A major division occurs between techniques using normal gravitational forces and those using centrifugal forces to increase sedimentation rates.

Using gravitational techniques the maximum PS which may be measured is limited by the difference in density between the solid and the fluid (and is approximately 100 \(\mu\)m for PVC). The smallest size capable of accurate measurement is limited by Brownian and thermal motion of particles and is usually in the order of 1 - 3 \(\mu\)m. Determination of the PSD within a liquid can be achieved using a micromeritics Sedigraph 5000 (Micromeritics, Coulter U.K.). Using an X-ray measuring system, this system is claimed to operate over a PS range of 0.18 - 50 \(\mu\)m. To minimise analysis time the position of the sedimentation cell, with respect to the finely collimated X-ray beam, is continuously changed. The PSD of a dry PVC powder may be characterised using a Sharples Micromerograph which uses a gas as the sedimentation fluid. The sample is injected through a deagglomerator into the top of a 7 foot column by a blast of compressed nitrogen. The particles then fall down the sedimentation tube onto the pan of a servo - electric
balance and the accumulating weight is recorded against time on a strip chart. The makers of the instrument claim a PS range of 1 to 250 μm.

The application of centrifugal forces to the sedimentation technique have enabled the minimum measurable size to be reduced. By this method, the settling rate is increased and interference from factors such as convection, diffusion and Brownian motion reduced. The calculation of data is complicated by the fact that the sedimentation forces increase as the distance the particles have travelled from the axis increases. Techniques used to reduce this complication include the use of a long armed centrifuge or the two layer technique. This latter technique involves introducing a thin layer of concentrated suspension into the surface of the sedimentation (spin) fluid - thus causing all particles to start at the same distance from the axis. Unfortunately, this technique can suffer from problems due to 'streaming', which is the name given to unstable, non-uniform sedimentation. The technique has therefore been extended to three layers or to a buffered start in an attempt to overcome 'streaming' problems.

In the Joyce - Loebl Disc Centrifuge the basic techniques have been refined and automated in an attempt to speed up and reduce the tedium of the manual methods. These involve removal of samples from the centrifugal cell at fixed times. A continuous trace of turbidity versus time can be recorded, as the instrument is fitted with a photoelectric detector operating at a fixed radius from the centre of the transparent disc cell. The photoelectric detector must, however, be carefully calibrated as PS and therefore optical properties are continually changing with time. Other instruments include the Kaye Disc Centrifuge which uses only a phototechnique for following sedimentation rates.

The Ladal X-ray Centrifuge uses the same technique as employed in the Sedigraph gravitational instrument.
1.7.4 Electrical Sensing Zone Method (Coulter Principle)

The Coulter technique involves the preparation of a dilute dispersion of the material to be examined in a electrolyte solution. The suspended particles are then caused to pass through a small orifice, on either side of which is immersed an electrode. The particle concentration should be low enough to ensure that most particles transverse the aperture one at a time. As each particle passes through the orifice, it displaces a quantity of electrolyte equal to its own volume. This displacement changes the resistance between the two electrodes which generates a voltage pulse proportional to the size of the particle passing through. The pulses are amplified, sized and counted. The FSD of the suspended phase can then be determined from the derived data. The Coulter Counter operates over a particle size range of 1 - 400 μm, although several different orifice sizes may be required. The main limitation of this instrument is at the lower end of the FSD range for any given orifice tube. The instrument can pick up electrical interference ('noise') which can result in an unduly high particle count in the lowest two size channels. Unfortunately, noise cannot be completely eliminated and may, to some extent, be inherent in the measuring technique itself.

1.7.5 Optical Techniques

The modulation of light by particles placed in its path can be used in several ways to obtain particle size information. When a particle is of much greater size than the wavelength of the incident radiation, diffraction occurs. The Malvern (2200/3000) Particle Sizer uses a He/Ne laser and has a measurement range of 1.2 to 500 μm. When the laser beam falls on a spherical or non-circular particle, a diffraction pattern is formed, whereby some of the light is deflected by an amount dependant upon the size of the particle.

If particles of different diameters are present in the laser beam then, after suitable optical treatment, a series of 'focused' rings will be generated at various radii. Each focussed ring is a function of a
different PS. In the Malvern Particle Sizer the diffraction pattern is measured by a multi-element detector, consisting of a series of detectors of increasing radius. The detectors are rapidly scanned electronically and the output taken to a signal processor to form the basis of the PSD data. With suitable computation multimodal PSD's can be measured.

When the wavelength of the incident radiation is greater than or equivalent to the diameter of the particles, then scattering occurs. Leeds and Northrop have recently developed a light scattering instrument which is capable of measuring particle sizes down to 0.1 μm.

A further optical technique used for PS analysis is that of light blockage. Instruments based on this principle are produced by HIAC Corporation and Royco Instruments Inc. A dilute slurry of the sample to be examined is pumped through a cell, through which light passes to a photodetector. Pulses generated by the 'shadows' of the particles are processed to give the PSD. The measurable size range is 1 to over 1000 μm.

1.7.6 Application of Techniques to PVC Latices and Plastisols

The Joyce Loebl Disc Centrifuge has been used for many years to characterise the PSD of PVC latices. It is particularly suitable because such latices are usually stabilised by surfactants and so streaming is less of a problem. It is easy to present the sample as a uniform dispersion. The instrument is capable of detecting particles between 0.01 and 10.0 μm; it is therefore able to characterise the whole latex PSD. Problems may, however, be encountered if the difference between the largest and smallest particle is greater than an order of magnitude.

Underdal et al sought to determine the PSD of commercial PVC paste polymers because they were trying to establish correlations between plastisol rheology and PSD. Unfortunately, due to the broad distribution of sizes within these systems, they were unable to cover
the whole PS range using one instrument. A Coulter Counter (mod. TA2) was used to measure the secondary particle size distribution. The resins were dispersed in dioctyl phthalate (DOP) and diluted in an electrolyte consisting of 4% ammonium thiocyanate in isopropanol. The instrument range was 1.76 to 71.2 μm. Erronious results may have been obtained because a pre-condition of selecting the technique is that the particles should not be soluble in the electrolyte or conduct electrical current. To measure the distribution of primary particle sizes, they found it necessary to use an analytical centrifuge after dispersing the powder by ultrasound in a 10% ethanol solution. Sizes between 0.15 and 1.5 μm were registered. This work demonstrates several of the problems encountered when attempting to measure a broad PSD within a non-aqueous suspension. Correlations between plastisol rheology and PSD may be subject to error because the PSD of a dry resin can be significantly altered when the resin is mixed with a plasticiser. The shear created during mixing and the solvation action of the plasticiser can influence the PSD of the PVC resins. Underdal et al's correlations assume that the PSD within a plastisol may be represented by the distributions measured by a combination of the centrifuge and Coulter instruments. Such an assumption must be called into question because the sample tested in the centrifuge was not subjected to the mixing and solvation effects experienced during plastisol preparation.

In a recent paper, Moran** applied a photometric centrifuge technique to the particle size analysis of two commercial paste polymers. This method may overcome the problems encountered by Underdal et al because the instrument can cover the whole PS range for certain paste polymers dispersed in a plasticiser. The primary disadvantage of the technique is that the laws of geometric optics breakdown as the PS approaches the wavelength of the incident radiation. However, this breakdown can be accounted for by the insertion of an extinction coefficient (K) into the calculations. Unfortunately, Moran was unable to obtain a range of monodisperse PVC latices to calibrate the system and determine K. He therefore, determined K using the theory developed by Mie**, which elucidates the fundamental relationships between light extinction and particle size. In his paper he used this
technique to characterise the PSD of two paste polymers. The technique seems reproducible and further work is being undertaken to substantiate the accuracy of the method. His main problem seems to be the difficulty in obtaining monodisperse PVC standards to evaluate and calibrate the system. Application of this technique to paste polymers may also be difficult due to:

(i) The broad PSD of commercial paste polymers.

(ii) Calibration problems, and

(iii) Changes in the spin fluid required for different PS ranges

Hoffmann and Garcia22 overcome the problems encountered in the particle size analysis of plastisols by the application of the Sedigraph 5000. This instrument is capable of covering the PS range of 0.15 to 70.0 μm which is encountered in many PVC paste polymer resins. They used this instrument to highlight the shifts in PSD which occur during heat ageing of a plastisol. They used dibutyl sebacate as the suspending medium due to its low density, activity and, most importantly, its viscosity.

1.8 CRITICAL PRESSURE MERCURY POROSIMETRY

In a series of papers, J.A. Davidson applied Mercury Porosimetry to the characterisation of the porosity within Mass and Suspension PVC powders.

In his first paper113, he demonstrated that low melting alloy intrusion experiments offer a convenient and simple technique to aid the interpretation of mercury intrusion curves. By substituting a low melting alloy (Cerrelow • 117, mp 47°C) for mercury in an intrusion experiment, it is possible to "freeze" the intrusion process at any given pressure merely by cooling the alloy below its freezing point. He was then able to section the frozen sample and examine it under the
microscope to see how the metal was entering the structure. From his study of two PVC samples, produced by mass or suspension polymerisation (average PS = 136 and 253 μm), he found that bed depacking rather than bed penetration was the mechanism of intrusion.

In any determination of internal porosity (intraparticle porosity) by mercury porosimetry, the penetration curve must be interpreted in such a way that the contribution of inter and intraparticle porosity may be separated. In his second paper114, Davidson evaluated the performance of two techniques which enable such a distinction to be made. The first relies upon the control of interparticle bed packing by mounting the particles upon a transparent adhesive substrate. The pressure at which interparticle penetration occurs (critical pressure) is measured by observing the penetration process directly in a microscope pressure cell (TAPE METHOD). A mercury intrusion experiment is then run on a similarly mounted sample and the value of critical pressure, obtained previously, used to define the interparticle volume.

In the second method, the critical pressure is determined by running a mercury intrusion experiment on a powder sample whose interparticle volume has been filled with a wetting agent such as DOP (DOP FILLED METHOD). Such a technique depends upon the observation made in his previous paper that bed depacking rather than bed penetration is the initial step of the penetration process.

FIGURE 1.34 - MERCURY INTRUSION CURVES. FROM Ref. 114
Figure 1.34 shows the use of critical pressure in the characterisation of intraparticle porosity. Intrusion volumes below the critical pressure are due to bed depacking, volumes above the critical pressure are due to intraparticle porosity.

Total intraparticle volumes determined by both of these methods were compared with those obtained by the uptake of a wetting agent. Although Davidson found an excellent degree of correlation between the two methods, the DOP uptake volumes were found to be high by a constant amount. This was demonstrated to be due to plasticiser being retained in the interparticle volume. The non-linear relationship between DOP uptake and critical pressure mercury porosimetry may indicate the pressure of very fine pores, not filled by mercury, which may be reduced in size by compression of the fragile PVC particles. Davidson found that the volume of critical pressure was different for each sample and did not correspond to any feature observed in the penetration curve.

In his final paper, Davidson checked the validity of the Critical Pressure Technique using image analysis and DOP absorption. When evaluating the porosity of mass and suspension PVC resins Davidson experienced problems in obtaining satisfactory agreement between the DOP absorption of mass resins and mercury porosimetry. He attributed these problems to the large number of fines present in these resins. He believed that DOP absorption results could be prejudiced due to plugging in the screens of the filter tubes when numerous fines are present. For SiC, anomalous results were obtained when the particle size fell below 70 μm. He also believed that the rough surface of mass resins may retain plasticiser.

Davidson concluded his work by pointing to the high correlation between image analysis and critical pressure mercury porosimetry. The use of image analysis, at least for PVC, should enable a porosity distribution on a particle-particle basis to be made. Such an optical technique negates the problems in the DOP uptake and mercury porosimetry techniques where pore size, retention of plasticiser and distortion lead to anomalous results.
1.9 AIM OF STUDY

The purpose of this study is to investigate the factors controlling the rheology of filled and unfilled PVC plastisols. At the present time, commercial manufacturers take great care to control the particle size (PS) and particle size distribution (PSD) of a polymer latex, as these exert a strong influence over the flow characteristics of an uncompounded plastisol. However, the fundamental mechanisms controlling viscosity are not clearly understood. By measuring the viscosity over an extended shear rate range and the PSD of PVC plastisols prepared from carefully selected paste polymers, the combined effects of polymerisation technique, emulsifier type, spray drying, milling and plastisol preparation technique on plastisol rheology will be established. Such an understanding will enable paste polymer manufacturers to design plastisol systems more efficiently.

Having elucidated the factors controlling the rheology of unfilled systems, the second objective is to quantify the effect of filler incorporation on plastisol rheology. Unfilled plastisols are seldom used, for many applications plastisols contain mineral fillers which improve the product physical properties and reduce cost. These fillers may have a PS similar to that of the paste polymer. Addition of these materials can drastically change the order of performance between grades. Unfortunately, it is not possible to predict how a particular plastisol system will respond to filler additions, as the interrelationships between filler plasticiser absorption and particle packing considerations have received little attention in the literature. By considering the effect of various fillers on the rheology of filled plastisols prepared from carefully selected paste polymers, it should be possible to evaluate the factors controlling filled plastisol rheology.

From the models which will be developed in this work it is hoped that manufacturers will find it easier to design paste polymers which confer specific rheological properties to plastisols.
Compounders should also find it easier to predict the response of a plastisol to filler addition by considering filler plasticiser absorption and particle packing efficiency.

A statistical approach which enables the flow curve of a plastisol to be generated from volume fraction and PSD measurements will be presented. The predictive power of this model will be investigated.
CHAPTER 2: EXPERIMENTAL

2.1 MATERIALS

The polymers used in this study are listed in Tables 2.1 and 2.2.

TABLE 2.1 - PASTE POLYMER CHARACTERISTICS

<table>
<thead>
<tr>
<th>Polymerisation Technique</th>
<th>Code</th>
<th>Latex PSD (μm)</th>
<th>Porosity of Secondary Particles (g/cc)</th>
<th>Drying Severity Outlet Temp(°C)</th>
<th>Milled</th>
<th>Emulsifier Content (%)</th>
<th>K+ Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Conventional Emulsion</td>
<td>E1</td>
<td>Narrow Unimodal</td>
<td>0.14</td>
<td>80</td>
<td>Yes</td>
<td>1.0</td>
<td>69</td>
</tr>
<tr>
<td></td>
<td>E2</td>
<td>0.15 Unimodal</td>
<td></td>
<td>68</td>
<td></td>
<td></td>
<td>69</td>
</tr>
<tr>
<td>Seedled Emulsion</td>
<td>S1</td>
<td>Bimodal* 0.25 and 1.00</td>
<td>0.10</td>
<td>60</td>
<td></td>
<td>2.0</td>
<td>73</td>
</tr>
<tr>
<td></td>
<td>S2</td>
<td>Bimodal* and 0.70 (33% small particles)</td>
<td>0.10</td>
<td>66</td>
<td></td>
<td>1.0</td>
<td>70</td>
</tr>
<tr>
<td>Micro-suspension</td>
<td>M1</td>
<td>Broad, Unimodal 1.10</td>
<td>0.40</td>
<td>60</td>
<td>Yes</td>
<td>1.0</td>
<td>73</td>
</tr>
<tr>
<td></td>
<td>M2</td>
<td></td>
<td></td>
<td></td>
<td>No</td>
<td></td>
<td>73</td>
</tr>
</tbody>
</table>

* 33% by weight small particles

Note: Milling has the effect of reducing the concentration of secondary particles within a plastisol

+ standard measure of PVC relative molecular mass (RMW). Higher values denote higher RMW. (7)
<table>
<thead>
<tr>
<th>Grade</th>
<th>Spray Drying Severity</th>
<th>Code</th>
<th>Spray Drying Temp (°C)</th>
<th>Porosity of Secondary Particles</th>
</tr>
</thead>
<tbody>
<tr>
<td>E1</td>
<td>1</td>
<td>E1.1</td>
<td>55</td>
<td>0.14</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>E1.2</td>
<td>65</td>
<td></td>
</tr>
<tr>
<td>E2</td>
<td>1</td>
<td>E2.1</td>
<td>55</td>
<td>0.14</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>E2.2</td>
<td>65</td>
<td></td>
</tr>
<tr>
<td></td>
<td>3</td>
<td>E2.3</td>
<td>76</td>
<td></td>
</tr>
<tr>
<td>S1</td>
<td>1</td>
<td>S1.1</td>
<td>56</td>
<td></td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>S1.2</td>
<td>64</td>
<td></td>
</tr>
<tr>
<td></td>
<td>3</td>
<td>S1.3</td>
<td>68</td>
<td>0.10</td>
</tr>
<tr>
<td></td>
<td>4</td>
<td>S1.4</td>
<td>72</td>
<td></td>
</tr>
<tr>
<td>S2</td>
<td>1</td>
<td>S2.1</td>
<td>55</td>
<td></td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>S2.2</td>
<td>65</td>
<td>0.10</td>
</tr>
<tr>
<td></td>
<td>3</td>
<td>S2.3</td>
<td>75</td>
<td></td>
</tr>
<tr>
<td>M1</td>
<td>1</td>
<td>M1.1</td>
<td>50</td>
<td></td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>M1.2</td>
<td>60</td>
<td>0.40</td>
</tr>
<tr>
<td></td>
<td>3</td>
<td>M1.3</td>
<td>70</td>
<td></td>
</tr>
<tr>
<td></td>
<td>4</td>
<td>M1.4</td>
<td>80</td>
<td></td>
</tr>
<tr>
<td>M2</td>
<td>1</td>
<td>M2.1</td>
<td>50</td>
<td></td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>M2.2</td>
<td>60</td>
<td>0.40</td>
</tr>
<tr>
<td></td>
<td>3</td>
<td>M2.3</td>
<td>70</td>
<td></td>
</tr>
<tr>
<td></td>
<td>4</td>
<td>M2.4</td>
<td>80</td>
<td></td>
</tr>
</tbody>
</table>

The materials described in Table 2.2 were obtained by spray drying the latices, used to prepare the paste polymers described in Table 2.1, under a broad range of spray drying conditions. Each of the paste polymers
shown in Table 2.1 may be considered as a typical sample of the materials derived by the various polymerisation techniques.

The range of fillers selected for this study are described in Tables 2.3, 2.4 and 2.5. Fillers of differing PS, PSD, surface treatment, chemical composition and plasticiser absorbtions, were chosen.

**TABLE 2.3 - GROUND CALCIUM CARBONATE FILLER SPECIFICATIONS.**

<table>
<thead>
<tr>
<th>Filler</th>
<th>Particle Size (&lt;% below 2μm)</th>
<th>Surface Coating</th>
<th>Specific Gravity</th>
</tr>
</thead>
<tbody>
<tr>
<td>Polycarb</td>
<td>86.0</td>
<td>--</td>
<td>2.65</td>
</tr>
<tr>
<td>Polycarb S</td>
<td>2.65</td>
<td>1.0% Steric Acid</td>
<td></td>
</tr>
<tr>
<td>Q60</td>
<td>57.0</td>
<td>--</td>
<td>2.65</td>
</tr>
<tr>
<td>Q60 S</td>
<td>1.0% Steric Acid</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Q300</td>
<td>38.0</td>
<td>--</td>
<td>2.65</td>
</tr>
<tr>
<td>Q300 S</td>
<td>1.0% Steric Acid</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
TABLE 2.4 - TIOXIDE 96 PIGMENT CHARACTERISTICS.

<table>
<thead>
<tr>
<th>Pigment</th>
<th>Chemical Composition</th>
<th>Specific Gravity</th>
<th>Crystal PSD (µm)</th>
<th>Surface Area (m²/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>RFC5</td>
<td>Rutile</td>
<td>4.05</td>
<td>0.18</td>
<td>8.00</td>
</tr>
<tr>
<td>RTC60</td>
<td>Rutile</td>
<td>4.05</td>
<td>0.22</td>
<td>4.05</td>
</tr>
</tbody>
</table>

TABLE 2.5 - SPHERIGLASS : GLASS MICRO SPHERES.

<table>
<thead>
<tr>
<th>Filler</th>
<th>Chemical Composition</th>
<th>Specific Gravity</th>
<th>Particle Size (µm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>5000 CPC3</td>
<td>Soda-Lime Glass</td>
<td>2.475</td>
<td>8.00</td>
</tr>
</tbody>
</table>

The reasons for selecting these materials are given in the following sections;

2.1.1 Selection of Paste Polymers

2.1.1.1 Unimodal Latices

2.1.1.1.a Conventional Emulsion Paste Polymers

The two emulsion paste polymers which have been selected, were prepared by ICI, from similar latices. Differences in secondary particle morphology, due to different drying conditions, should enable the effect of deagglomeration, on plastisol rheology, to be studied.
The severe drying conditions employed in the drying of E1 were achieved by having a high dryer outlet temperature. This high temperature should thoroughly fuse the secondary particles, making them resistant to deagglomeration during plastisol preparation. E2 was dried under mild conditions (lower dryer outlet temperature) and so the secondary particles should be easily broken down during plastisol preparation.

2.1.1.1.b Microsuspension Paste Polymers

The two microsuspension paste polymers selected for this study were prepared by ICI from the same latex, however, M2 was unmilled. The milling technique is usually employed during commercial preparation of paste polymers, in order to limit the maximum PS in the system. Such control of PS may be necessary to prevent poor surface finish in applications requiring thin coatings. By considering the behaviour of M1 and M2, it will be possible to study the effect of the milling process on plastisol rheology and filler tolerance.

In both the emulsion and the microsuspension processes, the unimodal primary PSD prevents efficient packing of particles during the spray drying process. Secondary particle porosity should, therefore, be high compared with the secondary particle porosity of paste polymers derived from a bimodal latex.

2.1.1.2 Bimodal Latices

2.1.1.2.a Seeded Emulsion Paste Polymers

By comparing the rheology of plastisols prepared from the seeded emulsion paste polymers, manufactured by ICI, it should be possible to quantify the effect of average PS, emulsifier level and the inter-relationships between PSD and plastisol rheology. Comparison of the performance of the paste polymers, prepared from the unimodal and bimodal latices, should enable the effect of secondary particle porosity to be established.
2.1.1.3 Experimental Grades (Spray Drying Experiments)

To establish a model which will allow paste polymer systems to be designed more accurately, the paste polymers used in the initial part of this study have been spray dried under widely differing conditions.

All the materials described in Table 2.2 apart from the M2 modified grades, were milled after spray drying. The numbers in column 2, of Table 2.2, refer to the severity of spray drying. The higher numbers denote a more severe drying regime, achieved by increasing the drier outlet temperature. Consequently, a paste polymer with a drying severity of 4 would contain more thoroughly fused secondary particles (due to the higher temperatures experienced) than a paste polymer with a drying severity of 1.

2.1.2 Selection of Fillers

A plastisol prepared from a spray dried latex should contain two size distributions, one being the primary PS defined by the polymerisation technique, the second being controlled by the spray drying conditions. When considering the effect of filler introduction in these systems, it is unclear how packing efficiency will be affected. It is, therefore, necessary to consider the effect of a range of fillers, of differing PS, if an understanding of filler response is to be achieved. The selection of this range of fillers is described in the following sections.

2.1.2.1 Calcium Carbonate Fillers (Coated and Uncoated)

A range of ground calcium carbonate (GCC) fillers have been selected from the extensive range of mineral fillers manufactured by ECC®, see Table 2.3. This is because of their symmetrical shape and frequent use in commercial plastisol formulations. Kaolite and Talc fillers were not considered because of their plate-like or lamella type structure. Such anisotropic shapes retard plastisol flow, conferring very high viscosities to these systems, making them less attractive for
use in commercial formulations.

The range of particle sizes was chosen to reflect the maximum and minimum PS filler used in the industry. Q300, the coarsest material, is used in applications where low viscosity combined with high filler loadings is required. Polcarb, the finest material, is used as an economical alternative to precipitated calcium carbonate fillers, to impart high viscosities and control thixotropy.

The stearate coated versions of Q300, Q60 and Polcarb have been included in this study because it is interesting to speculate whether their reduced plasticiser absorption will have a significant effect on plastisol rheology and the effect of filler introduction.

2.1.2.2 Titanium Dioxide Pigments

Two Titanium Dioxide (TiO₂) pigments were selected from Tioxides range of products, see Table 2.4. These were selected because of their small crystal size (approximately 0.20 µm) which should enable the effect of filler introduction, on plastisol rheology, to be studied over an extended filler PS range. The small TiO₂ particles, being comparable in diameter to the latex particles, should interfere with the packing efficiency of the primary PSD. The larger GCC particles may interfere with the secondary PSD, as their size is comparable to the size of the spray dried agglomerates. The study of filler effects over this extended size range, in different plastisol systems, should provide an insight into the mechanisms controlling plastisol rheology.

2.1.2.3 Spheriglass Fillers

The interpretation of results obtained from TiO₂ and GCC modified plastisols may be complicated by the absorption of plasticiser and the slightly irregular shape of the filler particles. To overcome the problems of interpretation, it was decided to investigate the rheology of model systems, based on the addition of glass spheres to selected plastisols. Such particles are spherical and non-plasticiser
absorbing. A range of glass microspheres with average sizes ranging from 0.2 \( \mu m \) to 10.0 \( \mu m \) would be ideal for this study. The latest development product, developed by Potters Industries\(^7\), is Spheriglass 5000 CP03; it has an average PS of approximately 8.0 \( \mu m \) (as determined by the Sedigraph 5000 ET Particle Size Analyser). Although this material does not have a small enough average PS to be considered ideal for this study, it is the finest glass microsphere filler available. It was therefore adopted for several model systems, as its average size is comparable to that of the coarsest GCC filler, Q300.

2.1.3 Mix Formulations

2.1.3.1 Calcium Carbonate Filler Systems

2.1.3.1.a Filler Dispersion Additions

TABLE 2.5 - GCC FILLED PLASTISOL FORMULATIONS - BASED ON FILLER DISPERSION ADDITIONS

<table>
<thead>
<tr>
<th>CALCIUM CARBONATE (% by volume of solids)</th>
<th>0</th>
<th>4.5</th>
<th>9.0</th>
<th>13.5</th>
<th>18.0</th>
</tr>
</thead>
<tbody>
<tr>
<td>PVC (Parts by weight)</td>
<td>100</td>
<td>95.51</td>
<td>91.00</td>
<td>86.51</td>
<td>82.39</td>
</tr>
<tr>
<td>GCC Filler Paste *</td>
<td>-</td>
<td>20.97</td>
<td>42.02</td>
<td>62.99</td>
<td>82.17</td>
</tr>
<tr>
<td>DIOP</td>
<td>50.00</td>
<td>37.24</td>
<td>24.43</td>
<td>11.67</td>
<td>-</td>
</tr>
<tr>
<td>ADDITIONAL DIOP FOR E1 ONLY</td>
<td>10.00</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>ADDITIONAL DIOP FOR E2 ONLY</td>
<td>40.00</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

* 40% SOLIDS IN DIOP, prepared using Silverson, according to 2.6.2.

Calculation of the mix formulations necessary to maintain a
constant solids to liquid ratio while increasing the proportion of calcium carbonate is described in Appendix 1.

2.1.3.1.b Dry Filler Additions

TABLE 2.6 - GCC FILLED PLASTISOL FORMULATIONS - BASED ON DRY FILLER ADDITION

<table>
<thead>
<tr>
<th>CALCIUM CARBONATE (&lt;% by volume of solids&gt;)</th>
<th>0</th>
<th>4.5</th>
<th>9.0</th>
<th>13.5</th>
<th>18.0</th>
</tr>
</thead>
<tbody>
<tr>
<td>PVC (parts by weight)</td>
<td>100</td>
<td>95.51</td>
<td>91.00</td>
<td>86.51</td>
<td>82.39</td>
</tr>
<tr>
<td>GCC</td>
<td>--</td>
<td>8.51</td>
<td>17.04</td>
<td>25.55</td>
<td>33.34</td>
</tr>
<tr>
<td>DIOP</td>
<td>50.00</td>
<td>-------------------------------→</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>ADDITIONAL DIOP</td>
<td>FOR E1 ONLY</td>
<td>10.00</td>
<td>-------------------------------→</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>FOR E2 ONLY</td>
<td>40.00</td>
<td>-------------------------------→</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Calculation of the mix formulations necessary to maintain a constant solids to liquid ratio while increasing the proportion of GCC is described in Appendix 2.
TABLE 2.7 - T\textsubscript{2}O\textsubscript{2} FILLED PLASTISOL FORMULATIONS - BASED ON FILLER DISPERSION ADDITIONS

<table>
<thead>
<tr>
<th>TITANIUM DIOXIDE (% by volume of solids)</th>
<th>0</th>
<th>1</th>
<th>2</th>
<th>4</th>
</tr>
</thead>
<tbody>
<tr>
<td>PVC</td>
<td>100</td>
<td>99.01</td>
<td>98.00</td>
<td>95.99</td>
</tr>
<tr>
<td>T\textsubscript{2}O\textsubscript{2} FILLER PASTE *</td>
<td>-</td>
<td>7.10</td>
<td>14.19</td>
<td>28.38</td>
</tr>
<tr>
<td>DIOP</td>
<td>50.00</td>
<td>45.66</td>
<td>41.32</td>
<td>32.64</td>
</tr>
<tr>
<td>ADDITIONAL DIOP</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>FOR E1 ONLY</td>
<td>10.00</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>FOR E2 ONLY</td>
<td>40.00</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

* 40% SOLIDS IN DIOP, prepared using Silverson, according to 2.6.2

Calculation of the mix formulations necessary to maintain a constant solids to liquid ratio while increasing the proportion of titanium dioxide is described in Appendix 3.
2.1.3.3 Spheriglass Model Systems

TABLE 2.8 - SPHERIGLASS FILLED PLASTISOL FORMULATIONS - BASED ON FILLER DISPERSION ADDITION.

<table>
<thead>
<tr>
<th>SPHERIGLASS 5000 CPO3 (% by volume of solids)</th>
<th>0</th>
<th>7</th>
<th>14</th>
<th>21</th>
<th>28</th>
</tr>
</thead>
<tbody>
<tr>
<td>PVC (parts by weight)</td>
<td>100</td>
<td>93.00</td>
<td>86.00</td>
<td>79.00</td>
<td>72.00</td>
</tr>
<tr>
<td>Spheriglass FILLER PASTE *</td>
<td>24.31</td>
<td>48.63</td>
<td>72.92</td>
<td>97.25</td>
<td></td>
</tr>
<tr>
<td>DIOP</td>
<td>50.00</td>
<td>37.65</td>
<td>25.29</td>
<td>12.96</td>
<td>0.59</td>
</tr>
<tr>
<td>ADDITIONAL DIOP</td>
<td>10.00</td>
<td>40.00</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>FOR E1 ONLY</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>FOR E2 ONLY</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

* 50% Solids in DIOP, prepared using Silverson, according to 2.6.2

Calculation of the mix formulation necessary to maintain a constant solids to liquid ratio while increasing the proportion of spheriglass is described in Appendix 4.

2.2 CONDITIONING

Underdal et al. demonstrated the need for careful control of humidity during the storage of paste polymers. Plastisols prepared from resins stored at 30% rh and 65% rh displayed drastically different low
shear viscosities. Therefore, all paste polymers used in this study were conditioned prior to plastisol preparation, according to the guidelines outlined in ISO R.291:

- Temperature: 23°C ± 2°C
- Humidity: 50% ± 5%
- Conditioning time: at least 72 hours

*Humidity was controlled by a Magnesium Nitrate Salt Solution.

2.3 MIXING TECHNIQUE

2.3.1 Evaluation of Mixing Technique

2.3.1.1 Thick Stage Plasticiser Level

Plastisols were prepared in a Hobart AE200 planetary mixer. This type of mixer operates at relatively low speeds (107 to 287 rpm) and depends upon the shear forces generated, by blending a dough-like mix to thoroughly wet out and disperse the paste polymer in the plasticiser. As a consequence of this need to shear a highly viscous mix, the two-stage thick/thin mix technique was adopted for plastisol preparation. Using this technique, sufficient plasticiser is added to the paste polymer to generate a highly viscous mass. Once the paste polymer has been thoroughly dispersed in this limited amount of plasticiser, further plasticiser is added to dilute the mix to the required level.

A reduction in the amount of plasticiser used to disperse the paste polymer, during the thick stage, causes an increase in the shear forces generated within the plastisol, as demonstrated by the increase in dilatancy of M1, see Figure 2.1.a. and a subsequent increase in temperature. ISO 4612 describes the optimum conditions for plastisol preparation using a single-stage mixing technique. The standard places a limit of 23°C ± 2°C on the temperature of the plastisol on completion of mixing. A significant temperature increase may cause excessive solvation and deagglomeration of secondary particles or even gellation.
Several experiments were carried out, using M1, to establish the minimum plasticiser level which could be used in the thick stage of this two stage mixing technique. M1 was considered the most suitable paste polymer for this experimental program, as it imparts a high degree of dilatancy to a plastisol. The flow instabilities leading to this dilatancy should enhance the shear forces and heat build-up generated during mixing. As a result of these trials, a thick stage plasticiser level of 45 phr was considered ideal for dispersion of the paste polymer. Higher plasticiser levels reduced plastisol viscosity excessively, considerably reducing the shear forces necessary for efficient mixing. Lower plasticiser levels caused excessive heat build-up during mixing, so that the temperature on completion of mixing fell outside the range considered acceptable by ISO 4612.

The mix formulations used to prepare the paste characterised by Figure 2.1.a are described in Table 2.9. Thick stage mixing times were limited to 10 minutes, at speed 2 (198 rpm).

### TABLE 2.9 - FORMULATIONS USED TO PREPARE THE PLASTISOLS CHARACTERISED BY FIGURE 2.1.a

<table>
<thead>
<tr>
<th>PLASTICISER LEVEL (phr)</th>
<th>45</th>
<th>50</th>
<th>55</th>
<th>60</th>
</tr>
</thead>
<tbody>
<tr>
<td>PVC (for grades M and S)</td>
<td>100</td>
<td>--</td>
<td>--</td>
<td>--</td>
</tr>
<tr>
<td>DIOP Thick stage</td>
<td>45</td>
<td>--</td>
<td>--</td>
<td>--</td>
</tr>
<tr>
<td>DIOP Thin stage</td>
<td></td>
<td>5</td>
<td>10</td>
<td>15</td>
</tr>
</tbody>
</table>

Plastisols prepared from the emulsion paste polymers (E1 and E2) displayed a much higher viscosity. It was therefore found necessary to
increase the thick stage plasticiser levels to 55phr for E1 and 65 phr for E2.

2.3.1.2 Thick Stage Mixing Time

Having established the optimum thick stage plasticiser level, the next step in the development of a standard mixing regime was to determine the optimum mixing time. During the dispersion of a paste polymer in a plasticiser, there may be a limited amount of secondary particle deagglomeration which can lead to a change in plastisol rheology. The change in rheology and heat build up, with increasing mixing times, were used as the criteria for determining the most suitable thick stage mixing time (TS). At this early stage of the research programme, it was not possible to follow the change in PSD, with mixing time, because of the lack of equipment. However, the results described in Section 3.1.2.4.a, which were obtained later in the research programme, suggest that any change in PSD during mixing is extremely difficult to detect.

A mix design based on a 100/45 plastisol (100 parts PVC : 45 parts DIOP) produced from M2 was considered ideal for the evaluation of mixing time, for two reasons:

(i) the dilatant nature of the plastisol made it sensitive to shear history, and
(ii) the greater concentration of secondary particles compared with M1 made the system more sensitive to deagglomeration.

To evaluate the thick stage mixing time (TS), five plastisols were prepared by blending 1000 grams of M2 and 450 grams of DIOP for various times. For the first mix, each of the two components were charged to the 10 quart mixing bowl of a Hobart AE200 planetary mixer. A pre-mix was prepared by folding the PVC into the DIOP with a pallet knife, this was necessary in order to prevent sample loss when the mixing rotor was engaged. Mixing was then carried out at speed 1 (107 rpm) for two minutes. Having achieved a crude blend, the rotor was
stopped and the excess plastisol scraped down from the bowl walls into the body of the plastisol. Mixing was then continued at speed 2 (198 rpm) for a further 3 minutes, taking the total mixing time to 5 minutes. This process was repeated for each of the 5 remaining plastisols, but the total mixing time was increased as shown in Table 2.10.

**TABLE 2.10 - TS EVALUATION : MIXING REGIME (SEE FIG. 2.1.b)**

<table>
<thead>
<tr>
<th>TS mixing time</th>
<th>5</th>
<th>10</th>
<th>15</th>
<th>20</th>
<th>30</th>
<th>40</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mixing time (minutes)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Speed 1 (107 rpm)</td>
<td>2</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Speed 2 (198 rpm)</td>
<td>3</td>
<td>8</td>
<td>13</td>
<td>18</td>
<td>28</td>
<td>38</td>
</tr>
</tbody>
</table>

Each plastisol was deaerated in a 5L vacuum flask under a vacuum of 760 mm of mercury, for 30 minutes. The flask was fitted with a mechanical stirrer to ensure optimum air release. These deaerated plastisols were conditioned for 24 hours at 23°C ± 0.1°C prior to characterisation in the Brookfield, Rotovisko and Severs rheometers. The viscosity profiles of these plastisols are displayed in Figure 2.1.b.

From this data, there seems to be little benefit in increasing the TS mixing time from 5 to 15 minutes, as the plastisols prepared with mixing times of 5, 10 and 15 minutes displayed the same low shear viscosity. It is only after 20 minutes mixing (2 minutes at speed 1, and 18 minutes at speed 2), that viscosity starts to fall. However, after such protracted mixing times the frictional heat generated within the system starts to cause an unacceptable temperature rise. There is evidence to suggest that the fall in viscosity after 20 minutes is due to secondary particle deagglomeration brought about by a combination of the shear forces and frictional heat generated during mixing. In Section 3.2.1.3.a it has been clearly demonstrated that a reduction in the concentration of secondary particles (simulated by a change in the spray
drying parameters) within a plastisol prepared from M2, results in a fall in low shear viscosity. I believe that, the primary PSD is better for low shear viscosity, due to efficient particle packing, than the highly porous secondary particles. As there seems to be no benefit in increasing mixing times above 10 minutes, this time was adopted as the standard for all further plastisol preparations.

2.3.1.3 Batch Size

A study of mixing conditions would not be complete without considering the effect of batch size on mixing efficiency. It seemed reasonable to assume that an increase in the volume of plastisol within the mixing bowl, during mixing, would have an effect on plastisol rheology. A higher volume of plastisol should mean that a smaller proportion of the total mix is being subject to shear between the bowl walls and the rotor, at any given time. To study this effect, four 100/45 plastisols were prepared from M2, this grade being chosen because of its sensitivity to shear forces. The batch sizes were based on 500, 1000, 1500 and 2000 grams of PVC. The Hobart prepared each plastisol according to the 10 minute mix method. Deaeration was achieved as before. Each plastisol was stored for 24 hours at 23°C ± 0.1°C prior to characterisation by the Brookfield, Rotovisko and Severs rheometers. The data obtained from these plastisols is presented in Figure 2.1.c. As suspected, an increase in plastisol volume reduces the shear applied to the system. This reduction in shear is accompanied by an increase in plastisol low shear viscosity, as the degree of secondary particle deagglomeration is reduced. It has already been shown that a higher concentration of secondary particles, within a plastisol prepared from M2, results in a higher plastisol viscosity because of the high porosity of these secondary particles. Anything which prevents the deagglomeration of these secondary particles must, therefore, increase low shear viscosity. I decided to adopt a batch size based on 1000 grams of PVC as the standard size because such a volume provides sufficient material for testing. Higher volumes are unnecessary and may reduce mixing efficiency within the Hobart.
2.3.1.4 Deaeration Time

The final step in designing a standard mixing technique was to consider the effect of deaeration time (DAT) on plastisol rheology. This was achieved by measuring the rheology of plastisols prepared from S1 as a function of deaeration time, see Figure 2.1.d. The seeded emulsion paste polymer, S1, was considered ideal for this study because plastisols prepared from this material were "Newtonian". The absence of any dilatancy means that the system should be less sensitive to slight changes in shear history, and so any differences in low shear viscosity should be due to entrapped air. The release of entrapped air becomes more difficult the higher the plastisol viscosity. It was, therefore, decided to select a plasticiser level of 45 phr, so that one could consider the worst case in which air release was inhibited by a high plastisol viscosity.

Six plastisols were prepared from 1000g of S1 and 450g of DIOP. The 10 minute mixing regime was adopted and deaeration was achieved as follows: 0, 10, 20, 30, 45 and 60 minutes under a vacuum of 760 mm of mercury. After conditioning, for 24 hours at 23°C ± 0.1°C the rheology of the systems was measured using the Brookfield, Rotovisko and Severs rheometers. From Figure 2.1.d it seems that the majority of air removal is achieved after 20 minutes. There seems to be little effect on low shear viscosity when deaeration times are increased from 20 to 45 minutes; all the flow curves of these mixes lie on top of one another. Only after 60 minutes does there appear to be a further minimal drop in viscosity. It was, therefore, decided to adopt 30 minutes as the standard deaeration time. 20 minutes was probably the minimum time that could be considered sufficient to achieve deaeration but a further 10 minutes (making a total of 30 minutes) was not considered excessive in ensuring that thorough deaeration had been achieved.

2.3.2 Standard Mixing Technique

From the mix trials, the following conditions were adopted for preparation of subsequent plastisols:
Thick Stage: Plasticiser level, 45 phr (55 for E1 and 65 for E2).

Mixing Time, 10 minutes; 2 minutes at speed 1 and 8 minutes at speed 2.

Batch Size: based on 1000g of Polymer.

On completion of the thick stage, any remaining plasticiser (eg. 5phr for a 100/50 mix) should be added to the plastisol and mixing continued at speed 1 for 2 minutes. The rotor should then be stopped and the material from the walls of the bowl scraped down into the body of the plastisol. Mixing should then be continued at speed 2 for 8 minutes. After mixing, plastisols should be stored for 24 hours at 23°C ± 0.1°C prior to viscosity measurement.

For the filled plastisols, all ingredients were charged to the mixer. These materials were then blended according to the standard thick stage conditions, described above.

2.4 RHEOMETER MEASUREMENTS

2.4.1 Brookfield Viscometer

The viscosity of each plastisol was determined by a Brookfield Synchro-Lectric Viscometer (model RVT), 24 hours after plastisol preparation, according to the procedure outlined in ASTM D1824. The viscosity of each plastisol was calculated from the torque required to drive the spindle at a given speed using the Brookfield "factor finder" chart, after 10 revolutions at speed 10 (10 rpm). Care was taken to select a spindle which would give a reading of 25 - 75% of full scale deflection.

When using the Brookfield to determine the viscosity of the filler dispersions, it was necessary to use the 'T' range of spindles and the Brookfield Motor Driven Stand, described in the literature. The use of this arrangement ensures that the 'T' spindle follows a helical path.
in the sample, during testing. This is necessary when dispersions which
tend to segregate are being characterised. To give an indication of
shear sensitivity, the filler dispersions were tested over a range of
speeds: 1, 2.5 and 5 rpm, after 10 revolutions. When evaluating filler
dispersions, the operation of the instrument was carried out in
accordance with ASTM D1824, while the motor driven stand raised the
viscometer.

2.4.2 Rotovisko Rheometer

The Rotovisko RV2 rheometer was used to measure the viscosity of the
plastisols over an extended shear rate range, of approximately 0.1 to
300 reciprocal seconds, 24 hours after plastisol preparation. This
instrument uses a similar principle to the Brookfield viscometer,
measuring the torque (S) required to drive a measuring head at a given
speed (N). However, careful design of the sensor system enables the
apparent viscosity, shear stress and shear rate to be accurately
calculated from N and S. The coaxial cylinder configurations were
selected because the particulate nature of plastisols may cause problems
when using the cone and plate configurations. This is because the PVC
particles can jam in the gap between the two shearing surfaces, leading
to artificially high torque readings. The calculation of apparent
viscosity and shear rate from rheology data derived from the coaxial
cylinder system is described in Appendix 5. Although, the instrument
operating procedures are clearly described in the Rotovisko manual\textsuperscript{12},
it was necessary to carry out several experiments to evaluate the
performance of the instrument and to select the combination of sensor
heads which would cover the widest possible shear rate range. The
results of these tests are considered in the following sections.

2.4.2.1 Performance of the Rheometer

Unfortunately, the Rotovisko rheometer relies on the deflection of
a torsion spring, as measured by a potentiometer, to determine the
torque applied to the measurement spindle. This dependence of torque
measurement on the deflection of a potentiometer means that the
Rotovisko spindle must rotate a certain amount before accurate readings are obtained. It was therefore necessary to carry out several tests, at low speeds, to determine at what point sufficient time had been allowed for reliable torque readings to be made.

FIG 2.4 - ARRANGEMENT OF COAXIAL CYLINDERS WITHIN THE ROTOVISKO RHEOMETER.

<table>
<thead>
<tr>
<th>SENSOR SYSTEM</th>
<th>MV I</th>
<th>MV II</th>
<th>MV III</th>
</tr>
</thead>
<tbody>
<tr>
<td>Rotor (BOB) radius Ri (mm)</td>
<td>20.04</td>
<td>18.4</td>
<td>15.2</td>
</tr>
<tr>
<td>height L (mm)</td>
<td>60</td>
<td>60</td>
<td>60</td>
</tr>
<tr>
<td>STATOR (CUP) radius Ra (mm)</td>
<td>21</td>
<td>21</td>
<td>21</td>
</tr>
<tr>
<td>RADI RATIO Ra/Ri</td>
<td>1.05</td>
<td>1.14</td>
<td>1.38</td>
</tr>
<tr>
<td>SAMPLE VOLUME V (cm³)</td>
<td>40</td>
<td>55</td>
<td>70</td>
</tr>
<tr>
<td>TEMPERATURE: max. (°C)</td>
<td>150</td>
<td>150</td>
<td>150</td>
</tr>
<tr>
<td>min. (°C)</td>
<td>-30</td>
<td>-30</td>
<td>-30</td>
</tr>
<tr>
<td>CALCULATION FACTORS</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>A (Pa/scale grad.)</td>
<td>3.22</td>
<td>3.76</td>
<td>5.44</td>
</tr>
<tr>
<td>M (min/s)</td>
<td>2.34</td>
<td>0.9</td>
<td>0.44</td>
</tr>
<tr>
<td>G (mPa·s/scale grad.·min)</td>
<td>1374</td>
<td>4171</td>
<td>12375</td>
</tr>
</tbody>
</table>

The tests were performed, by placing a sample of a high viscosity plastisol in the MVII cup, which was then placed in the rheometer, so that the MVII bob slid into the MVII cup, displacing the plastisol into the gap between the coaxial cylinders, as shown in Figure 2.4. An initial speed of 0.1 rpm (the lowest possible on the unmodified instrument) was selected and the torque measured as a function of time. Once a stable torque reading had been achieved, the speed was then increased in steps and the time required to achieve stable readings noted. Such experiments lead to Table 2.11, which describes the time required between successive torque readings before stable deflections were achieved. As a result of these tests, all future viscosity measurements were carried out as dictated by Table 2.11. Apart from the need to achieve stable readings, it was also necessary to adhere closely to this schedule because the non-Newtonian nature of plastisols causes sample loss from the gap between the concentric cylinders. If accurate comparison between plastisols is to be made, excessive loss of sample...
should be avoided by increasing the rheometer speed to the next level once the torque had been measured.

**TABLE 2.11 - TIME ELAPSED BETWEEN STABLE DEFLECTIONS**

<table>
<thead>
<tr>
<th>Speed (rpm)</th>
<th>Time (min)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.1</td>
<td>3½</td>
</tr>
<tr>
<td>0.141</td>
<td>3½</td>
</tr>
<tr>
<td>0.2</td>
<td>1½</td>
</tr>
<tr>
<td>0.283</td>
<td>1½</td>
</tr>
<tr>
<td>0.4</td>
<td>1</td>
</tr>
<tr>
<td>0.566</td>
<td>1</td>
</tr>
</tbody>
</table>

30 seconds for remainder of readings

2.4.2.2 Selection of Various Measurement Head Configurations

Having established the optimum length of time between rheometer torque readings, as indicated in Table 2.11, the next step was to select a combination of coaxial cylinders which would provide rheology data over the widest range of shear rates, while displaying accurate correlations between the two sets of coaxial cylinders. Plastisols prepared from M1 were used to aid selection, because of their highly dilatant nature. This should highlight any errors in the calculation of apparent viscosity and shear rate for the various sets of cylinders. The flow curves of plastisols prepared from M1, with plasticiser contents of 60 phr and 45 phr, are presented in Figure 2.2. Care was taken to follow the guidelines given in Table 2.11 and the operating procedures outlined in the Rotovisko manual. Both measurement ranges, 50 and 500, were used, so that the largest range of shear rates could be covered. Using the MV and SV sets of concentric cylinders to derive these flow curves, it is obvious that the apparent viscosity of the plastisol depends upon which set of cylinders has been used to measure
viscosity. This was expected, as the calculation of apparent viscosity and shear rate from torque and speed, for the coaxial cylinder system, is based on the assumption that the fluid under test is Newtonian. Plastisol, however, rarely display Newtonian characteristics and it is this factor which explains the differences in apparent viscosity and shear rate derived from various sensor systems. There appears to be a greater spread in the results for the 100/45 plastisol than for the 100/60 plastisol. This is because the 100/60 plastisol displays almost Newtonian properties and so the assumptions made in the calculations are correct for this material, while the assumption of Newtonian flow for the 100/45 plastisol is clearly incorrect. A detailed analysis of non-Newtonian flow in concentric cylinders is given in Appendix 5.

From Figure 2.2.b it seems that rheology data obtained from a combination of the MV III and SV II sets of cylinders covers the widest range of shear rates, thus making such an arrangement the most suitable for this study. However, such data obtained from the MV III set of cylinders is less reliable than that obtained from the MV II set of cylinders because the gap between the cylinders is too large\(^{20}\), making it less credible to assume laminar flow. I therefore decided to adopt a combination of the MV II and SV II systems for all further work, as they cover the widest, accurately characterised, shear rate range and provide excellent correlation between each other. This agreement is clearly shown in Figure 2.2.b where the green triangles for the MV II data and the black crosses for the SV II data lie on the same line.

2.4.3 Severs Capillary Rheometer

The apparent viscosity of each plastisol was measured over a shear rate range of approximately 300 to 15,000 reciprocal seconds, 24 hours after preparation, using the Severs rheometer as described in ISO 4575. Using this standard, viscosities and shear rates were derived from the pressure required to force a fluid through a tube die at a given flow rate. Three dies were available for the instrument, having internal diameters of 1.0, 1.5 and 2.0 mm. The large diameter die was used for high viscosity materials, the smaller diameter dies being used
for less viscous plastisols.

The formulae governing derivations of apparent viscosity from flow rate and pressure data are due to Poiseuille\textsuperscript{102}.

Assuming the plastisol is Newtonian, then the shear rate at the wall of the die

\[ \frac{4D}{\pi r^3 \rho} \] (2.1)

and the apparent viscosity = \( 10^3 \frac{\pi r^4 P \rho}{8 h D} \) (2.2)

D is the plastisol flow rate in grams per second at pressure P
P is the applied pressure in Kilo pascals
r is the radius of the die in centimetres
h is the height of the cylindrical die tube in centimetres
\( \rho \) is the density of the paste in grams per cubic centimetre (as measured at 23°C)

(Note: the die constants were calculated in Appendix 6, using the units specified by ISO 4575).

2.4.3.1 Effect of Die Diameter on Rheometer Performance

The use of equations 2.1 and 2.2 for the calculation of apparent viscosity and shear rate from flow rates and pressure data is based on the assumption that the fluid under test is Newtonian. Unfortunately, as demonstrated in the preceding sections, plastisols may display a non-Newtonian flow curve. It therefore seemed prudent to compare the performance of the various Severs dies, so that the effect of deviations from Newtonian flow could be established. The high shear viscosities of plastisols prepared from M1 have been characterised using the various dies and the data has been displayed in Figure 2.2. From this data, derived from a 100/45 and a 100/60 plastisol, it seems that the die diameter has little effect on the apparent viscosity at high shear rates.
as determined by the 1.0, 1.5 and 2.0 mm dies. Data for the 1.0 mm die does not appear in Figure 2.2.b because the extremely high viscosity of the 100/45 plastisol prevented sufficient flow through the small diameter die to determine flow rates. From these observations, it was decided to select the die to be used, for the evaluation of a given plastisol, according to plastisol viscosity. To reduce any errors which may be due to changing the die, a single die would be used, if possible, for a specific set of experiments. A more detailed evaluation of the effect of non-Newtonian flow in a capillary rheometer is given in Appendix 6.

2.4.4 Calibration of Rheometers and Computer Program

To ease the processing of rheology data, a computer program has been developed which uses the Rotovisko and Severs formulae outlined in the Appendices to generate the viscosity-shear rate relationships. Such manipulations are necessary, as some of the plots described in this work may contain 250 points. The program is also capable of using the University Telegraf package to plot the graphs presented in this work.

The Rotovisko and Severs rheometers have been calibrated using a standard E30,000 calibration fluid, with a viscosity of 34.87 Pa.S, supplied by Haake®. Figure 2.3.a shows a flow curve derived from the calibration fluid using the uncalibrated rheometers; there seems to be only a limited error in the results. The introduction of a calibration factor ($K$) into the computer program has been used to improve the accuracy of the instruments. Figure 2.3.b shows the agreement between the viscosity of the calibration fluid and the viscosity according to the calibrated rheometers.

Note: $K = \text{Viscosity of calibration fluid.}$

Average viscosity of calibration fluid as suggested by the rheometers.
Fig. 2.1 – Evaluation of Mixing Technique

a, Thick Stage Plasticiser Level (M1)

b, Thick Stage Mixing Time (M2 100/45).

* Units of shear rate are s⁻¹, computer package not capable of rendering this notation
Fig. 2.1 -

c, Batch Size (M2 100/45)

d, Deaggregation Time (S1 100/45)
Fig. 2.2 – Rheometer Performance

a, M1 100/60

b, M1 100/45
Fig. 2.3 - Calibration of Rheometer/Computer Output

a, Uncalibrated

b, Calibrated
2.5 PARTICLE SIZE MEASUREMENTS

2.5.1 Scanning Electron Microscopy

Scanning electron microscopy was used to examine paste polymer and filler samples, in order to elucidate the particle morphology of these materials, using a Cambridge Stereoscan type 2A Scanning Electron Microscope. The samples were mounted on the stub using double sided sticky tape and then sputter coated with gold. Coating levels were high, because of the need to remove the charge build up on the samples, when in the electron beam. Such charge build up is a commonly encountered problem when studying powdered materials by electron microscopy. The possibility of bursting the gold coating, during evacuation of the microscope sample chamber, was minimised by only applying a light dusting of sample onto the mounting stub, prior to coating.

2.5.2 Joyce Loebl Disc Centrifuge

The particle size distribution of the uncoated calcium carbonate fillers and the two titanium dioxide pigments, RFC5 and RTC60, was determined using the Joyce Loebl Disc Centrifuge, according to the procedures described in the operators manual. Preliminary experiments were carried out to determine the most suitable dispersant for each sample, from the recommended materials described in the JLDC operators manual. The best spin fluid was selected from a range of materials based on glycerol/distilled water mixtures. The sample dispersions had to be stable in the centrifuge and be of lower density than the spin fluid, in order to prevent the hydrodynamic instability known as streaming. This phenomenon is caused when a more dense fluid moves en masse through the less dense fluid. After testing the range of recommended dispersants and the spin fluids based on mixtures of glycerol and distilled water, the conditions described in Table 2.12 were considered the most suitable for particle size analysis. The sample dispersions were sonicated in an ultrasonic bath for 60 seconds to break up the loose aggregates and form a uniform suspension.
<table>
<thead>
<tr>
<th>Filler</th>
<th>Ground Calcium Carbonate (uncoated)</th>
<th>Titanium Dioxide</th>
</tr>
</thead>
<tbody>
<tr>
<td>Technique</td>
<td>Buffered Line Start</td>
<td>Buffered Line Start</td>
</tr>
<tr>
<td>Density (g/ml)</td>
<td>2.65</td>
<td>4.05</td>
</tr>
<tr>
<td>Sample Dispersions</td>
<td>Sodium Pyrophosphate Solution</td>
<td>Sodium Pyrophosphate Solution</td>
</tr>
<tr>
<td></td>
<td>(0.89g/litre) + 1 drop Lissapol *</td>
<td>(0.89g/litre)</td>
</tr>
<tr>
<td>Buffer Layer</td>
<td>1 ml Distilled Water</td>
<td>1 ml Distilled Water</td>
</tr>
<tr>
<td>Spin Fluid (30 cc)</td>
<td>60% w/v Glycerol/20% w/v Glycerol/</td>
<td>Distilled Water</td>
</tr>
<tr>
<td>Spin Speed (rpm)</td>
<td>1,000</td>
<td>1,000</td>
</tr>
<tr>
<td>Total Centrifuge Time (minutes)</td>
<td>86</td>
<td>45</td>
</tr>
</tbody>
</table>

* T.02 was dispersed in Lissapol, prior to dilution with Sodium Pyrophosphate solution.

Generation of the PSD of each sample from the trace of turbidity against time, obtained from the JLDC, was achieved by using a computer package developed by the Particle Sizing Group at Loughborough University. The program is based on the application of Stokes Law for settling velocities and the Mie light Scattering Theory, as described in the literature search, section 1.76.
2.5.3 Coulter Counter Particle Size Analyser

All dispersions of the stearate coated GCC fillers displayed streaming, to some extent, in the spin fluid of the JLDC. The size of the Spheriglass, coated and uncoated GCC filler particles in the range 1.0 to 20.0 μm were, therefore, analysed by a Coulter Counter, model TA II. Each filler was dispersed in a non-aqueous electrolyte consisting of 2.5% ammonium thiocyanate in propan-2-ol. Sonication times of 60 seconds were used, to ensure a uniform dispersion of particles. Particle size analysis was carried out in accordance with the instructions given in the Coulter Counter hand book. Unfortunately, the TiO₂ pigment could not be sized in a similar manner because the lower size limit of the instrument is approximately 0.7 μm.

2.5.4 Malvern Autocorrelation Particle Size Analysis

The autocorrelation technique, developed by Malvern Instruments, was used to characterise the size of the very small diameter TiO₂ particles (0.20 μm). This technique uses laser light scattering to measure the degree of Brownian motion experienced by particles in a dispersion. The smaller the diameter of the particles then the greater the degree of Brownian motion. Unfortunately, the instrument, Model K7025, available, does not characterise the whole PSD, but gives an average particle size. (The latest model 4600, which has been recently developed by Malvern Instruments, is capable of generating a PSD, by performing a complex series of curve fitting calculations).

As the technique is sensitive to the existence of the very small diameter TiO₂ particles, it was used to determine the average PS of RFC5 and RTC60, even though I would prefer to characterise the whole PSD and not an average PS. Although, a detailed account of the operation of this instrument is given in the Malvern hand book, the particular conditions, obtained by experimentation, which gave the most reliable analysis are given below:
Sample Dispersion:

0.01 % V/V TiO₂/Propan-2-ol, subject to 30 seconds ultrasound

Instrument Parameters:

K7025 Multibit Correlator
Auto-correlation, Delay out, Multibit
ST = 150, ED = 6,000,000, AP = 4, BP = 4

Experiment

TE = 18, VI = 1.019, RI = 1.33, LW = 6328, MA = 90

2.5.5 Malvern Diffraction Particle Size Analysis

Unfortunately, as the autocorrelation technique is limited to the measurement of sub-μm particles, it was not possible to size the paste polymer and calcium carbonate fillers by this technique because their average size is of the order of several μm’s. To overcome this problem another technique developed by Malvern Instruments was used. The Malvern 2200/3300 Diffraction Particle Size Analyser is capable of measuring the size of particles in the range of 1.0 μm to 560 μm, it relies on the diffraction of laser light to measure PS as opposed to the scattering of laser light used in the autocorrelation technique.

The PSD of fillers and paste polymers were measured using this laser diffraction technique developed by Malvern Instruments. The operation of the instrument is simplified by the menu driven computer system supplied with the instrument. By following the instructions given in the manual, rapid particle size analysis (PSA) of the samples was possible. However, as the technique requires the sample to be presented as a dilute dispersion (0.01%), problems may be experienced in obtaining representative PSA. Segregation of the dispersion can occur during the transport of sample from the beaker, used to dilute the concentrated filler dispersions or plastisols, to the sample cell. Initial tests
produced results of poor reliability. When a filler dispersion or plastisol was diluted with DIOP, for presentation to the sample cell, the large particles were attracted preferentially to the sides of the beaker. Such an effect was magnified when the sample was transferred using a pipette, as the particles were again segregated. To overcome these problems a very small sample (0.01 grams) of the concentrated plastisol or filler dispersion was transported on the tip of a pin to the DIOP in the sample cell. This technique of presenting a minute amount of the concentrated dispersion to the sample cell was adopted for all evaluations using the Malvern Diffraction Instrument. The dispersion of the samples in the DIOP, contained in the sample cell, was achieved by the magnetic stirrer located in the bottom of the sample cell.

The model independant program supplied by Malvern Instruments was used for analysis of the raw diffraction data, as some distributions were bimodal.

2.5.6 Sedigraph Gravimetric Particle Size Analysis

Particle size measurements of the fillers and plastisols were made using the Sedigraph 5000 ET. This instrument operates on the principle of gravitational settling of the particles in the suspending medium. Stokes equation is used to calculate the diameter of the particles. The operation of the instrument is clearly described in the Sedigraph handbook. A detailed account of the test variables and calculation of the rate constants is given in Appendix 7.

2.6 PLASTICISER ABSORPTION

2.6.1 British Standard Technique

Oil absorption values of the calcium carbonate, titanium dioxide and Spheriglass materials were determined by BS 1795 : 1965. Samples were tested several times to establish the repeatability and accuracy of the technique.
2.6.2 Filler Dispersion Viscosity

To confirm the results obtained by BS 1795 : 1965 and to rank the fillers in order of plasticiser demand, dispersions of each material were prepared, and the Brookfield viscosity of each determined. A plasticiser level of 209.6g to 242.1g filler (370g T2O2 – see Appendix 8) was chosen. At this level, the viscosity of the least viscous dispersion (Q300S) was the minimum capable of accurate determination using an RVT Brookfield Viscometer fitted with an AT spindle and motorised stand.

Dispensions of Polcarb, RFC5 and RTC60, due to their high viscosity, were prepared in a Hobart AE200. Both components were charged to the mixer and blended at speed 1 for 60 seconds. The mixer was then stopped. Material from the bowl walls was scraped down into the body of the dispersion and mixing continued at speed 2 for 30 seconds. The mixer was again stopped and the material from the bowl walls scraped down into the body of the dispersion. Mixing was completed after a further 30 seconds at speed 3 (287 rpm).

The remaining dispersions, being less viscous, were prepared on a Silverson High Speed Mixer, the rotor was run at minimum speed until the filler was completely wetted out. The speed was then increased to a maximum and the mixing continued for 2 minutes. The mixer was then stopped. Material from the beaker walls was scraped down into the body of the dispersion, and mixing completed after a further 2 minutes at the maximum speed.

2.7 SECONDARY PARTICLE POROSITY

Secondary particle porosity was measured at ICI using a mercury porosimetry technique. For paste polymers, the separation of intra and interparticle porosity is complicated by the small size of these agglomerates (≈ 8.0 to 20 μm) compared with the secondary particles produced by the mass or suspension technique (136 to 253 μm), which leads to problems in bed depacking and penetration. To overcome these
difficulties special procedures which involve dispersing the paste polymer particles in mercury by ultrasonic means are under development at ICI. Although the technique requires further work to improve its resolution, preliminary results are presented in Table 2.1.

2.8 CURVE FITTING TECHNIQUES

To ease the prediction of plastisol viscosity from filler and paste polymer concentrations, polynomial expressions have been fitted to experimental data presented throughout this thesis. These expressions and the data to which they refer are presented in Appendix 11. The six graphs presented in this Appendix show the correlation between these mathematical expressions and the actual viscosity of plastisols containing various levels of filler and paste polymer.
CHAPTER 3 : UNFILLED PLASTISOLS

3.1 RESULTS

3.1.1 Rheological Characterisation of Plastisols over an Extended Shear Rate Range

3.1.1.1 Effect of Paste Polymer Type

3.1.1.1.a Unimodal Latices

(1) Microsuspension Paste Polymers

The flow curves of plastisols, with DIOP contents of 45, 50, 55 and 60 phr, prepared from the unimodal microsuspension paste polymer, M1, are shown in Figure 3.1.a. Within the shear rate range considered, all the plastisols derived from this material displayed dilatancy. The severity of this flow instability appears to increase dramatically as the concentration of DIOP was reduced from 60 phr to 45 phr. A reduction in the plasticiser level also causes the onset of dilatancy to move to lower shear rates. For the plastisol containing 60 phr of DIOP, the onset of dilatancy occurs at around 200 reciprocal seconds. For the plastisol containing only 45 phr of DIOP, dilatancy starts to appear at a lower shear rate, of approximately 30 reciprocal seconds. The earlier onset of dilatancy and the severity of this instability appears to be proportional to the paste polymer level. The validity of expressions which have been proposed to explain this relationship is discussed in Section 3.2.1.1. A plasticiser level of 45 phr confers such a high degree of dilatancy that the plastisol may be unprocessable.

A similar set of flow curves, for plastisols prepared from M2, which is the unmilled version of M1, is described in Figure 3.1.b. Again all the plastisols displayed dilatancy, the earlier onset and severity of which appears to be proportional to paste polymer content. However, the severity of this instability is lower and occurs at higher shear rates when compared with plastisols prepared from M1. The milling of M2, to
produce #1, appears to enhance the severity of any dilatancy, causing it to occur at lower shear rates.

(ii) Emulsion Paste Polymers.

Figure 3.1.c shows the flow curves of plastisols prepared from E1. A range of plasticiser levels between 55 and 70 phr were studied. These higher concentrations of DIOP were necessary because of the high viscosity of plastisols prepared from this emulsion paste polymer, compared with those prepared from the microsuspension materials. As clearly shown in Figure 3.1.c., all the plastisols tested, displayed a limited degree of dilatancy at low shear rates, typically between 0.3 to 100 reciprocal seconds. Although dilatancy occurred at much lower shear rates, compared with the microsuspension materials, the onset of dilatancy moved to lower shear rates and the severity of this instability increased with an increase in the paste polymer concentration.

The results described in Figure 3.1.c., highlight some of the problems which may be encountered in a study of plastisol rheology. Some compounders consider plastisols prepared from E1 to be pseudoplastic. Indeed, if the flow curve of a 100/55 plastisol (100 parts PVC, 55 parts plasticiser) was characterised between 10 and 10,000 reciprocal seconds it would appear to be pseudoplastic. By measuring viscosity over an extended shear rate range and considering a range of plasticiser levels, I hope to be able to characterise fully the shear rate dependence of apparent viscosity. The dilatancy in E1 plastisols was discovered by adopting this approach.

The flow curves of plastisols prepared from E2 are described in Figure 3.1.d. These E2 plastisols were extremely difficult to characterise. Figure 3.1.d., only contains the complete flow curve for a 100/90 plastisol. The extremely high viscosity of the 100/65 plastisol could only be measured by the Rotovisko rheometer, using very low speeds. Full scale deflection on the measurement head was achieved at only 0.6 rpm and so measurements at higher speeds (i.e. higher shear rates) could not be made. For the 100/100 plastisol, plasticiser separates out from
the plastisol between the concentric cylinders of the Rotovisko. Problems were also encountered using the Severs rheometer. The high low shear rate viscosity caused difficulties in filling the rheometer barrel, while the low high shear rate viscosity caused excessively high flow rates through the Severs 1.0 mm die.

The complete 100/90 flow curve in Figure 3.1.d., highlights the extremely pseudoplastic nature of plastisols prepared from E2. Within industry, this property is used to aid spread coating on open weave cloth. A low high shear viscosity is required to ease application by the doctor knife, while, the high low shear viscosity is necessary to prevent 'strike through', where the plastisol passes through the weave of the cloth.

3.1.1.1.b Bimodal Latices

The flow curves of plastisols derived from the seeded emulsion paste polymers, with plasticiser contents of 45 to 60 phr, are shown in Figure 3.2.a and 3.2.b.

The plastisols derived from S1, see Figure 3.2.a., display an almost Newtonian flow curve, which shifts to higher viscosity levels with a reduction in the plasticiser level. It is only at shear rates above 1000 reciprocal seconds that viscosity starts to fall, with a further increase in shear rate. Unfortunately, there is a discrepancy in the viscosity measured by the Rotovisko and Severs rheometers. For the 100/45 S1 plastisol the viscosity, at a shear rate of 100 S$^{-1}$, determined by the Rotovisko is lower than that measured by the Severs rheometer. This lack of overlap in data, shown by a gap in the flow curves, see Figure 3.2.a., is due to sample loss from the concentric cylinders and over simplification in the calculation of apparent viscosity, see Appendix 5. This sample loss occurs because plastisols are not Newtonian fluids, so plastisol flows from the gap between the cylinders. To minimise these problems the viscosity of the plastisols was determined, using the Rotovisko, as described in Table 2.11. These procedures minimise the sample loss and ensure that any loss is similar for all grades and tests.
Figure 3.2.b., contains the flow curves of plastisols derived from the S2 paste polymer. These materials display a limited degree of pseudoplasticity, the severity of which increases with a reduction in plasticiser content. Compared with the S1 plastisols, low shear viscosities tend to be higher, but the high shear rate viscosities tend to be lower.

3.1.1.1.1 Paste Polymer Blends

Figure 3.3.a., shows the effect of blending a microsuspension paste polymer and an emulsion paste polymer on the rheological behaviour of the resulting 100/55 plastisol. For a plastisol prepared from the microsuspension paste polymer, the onset of dilatancy occurs at approximately 100 S⁻¹. Increasing the proportion of El, however, shifts the onset of dilatancy down the shear rate axis, until for an El plastisol, dilatancy starts to appear at approximately 0.3 S⁻¹.

The addition of El has a different effect at low and high shear rates. At a shear rate of 1.0 reciprocal second, see Figure 3.3.b., the viscosity rises continuously, with the addition of El. At higher shear rates (1000 S⁻¹), the viscosity initially falls, below that predicted by the law of mixtures (see the solid line in Figure 3.3.c) but then rises again with further additions of El.
Fig. 3.1 – Rheological Evaluation of Plastisols [Unimodal Latices]

a, – M1

b, – M2
Fig. 3.1 -

c, - E1

![Graph of Shear Rate vs. Apparent Viscosity for c, - E1]

Plasticiser (phr)
- 10.0
- 15.0
- 20.0
- 25.0

d, - E2

![Graph of Shear Rate vs. Apparent Viscosity for d, - E2]

Plasticiser (phr)
- 10.0
- 15.0
- 20.0
- 25.0

-119-
Fig. 3.2 - Rheological Evaluation of Plastisols [Bimodal Latices]

\[ \text{a, } - \text{ S1} \]

\[ \text{b, } - \text{ S2} \]
Fig. 3.6 – Effect of Ageing on Plastisol Rheology [Unimodal Latices]

\[ a, - M1 \]

\[ b, - M2 \]
Fig. 3.6 -

c, - E1

\[ \text{SHEAR RATE / S}^{-1} \]

\[ \text{APPARENT VISCOSITY / Pa.s} \]

Plasticiser (phr)
- 50.0
- 55.0
- 60.0
- 70.0

\[ \text{SHEAR RATE / S}^{-1} \]

\[ \text{APPARENT VISCOSITY / Pa.s} \]

Plasticiser (phr)
- 50.0
- 55.0
- 60.0
- 70.0

-132-
Fig. 3.7 – Effect of Ageing on Plastisol Rheology [Bimodal Latices]

a, - S1

b, - S2
3.1.1.2 Effect of Spray Drying Parameters.

3.1.1.2.a Unimodal Latices

Figures 3.4.a and 3.4.b show the rheological behaviour of plastisols prepared from the microsuspension paste polymers, dried under differing conditions. The plastisols considered in Figure 3.4.a were milled while those in Figure 3.4.b were unmilled. There are similarities in the behaviour of the two systems. The viscosity, measured at 4 s⁻¹, falls as the spray drying severity is increased from 1 to 2, but then rises as the drying severity is further increased. The high shear viscosity of M2 plastisols, measured at approximately 1000 S⁻¹, behaves in the same way. The viscosity initially falls but then increases with drying severity. The minimum, however, occurs at severity 3 and not 2, as in the case of the low shear viscosity. This effect, however, is hardly perceptible for the milled material, M1, the high shear viscosity hardly changing with drying severity. The milling process seems to limit the effect of the spray drying process. The plastisols prepared from the unmilled materials have a lower high shear viscosity but a higher low shear viscosity. The largest difference in behaviour of the two systems is in the rheological properties of the plastisols prepared under the most severe drying conditions, severity 4. The unmilled material, Figure 3.4.b., exhibits severe dilatancy, the onset of which occurs at 0.3 S⁻¹. The milled material, however, displays a lower degree of dilatancy which does not appear until approximately 10 S⁻¹. This, again, shows that the milling process seems to limit the effect of spray drying variations.

Figures 3.4.c and 3.4.d show the rheological behaviour of plastisols prepared from the emulsion paste polymers dried under different conditions. For these materials it is possible to directly compare the flow curves because the drying temperature at each severity was the same for E1 and E2, see Table 2.2. The plastisols prepared from these paste polymers respond in a similar way to drying conditions. As the drier temperature is increased the resultant plastisols become less pseudoplastic. Although E1 plastisols appear to be slightly more sensitive to drying temperature, as shown by the fall in low shear
viscosity on increasing the drying severity from 1 to 2, I suspect one should be cautious in drawing any conclusions from such an observation. At this stage one should assume that each system responds in a similar manner. There is no reason to believe the S1 paste polymer is more sensitive to drying temperature, as both systems are derived from similar latices.

3.1.1.3.b Bimodal Latices

Figure 3.5.a. describes the rheological behaviour of plastisols prepared from the S1 paste polymer dried under a range of drying severities. Compared with the microsuspension polymers a change in spray drying severity seems to have less of an effect on viscosity, the flow curves being relatively close together. Although the viscosity at 100 S\(^{-1}\) does rise continuously with drying severity, the viscosity at higher shear rates, 200 to 20000 S\(^{-1}\), does not seem to be affected. It is only when the most severe drying conditions are employed that the shape of the flow curve changes. The plastisol becomes dilatant, although the effect is limited compared with the increase in dilatancy observed by spray drying the unmilled microsuspension paste polymer, see Figure 3.4.b., under severity 4.

Figure 3.5.b describes the rheological behaviour of plastisols prepared from the S2 paste polymer dried under a range of drying severities. As in the case of the S1 paste polymer, increasing the drying severity from 1 to 3 has only a limited effect on the viscosity, measured between 5.0 S\(^{-1}\) and 2000 S\(^{-1}\). Dilatancy at these intermediate and high shear rates is totally suppressed. However, at low shear rates the two systems behave in a totally different manner. The S1 plastisol viscosity is relatively unaffected by drying conditions, while, the S2 plastisol viscosity initially rises, making the system highly pseudoplastic, and then falls resulting in a more "Newtonian" system, as drying temperatures are increased. Presumably, because of this peak in low shear viscosity, there must be two different drying temperatures which confer the same low shear viscosity.
Fig. 3.4 – Effect of Spray Drying [Unimodal Latices]

a, M1 100/65

b, M2 100/65
Fig. 3.4 -

c, E1 100/90

![Graph a](image1)

![Graph b](image2)

-126-
Fig. 3.5 – Effect of Spray Drying [Bimodal Latices]

a, S1 100/65

b, S2 100/65

Severity

○ 1
△ 2
+ 3
× 4
3.1.1.3 Effect of Ageing Plastisols

3.1.1.3.a Unimodal Latices

Although it has been reported that plastisol viscosity may fall upon ageing, the viscosity of all my plastisols increased with time. This is clearly demonstrated by the green lines which represent the viscosity of the aged plastisols.

(i) Microsuspension Paste Polymers

The change in rheology as a function of time for plastisols prepared from the microsuspension paste polymers, is described in Figures 3.6.a and 3.6.b. The viscosity of the plastisols was determined 24 (black lines) and 72 hours (green lines) after plastisol preparation. For both these systems the shape of the flow curve, on a log-log plot, does not appear to change dramatically when the time between preparation and testing is increased, although there is a tendency for the M2 plastisols to become a little more pseudoplastic at low shear rates. The plastisols remain dilatant, the magnitude of which increases with a reduction in the amount of plasticiser. The viscosity over the whole shear rate range does, however, rise as a function of time. As the viscosity against shear rate graph is plotted on a log axis, it should be pointed out that the rise in viscosity with time is not the same for each plastisol. The viscosity, determined at 1.0 S⁻¹, of the most dilute system (100/60 M₂ plastisol) rises by approximately 1.0 Pa.S after ageing for 72 hours while that of the most concentrated system rises by approximately 20 Pa.S. Neither is this rise in viscosity constant with shear rate. For the most concentrated plastisol, see Figure 3.6.a., although the rise in viscosity at 1.0 S⁻¹ is approximately 20 Pa.S it is around 100 Pa.S at 100 S⁻¹. Similar trends are also evident in the change in rheology of the M₂ plastisol with time, see Figure 3.6.b., although low shear rate viscosities tend to be influenced more by time than the high shear rate viscosities.

(ii) Emulsion Paste Polymers

The change in rheology of the emulsion paste polymer plastisols,
as a function of time, is described in Figures 3.6.c and 3.6.d.

For the plastisols prepared from the E1 paste polymer the shape of the flow curve changes drastically with time. This paste polymer ages rapidly, especially for the dilute systems. For the 100/70 plastisol, the viscosity, measured at 0.3 S⁻¹, rises from 10 PaS to 60 PaS, a six fold increase. For a 100/55 plastisol the viscosity, measured at the same shear rate, rises from 120 to 210 Pa S. This rapid ageing, of the dilute systems, causes a change in the shape of the flow curve. Although the 100/60 plastisol retains a degree of dilatancy after ageing, the 100/70 plastisol is transformed from a dilatant material to a pseudoplastic one, on increasing the ageing time from 24 to 72 hours.

In contrast to the E1 paste polymers, for plastisols prepared from the E2 paste polymers the shape of the flow curve is largely unaffected by ageing. This highly pseudoplastic material merely becomes even more pseudoplastic on increasing the time between preparation and testing from 24 to 72 hours. Such an increase in viscosity made it very difficult to test this material and so it was not possible to look at plastisol stability over a range of plasticiser levels. The ageing observation is therefore limited to a 100/90 plastisol.

3.1.1.3.b Bimodal Latices

Figure 3.7.a demonstrates the change in rheology, as a function of time, for a series of S1 plastisols, with plasticiser levels of 45, 50, 55 and 60 phr of DIOP. These 'Newtonian' plastisols retain their excellent flow properties on increasing the ageing time from 24 to 72 hours, the shape of the flow curve remaining constant. The viscosity does, however, increase with time. The most concentrated system (100/45 plastisol) experiences a viscosity increase of approximately 20 PaS, over the whole shear rate range. For the most dilute system (100/60 plastisol) the viscosity increases by approximately 3.0 Pa S over the whole shear rate range.

A similar set of results for the S2 plastisols is presented in
Figure 3.7.b. These systems do not retain their rheological properties with time. These mildly pseudoplastic systems become more pseudoplastic with time, because of the rapid increase in low shear viscosity. The greatest increase in viscosity is for the more dilute plastisols.
Fig. 3.6 – Effect of Ageing on Plastisol Rheology [Unimodal Latices]

a, - M1

b, - M2
Fig. 3.6 –

c, – E1

![Graph showing apparent viscosity vs. shear rate for E1 with different plastisizer concentrations.]

<table>
<thead>
<tr>
<th>Plastisizer (phr)</th>
<th>55.0</th>
<th>49.5</th>
<th>49.0</th>
<th>45.0</th>
<th>40.0</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

d, – E2

![Graph showing apparent viscosity vs. shear rate for E2 with different plastisizer concentrations.]

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Fig. 3.7 – Effect of Ageing on Plastisol Rheology [Bimodal Latices]

a, – S1

b, – S2
3.1.1.4 Mixing Constraints

The results described in Figure 3.8 are an extension of the work reported in Figure 2.1. The objective being to further evaluate the effect of mixing variables on both unfilled and filled plastisol rheology, so that the interpretation of future results will not be confused by paste polymer deagglomeration. Such deagglomeration could be brought about by the hard, angular filler particles and changes in the mixing conditions.

Figure 3.8.a shows the change in rheology of a 100/45 M1 plastisol, as a function of time. The flow curve does not change on increasing the mixing time from 5 to 10 minutes. Nor does it change for a 100/50 M1 plastisol containing 4% RFC5, as shown in Figure 3.8.b. Such a level of T.o~ was chosen as it was the maximum level used in this study and has been reported as a cause of deagglomeration in plastisols. It is only after 25 minutes of mixing that the low shear viscosity starts to fall. After such a protracted mixing time, it maybe the resultant heat build up which causes this fall in viscosity. The addition of 4% RFC5, the maximum used in this study, does not change the effect of mixing time.

The results described in Figure 3.8,c are extremely important. In the next chapter, which considers the rheology of filled systems, all the formulations are designed on the assumption that the filler is added as a dispersion in DIOP. As it was not possible to measure the PSD of a filled system, during the initial stages of this work, I decided to add filler as a pre-dispersion so that any paste polymer deagglomeration due to filler particles would be minimised. This would enable interactions between PSD and rheology to be assessed more easily. Figure 3.8.c shows the rheology of a 100/50 S2 plastisol containing two levels of Polcarb filler. The plastisols characterised by the black lines contain filler, added as a pre-dispersion in DIOP, the formulations are given in Table 2.5. The red lines are for similar systems, the filler being added as a dry powder, the formulations are given in Table 2.6. From Figure 3.8.c it does not seem to matter in which form the filler was added, the flow curve for the dry filler and the pre-dispersed filler additives are
identical.

All the filled plastisol formulations are based on a 100/50 plastisol, all the ingredients being charged to the Hobart mixing bowl at the start of the mixing process. In effect, this increases the thick stage plasticiser level to 50 phr, for the (M and S) filled systems. Figure 3.8.d clearly shows that for a 100/50 plastisol, prepared from S1, it does not matter whether the plasticiser is added in two stages, 45 parts and then 5 parts, or in one stage, 50 parts.
Fig. 3.8 – Mixing Constraints

a, Effect of Mixing Time (M1 100/45)

b, Effect of Mixing Time (M1 100/50 + 4% RFC5)
c, Filler Dispersion Problems (S2 + Polcarb)

![Graph showing Filler Dispersion Problems (S2 + Polcarb).]

---

d, Effect of Plasticiser Level (S1)

![Graph showing Effect of Plasticiser Level (S1).]

---

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3.1.2 Measurement of Particle Size Distributions

3.1.2.1 Electron Microscope Examination of Paste Powders.

Figures 3.9.a and 3.9.b contain micrographs of the seeded emulsion paste polymers, at a magnification of 11000 X. For both of these samples, one can see the distinct bimodal distribution of particle sizes. Each sample has a size ratio of large (L) to small (S) primaries of \( \approx 4:1 \). From these micrographs, one can also see that the only difference between the two grades is the average size of the particles, both the L primaries and S primaries are smaller in the S2 material.

For the M1 paste polymer, one can see from Figure 3.9.c that there is no evidence of two families of particles, there is a continuous gradation of sizes as one would expect. At a magnification of 11000 X, using the scale shown, one can see that the average size of the primaries is \( \approx 1.1 \mu m \).

Figures 3.9.d, e and f contain micrographs of the emulsion paste polymers at different magnifications. From Figure 3.9.d, using a magnification of 55000 X, one is able to isolate the presence of the 0.15 \( \mu m \) primaries. Unfortunately, at this magnification the electron microscope is operating at the limit of its range and it is therefore not possible to clearly identify the particle boundaries. To isolate the differences between the E1 and E2 paste polymers, samples of each were examined under a magnification of 55 X, see Figures 3.9.e and 3.9.f. Although these micrographs do not represent statistically representative samples, and thus it is not possible to characterise the PSD, one can see that the E2 material appears to contain a large number of fragments. One would expect this as the material is dried under milder conditions and should therefore be composed of less thoroughly fused secondaries.
FIG. 3.9 -
SEM MICROGRAPHS

A. S1 1 μM

B. S2 1 μM

C. M1 1 μM
3.1.2.2 Uncompounded Plastisols

3.1.2.2.a Unimodal Latices

(1) Microsuspension Paste Polymers

Figure 3.10.a contains the particle size analysis of a 100/45 plastisol prepared from the microsuspension paste polymer, M1. This data was obtained using the Sedigraph 5000 ET. The instrument detected the unimodal primary PSD which extends from 0.3 to 2.0 μm and accounts for 80%, by weight, of the distribution. The remaining 20% of the distribution is made up of agglomerates of the primary particles and extends from 2.0 to 80 μm. The average size of the primary particles, determined at 50% by weight of the PSD, is 1.1 μm. The average size of the secondary particles is approximately 6 μm. The Particle Size Analysis (PSA) displayed in Figure 3.10 also contains data for plastisols aged for 72 and 168 hours, this data will be examined in Section 3.2.1.4.

Figure 3.10.b contains the PSA of a 100/45 plastisol prepared from the unmilled microsuspension paste polymer, M2. A direct comparison with the PSD presented in Figure 3.10.a reveals the higher proportion of secondary particles in the unmilled material. For this paste polymer the primary PSD extends from 0.3 to 2.0 μm and accounts for only 70%, by weight, of the distribution. Again the average size of the primaries is ~ 1.1 μm. However, the average of the secondaries, determined at 50% by weight, is approximately 20 μm. These findings show that the milling of the microsuspension paste polymer reduces the size and concentration of secondary particles within the plastisol.

(ii) Emulsion Paste Polymers

Figure 3.10.c represents the PSD of a 100/45 plastisol prepared from E1. As the primary PSD has an average size of 0.15 μm, the distribution shown in Figure 3.10.c. must be composed of only secondary particles, The size of which ranges from 1.0 to 80 μm, with an average size of approximately 17 μm.

Sedigraph particle size analysis of a 100/90 plastisol, prepared
from E2, revealed two size distributions, see Figure 3.10.d. The first PSD accounts for up to 34% of the total distribution. From the Sedigraph data, the average size of the first PSD appears to be about 0.4 μm. The average size of the larger particles appears to be approximately 13 μm.

3.1.2.2.b Bimodal Latices

The particle size analysis (PSA) of a 100/45 S1 plastisol reveals three distinct size distributions, see Figure 3.10.e. The bimodal primary PSD is clearly shown, it accounts for approximately 58% of the total size distribution. The average size of the small primary particles (S primaries) according to the Sedigraph, is around 0.25 μm. The average size of the large primary particles (L primaries) is approximately 1.1 μm. These results agree with those provided by ICI, which are based upon the PSA of a latex prior to spray drying, using a Joyce-Loebl Disc Centrifuge. The remainder of the size distribution is composed of secondary particles (or agglomerates) which have an average size of ≈ 17 μm and occupy 42% of the distribution.

Unfortunately, the results of a PSA of a 100/45 S2 plastisol did not highlight the bimodal primary PSD as clearly as in the case of the S1 plastisol, see Figure 3.10.f. The system appears to be bimodal, the secondary PSD accounting for 50% of the distribution, with an average size of ≈ 17 μm. The primary PSD seems to be almost 'Unimodal', although the inflection in the curve, at 0.3 μm, suggests the presence of another family of primary particles.
Fig. 3.10 – Plastisol Particle Size Analysis [Unimodal Latices]

a, M1 (Milled)

b, M2 (Unmilled)
Fig. 3.10 –

c, E1

![Graph showing cumulative mass percent vs. equivalent spherical diameter for E1.]

Time
- 24 hrs
- 72 hrs
- 168 hrs

d, E2

![Graph showing cumulative mass percent vs. equivalent spherical diameter for E2.]

Time
- 24 hrs
- 72 hrs
- 168 hrs
Fig. 3.10 -

e, S1

![Graph showing cumulative mass percent vs. equivalent spherical diameter for S1, with data points at 24, 72, and 168 hours.]

f, S2

![Graph showing cumulative mass percent vs. equivalent spherical diameter for S2, with data points at 24, 72, and 168 hours.]

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3.1.2.3 Effect of Spray Drying Conditions on Plastisol PSD

3.1.2.3.a Unimodal Latices

Figure 3.11 contains the PSA of plastisols prepared from various unimodal paste polymer latices, dried under different spray drying conditions.

The PSA of M1 plastisols reveals an increase in the size and concentration of secondary particles as the drying severity is increased, see Figure 3.11.a and Table 3.1.

Table 3.1 - PSA of Plastisols Derived from M1, Dried Under Differing Conditions

<table>
<thead>
<tr>
<th>Severity</th>
<th>Primary PSD</th>
<th>Secondary PSD</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>% of Total</td>
<td>Average size (μm)</td>
</tr>
<tr>
<td>1</td>
<td>92.0</td>
<td>2.3</td>
</tr>
<tr>
<td>2</td>
<td>88.0</td>
<td>4.0</td>
</tr>
<tr>
<td>3</td>
<td>88.0</td>
<td>4.0</td>
</tr>
<tr>
<td>4</td>
<td>67.0</td>
<td>7.0</td>
</tr>
</tbody>
</table>

The data presented in Table 3.1 was extracted from Figure 3.11.a, assuming the primary PSD account for all particles smaller than 2.0 μm.

A similar analysis of the size of particles within a series of M2 plastisols, derived from paste polymers dried under various conditions, led to the data displayed in Figure 3.11.b and Table 3.2.
TABLE 3.2 - PSA OF PLASTISOLS DERIVED FROM M2, DRIED UNDER DIFFERING CONDITIONS.

<table>
<thead>
<tr>
<th>Severity</th>
<th>Primary PSD</th>
<th>Secondary PSD</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>% of Total</td>
<td>Average Size</td>
</tr>
<tr>
<td></td>
<td></td>
<td>(μm)</td>
</tr>
<tr>
<td>1</td>
<td>89.0</td>
<td>4.0</td>
</tr>
<tr>
<td>2</td>
<td>90.0</td>
<td>7.0</td>
</tr>
<tr>
<td>3</td>
<td>81.0</td>
<td>9.0</td>
</tr>
<tr>
<td>4</td>
<td>29.0</td>
<td>14.0</td>
</tr>
</tbody>
</table>

Again, an increase in drying severity led to a significant increase in the size and concentration of secondary particles.

By comparing the data in Tables 3.1 and 3.2, the effect of milling the paste polymer becomes clear. When the paste polymer was dried under severity 4, the milling process appears to reduce the concentration and size of secondary particles. The unmilled system contains 14.0 μm particles which account for 71% of the distribution, while the milled system contains 7.0 μm particles which account for only 33% of the distribution. Milling seems to limit the effect of spray drying variations. Similar decreases in size and concentration of secondary particles occur for materials dried under severity 3 but the change is less marked, as these drying conditions generate fewer secondary particles.

Figures 3.11.c and 3.11.d contain the PSD of plastisols prepared from the emulsion paste polymers, dried under differing severities. Initial inspection of these figures suggest the presence of two size distributions, shown by the inflection at 1.0 μm. This data combined with the micrograph presented in Figure 3.9.f confirms my belief that there are indeed two distributions. The larger particles are in fact intact secondary particles, while the smaller particles are fragments of these secondaries.
For the emulsion paste polymers it is possible to directly compare the PSD generated from each drying severity, as they were dried under identical conditions, see Table 2.2. These grades respond in a similar way to spray drying, the PSD generated from the paste polymers, dried under each severity, are approximately the same. Increased drying severity results in the formation of larger quantities of secondary particles.

It is interesting to note that the emulsion paste polymers are more sensitive to drying temperatures. A plastisol prepared from an E1 paste polymer, dried at 55°C (severity 1), contains 35% intact secondary particles, while a similar plastisol prepared from the M1 paste polymer dried at 55°C (severity 1.5) contains only 10% secondary particles. Such behaviour may be expected, one would expect the emulsion paste polymers to generate a larger proportion of intact secondary particles because of the smaller size of the primary particles (< 0.15 \( \mu m \)), see Figure 3.9.d. Such particles should soften more easily, during spray drying, and thus fuse into the secondary particles more thoroughly.

3.1.2.3.b Bimodal Latices

The effect of spray drying variations on plastisol PSD, for bimodal latices, is shown in Figure 3.12.

For the series of S1 plastisols, increasing the severity of the drying conditions causes an increase in the concentration of secondary particles, see Table 3.3.
TABLE 3.3 - PSA OF PLASTISOLS DERIVED FROM S1, DRIED UNDER DIFFERING CONDITIONS.

<table>
<thead>
<tr>
<th>Severity</th>
<th>Primary PSD</th>
<th>Secondary PSD</th>
<th>% of Total</th>
<th>Average Size ($\mu m$)</th>
<th>% of Total</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>78.0</td>
<td></td>
<td>9.0</td>
<td>22.0</td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>76.0</td>
<td></td>
<td>10.0</td>
<td>24.0</td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>54.0</td>
<td></td>
<td>8.0</td>
<td>46.0</td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>36.0</td>
<td></td>
<td>8.0</td>
<td>64.0</td>
<td></td>
</tr>
</tbody>
</table>

The data presented in Table 3.3 was extracted from Figure 3.12.a assuming the primary PSD accounts for all particles smaller than 1.4 $\mu m$.

The ratio of large primaries ($L$) to small primaries ($S$) appears to remain constant, at 3:1, there is no evidence of preferential agglomeration during spray drying. The system does, however, seem more sensitive to the drying conditions when compared with the microsuspension system. When dried under severity 3, the S1 secondaries account for 46% of the distribution, the M1 and M2 secondaries account for 12 and 19%, respectively.

Unlike the S1 plastisols, for the series of S2 plastisols there is no evidence of the bimodal primary PSD (see Figure 3.12.b) which was evident in the micrographs. The primary particles appear to be fused together, as in the case of the E2 plastisols, the particles smaller than 1.1 $\mu m$ are likely to be fragments of secondary particles.

From Figure 3.12.b one can see that the more severe drying conditions result in the formation of more intact secondary particles.

The apparent absence of independent 0.2 and 0.7 $\mu m$ primaries may be due to the failure of the Sedigraph to resolve these two families of particles. Evidence to support the theory that structure development may cause problems in PSA, by sedimentation, will be presented in Section 4.2.2.3.b.
Fig. 3.11 – Effect of Spray Drying [Unimodal Latices]

a, M1 100/65

b, M2 100/65
c, E1 100/90

d, E2 100/90
Fig. 3.12 – Effect of Spray Drying [Bimodal Latices]

a, S1 100/65

b, S2 100/65
3.1.2.4 Particle Stability

3.1.2.4.a During Plastisol Preparation

As stated in Section 3.1.1.4, during the initial stages of this work, it was not possible to accurately measure the PSD within a filled plastisol. However, the use of the Sedigraph has made an approximate measure of PSD possible. Figure 3.13.a and 3.13.b show the change in PSD caused by increasing the mixing time, of an unfilled and a filled plastisol, from 2 to 25 minutes.

For the unfilled system, see Figure 3.13.a, there appears to be a 3 to 4% reduction in the concentration of secondaries and a similar increase in the concentration of primaries. These tests were carried out on the materials presented in Figure 3.8.a. As there seems to be little change in rheology, the importance of this small change in PSD should not be exaggerated. The experimental error experienced in the Sedigraph is ± 1.5%.

A similar set of results is presented in Figure 3.13.b. The rheology data for these filled plastisols is presented in Figure 3.8.b. Again, the limited shift of the PSD, to larger sizes, may be attributed to experimental error.

3.1.2.4.b During Paste Blending

The development of the Malvern 2200/3300 PSA technique has made the accurate assessment of the PSD of a filled plastisol possible. Figures 3.14 and 3.15 contain the data obtained from the analysis of filled and unfilled systems, using this instrument.

Figure 3.14.a contains the PSD of an E1 and a Q60 dispersion, the quantity of DIOP being equivalent in volume ratio to a 100/50 plastisol. The PSA was duplicated to assess the repeatability of the technique. As clearly shown, both systems are unimodal, the Q60 particles being smaller than the E1 particles. Figure 3.14.b contains a duplicated PSA,
of a filled plastisol, based on a ratio of solids to liquid equivalent to a 100/50 plastisol. The solids fraction containing 18% by volume Q60. The two lines indentified by crosses represent the PSA predicted from the Q60 and E1 dispersion data. These predicted values being obtained by adding 70.65% of the E1 values to 29.35% of the Q60 values, presented in Figure 3.14.a, and plotting these points against sizes, in Figure 3.14.b. A value of 29.35% by weight was used because this is equivalent to 18% by volume. The agreement between the PSD predicted by combining the distributions presented in Figure 3.14.a and the PSD of the filled plastisol presented in Figure 3.14.b is very close.

A similar set of results for an S1 filled plastisol is presented in Figure 3.15, again the agreement between actual and predicted values is quite close.

3.1.2.4.c During Rheological Characterisation

Figure 3.16 contains the PSD’s and flow curves of plastisols before and after the application of shear. The black lines represent the PSD and rheology measurements carried out 24 hours after plastisol preparation. The data represented by the green lines was obtained from the same material, immediately after passing the plastisol through the 1.0 mm die of the Severs rheometer, under an applied pressure of 1000 psi.

Figures 3.16.a and 3.16.b contain the data derived from a 100/90 plastisol prepared from the E2 paste polymer. Although there seems to be a shift in the PSD, to the larger sizes, there is only a minimal fall in the flow curve, the shape of which does not change.

A similar set of results for a 100/55 E1 plastisol is presented in Figures 3.16.c and 3.16.d. For this material the shear forces seem to have an extremely limited effect. The PSD does not appear to change and there is only a limited change in the Severs viscosity.
Fig. 3.13 – Particle Stability – During Plastisol Preparation

a, Unfilled Systems (M1 100/45) – see 3.8.a

b, Filled Systems (M1 100/50 + 4.5% RFCS) – see 3.8.b
Fig. 3.14 – Particle Stability – During Paste Blending

a, DIOP Dispersions (100/50)

b, Filled Plastisols
Fig. 3.15 – Particle Stability – During Paste Blending

a, DIOP Dispersions (100/50)

b, Filled Plastisols
Fig. 3.16 – Particle Stability – During Rheological Characterisation

a, Effect of Shear on PSD (E2 100/90)

b, Effect of Shear on Rheology (E2 100/90)
c, Effect of Shear on PSD (E1 100/55)

d, Effect of Shear on Rheology (E1 100/55)
3.1.2.5 Evaluation of the Plasticiser Absorption of Paste Polymers

Figure 3.17 contains the plasticiser absorption values of each of the paste polymers, determined according to BS 1795 : 1965. Each value is expressed in terms of unit weight and unit volume.
Fig. 3.17 – Paste Polymer Plasticiser Absorption

a, Per Unit Weight

b, Per Unit Volume
3.2 DISCUSSION OF RESULTS

3.2.1 Relationships between Plastisol PSD and Rheology

3.2.1.1 Effect of Concentration of the Dispersed Phase

As described in Section 1.3.1, of the literature search, many workers have tried to formulate mathematical relationships between suspension rheology and the concentration of the dispersed phase, each relationship being limited to a particular concentration range. In 1971 Chong et al. developed an empirical relationship between plastisol viscosity and polymer concentration, as shown in Figure 1.19. Such a correlation assumes that the relative viscosity of a suspension of spherical particles is independent of PS and PSD, and is only a function of reduced volume fraction \(\phi/\phi_0\). To test this suspect assumption, the viscosity of each plastisol, described in Figures 3.1 and 3.2 was plotted against \(\phi/\phi_0\). Appendix 9 describes the calculation of \(\phi/\phi_0\) for each system.

The black line in Figure 3.18.a represents the empirical equation developed by Chong et al.:

\[
n = n_0 \left[ 1 + 0.75 \frac{\phi/\phi_0}{1-\phi/\phi_0} \right]^2
\]

The considerable degree of scatter in the results presented in Figure 3.18.a casts doubt on Chong et al.'s assumption of a simple relationship between viscosity and concentration. As plastisols are colloidal suspensions, viscosity is also influenced by the PS and PSD of the dispersed phase through the effects of particle packing efficiency, porosity, hydrodynamic and non-hydrodynamic forces, surface area and electrostatic forces.

The bimodal systems, S1 and S2, appear to have a higher viscosity than predicted by the empirical equation, while, the unimodal, microsuspension systems appear to have a lower viscosity than expected. The considerable departure of the E2 plastisol viscosity from the
expected values is not an erroneous result; as will be shown later, in sections considering El plastisol rheology (Section 3.2.1.2.b), the small size of the primary particles (0.15μ) enhances the effect of the non-hydrodynamic forces, which considerably increase viscosity. Later experiments have cast doubt on these conclusions, see Section 5.2.1.

3.2.1.2 Effect of Paste Polymer Type

As shown in sections 1.5.1.1 and 1.5.1.2 of the literature search, considerable care must be taken when considering relationships between paste polymer PSD and plastisol rheology. Shtarkman and Varonkova attempted to relate the plastisol flow curve to the latex PSD, as demonstrated in section 1.5.1.1. However, it is obvious from their results that the rheology of their systems was related to the PSD within the plastisol, at the time of testing, and not the latex PSD. Kaltwasser et al also had problems in accounting for the behaviour of their bimodal systems, see section 1.5.1.2. They characterised the latex PSD but were unsure of the PSD within the plastisol and so found it impossible to explain the conflicting behaviour of two systems. To avoid these problems, I characterised the PSD of the paste polymers within the plastisol, using the Sedigraph, and the rheology of the systems, 24 hours after plastisol preparation. A summary of the PSD and rheology data presented in section 3.1 is presented in Figure 3.19.

3.2.1.2.a Microsuspension Paste Polymers

The microsuspension polymerisation technique employed in the manufacture of M1 produces a broad unimodal distribution of primary particle sizes, ranging from approximately 0.3 - 2.0 μm, with a mean of 1.1 μm. As the spray drying process is carried out under mild conditions, the superficial agglomerates, formed during the drying stage, tend to breakdown during dispersion of the paste polymer in the plasticiser. According to Figure 3.19.a the primary PSD accounts for 80% of the total, by weight. This broad distribution of primary particle sizes appears to have a dominant effect on plastisol rheology. The continuous gradation of sizes minimises void volume, as the small
particles fit into the interstices of the larger particles. This efficient packing releases plasticiser from the interstices between the larger particles and results in a comparatively low viscosity plastisol. As can be seen from Figure 3.19.b the microsuspension paste polymers confer the lowest low shear viscosity of all the paste polymers tested. The absence of any pseudoplasticity, at low shear rates, may be attributed to the careful control of the homogenisation process, which may be used to limit the lower size of the PSD, to 0.3 μm. Particles smaller than this lead to a pronounced increase in low shear viscosity which results in pseudoplasticity. The influence of particles smaller than 0.3 μm will be discussed in the section considering emulsion paste polymers.

Unfortunately, although the primary PSD produced by the microsuspension technique produces a low shear viscosity at low shear rates, the unimodal nature leads to dilatancy at higher shear rates. Hoffman observed similar dilatant behaviour in suspensions containing monosized 1.25 μm spheres of PVC. He proposed a model to account for this behaviour, based on the theory that 1.25 μm PVC particles flow in hexagonal layers below the discontinuity point. As the shear forces are further increased, disordered flow occurs which results in a discontinuous jump in viscosity at the instability point. Far above this point ordered flow occurs once again. Hoffman supported his theory by light diffraction studies and photographic techniques. In a study of particle packing, Westman and Hugill provided evidence to support Hoffman's model. They were able to show that spheres of uniform size pack into hexagonal planes.

The M1 plastisols displayed dilatancy and not a discontinuous jump in viscosity, as occurred in Hoffman's work. The broad distribution of sizes, present in the M1 plastisol, probably reduces the degree of perfection in the hexagonal planes and so the breakup of ordered flow occurs over a range of shear rates and not at an instability point. For Hoffman's samples, the discontinuity shear rate goes to zero when the volume fraction of solids is raised to 0.60. This could be predicted from the model, as planes of hexagonally packed spheres placed over one another have 0.605 volume fraction of solids when the planes just meet.
The onset of dilatancy for an M1 plastisol, with a solids volume fraction of 0.609 (45 phr DIOP), does not occur until 35 s⁻¹, as shown in Appendix 10. The improvement in packing efficiency and disruption of the hexagonal planes of particles retards the onset of dilatancy.

The dilatancy of plastisols derived from microsuspension paste polymers may be suppressed. As demonstrated, in section 1.5.2.1., by Kaltwasser et al., an increase in the width of the latex PSD may be used to suppress dilatancy. Collins and Hoffmann were able to achieve a similar effect by spray drying the latex under more severe conditions, the generation of secondary particles increasing the width of the whole PSD.

It is clear from Figure 3.19.b that the secondary particles are not present in sufficient quantities to suppress dilatancy, they occupy only 20% of the distribution. These particles tend to be porous, having a high void content, as they are derived from a unimodal latex. From this discussion it is obvious that the concentration of secondary particles is very important. Too low a level results in the dilatancy exhibited by the M1 plastisol. Too high a level would increase the viscosity of the plastisol as the high plasticiser absorption of the secondary particles becomes the dominant factor controlling viscosity. For the El plastisols, it is the high plasticiser absorption of the secondary particles which controls viscosity, see section 3.2.1.2.b.

By comparing the rheology and PSD for the two microsuspension systems, it is possible to evaluate the effect of the milling process. The primary PSD of the M2 plastisol accounts for 70% of the total distribution. The milling process reduces the concentration of secondary particles. The primary PSD of the M1 plastisol accounts for 80% of the total. The reduction in the size and concentration of secondary particles reduces the defects in the hexagonal planes which lead to dilatancy. This results in an unwanted increase in the flow instabilities which lead to dilatancy. For these particular systems, the milling process reduces the width of the PSD and results in an increase in dilatancy. From these observations, it may seem that the milling process leads to problems in
the flow behaviour of the system. Although this is true, the main purpose of the milling process, in this particular case, is not to control rheology but to reduce the maximum size of the secondary particles. For applications which require thin coatings, such as in wall paper coatings, large particles may impair the surface finish. For M1 plastisols, the milling process is used to improve suitability for such applications even though rheology may suffer.

3.2.1.2.b Emulsion Paste Polymers

The emulsion polymerisation technique, employed in the manufacture of E1 and E2, produces a latex with a very narrow distribution of sizes, the mean size being ≈ 0.15 μm (see Figure 3.9.d). For the E1 paste polymers the latex is spray dried under severe conditions. As can be seen from Figure 3.19.a, this treatment results in the formation of large 17 μm secondary particles, which remain intact in the plastisol. There is no evidence of any independent primary particles. Boisain and Feldman showed that the secondary particles produced at high temperatures become resistant to breakdown.

The secondary particles produced by this process tend to be porous, as the packing efficiency of unimodal systems tend to be low. If the secondary particles in E1 were of low porosity their large size would result in the plastisol having a lower viscosity than an M1 plastisol. However, the porous nature of these particles leads to the immobilisation of considerable quantities of plasticiser which results in a high plastisol viscosity. From Figure 3.19.b one can see that the low shear viscosity of the E1 plastisol is the second highest of all the systems tested. The low shear viscosity of the E2 plastisol is not presented in Figure 3.19.a because, at a DIOP content of 55 phr, it was too high to be measured.

The E1 plastisol exhibits dilatancy at low shear rates, the onset of which occurs at ≈ 0.7 S⁻¹. For an M1 plastisol it occurs at 35 S⁻¹.

According to Williams and Bergen's study, section 1.3.2.1.c., the
onset of dilatancy is a function of the reduced volume fraction of solids
and may be predicted from the least-squares equation developed by these
workers:

\[
\log_{10} \dot{\gamma}_d = -9.8568 + 10.437/\theta R \tag{3.2}
\]

where \( \theta R = \theta / \theta \infty \)

To test the validity of this claim the onset of dilatancy for the M1
and E1 plastisols was plotted as a function of the reciprocal of the
reduced volume fraction (RVF), see Figure 3.18.b. The red line in this
figure represents data derived from equation (3.2), this data relates the
discontinuity shear rate to the volume fraction of polymer and was
derived from suspensions containing monodispersed 1.7 \( \mu m \) diameter PVC
particles.

The M1 and E1 plastisols are not monodispersed, each contains a
range of particle sizes. It is the difference in PS and PSD between the
paste polymers used in my study and the materials used in Williams and
Bergens study which explains the considerable variation in the
correlation between discontinuity and reduced volume for each system,
shown in Figure 3.18.b. The broad distribution of sizes within the M1
plastisol causes progressive breakdown of the hexagonal planes of
particles, when subjected to increasing shear forces. This results in
dilatancy and not a discontinuity in the flow curve. To ease comparison
between the various systems, the apparent discontinuity point was taken
as the most steeply rising portion of the dilatancy curve, which was
determined by differentiation.

From Figure 3.18.b it is apparent that for dilute M1 plastisols
the "discontinuity" occurs at lower shear rates than predicted by equation
3.2. This premature "discontinuity" is a result of the broad distribution
of sizes, which results in less perfect hexagonal planes of particles
which breakup at lower shear rates because of these imperfections.

The results for the E1 plastisol show an even greater deviation
from the values expected by Williams and Bergen. It is unlikely that the
deviation is a result of the high secondary particle porosity of the E1 secondary particles because this is taken into account in the calculation of $\delta R$, which measures the deviation from the maximum amount of PVC which can be incorporated into a plastisol. At the maximum PVC level, the porous structure of the E1 secondary particles will be saturated with plasticiser.

The low shear dilatancy of the E1 plastisol is a result of the size of the E1 secondaries. For unimodal systems, larger particles require more time to flow around one another. As the shear rate is increased, the time for cooperative movement is reduced and so dilatancy occurs at low shear rates for systems containing large particles.

The application of equation 3.2 is, therefore, limited to monodispersed samples with particle sizes in the region of 2.0 $\mu$m. Larger particles or a significant proportion of secondary particles (>20% by weight) causes the performance of plastisols to deviate from the behaviour predicted by equation 3.2.

The onset of dilatancy, for the E1 and X1 plastisols, may be predicted from the following least-square equations, which were derived in a similar manner to the equation due to Williams and Bergen;

$$\text{X1 plastisols : } \log_{10} \dot{\gamma}_d = -2.5805 + 3.7582/eR$$  \hspace{1cm} (3.3)

$$\text{E1 plastisols : } \log_{10} \dot{\gamma}_d = -7.8109 + 6.8108/eR$$  \hspace{1cm} (3.4)

The solid lines in Figure 3.18.b represent the least-squares equation data. The symbols represent viscosity data for the X1 and E1 plastisols respectively.

As in the case of E1, the E2 material consists of a narrow unimodal latex PSD, with a mean diameter of $\approx 0.15 \mu m$. However, the mild drying conditions lead to a broad distribution of sizes within the plastisol, as shown in Figure 3.19.a. The secondary particles tend to be porous, as they are derived from a unimodal latex.
A plastisol prepared from the E2 paste polymer has a very high low shear viscosity (1000 Pa S at a shear rate of 0.1 S⁻¹, for a 100/90 plastisol), as shown in Figure 3.1.d., and is extremely pseudoplastic. Such a high low shear viscosity is probably a function of the small (≈ 8.0 µm) porous secondary particles which occupy 35% of the distribution. These particles have a large surface area, high internal porosity and immobilise large quantities of plasticiser, which is no longer available to facilitate flow. It should, also, be noted that the independent 0.15 µm primary particles, within the plastisol, have a disproportionate effect on low shear viscosity. According to the DLVO theory of colloidal stability\(^\circ\), section 1.3.2.2., the importance of thermal (Brownian), electrical and London-Van der Waal's forces increases dramatically as the PS decreases below 0.5 µm. Such non-hydrodynamic forces increase the viscosity at low shear rates. At high shear rates their effect is negligible. In addition, the structure contribution depends upon the square of the number of particles and so this effect increases rapidly with a reduction of PS. This relationship between PS and the magnitude of the forces acting upon it is very important. In section 1.5.1.1, Kaltwasser et al\(^\circ\) have demonstrated the change over from dilatant to pseudoplastic flow on decreasing the PS of a unimodal system, below 0.45 µm.

The broad distribution of sizes within an E2 plastisol prevent dilatancy at high shear rates, making the system pseudoplastic. The absence of dilatancy in unimodal systems of particles smaller than 0.45 µm may also be due to the Brownian motion, which prevents the formation of the hexagonal planes proposed by Hoffman\(^\circ\).

3.2.1.2.c Seeded Emulsion Paste Polymers

The seeded emulsion polymerisation technique is employed in the manufacture of the S1 paste polymer. The latex PSD contains two narrow distributions of particles with diameters of 0.25 and 1.0 µm. The small, 0.25 µm, particles account for 33% of the latex PSD, by weight.

During the spray drying process, the primary particles fused
together forming secondary particles. The porosity of these secondaries tends to be lower than the porosity of the secondary particles derived from a unimodal latex, as a unimodal distribution of particles does not pack together as efficiently. When the S1 paste polymer is dispersed in DIOP, to form a plastisol, many of the secondary particles break down, liberating independent primary particles. From Figure 3.19.a one can see that the independent primary PSD accounts for 60% of the distribution.

The rheology of the S1 plastisols is controlled by both the primary and secondary particles. The efficient packing of the independent 0.25 and 1.0 μm particles minimises void volume and, thus, imparts a low viscosity, at low shear rates. The plastisols are almost Newtonian, any dilatancy at high shear rates is totally suppressed. The small primary particles (S primaries) separate the large primary particles (L primaries) sufficiently to allow the 1.0 μm particles to flow easily past each other, without the flow instabilities which lead to dilatancy. The low shear viscosity of the S1 plastisol is higher than that of the M1 plastisol. According to the practical experiments carried out by McGeary, Westman and Hugill, section 1.4.1, the size ratio between the large and small particles should be at least 7 : 1 (and preferably 10 : 1) in order to achieve optimum packing. It is, therefore, clear that the size ratio of 4 : 1, employed in the production of the S1 paste polymer is insufficient to achieve the lowest void volume in the plastisol. The size of the L primaries is limited, by the seeded emulsion process, to approximately 1.1 μm. The lower size of the particles is limited by surface area effects, which eventually increase plastisol viscosity, to approximately 0.2 μm. The lowest void content appears to be achieved by employing a continuous gradation of sizes, as in the case of M1.

The large secondary particles in the S1 plastisol, which account for 40% of the distribution, are of low porosity and immobilise relatively small amounts of plasticiser. These particles help to suppress dilatancy and maintain a low shear viscosity at low shear rates by acting as blending resin particles.
Although 20% of the S1 plastisol PSD is composed of particles with a diameter below 0.25 μm, the pseudoplasticity which would be expected is prevented by the addition of a viscosity depressant.

The S2 paste polymer is manufactured in a similar way to the S1 material. The latex PSD contains two narrow distributions of particles with diameters of 0.2 and 0.7 μm. Again, the small particles account for 30% of the latex PSD and the size ratio of the large to small particles is ≈ 4 : 1.

When the latex was spray dried, the primary particles agglomerated to form fused secondary particles. It appears that the smaller size of the S2 primaries, compared with the S1 primaries, results in more thoroughly fused secondary particles, this higher level of secondary particle fusion is a primary factor in accounting for the difference in rheological properties between the S1 and S2 plastisols. Although, both grades are prepared by the seeded emulsion polymerisation technique, the PSD within each plastisol is very different, as shown in Figure 3.19.a.

The secondary particles in S2 plastisols resist breakdown in the plasticiser. According to the Sedigraph measurements there appears to be only limited evidence of the bimodal primary PSD. Many of the primary particles must have been thoroughly fused together, during the drying process, to form stable low porosity secondary particles, which do not liberate independent primary particles during plastisol preparation. S2 plastisol rheology can not be controlled by the efficient packing of independent primary particles, as many of the primaries seem to be fused together. Nor could dilatancy be controlled by the interaction of the large (0.7 μm) and small (0.2 μm) independent primary particles.

The S2 plastisols are pseudoplastic over the whole shear rate range. The PSD of these systems is extremely broad. Although the system contains a high concentration of small secondary particles (38% smaller than 0.8 μm and 15% smaller than 0.25 μm), the porosity of these particles is very low and it is this factor combined with the broad size
distribution which maintains the low viscosity and pseudoplasticity of the system. The role of structure development in S2 plastisol rheology will be evaluated in Chapter 4.

3.2.1.2.d Paste Polymer Blends

Throughout the preceding discussions and the literature search, it has been assumed that the viscosity of a bimodal suspension is lower than the viscosity of either of the unimodal suspensions from which it is derived. To check this assumption several 100/55 plastisols have been prepared from a blend of E1 and M1 paste polymers. The rheology of these plastisol blends is presented in Figure 3.3. The large particles are provided by the E1 paste polymer, the small particles by the M1 material. Figure 3.3.a indicates a rise in low shear viscosity and a fall in dilatancy, on increasing the concentration of E1 up to 35% by weight. The continuous rise in low shear viscosity, with E1 content, shown in Figure 3.3.b, is due to the high porosity of the E1 secondary particles. These particles immobilise considerably more plasticiser than a corresponding quantity of M1 particles. The fall in high shear viscosity, below that predicted by the law of mixtures, represented by the solid line in Figure 3.3.c., is caused by the fall in dilatancy. The inclusion of a second family of particles clearly disrupts the formation of the hexagonal planes of particles within the system and so reduces dilatancy.

It is interesting to note that the high shear viscosity of all the plastisols tested in this project appears to fall with a continued increase in shear rate. This reduction in viscosity may be due to the low rigidity of the solvated PVC particles, which must deform under these high shear forces.
Fig. 3.18 – Effect of Concentration of the Dispersed Phase

a, Dependence of Viscosity on Solids Concentration

b, Correlation between Discontinuity S−1 and Reduced Vol
Fig. 3.19 – Relationships Between PSD and Rheology

a, Particle Size Distributions

b, Rheology of [100/55] Plastisols
3.2.1.3 Effect of Spray Drying Conditions.

Kaltwasser et al. were some of the first workers to appreciate the complexity of relating PSD to rheology. They were unable to explain the behaviour of several bimodal systems because they did not measure the PSD in the plastisol but the PSD of the latex prior to spray drying. Such results were presented to highlight the problems of interpretation. To overcome these problems and to gain a better understanding of plastisol rheology, each of the paste grades discussed so far were dried under a range of conditions. The PSD and rheology of plastisols prepared from these materials are displayed in the results section, see Figure 3.4, 3.5, 3.11 and 3.12. To ease interpretation these results are summarised in Figures 3.20 to 3.25.

3.2.1.3.a Microsuspension Paste Polymers

The behaviour of the M2 paste polymers, dried under severity 1 to 3, demonstrate the contribution of particle morphology and particle-packing interactions to plastisol viscosity, as shown in Figure 3.20. As the severity of spray drying is increased, the viscosity at 0.4 S⁻¹ falls and then increases, the minimum occurring at severity 2. At 100 S⁻¹ the viscosity continues to fall, the minimum occurring at severity 3. From Furnas's theoretical treatment of particle packing, section 1.4.1.2, it is apparent that there is only one optimum ratio of large to small particles for minimum void volume. However, we see from the viscosity of a plastisol several optimum PSD's, depending upon shear rate. At a shear rate of 1000 S⁻¹, increasing the proportion of large secondary particles, by increasing the drying severity from 1 to 3 minimises dilatancy and high shear viscosity. This effect must be due to an improvement in packing efficiency and the disruption of the hexagonal planes of particles, by a second family of particles, which leads to dilatancy. At lower shear rates (0.4 S⁻¹) increasing the severity from 2 to 3 must improve packing efficiency, by the addition of more porous secondary particles. However, these secondaries must immobilise considerable quantities of plasticiser within their porous structure and so increase plastisol viscosity. As shear rate is increased the
importance of this immobilised plasticiser contribution decreases and viscosity is controlled by the disruption of hexagonal packing and the improvement in primary and secondary particle packing during flow.

Increasing the drying severity to 4 (80°C) has a considerable effect on the concentration of secondary particles, which increases from 20 to 70% of the distribution. As the drying temperature approaches the glass transition temperature \( T_{\text{gl}} \) of PVC (which is \( \approx 80^\circ \text{C} \)) the secondary particles become sintered together as the primaries soften and adhere to one another. This large proportion of sintered porous secondary particles has a considerable effect on plastisol rheology. Their large size reduces the onset of dilatancy to \( \approx 0.7 \text{ s}^{-1} \), while their porous nature increases viscosity.

By comparing the behaviour of the M1 and M2 plastisols it is possible to evaluate the interaction between the milling and spray drying process. From Figure 3.21 it becomes apparent that the milling process has reduced the concentration of secondary particles within the plastisols for each of the drying conditions. A consequence of this reduction is that the drying process has less of an effect on the high shear viscosities. The greatest reduction in secondary particle concentration occurs in the paste polymer dried under severity 4. The reduction, by milling, in secondary particle concentration for the systems dried under mild conditions is less, because under these temperatures they are only superficial agglomerates and tend to breakdown whether the system is milled or not.

The M1 plastisols, characterised by Figure 3.21, tend to have a lower low shear viscosity and a higher high shear viscosity than the M2 plastisols shown in Figure 3.20. Such behaviour is expected. The primary PSD maintains a low viscosity at low shear rates but confers dilatancy at higher shear rates. The higher concentration of porous secondary particles in the M2 system increases low shear viscosity and suppresses dilatancy by increasing the porosity and PSD width of the system.
A lower level of secondary particles in the M1 system pushes the onset of dilatancy to higher shear rates. This is because, as shown in the previous section, a reduction in the average size of the particles in a unimodal plastisol pushes dilatancy to higher shear rates; smaller particles require less time for cooperative movement.

3.2.1.3.b Emulsion Paste Polymers

In comparison to the microsuspension paste polymers the response of the emulsion systems to changes in spray drying conditions is far less complicated. By considering Figures 3.22 and 3.23, which show the effect of drying temperature on the PSD and rheology of emulsion plastisols, one can see that a higher dryer outlet temperature results in more thoroughly fused secondary particles which resist breakdown in the plasticiser. This resistance to breakdown results in a higher concentration of secondary particles within the plastisol and a reduction in low shear viscosity (and pseudoplasticity). It is quite clear that the secondary particles confer a lower viscosity to a plastisol and so an increase in the concentration of such particles, brought about by increasing drying temperature, results in a fall in viscosity. From Figure 3.23, one can see that even under severity 3, which corresponds to a drying temperature of 76°C, there is still a high proportion of fragmented secondary particles (34% smaller than 1.0 μm) which lead to a high low shear viscosity and pronounced pseudoplasticity. It is only when a drying temperature of ≈ 80°C is employed that plastisol viscosity approaches an acceptable level. At such temperatures, which correspond to the Tg of the PVC, the secondary particles become thoroughly fused and resist fragmentation within the plastisol.

3.2.1.3.c Seeded Emulsion Paste Polymers

As shown in Figure 3.24, increasing the spray drying temperature, of the S1 latex, increases the concentration of secondary particles in an S1 plastisol. There appears to be no preferential agglomeration of particles, the ratio of L primaries to S primaries for each of the spray dried materials remains the same, at approximately 3 : 1. There is only a limited increase in viscosity and dilatancy. The plastisols seem to retain their 'Newtonian' character with increasing drying severity. The
low porosity secondary particles seem to have a minimal effect on increasing viscosity. Only the most severely treated material exhibits a degree of dilatancy.

The effect of secondary particle size, for unimodal systems, on the onset of dilatancy can, again, be confirmed by comparing the PSD and rheology of the S1 and M1 plastisols, prepared from materials dried under severity 4. The data in Tables 3.2 and 3.3 show that the average size of the secondary particles for S1.4 and M2.4 plastisols is 8.0 and 14.0 μm, respectively. Increasing the size of the secondary particles reduces the onset of dilatancy from 1 s−1 for the S1.4 system to 0.3 s−1 for the M1.4 system.

Although the S1.3 and S1.4 paste polymers were dried under similar conditions to the M1.3 latex, plastisols prepared from these materials have a much higher level of secondary particles. This may be due to the much higher emulsifier level employed in the production of the S1 paste polymers. Both Merinov et al., section 1.2.2.3, and Kaltwasser et al., section 1.5.2.2, have shown the effect of emulsifier level. Kaltwasser et al demonstrated the effect, using different coating levels. With a high coating level, secondary particles tended to remain intact in the plastisol.

According to Table 3.3, the size of the secondary particles within the plastisols displayed in Figure 3.24 tends to decrease with increasing drying severity from 10.0 μm to 8.0 μm. Although this evidence is extremely limited and may be a result of experimental error in extracting the data from the graph, such an effect should occur. Increasing drying severity is achieved by raising the dryer outlet temperature. Commercially this is achieved by reducing the feed rate to the dryer atomiser. Fieldman et al. have shown that decreased feed rates reduce droplet size. As the droplets are smaller, this should result in reduced agglomeration within a plastisol as drying severity is increased.

In the previous sections, discussing the relationships between PSD and rheology for unimodal and bimodal systems, it was stated that the
porosity of secondary particles is lower when they are derived from unimodal latices. For an S1 plastisol, the primary particles confer a higher viscosity than the M1 primary particles but the S1 secondary particles confer a lower viscosity than the M1 secondary particles.

The spray drying experiments allow these facts to be tested. Comparison of the rheology of the M2 and S1 plastisols shown in Figures 3.20 and 3.24, respectively, allows the following conclusions to be drawn:

(i) Under severity 1, the high concentration of primary particles in each system dominates rheology. The M2 plastisol displays a lower viscosity over the whole shear rate range, which suggests that the M2 primary PSD is better at maintaining a low viscosity.

(ii) Under the most severe spray drying conditions (severity 4) the rheology of each system is dominated by the secondary particles which account for ~70% of the distribution. The higher viscosity of the M2 plastisol must be due to the higher porosity of the secondary particles.

As shown in Figure 3.25, increasing the spray drying temperature of the S2 latex increases the concentration of secondary particles in an S2 plastisol, in a similar manner to an S1 plastisol. However, the response of the plastisol viscosity to such changes in PSD differs significantly from that of the S1 plastisol. With increasing drying temperature, S2 plastisol low shear viscosity initially rises and then falls. In contrast, the S1 plastisols seem to retain their "Newtonian" character as drying temperature is increased. I suspect this behaviour is due to differences in secondary particle porosity. From Figures 3.24.a and 3.25.a, one can see that the secondary particles in each of the seeded plastisols are of comparable size. Since we know that the primary particles which make up these secondary particles are smaller in the case of the S2 material, the porosity of the S2 secondary particles should be considerably higher, providing the particulate nature of the secondary particles is not damaged significantly during spray drying. An increase in the proportion of highly porous S2 secondary particles may therefore cause an increase in plastisol viscosity because of the immobilisation of...
considerable quantities of plasticiser. The fall in plastisol viscosity with a further increase in secondary particle concentration may be attributed to an increase in the width of the PSD which increases particle packing efficiency. Such improvements may also account for the continued fall in high shear viscosity with increasing secondary particle concentration.

I suspect that a further increase in secondary particle concentration would cause another increase in low shear viscosity as the porosity of the secondary particles becomes the dominant factor controlling viscosity.
Fig. 3.20 – Effect of Drying Severity (M2 100/65)

a, Agglomerate Formation

b, Enhanced Dilatancy
Fig. 3.21 – Effect of Drying Severity (M1 100/65)

a, Agglomerate Formation

Cumulative Mass Percent

Equivalent Spherical Diameter / μm

b, Enhanced Dilatancy

Apparent Viscosity / Pa.s

Shear Rate / S⁻¹

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Fig. 3.22 – Effect of Drying Severity (E1 100/90)

a, Agglomerate Formation

b, Reduction in Low Shear Viscosity
Fig. 3.23 - Effect of Drying Severity (E2 100/90)

a, Agglomerate Formation

b, Reduction in Low Shear Viscosity
Fig. 3.24 - Effect of Drying Severity (S1 100/65)

a, Agglomerate Formation

b, Enhanced Dilatancy
**Fig. 3.25 – Effect of Drying Severity (S2 100/65)**

**a, Agglomerate Formation**

- Cumulative Mass Percent vs. Equivalent Spherical Diameter / \( \mu \text{m} \)

**b, Enhanced Low Shear Viscosity**

- Apparent Viscosity / Pa.s vs. Shear Rate / s\(^{-1}\)
3.2.1.4 Effect of Ageing Plastisols

3.2.1.4.a Increase in Apparent Solids Volume

Several workers have considered deagglomeration to be a dominant factor in the ageing of PVC plastisols, as discussed in section 1.3.3. Unfortunately, the studies have been limited to observations at one shear rate. If deagglomeration is a dominant factor, the change in plastisol PSD should have a considerable effect on the shape of the plastisol flow curve. To evaluate this proposal, I have measured the change in plastisol PSD and viscosity, over an extended shear rate range, see Figures 3.6, 3.7 and 3.10.

For the M1, M2 and S1 plastisols there appears to be no evidence of deagglomeration. This is confirmed by the retention of the flow curve shape. For each of these systems the rise in viscosity is consistent with what would be expected upon increasing the volume fraction of solids. This is confirmed by comparing the change in viscosity with volume fraction, with the change in viscosity with time, see Figure 3.26. As shown, an increase in time or volume fraction raises the flow curve, while retaining its shape. Ageing the M1 plastisol, for 72 hours at 23°C, must cause an increase in the plasticiser bound to the surface of the particles and a certain degree of particle swelling, which increases the apparent volume fraction of solids. There is no evidence of deagglomeration or the development of structure. An increase in structure should raise the low shear viscosity, making the system more pseudoplastic. From Figure 3.26, it is obvious that there is no increase in pseudoplasticity which could not be accounted for by an increase in apparent volume fraction of solids. Similar observations may be made for the M2 and S1 systems. I have not combined the effect of volume fraction and time plots, for the M2 and S1 systems, although the data is available from Figure 3.6, 3.7 and 3.10, because I would only be repeating the observations I have made for the M1 plastisols. The M1, M2 and S1 plastisols age relatively slowly.
The effect of ageing on the behaviour of the S2 and E1 plastisols cannot be explained by a simple increase in apparent volume fraction of solids.

3.2.1.4.b Increase in Primary Particle Size

For the S2 plastisol the ageing process results in a considerable increase in the low shear viscosity, making the system even more pseudoplastic. Such an increase cannot be explained, as previously, by an increase in the volume fraction of solids because the shape of the flow curve changes more than can be explained by the solids content. There also appears to be an increase to the size of the 0.2 \( \mu \)m particles. Hoffmann and Garcia were able to characterise plastisols as either high or low ageing systems. They found that the high ageing resins were composed of smaller primary particles. Such results agree with my observations. The S2 plastisol appears to age more rapidly than the S1 system and has a smaller latex PSD, 0.2 and 0.7 \( \mu \)m compared with 0.25 and 1.0 \( \mu \)m, for the S1 system. From Figure 3.27 the increase in the S primaries PS and the rise in low shear viscosity for the S2 system suggests that the swelling of the particles increases the apparent volume fraction of solids and results in a significant increase in the structure development within the system.

3.2.1.4.c Increase in Secondary Particle Size

For plastisols which contain particles of approximately 0.2 \( \mu \)m, or less, ageing seems to cause a rapid swelling of these particles which increases pseudoplasticity and structure development. To test this suggestion the ageing characteristics of the E1 and E2 plastisols were investigated because their primary PSD is composed of 0.15 \( \mu \)m particles. The results of these investigations are presented in Figures 3.28 and 3.29, where the changes in rheology and PSD are displayed, for ease of comparison.

Many workers have shown that a higher dryer temperature produces stable plastisols, the highly fused secondary particles tending to remain
intact. This is the case for E1 paste polymers. From Figure 3.28 it is obvious that the severe drying conditions enable the secondary particles to remain intact during plastisol preparation. The PSD of the E1 plastisol being composed of fused secondary particles, there is no evidence of the 0.15 μm primary particles. Ponizil, as disclosed in section 1.6.1.2.a, evaluated the ageing behaviour of a similar system, which was composed of large secondary particles. During the ageing of these systems, he found that some of the secondary particles broke down to liberate the primary particles. The resultant change in PSD produced a lower plastisol viscosity. Ponizil was able to accelerate the breakdown of the secondary particle skin using glycol ether derivatives. We can see from Figure 3.28 that the rapid increase in low shear viscosity is not accompanied by deagglomeration. Indeed, there appears to be considerable swelling of the 17 μm secondary particles. If the increase in size controls viscosity the low shear viscosity should fall. However, as these particles are highly porous, the swelling must be accompanied by the absorption and immobilisation of considerable quantities of plasticiser. It is this absorption of plasticiser which increases viscosity.

The absence of deagglomeration in the systems I have been considering may not be as difficult to reconcile, as one may expect. In Ponizil's study the deagglomeration of particles was accelerated by the presence of viscosity depressants, while Hoffmann and Garcia carried out their ageing studies at elevated temperatures. Ageing conditions of 24 hours at 41.5°C may not only accelerate particle deagglomeration, particle swelling, particle dissolution, particle solvation and plastisol structure development but may destroy the crystallinity within the PVC structures and emulsifier coating, which hold the secondary particles together. I suspect that heat ageing and room temperature ageing studies can not be compared, reliably. High temperatures can cause a change in properties which would not occur until protracted times at room temperature, if at all. It may be that heat ageing studies are the only way to observe deagglomeration in the systems I have been considering.

For the E2 plastisol, the Sedigraph failed to detect a change in
PSD on increasing the ageing time from 24 to 72 hours, as shown in Figure 3.29.a. I therefore suspect that the increase in pseudoplasticity with time, shown in Figure 3.29.b, is a result of secondary particle plasticiser absorption and structure development, not an increase in the size of the secondary particles as in the case of the El plastisol. Such a difference in performance may be due to the different emulsifier/surfactant blends used in the production of these emulsion paste polymers.
Fig. 3.26 – Ageing of M1 Plastisols

a, Effect of Volume Fraction – see 3.1.a

b, Effect of Time – see 3.6.a
Fig. 3.27 – Ageing of S2 Plastisols

a, Limited Change in PSD – see 3.10.f

b, Increase in Pseudoplasticity – see 3.7.b
Fig. 3.28 – Ageing of E1 Plastisols

a, Increase in Agglomerate Size – see 3.10.c

b, Increase in Pseudoplasticity – see 3.6.c
Fig. 3.29 – Ageing of E2 Plastisols

a, Limited Change in PSD – see 3.10.d

![Graph showing cumulative mass percent against equivalent spherical diameter (µm)](image)

b, Increase in Pseudoplasticity – see 3.1.d

![Graph showing apparent viscosity against shear rate (S-1)](image)
3.2.1.5 Particle Stability and Resistance to Deagglomeration during Plastisol Preparation

From the rheological and PSD data presented in Figures 3.8 and 3.13, respectively, it seems that the majority of deagglomeration and rheological changes take place in the first couple of minutes mixing. There appears to be little change in rheology, see Figure 3.8.a and 3.8.b., on increasing the thick stage mixing time from 5 to 10 minutes. This stability during mixing is very important, it means that differences in rheology due to paste polymer type or filler interactions will not be confused with changes due to deagglomeration of the PVC particles.

3.2.1.6. Particle Stability during Paste Blending

The results in Figures 3.14 and 3.15 are of crucial importance. One of the problems encountered in the particle size analysis of PVC plastisols is that the Sedigraph instrument is incapable of measuring the PSD of a mixture of different particles. The technique relies on the application of Stokes Law, to derive PSD from settling velocity. All the particles, therefore, must be of the same density or else erroneous results will be observed because particles of the same size but different densities will settle at different velocities. The Malvern 2200/3300 instrument is capable of measuring the PSD of mixtures but has a lower size limit of 1.2 μm. In the next chapter, when considering the interactions between filled plastisol rheology and PSD, it will be assumed that the Sedigraph analysis of the unfilled plastisol can be used to represent the PSD of the PVC particles in a filled plastisol. The PSD of the filled system being the sum of the PSD of the unfilled system and the PSD of a filler dispersion, using the Sedigraph. In other words, the addition of the filler does not change the PVC PSD. To check this assumption, the PSD of an unfilled plastisol and a filler dispersion were characterised using the Malvern 2200/3300. The PSD calculated from the addition of these two distributions was compared with the PSD of an equivalent filled plastisol, characterised by the 2200/3300.

From Figures 3.14 and 3.15 it appears that the filled plastisol
PSD is the sum of the unfilled plastisol PSD and the filler PSD. It therefore seems reasonable to extend the assumption of zero particle deagglomeration to the Sedigraph analysis, which should allow particles below 1.2 μm to be evaluated.

3.2.1.7 Particle Stability during Rheological Characterisation

When considering the relationship between rheology and PSD it has occurred to me that the PSD may change, as the system is subject to high shear rates. Under such circumstances, it would be incorrect to relate high shear viscosity to a PSD which was obtained from a plastisol which had not been subject to the high shear forces experienced in the Severs die. I, therefore, measured the PSD and rheology of E1 and E2 plastisols before and after the application of shear, see Figure 3.16.

The shear forces seem to cause a slight increase in the size of the E2 sub-μm particles, although there is only a limited effect on rheology. It is unlikely that the sub-μm particles actually increase in size on one passage through the die. This experiment may highlight a limitation of the Sedigraph. One passage through the Severs die may reduce the structure development in the plastisol. This would explain the reduction in the plastisol viscosity over the whole shear rate range. A reduction in structure may also accelerate sedimentation, as there is a reduction in particle-particle attractive forces.

Such an acceleration of sedimentation would result in apparently larger sub-μm particles, the smaller sizes being affected more than the larger sizes, as shown in Figure 3.16.a.

The interpretation of the data for the E1 plastisols is less complicated. The shear forces appear to have no effect on PSD or rheology. I suspect that one passage through the Severs die does not change the PSD of either system.
CHAPTER 4 : FILLED PLASTISOLS

4.1 RESULTS

4.1.1 Characterisation of Filler PSD

4.1.1.1 Calcium Carbonate and Spheriglass Fillers

The PSD of each of the uncoated calcium carbonate fillers, derived from the Joyce Loebi Disc Centrifuge (JLDC), are displayed in Figure 4.1. Polcarb has the smallest average PS, followed by Q60 and then Q300. From the initial evaluation, Q60 appeared to be trimodal. A retest, however, indicated that all the fillers were in fact unimodal. Difficulties experienced in obtaining consistent PSA suggest that the analysis of Ground Calcium Carbonate (GCC) is susceptible to "streaming" problems.

Using the Coulter Counter it was possible to determine the PSD of the uncoated and coated GCC, as well as the Spheriglass filler. The data presented in Figure 4.2.a agrees with the JLDC analysis. Polcarb being the smallest filler, followed by Q60 and then Q300. The coated versions of the GCC fillers have a similar PSD to the uncoated materials. Spheriglass 5000 CF03 has the largest PS, with an average of ≈ 7.0 to 8.0 μm.

Sedigraph analysis of the spheriglass and GCC fillers reveals the PSD's presented in Figure 4.2.b. This technique ranks the fillers in the same order of size as the JLDC and Coulter techniques. The average size of the filler particles, according to the Sedigraph technique, is displayed in Table 4.1.

A comparison of the PSD of Q60, determined by various methods, is presented in Figure 4.3.a. From this comparison, it is obvious that the apparent size of particles depends upon the measurement technique employed. One can see that the average size, at 50% cumulative mass, ranges from 2.0 μm, according to the Sedigraph, to 6.0 μm, according to
the JLDC. While there seems to be fair agreement between the Coulter and Malvern instruments.

4.1.1.2 Titanium Dioxide Pigments

Figure 4.4 contains the PSD of the two titanium dioxide samples. The initial evaluation suggests that RTC60 contains larger particles. The retest, however, suggest that the fillers are of similar PS. The JLDC may be incapable of resolving the difference in the size of these small particles. According to the Autocorrelation technique, the average size of the two pigments are as follows:

RFC5 = 0.306 μm
RTC60 = 0.275 μm

<table>
<thead>
<tr>
<th>Table 4.1 - Filler Particle Size Analysis</th>
</tr>
</thead>
<tbody>
<tr>
<td>Filler</td>
</tr>
<tr>
<td>--------</td>
</tr>
<tr>
<td>Polcarb</td>
</tr>
<tr>
<td>Polcarb S</td>
</tr>
<tr>
<td>Q60</td>
</tr>
<tr>
<td>Q60 S</td>
</tr>
<tr>
<td>Q300</td>
</tr>
<tr>
<td>Q300 S</td>
</tr>
<tr>
<td>RTC60</td>
</tr>
<tr>
<td>RFC5</td>
</tr>
</tbody>
</table>

* PS determined by Sedigraph Particle Size Analysis
Fig. 4.1 – JLDC Particle Size Analysis of GCC Fillers

a, Initial Evaluation

\[
\text{Cumulative \% \ Under \ Size} \\
\text{Equivalent Stokes Diameter / \( \mu \text{m} \)}
\]

- \( \text{Polcarb} \)
- \( \text{Q60} \)
- \( \text{Q300} \)

b, Retest

\[
\text{Cumulative \% \ Under \ Size} \\
\text{Equivalent Stokes Diameter / \( \mu \text{m} \)}
\]

- \( \text{Polcarb} \)
- \( \text{Q60} \)
- \( \text{Q300} \)
Fig. 4.2 – PSA of Coated and Uncoated Fillers

a, Coulter Counter PSA

Cumulative % Under Size

Diameter / μm

0 5 10 15 20 25 30

0 20 40 60 80 100

b, Sedigraph PSA

Cumulative Mass Percent

Equivalent Spherical Diameter / μm

0.1 1 10 100

0 20 40 60 80 100
Fig. 4.3 – Comparison of PSD Derived by Various Techniques

a. Uncoated Calcium Carbonate Filler (Q60)
Fig. 4.4 – JLDC PSA of Titanium Dioxide

a, Initial Evaluation

b, Retest
4.1.2 Plasticiser Absorption Characteristics

4.1.2.1 British Standard Test

The plasticiser absorption characteristics of the fillers are displayed in Figure 4.5 as a function of filler weight and filler volume. An increase in size of the GCC fillers reduces the plasticiser absorption from 39.95 g/100g to 25.1 g/100g. The stearate coating further reduces the plasticiser absorption of the fillers. However, the fall in plasticiser uptake of the coated fillers does not seem to be directly related to PS. The plasticiser absorption of the Q60 S is higher than that of the Polcarb S filler. On a weight basis the Q300 filler absorbs similar quantities of plasticiser to the titanium dioxide fillers. The plasticiser absorption of the small PS RTC60 is higher than that of the larger PS RFC5. If one compares the performance, of the fillers, on a volume basis, which takes differences in filler density into account, the titanium dioxide fillers have similar plasticiser absorption characteristics to the Polcarb filler.

4.1.2.2 Viscosity of Comparable Filler Dispersions.

The viscosity of a filler dispersion, as a function of filler type and shear rate, is displayed in Figure 4.5.c. All the dispersions tested seem to be pseudoplastic, the viscosity falling as the test speed was increased from 1.0 to 5.0 rpm. An increase in filler PS reduces viscosity, as does the application of a stearate coating. The viscosity of the titanium dioxide dispersions is comparable to the Polcarb dispersion.
Fig. 4.5 – Plasticiser Absorption Characteristics

a, BS 1795 : 1965 (Per Unit Weight)

b, (Per Unit Volume)
Fig. 4.5 –

c. Viscosity of Comparable Filler Dispersions

![Graph showing viscosity of comparable filler dispersions with speed variations.](image-url)
4.1.3 Effect of Filler Type and PSD on Filled Plastisol Rheology

4.1.3.1 Milled Microsuspension Paste Polymers

The effect of GCC filler substitution on a series of 100/50 plastisols, prepared from the M1 paste polymer, is shown in Figures 4.6.a, b and c. All the plastisols had a solids to liquid ratio equivalent to a 100/50 plastisol but the concentration of filler was increased from 0 to 18%, by volume of the solids. From these observations it is obvious that an increase in the concentration of GCC filler causes a dramatic increase in both low shear pseudoplasticity and high shear dilatancy. The effect is more pronounced for the smaller PS fillers. For the coarse, Q300, filler there is only a limited increase in dilatancy. However, for the Polcarb filler the increase in dilatancy is more pronounced. The addition of a fine GCC filler also moves the onset of dilatancy to lower shear rates.

Figure 4.6.d considers the effect of filler incorporation on plastisol viscosity, at a shear rate of $0.18 \text{ s}^{-1}$. From this figure it seems that filler addition, irrespective of PS, causes a continuous rise in viscosity. A series of polynomial expressions have been fitted to the data points presented in this figure and subsequent summary plots, the coefficients and measures of correlation are presented in Appendix 11.

A similar set of graphs, for the substitution of titanium dioxide fillers is shown in Figures 4.6.g and 4.6.f. Again, an increase in the concentration of filler causes a rapid rise in low shear pseudoplasticity but has only a limited effect on high shear dilatancy. The small PS of these fillers results in a greater rise in low shear viscosity, that is why filler levels of only 1.0 and 2% have been considered, compared with up to 18% for the GCC fillers.
Fig. 4.6 - Milled Microsuspension Plastisols: Effect of filler

(a) Polcarb Addition

(b) Q60 Addition
Fig. 4.6 –

c, Q300 Addition

\[ \text{APPARENT VISCOSITY / Pa.s} \]
\[ \text{SHEAR RATE / s}^{-1} \]

\[ \% \text{ Q300} \]
\[ \text{0} \]
\[ \Delta 4.5 \]
\[ + 9 \]
\[ \times 13.5 \]
\[ \diamond 18 \]

\[ \text{d, Effect of GCC Fillers on Low Shear Viscosity (0.1 \text{ s}^{-1})} \]

\[ \text{APPARENT VISCOSITY / Pa.s} \]
\[ \% \text{ Filler} \]

\[ \text{Filler} \]
\[ \Delta \text{ Polycarb} \]
\[ \times \text{ Q60} \]
\[ \square \text{ Q300} \]
Fig. 4.6 -

e. RTC60 Addition

\[
\text{APPARENT VISCOSITY / Pa.s}
\]

\[
\text{SHEAR RATE / S}^{-1}
\]

f. RFC5 Addition

\[
\text{APPARENT VISCOSITY / Pa.s}
\]

\[
\text{SHEAR RATE / S}^{-1}
\]
4.1.3.2 Unmilled Microsuspension Paste Polymers

Figures 4.7.a to 4.7.d show the effect of GCC introduction on a series of M2 plastisols. These systems responded to filler introduction in a similar manner to the M1 plastisols. Low shear viscosity rose rapidly with an increasing filler content and a reduction in filler PS. Filler introduction also increased high shear viscosities, the effect being more pronounced for the small PS fillers, but the lower dilatancy in these unmilled systems ensures that the dilatancy in the filled M2 plastisols is lower than that in the filled M1 plastisols.

The M2 filled systems display a higher low shear viscosity than the corresponding M1 plastisols.

Again, the M2 plastisols respond to titanium dioxide filler introduction in a similar manner to the M1 plastisols, as shown in Figures 4.7.e and 4.7.f. The titanium dioxide (TiO₂) fillers impart high low shear viscosities. The RTC60 filled system displays a higher viscosity than the RFC5 system. The M2 TiO₂ filled plastisols have a higher viscosity than the M1 systems.
Fig. 4.7 – Unmilled Microsuspension Plastisol: Effect of Filler

a. Polcarb Addition

b. C60 Addition
Fig. 4.7 –

c. Q300 Addition

\[
\begin{array}{c}
\text{APPARENT VISCOSITY / Pa.s} \\
\text{SHEAR RATE / s}^{-1}
\end{array}
\]

\[
\frac{\text{% Q300}}{\begin{array}{c}
\circ 0 \\
\Delta 4.5 \\
\ast 9 \\
\times 13.5 \\
\diamond 18
\end{array}}
\]

d. Effect of GCC on Low Shear Viscosity (0.18 s\(^{-1}\))

\[
\begin{array}{c}
\text{APPARENT VISCOSITY / Pa.s} \\
\text{% FILLER}
\end{array}
\]

\[
\frac{\text{Filler}}{\begin{array}{c}
\Delta \text{ Polycarb} \\
\times \text{ Q60} \\
\square \text{ Q300}
\end{array}}
\]
Fig. 4.7 -

e. RTC60 Addition

f. RFC5 Addition
4.1.3.3 El Emulsion Paste Polymers

The effect of GCC filler introduction on the rheological properties of El plastisols has been evaluated in plastisols with DIOP contents equivalent to a 100/60 mix. This was necessary because of the high viscosity of unfilled El plastisols. From Figures 4.8.a to 4.8.c one can see that the low shear dilatancy of an unfilled El plastisol is transformed into pseudoplastic flow, which extends over the whole shear rate range. This transformation is complete when the plastisol contains 18% Polcarb. Plastisols containing lower levels of filler and/or larger PS fillers retain a certain degree of dilatancy. According to Figure 4.8.c a plastisol containing 18% of the coarse, Q300, GCC filler retains a degree of low shear dilatancy.

The effect of filler introduction on low and high shear viscosity has been considered in Figures 4.8.d and 4.8.e. One can see from Figure 4.8.d that the rise in viscosity, at 0.18 S⁻¹, is not proportional to filler level, although it is more pronounced the smaller the filler PS. For each of the GCC filled plastisols, the low shear viscosity initially rises to a peak, at ≈ 4.5% filler, the viscosity then falls, at ≈ 9 - 13.5% filler, and then rises with continued introduction of filler. The minimum in low shear viscosity depends upon the size of the filler particles. The relationship between the position of this minimum and filler PS is shown in Table 4.2.

**TABLE 4.2. - RELATIONSHIP BETWEEN THE DROP IN EL PLASTISOL VISCOSITY AND FILLER PS. DATA TAKEN FROM 4.8.d.**

<table>
<thead>
<tr>
<th>Filler</th>
<th>Particle Diameter (μm)</th>
<th>Position of Viscosity Minimum (% Filler)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Polcarb</td>
<td>1.1</td>
<td>6</td>
</tr>
<tr>
<td>Q60</td>
<td>2.0</td>
<td>9</td>
</tr>
<tr>
<td>Q300</td>
<td>2.9</td>
<td>13</td>
</tr>
</tbody>
</table>
The rheological response at high shear rates, 64.1 \text{s}^{-1}, is rather unusual. The high shear viscosity falls with filler introduction, see Figure 4.8.e. This fall in viscosity is more pronounced for the small PS GCC fillers. E1 plastisols are the only systems to behave in this manner, the high shear viscosity falling with the incorporation of small PS GCC fillers.

Titanium dioxide fillers have a pronounced effect on the shape and position of the flow curve. RTC60 introduction, see Figure 4.8.f, causes a rapid increase in low shear viscosity, making the system more pseudoplastic. Introduction of 4% RFC5, not only increases low shear viscosity but causes a rise in high shear rate viscosity. The whole flow curve moves to higher viscosities, see Figure 4.8.g.

The effect of Spheriglass incorporation on the flow curve of a 100/60 E1 plastisol is shown in Figure 4.8.h. There is a limited rise in low shear viscosity but the shape of the flow curve is largely retained, as in the case of Q300 introduction.
Fig. 4.8 - E1 Emulsion Plastisols: Effect of Filler

a. Polcarb Addition

b. O60 Addition
Fig. 4.8 -

(c) Q300 Addition

(d) Effect of GCC on Low Shear Viscosity (0.18 s⁻¹)
Fig. 4.8 -

e, Effect of GCC on High Shear Viscosity (641 s⁻¹)

[Graph showing the effect of GCC on high shear viscosity with different fillers: Polcarb, Q60, Q300]
Fig. 4.8 -

**f, RTC60 Addition**

- **g, RFC5 Addition**
Fig. 4.8  

h. Spheriglass 5000 CPO3 Addition
4.1.3.4 E2 Emulsion Paste Polymers.

As discussed in section 3.2, plastisols prepared from E2 have an extremely high low shear viscosity and are highly pseudoplastic. It was, therefore, necessary to adopt a plasticiser level equivalent to a 100/90 plastisol, when considering the effect of filler inclusion. The effect of GCC fillers on E2 plastisol rheology is shown in Figures 4.9.a and 4.9.b. From this study it is clear that the introduction of calcium carbonate reduces viscosity over the whole shear rate range, the greatest reduction occurring at the lower shear rates and with larger PS fillers. The low shear viscosity of the plastisol containing 18% Q300 is substantially lower than the system containing 18% Polcarb.

The introduction of RFC5; up to 8% by volume, seems to have little effect on the flow curve of a 100/90 E2 plastisol. There is only a slight fall in the Severs viscosity with RFC5 incorporation, see Figure 4.9.c.

The response of the E2 plastisol to Spheriglass inclusion is similar to the effect of Q300 addition, both plastisols experiencing a drop in viscosity over the whole shear rate range. However, the low shear viscosity of an E2, 9% Spheriglass filled plastisol, is lower than the corresponding system containing 9% Q300.
Fig. 4.9 – E2 Emulsion Plastisols: Effect of Filler

a, Polcarb Addition

b, Q300 Addition
c. RFC5 Addition

d. Spheriglass Addition
4.1.3.5 S1 Seeded Emulsion Paste Polymer

The effect of GCC filler substitution on a series of S1 plastisols is presented in Figures 4.10.a,b and c. Each plastisol had a solids to liquid ratio equivalent to a 100/50 plastisol but the concentration of GCC was increased from 0 to 18% by volume. From these graphs one can see that there is a rapid increase in low shear viscosity with the addition of the smaller PS fillers. There is only a limited effect on high shear viscosity and so the plastisols exhibit an increasingly pseudoplastic nature. In Figure 4.10.a the lines representing the 9, 13.5 and 18% Polcarb levels seem to bunch together. If one considers the effect of filler PS and concentration on the viscosity, measured at a shear rate of 0.18 S⁻¹, as shown in Figure 4.10.d, it becomes obvious that plastisol viscosity does not rise continuously with filler level. The low shear viscosity rises to a maximum at 9% substitution, the viscosity drops at 13.5% filler and then continues to rise with filler level. The viscosity at 9% filler substitution and 18% filler are identical.

All the plastisols, irrespective of GCC filler PS, behave in a similar manner, although the rise in low shear viscosity is greater for the smaller PS fillers. Unlike the E1 plastisols, the position of the minimum in low shear viscosity does not depend on filler PS. The drop in viscosity for the Polcarb, Q60 and Q300 systems occurs at 13.5% filler substitution as shown in Figure 4.10.d.

The incorporation of titanium dioxide fillers causes a rapid increase in S1 plastisol pseudoplasticity, see Figures 4.10.e and 4.10.f. The TiO₂ fillers impart a greater increase in low shear viscosity than the GCC fillers, which is why filler levels of only up to 4% were evaluated. As in the case of the microsuspension plastisols, the RTC60 filler causes a greater increase in viscosity compared with the RFC5 filler.

Spheriglass 5000 CP03 levels up to 9% cause a slight increase in viscosity, although the Newtonian character of the S1 plastisols is retained, see Figure 4.10.g.
Fig. 4.10 – S1 Seeded Emulsion Plastisols: Effect of Filler

a. Polcarb Addition

b. Q60 Addition
Fig. 4.10 -

c, Q300 Addition

\[ \text{APPARENT VISCOSITY / Pa.s} \]

\[ \text{SHEAR RATE / S}^{-1} \]

\[ 10000 \quad 1000 \quad 100 \quad 10 \quad 1 \quad 0.1 \quad 0.01 \]

\[ 0.01 \quad 0.1 \quad 1 \quad 10 \quad 100 \quad 1000 \quad 10000 \]

\[ 100000 \]

\% Q300

\( \circ \) 0

\( \Delta \) 4.5

\( + \) 9

\( \times \) 13.5

\( \diamond \) 18

d, Effect of GCC on Low Shear Viscosity (0.18 s\(^{-1}\))

\[ \text{APPARENT VISCOSITY / Pa.s} \]

\[ \% \text{ FILLER} \]

\[ 0 \quad 4.5 \quad 9 \quad 13.5 \quad 18 \]

\[ \text{Filler} \]

\( \Delta \) Polycarb

\( \times \) G60

\( \square \) Q300
Fig. 4.10 –

e, RTC60 Addition

f, RFC5 Addition
Fig. 4.10 -

g. Spheriglass 5000 CP03 Addition

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The effect of GCC inclusion on the rheology of S2 plastisols, with DIOP contents equivalent to a 100/50 plastisol, is represented by Figures 4.11.a,b and c. It is clear from this data that the S2 plastisols respond in a completely different manner to the S1 plastisols. Addition of 4.5% filler reduces the plastisol viscosity below that of the unfilled system, the plastisol becoming less pseudoplastic and more "Newtonian". The subsequent rise in viscosity achieved by further increasing the filler content is more pronounced for the finer fillers. For the Polcarb systems, 9% filler raises the plastisol viscosity back to the levels seen in an unfilled plastisol. However, even at filler levels of 18% the viscosity of the Q300 filled system is still below that of the unfilled S2 plastisol. Filler levels of 25% may be necessary before the Q300 filled system has a similar viscosity to the unfilled plastisol. Figure 4.11.d depicts this dependence of low shear viscosity on filler concentration and PS. Although the plastisols behave in the same manner, higher levels of the larger PS fillers are required to achieve the same increase in viscosity. Again, the position of the minimum is independent of filler PS, all systems displaying the minimum at 4.5% filler, by volume.

The T.02 filled systems behave in a similar manner, as shown in Figures 4.11.e and 4.11.f, although the minimum occurs at 1% filler substitution and the viscosity of the plastisol is restored to that of the unfilled system at ~ 2% filler substitution. As shown in previous sections, considering M1, M2 and S1 plastisol rheology, the RTC60 filler imparts a higher viscosity than the RFC5 material.

One can see from Figure 4.11.g that the Spheriglass filler behaves in a similar manner to the Q300 GCC filler.
Fig. 4.11 – S2 Seeded Emulsion Plastisols: Effect of Filler

a, Polcarb Addition

b, Q60 Addition
Fig. 4.11 -

c, Q300 Addition

---

d, Effect of GCC on Low Shear Viscosity (0.18 s⁻¹)
Fig. 4.11 -

e, RTC60 Addition

f, RFC5 Addition
Fig. 4.11 -

g, Spheriglass 5000 CP03 Addition

APPARENT VISCOSITY / Pa.s

SHEAR RATE / S⁻¹

% SPERIGLASS

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4.1.4 Effect of Stearate Coating

Figures 4.12.a and 4.12.c contain the flow curves for the seeded emulsion plastisols filled with various levels of Q60 S. A comparison of the flow curves derived from plastisols filled with 18% of the coated and uncoated fillers is presented in Figures 4.12.b and 4.12.d. The data for the uncoated materials was obtained from Figures 4.10.b and 4.11.b, respectively. From Figure 4.12.b one can see that the lower plasticizer absorption of the coated filler (see Figure 4.5) results in a slightly lower viscosity, over the whole shear rate range. However, for the S2 plastisol, the stearate coated material confers a slightly higher viscosity to the plastisol.

A similar set of results is presented in Figure 4.13, for a series of Polcarb filled plastisols. The data for the uncoated fillers, which enables a comparison to be drawn, is presented in Figures 4.11.a. and 4.8.a. Again, for the S2 plastisol, there seems to be little difference between the flow curves for the plastisols containing the coated and uncoated fillers. There is, however, a significant difference between the flow curve for the E1 plastisol containing 18% Polcarb and a similar system containing 18% Polcarb S. The coated filler imparts a much lower viscosity, over the whole shear rate range. (In this particular case the plastisols contained 60 phr of DIOP and not 50 phr as in the other plastisols).
Fig. 4.12 – Effect of Stearate Coating on Filled Plastisol Rheology

a, S1 100/50 Q60 S Addition

b, S1 100/50 Comparison of Q60 and Q60 S
Fig. 4.12 –

c, S2 100/50 Q60 S Addition

d, S2 100/50 Comparison of Q60 and Q60 S
Fig. 4.13 – Effect of Stearate Coating on Filled Plastisol Rheology

a, S2 100/50 Polcarb S Addition

b, S2 100/50 Comparison of Polcarb and Polcarb S
c, E1 100/60 Polcarb S Addition

![Graph showing comparison of Polcarb and Polcarb S](image)

d, E1 100/60 Comparison of Polcarb and Polcarb S

![Graph showing comparison of Polcarb and Polcarb S](image)
4.2 DISCUSSION OF RESULTS

4.2.1 Filler Particle Size Analysis and Plasticiser Absorbtion

4.2.1.1 Evaluation of PS Measurement Techniques

4.2.1.1.a Comparison of PSD Measured by Various Techniques

Initial PSA of the uncoated GCC was carried out using the Joyce Loebl Disc Centrifuge (JLDC). Table 4.3 contains the average PS of each grade, determined by this technique. The average values were obtained from the PSD's displayed in Figure 4.1.b.

TABLE 4.3 - JLDC ANALYSIS

<table>
<thead>
<tr>
<th>Filler</th>
<th>JLDC (Fig.4.1.b)</th>
<th>Coulter (Fig.4.2.a)</th>
<th>Sedigraph (Fig.4.2.b)</th>
<th>Malvern (Fig.3.14.a)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Polcarb</td>
<td>4.0</td>
<td>2.0</td>
<td>1.1</td>
<td>-</td>
</tr>
<tr>
<td>Polcarb S</td>
<td>-</td>
<td>-</td>
<td>1.1</td>
<td>-</td>
</tr>
<tr>
<td>Q60</td>
<td>6.0</td>
<td>2.7</td>
<td>2.0</td>
<td>3.0</td>
</tr>
<tr>
<td>Q60 S</td>
<td>-</td>
<td>3.1</td>
<td>2.1</td>
<td>-</td>
</tr>
<tr>
<td>Q300</td>
<td>9.0</td>
<td>3.5</td>
<td>2.9</td>
<td>-</td>
</tr>
<tr>
<td>Q300 S</td>
<td>-</td>
<td>4.0</td>
<td>4.3</td>
<td>-</td>
</tr>
</tbody>
</table>

Unfortunately, this technique proved to be unsuitable. Consistent results were very difficult to obtain. From Figure 4.1.a one can see that streaming was experienced in the analysis of Q60. This was shown by the apparent trimodal distribution which was displaced to the right of the diagram, suggesting an extremely large average PS. The technique was also unsuitable because it was incapable of characterising the PSD of the stearate coated materials. Using the dispersants recommended in the Coulter manual (i.e. Dispersal T and Calgon), it was not possible
to disperse the fillers in an aqueous phase and obtain stable sedimentation.

To overcome these problems the fillers were analysed in the Coulter Counter, which relies on the displacement of an electrolyte to measure the PSD. A non-aqueous electrolyte consisting of 2.5% ammonium thiocyanate in propan-2-ol was selected because the fillers were insoluble and readily dispersed in this medium. From the third column of Table 4.3, which was derived from Figure 4.2.a, one can see that the coated and uncoated GCC fillers have a similar average PS, they are also ranked in the same order of size as indicated by the JLDC.

For completeness, the Spheriglass PSD was also measured, it had an average PS of 8.0 μm.

One of the criteria when selecting the Coulter Counter Technique is that the particles should be insoluble in the electrolyte and be electrically non-conductive. Unfortunately, an emulsifier coated paste polymer particle suspended in a plasticiser violates both of these conditions. It was therefore not possible to use this technique when characterising the PSD within a plastisol. Once a Sedigraph instrument became available it was decided to measure the PSD of the GCC fillers using this technique because it would then be possible to directly compare the size of the filler and PVC particles, as the same instrument would be used to characterise PVC particles and filler dispersions.

Table 4.3 also contains the PSA derived from the Sedigraph, one can see that the coated and uncoated grades have a similar average PS, although the coated version of Q300 has a slightly larger average PS than the uncoated version.

The problems encountered when comparing the size of PVC and filler particles, derived by various techniques, are highlighted in the 3rd row of Table 4.3, which was derived from the data presented in Figure 4.3.a.
The apparent PS of a material depends upon what property is being measured as well as which technique is being employed. When one compares PS data it is essential to know which technique was being used and what quantity was being measured. Although the same filler was evaluated, by each of the techniques, the apparent average size of Q60 ranges from 2.0 to 6.0 μm.

The Sedigraph and JLDC techniques present the PSD as a function of equivalent spherical diameter, that is the diameter of a spherical particle which would settle at the same rate as the particle being considered. One may therefore consider it valid to directly compare the results from each instrument. Such an assumption would however be incorrect because the Sedigraph instrument measures the concentration of particles directly, using an X-ray source, while the JLDC calculates the concentration from turbidity measurements, using the Mie light scattering theory. So although both techniques characterise the size of the particles in the same manner, the concentration of particles is measured in a different way. The difference in average PS, of 4.0 μm, is not due to the differences in measurement techniques but problems in obtaining stable sedimentation in the JLDC sample disc. Streaming results in uneven, artificially large PSD, as the small particles travel en masse through the spin fluid.

The Coulter technique presents the PSD as a function of the volume of electrolyte displaced, in other words the size of the particle is measured as the size of a sphere which would displace the same volume of electrolyte as the particle being studied. This is why the results cannot be compared directly with the JLDC or Sedigraph data. It also explains why conductive or soluble particles cannot be considered. The Malvern 2200/3300 technique presents the PSD data as a function of the diameter of a spherical particle which would scatter the same amount of light as the particle being considered. The average size of the Q60 filler is similar for the Coulter and Malvern techniques but one must exercise care when considering data from various techniques.
For the TiO₂ fillers problems of streaming were encountered in the JLDC, using the dispersants recommended in the JLDC manual, it was therefore decided to use the Malvern Autocorrelation technique which gave the following analysis:

<table>
<thead>
<tr>
<th>RTC60</th>
<th>Average PS = 0.275 μm</th>
</tr>
</thead>
<tbody>
<tr>
<td>RFC5</td>
<td>Average PS = 0.306 μm</td>
</tr>
</tbody>
</table>

4.2.1.1.b Composite Plots

When considering the rheological response of filled plastisols it is necessary to characterise the PSD within a filled plastisol. To do this I have generated several composite plots which will be presented in later sections. Each is composed of the PSD of a plastisol and the PSD of a filler dispersion, these distributions being determined separately by the Sedigraph. The addition of a filler PSD and a plastisol PSD to produce such composite plots is necessary because the Sedigraph is incapable of characterising the PSD of mixtures of particles with different densities, PVC having a density of 1.4 g/cc and GCC a density of 2.65 g/cc. The PSD presented in these plots should represent that in the filled plastisols, as I have shown in Section 3.1.2.4.b the PSD of a filled system is the sum of the PSD in a plastisol and a filler dispersion. The data for the composite plots was obtained from the Sedigraph instrument and so problems in considering data from various techniques should be eliminated. I decided to use this technique because, apart from being very reliable, it covered the widest range of sizes encountered in a plastisol PSA.
4.2.1.2 Correlations between Filler PS and Plasticiser Absorption

TABLE 4.4 RELATIONSHIPS BETWEEN SEDIGRAPH AVERAGE PS AND PLASTICISER ABSORPTION

<table>
<thead>
<tr>
<th>Filler</th>
<th>Sedigraph Average PS (µm)</th>
<th>Plasticiser Absorbtion</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>- Figure 5.2.b</td>
<td>- Figures 4.5.a and 4.5.b</td>
</tr>
<tr>
<td></td>
<td></td>
<td>(g/100g)</td>
</tr>
<tr>
<td>Polcarb</td>
<td>1.1</td>
<td>39.95</td>
</tr>
<tr>
<td>Polcarb S</td>
<td>1.1</td>
<td>20.5</td>
</tr>
<tr>
<td>Q60</td>
<td>2.0</td>
<td>30.4</td>
</tr>
<tr>
<td>Q60 S</td>
<td>2.1</td>
<td>22.15</td>
</tr>
<tr>
<td>Q300</td>
<td>3.9</td>
<td>25.1</td>
</tr>
<tr>
<td>Q300 S</td>
<td>4.3</td>
<td>19.5</td>
</tr>
<tr>
<td>RTC60</td>
<td>0.275</td>
<td>26.45</td>
</tr>
<tr>
<td>RFC5</td>
<td>0.306</td>
<td>23.1</td>
</tr>
</tbody>
</table>

To ease evaluation, the results presented in Table 4.4, are presented graphically in Figure 4.14, such results confirm Skalski et al's belief that there is no general relationship between the plasticiser uptake of fillers and their mean PS. The plasticiser absorption of the stearate coated fillers appears to increase and then decrease with filler PS. Such behaviour may be due to differences in PSD, not accounted for by measuring the average PS. One can see from Figure 4.2.b that Q300 S, average PS 4.3 µm, has a much wider PSD than the other GCC fillers. An increase in distribution width should cause a reduction in plasticiser absorption. The accuracy of BS 1795 : 1965 must also be called into question. This technique relies upon manually evaluating the minimum amount of plasticiser which may be incorporated into a filler, using.
a palette knife. To ease comparison of filler absorption characteristics and to increase experimental accuracy, dispersions were prepared from each of the fillers while maintaining the same solids volume fraction. The viscosity of these dispersions as a function of filler PS is presented in Figure 4.14.b, the data was obtained from Figure 4.5.c. Although no general relationship exists between filler dispersion viscosity and mean PS, a correlation does exist between these two factors for individual groups of fillers of the same chemical composition (and surface structure).
Fig. 4.14 – Correlation Between Filler Absorption and PS

(a) Plasticiser Absorption

(b) Viscosity of Comparable Dispersions
4.2.2 Response of Plastisols to Filler Introduction

4.2.2.1 Microsuspension Paste Polymers

The response of the microsuspension plastisols to filler substitution may be explained by reviewing the factors controlling the rheology of the unfilled plastisol and evaluating the effect of substituting a portion of the plastisol PSD by filler particles.

In the unfilled state the rheology of M1 plastisols is controlled by the broad \(1.1 \mu m\) unimodal primary PSD which accounts for 80% of the distribution. The efficient packing of the primary PSD maintains a low plastisol viscosity although its unimodal nature confers dilatancy at intermediate (\(\approx 100 S^{-1}\)) shear rates. When one increases the proportion of porous \((0.4 \text{ cc/g}) 8.0 \mu m\) secondary particles, by changing the milling conditions, to 30%, the overall PSD is broadened sufficiently to suppress dilatancy. The low shear rate viscosity does not rise because the increase in porosity, on generating a further 10% of secondary particles, is balanced by the increase in PSD width. By considering the composite plots presented in Figure 4.15.a, it is possible to account for the change in the rheology upon introduction of GCC fillers. These plots were compiled by adding 70.65% of the M1 PSD, presented in Figure 3.19.a, to 29.35% of the GCC Sedigraph PSD's presented in Figure 4.2.b. These ratios were used because although the filler accounts for 18% of the distribution by volume, it accounts for 29.35% on a weight basis, and it is the PSD as a function of weight which is presented in the composite plots.

From Figure 4.15.a one can see that 18% Polcarb substitution does not change the PSD within the plastisol. By introducing the filler one is merely increasing the plasticiser absorption characteristics within the system. The plasticiser absorption of the M1 paste polymer is 48g / 100cc, for the Polcarb filler it is 106g / 100cc. The response of the M1 plastisol to Polcarb substitution is as expected, because there is no change in PSD but an increase in
plasticiser absorption the shape of the flow curve is largely retained; it is merely shifted to higher viscosities with increasing levels of filler, see Figure 4.6.a. There is a tendency for the curves to bunch together at 100 S⁻¹, this would be expected because the repulsive forces between the filler particles are weak and so dilatancy is reduced as filler is added. When the M1 plastisol is filled with a coarser filler, such as Q300, the plastisol PSD is changed. The curve moves to the right, indicating a broader size distribution. This increase in PSD width, combined with the lower plasticiser absorption (66.5g / 100cc), results in a less dramatic increase in low shear viscosity with filler substitution. The wider distribution also suppresses any increase in dilatancy with filler substitution.

The higher proportion of secondary particles within the M2 plastisol not only suppresses dilatancy but changes the response of the plastisol to GCC filler introduction. From Figure 4.15.b, one can see that 18% Polcarb substitution significantly narrows the PSD, as shown by a reduction in the difference in particle sizes between the 20% and 80% ogives, from 10 µm, for the unfilled system, to 3.8 µm, for the Polcarb filled system. This reduction in PSD width accompanied by an increase in plasticiser absorption, within the system, not only causes an increase in low shear viscosity but also leads to a consistent increase in the viscosity measured at 300 S⁻¹. Narrower distributions within suspensions enhance dilatancy. A similar increase in dilatancy also occurs for the Q60 filled system which also has a narrower PSD than the unfilled system. For Q300 addition there is a less significant effect at high shear rates due to the lower absorption of plasticiser and the broadening of the PSD by the filler particles.

From Figure 4.16.a and 4.16.b one can see that filler levels of 30% Polcarb cause a fall in high shear viscosity. As there would only be a limited change in PSD on adding 30% Polcarb, the reduction in dilatancy can not be explained by the disruption of the hexagonal planes of particles brought about by the addition of a second family
of different size particles. It is, therefore, more likely that the
fall in dilatancy is due to the reduction of interparticle forces
within the system. Unlike PVC particles suspended in DIOP, filler
particles experience only weak repulsive forces. This is clearly
shown by the rapid flocculation of a concentrated filler dispersion,
in which the short range London-Van der Waal attractive forces are
sufficient to overcome the repulsive forces. As the repulsive forces
within the system are reduced, by incorporating filler particles, the
formation of the hexagonal planes of particles which lead to
dilatancy becomes less pronounced and so dilatancy falls. If the
filler level was increased above 40%, the high shear viscosity would
rise as the high plasticiser absorption of the filler became the
dominant factor controlling viscosity.

By carefully comparing Figures 4.7.a and 4.6.a it becomes
obvious that the filled unmilled systems exhibit a higher low shear
viscosity. As these systems contain a lower concentration of primary
particles, which dominate low shear viscosity, addition of filler to
these systems results in the ratio of filler to primaries being
higher and so one would expect filler addition to have a greater
effect in these systems.

An initial inspection of Figures 4.17.a and b clearly
demonstrates the difference in filler tolerance at 0.18 S⁻¹ between
the microsuspension and seeded emulsion systems. One can see that
the unimodal systems have a poor filler tolerance; this must be due
to the efficient packing of the primaries, which control rheology.
In the seeded systems the size ratio between the S primaries and L
primaries is 3 : 1. There must, therefore, be a significant quantity
of voids within the system which may accommodate the filler particles
and retard any increase in viscosity. These factors will be more
thoroughly examined in the section considering the rheology of S1 and
S2 filled plastisols.

The response of the microsuspension systems to TiO₂ filler
substitution is in agreement with what would be expected when adding
a highly plasticiser absorbent small PS filler. The rise in viscosity with only 1.0% and 2.0% filler substitution is shown in Figures 4.6.e, 4.6.f, 4.7.e and 4.7.f. The plastisols become extremely pseudoplastic. This behaviour may be attributed to the \( \approx 0.3 \mu m \) filler particles which must be influenced by Brownian and other short range forces. As the shear rate is increased the viscosity falls rapidly. If one increases the \( T_{0,2} \) level up to 6%, by volume, one can see that dilatancy starts to fall, see Figure 4.18. In these circumstances, one is adding 0.3 \( \mu m \) particles to a system of \( \approx 1.1 \mu m \) particles. The second family of 0.3 \( \mu m \) particles must disrupt the hexagonal packing of the PVC particles and therefore lead to a reduction in dilatancy.
Fig. 4.15 – Microsuspension Plastisol Composite Plots

a, Effect of Filler on M1 Plastisol PSD

b, Effect of Filler on M2 Plastisol PSD
Fig. 4.16 – Extended Filler Loadings

a, Effect on M1 Plastisol Dilatancy

b, Effect on M2 High Shear Viscosity
Fig. 4.17 – Performance of Seeded and Microsuspension Plastisols

a, Effect of Polcarb Addition

b, Effect of Q60 Addition
c, Effect of Q300 Addition

![Graph showing the effect of Q300 addition on apparent viscosity. The graph includes data points for different fillers and polymers, with axes labeled for apparent viscosity (Pa.s) and filler percentage.]
Fig. 4.18 – Effect of RTC60 Addition on M1 Dilatancy

![Graph showing the effect of RTC60 addition on M1 dilatancy. The graph plots shear rate against apparent viscosity, with different symbols representing various percentages of RTC60. The x-axis is labeled 'SHEAR RATE / S^-1', and the y-axis is labeled 'APPARENT VISCOSITY / Pa.s'.]
4.2.2.2 Emulsion Paste Polymers

4.2.2.2.a El Plastisol Rheology

An understanding of the factors controlling the response of the El plastisol to filler incorporation may be achieved by first considering the similarities in the rheological behaviour of the unfilled El and M1 plastisols. Both these systems are dilatant as a result of the narrow unimodal distribution of particles which control rheology. However, when GCC filler is introduced into these plastisols, each system responds in a totally different manner. The M1 plastisol flow curve is shifted to higher viscosities, while the El plastisol is transformed from a dilatant to a pseudoplastic dispersion. The cause of these differences in plastisol filler response becomes clear when one considers the change in PSD, within the plastisol, on filler incorporation. From the composite plots, discussed in the previous section, it is clear that the introduction of GCC into an M1 plastisol has only a limited effect on the PSD. However, for an El plastisol, one can see, from Figure 4.19.a that an 18% substitution of GCC causes a dramatic increase in the width of the PSD. This change in PSD is characterised in Table 4.5, by considering the range of particle sizes between the 80% and 20% ogives.

**TABLE 4.5 - EFFECT OF FILLER TYPE ON EL PLASTISOL PSD.**

<table>
<thead>
<tr>
<th>Filler Type</th>
<th>20% Ogive PS/μm (d20)</th>
<th>80% Ogive PS/μm (d80)</th>
<th>PS Width/ (μm) (d80 - d20)</th>
</tr>
</thead>
<tbody>
<tr>
<td>No Filler</td>
<td>8.0</td>
<td>26</td>
<td>18.0</td>
</tr>
<tr>
<td>18% Polcarb</td>
<td>1.5</td>
<td>22</td>
<td>20.5</td>
</tr>
<tr>
<td>18% Q60</td>
<td>2.4</td>
<td>22</td>
<td>19.6</td>
</tr>
<tr>
<td>18% Q300</td>
<td>3.4</td>
<td>22</td>
<td>18.6</td>
</tr>
</tbody>
</table>
Table 4.5, apart from characterising the width of the PSD, highlights one of the problems in analysing PS data. If one merely considered the change in PSD width, measured by \( d_{\infty} - d_{15} \), it would appear that the incorporation of 18% Q300 broadened the distribution by 0.6 \( \mu m \). From Figure 4.19.a one can see that the addition of 18% Q300 causes a dramatic increase in the proportion of small particles, with diameters between 1.0 and 10.0 \( \mu m \), which is not characterised by the \( d_{\infty} - d_{15} \) value. It also causes a significant reduction in average PS, measured at 50% cumulative mass.

The transition from dilatant to pseudoplastic flow, the increase in low shear viscosity and the fall in high shear viscosity with GCC filler substitution are accelerated by a reduction in filler PS. As shown by Figure 4.19.a, these small PS fillers have the greatest effect on broadening the PSD, as well as increasing the plasticiser absorption characteristics within the plastisol.
Fig. 4.19 – Emulsion Plastisol Composite Plots

a, Effect of Filler on E1 Plastisol PSD

b, Effect of Filler on E2 Plastisol PSD
If one considers the behaviour of the E1 plastisol filled with Polcarb, the rise in viscosity, measured at 0.18 S⁻¹, with GCC filler incorporation suggests that, at these low shear rates, it is the high plasticiser absorption of the filler (106 g/100cc) compared with that of the paste polymer (57.68 g/100cc) which dominates rheology and not the increase in PSD width. The improvement in particle packing efficiency, caused by the 2.0 µm filler particles fitting into the interstices between the 17.0 µm paste polymer particles does however play a limited role at these low shear rates. The rise in low shear viscosity is not continuous with filler level, as in the case of M1. The viscosity initially rises as filler levels are increased up to 4.5%, it then falls, reaching a minimum between 5 and 14% filler (depending upon filler PS) and then rises as filler levels are further increased, see Figure 4.8.d and Table 4.2. The introduction of filler causes an increased demand for plasticiser within the system which results in an initial rise in low shear viscosity. As the filler level is increased above 4.5%, by volumes, the small filler particles (of < 2.0 µm diameter) start to fill the interstices between the large 17.0 µm paste polymer particles. The plasticiser released from the interstices contributes to lowering plastisol viscosity. However, at levels above ~ 13.5% the viscosity of the filled plastisol starts to rise with filler content. This rise in viscosity confirms the work of McGeary, Westman and Hugill, see section 1.4.1. They found, that providing the size ratio between the large and small particles was at least 7 : 1, as in the case of E1 filled with GCC, the optimum level of small particles for the minimum void volume was 27%, by volume. In a plastisol system, the optimum level of small particles would be below 27% because of the large surface area of the small particles which causes an increase in suspension viscosity before the optimum packing concentration can be achieved. These surface area effects which result in a premature rise in viscosity have been considered by spray drying a series of latices containing two families of particles, while progressively reducing the sizes of the S primaries, and measuring the viscosity of suspensions produced from these materials, see Figure 4.20.
This Figure shows that the larger the ratio of large to small particles the lower the plastisol viscosity and the concentration of small particles required to achieve the minimum viscosity. One can see that the plots bunch together as the size ratio is increased. At size ratios above 5:1 the viscosity of the plastisol may rise above that of the 5:1 system because the high surface area of the small particles causes a rise in viscosity, even though the optimum packing ratio should be at least 7:1.

From Table 4.6, one can see that the position of the minimum viscosity moves to lower filler levels as the PS ratio, $\phi$, was increased. This agrees with the fact that the smaller the filler particles the more efficiently they fit into the interstices between the polymer particles and so the lower the amount required to achieve the minimum viscosity. The higher plasticiser absorption of the smaller PS filler also means that the surface area effects dominate at lower filler levels and so this factor also shifts the minimum to lower filler levels.
## TABLE 4.6 - RELATIONSHIPS BETWEEN THE DROP IN E1 PLASTISOL VISCOSITY AND FILLER PS. DATA TAKEN FROM TABLES 4.1 AND 4.2.

<table>
<thead>
<tr>
<th>Filler</th>
<th>Particle Size (µm)</th>
<th>Particle size ratio</th>
<th>% Filler (small particles) to achieve minimum viscosity at 0.18 S⁻¹</th>
</tr>
</thead>
<tbody>
<tr>
<td>Q200</td>
<td>2.9</td>
<td>5.9 : 1</td>
<td>13</td>
</tr>
<tr>
<td>Q60</td>
<td>2.0</td>
<td>8.5 : 1</td>
<td>9.0</td>
</tr>
<tr>
<td>Polcarb</td>
<td>1.1</td>
<td>15.5 : 1</td>
<td>6.0</td>
</tr>
<tr>
<td>RFC5</td>
<td>0.306</td>
<td>55.6 : 1</td>
<td>-</td>
</tr>
<tr>
<td>RTC60</td>
<td>0.275</td>
<td>61.8 : 1</td>
<td>-</td>
</tr>
</tbody>
</table>

Note: E1 particle size = 17 µm

At shear rates of ≈ 1000 S⁻¹ the viscosity of the E1 plastisol falls with filler introduction of up to 18%, or even beyond. At these high shear rates there is no conflict between the opposing influences of plasticiser absorption and particle packing. It is the flow of particles past each other, and not the packing of particles at rest, which controls viscosity. The disruption of the hexagonal planes of particles, which lead to dilatancy, is of crucial importance in causing the fall in high shear viscosity. The finest PS filler, Polcarb, causes the greatest fall in high shear viscosity because the size ratio between these particles and the E1 particles is the largest and causes the greatest degree of disruption to the formation of the hexagonal planes of E1 particles.

As in the case of low shear viscosity there is a minimum in high shear viscosity with filler substitution. At high shear rates because the disruption of the hexagonal planes of particles is the primary factor controlling viscosity, the surface area effects are of little importance and so the minimum does not occur until filler levels above 18% have been achieved.
This behaviour is shown schematically in Figure 4.21, it is the shift in emphasis from surface area effects to flow behaviour (and disruption of hexagonal packing), with increasing shear rate, which accounts for the difference in viscosity minimum. This explanation is confirmed by the M2 spray drying experiments, see Section 3.1.1.2.a, in which the minimum in low shear viscosity occurred under severity 2. However, a further increase in secondary particle concentration, caused by increasing the drying severity, raised low shear viscosity but caused a further reduction in high shear viscosity. Although this increase in secondary particle concentration caused an increase in porosity and low shear viscosity, the improvement in flow behaviour caused a drop in high shear viscosity; such behaviour demonstrates the shift in emphasis with shear rate.

The response of E1 plastisol rheology to $T_dO_2$ incorporation also confirms the existence of the surface areas effects considered in the discussion of GCC fillers. The introduction of $T_dO_2$ causes an increase in low and high shear viscosity; there does not appear to be any evidence to suggest that changes in packing or flow behaviour have an effect on rheology. The PS ratio between the PVC and $T_dO_2$ particles is $\approx 55 : 1$. This ratio is so large that the $T_dO_2$ particles act by increasing the viscosity of the continuous phase, which when filled with $T_dO_2$ behaves as a fluid towards the PVC particles. The $T_dO_2$ filled system conforms to Farris's condition of zero interaction between large and small particles.
4.2.2.2.b E2 Plastisol Rheology

As a result of the mild drying conditions employed in the spray drying of the E2 paste polymer compared with the El material, the breakdown of secondary particles during plastisol preparation generates a broad size distribution within the plastisol. This extremely broad distribution of porous secondary particles results in an extremely pseudoplastic plastisol. Ninety parts of DICP were required to produce a plastisol of low enough viscosity to be characterised by the Rotovisco.

The incorporation of GCC fillers into E2 plastisols reduces the average PS from 8.0 to 2.0 µm, as shown in Table 4.7, which was derived from the composite plot presented in Figure 4.19.b.

TABLE 4.7 - AVERAGE PS OF FILLED E2 PLASTISOLS.

<table>
<thead>
<tr>
<th>FILLERS</th>
<th>AVERAGE PS (µm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>No Filler</td>
<td>8.0</td>
</tr>
<tr>
<td>18% Q300</td>
<td>4.7</td>
</tr>
<tr>
<td>18% Q60</td>
<td>5.0</td>
</tr>
<tr>
<td>18% Polcarb</td>
<td>2.0</td>
</tr>
</tbody>
</table>

The incorporation of these fillers reduces pseudoplasticity the greatest reduction occurring for the Q300 filler. This effect is rather surprising, one would expect the introduction of a highly plasticiser absorbent filler, such as Polcarb (106 g/100cc), and the consequent reduction in average PS to result in a rise in plastisol viscosity and pseudoplasticity. Figure 4.22.a shows that the reduction in pseudoplasticity is not due to the substitution of a filler dispersion which would in itself have a lower viscosity than the E2 plastisol. The viscosity of the plastisol initially falls, as Q300 S, the least absorbent filler, is introduced. Further additions cause a rise in viscosity, the Q300 S dispersion having a higher viscosity than the
unfilled plastisol. The initial drop in viscosity may be attributed to an improvement in packing efficiency, brought about by a shift in the PSD. I do however feel that, in this particular case, where the high viscosity of an unfilled E2 plastisol is a result of structure development and secondary particle porosity, the fall in viscosity and pseudoplasticity with filler introduction is a result of changes in interparticle repulsion and structure development.

In section 1.5.1.1 of the literature search it has been shown that the contribution of structure development to plastisol viscosity depends upon the square of the number of particles per cubic centimetre and becomes significant when the diameter of the paste polymer particles falls below 0.2 µm. Although the majority of the 0.15 µm primary particles, within an E2 plastisol, are present as agglomerates, I believe they still dominate plastisol rheology through structure development. Evidence to support this claim comes from the particle stability measurements made in section 3.2.1.7. During these experiments, I measured the viscosity of a 100/90 E2 plastisol before and after the application of shear forces. I detected a fall in viscosity and pseudoplasticity with the application of these shear forces, generated by one passage through the Severs 1 mm die. As demonstrated in Khanna's paper⁴⁶, the existence of this hysteresis loop, shown in Figure 4.22.b, is a result of structure development, in which the forces of attraction and repulsion between particles lead to the formation of a kinetically stable network, within the plastisol. This network resists deformation and contributes to a high viscosity. The application of shear forces can temporarily damage this structure and lead to a fall in viscosity.

In a filler dispersion, the repulsive forces between particles are relatively weak. The attractive London-van der Waals forces override these repulsive forces, causing the rapid flocculation of the system. The reduction in E2 plastisol viscosity with GCC filler incorporation may be explained. An increasing proportion of large filler particles within the plastisol reduces the magnitude of the interparticle forces, as the repulsive forces between filler particles are very weak, this results in the weakening of the structure within the plastisol and a

-263-
resultant fall in viscosity and pseudoplasticity. One can see from Figure 4.22.a that plastisol viscosity does finally start to increase again, with filler incorporation. This increase is due to the high plasticizer absorption of the filler (51.7 g/100cc) compared with that of the E2 paste polymer (37.52 g/100cc).

The substitution of RFC5 has little effect on rheology because the incorporation of up to 8% of the small ≈ 0.2 μm particles does not affect the development of structure within the system. The addition of Spheriglass 5000 CP03 on the other hand results in a dramatic reduction in pseudoplasticity due to the reduction of interparticle forces and structure development.
Fig. 4.22 – Structure Development in E2 Plastisols

a, Reduction of Interparticle Forces

b, Hysteresis Loop
4.2.2.3 Seeded Emulsion Paste Polymers

The high filler tolerance of the seeded emulsion plastisols compared with that of the microsuspension plastisols is a result of the bimodal primary PSD. If a size ratio of 7 : 1 or more had been employed the S primaries would be able to fit into the interstices within the L primaries, without disrupting their packing efficiency. However the size ratio employed in the manufacture of the S1 and S2 paste polymers was 4 : 1. At this level the S primaries are too large to fit into the triangular pores between the L primaries. This results in an expansion of the L primary network and the formation of a more open particle structure. A consequence of this more open structure is that filler particles may fit into this structure without disrupting the packing efficiency. This ability to accept filler particles limits the rise in plastisol viscosity with filler incorporation, as shown in Figure 4.17.

It is important to realise that the S1 and S2 plastisols respond in a different manner to filler incorporation. Although both systems eventually become increasingly pseudoplastic with the incorporation of increasing quantities of the smaller PS fillers. The S2 plastisol initially experiences a fall in low shear viscosity which causes the plastisol to become "Newtonian", while the S1 plastisol viscosity rises. This difference in filler response is clearly shown in Figure 4.23.

The factors controlling the rheology of the seeded emulsion plastisols will be further investigated in the next section. By comparing the effect of filler incorporation in the two systems, I will show that the rheology of the S1 plastisol is largely controlled by particle packing efficiency while structure development plays a significant role in the behaviour of the S2 plastisols.

4.2.2.3.a S1 Plastisol Filler Response

The "Newtonian" flow curve of the S1 plastisol has already been attributed to the combined effects of the low porosity secondary particles and the bimodal primary PSD, which is composed of independent
primaries. From Figure 4.23.a one can see that low shear viscosity rises with the incorporation of GCC, this increase becomes more pronounced as the PS of the filler is reduced. As the high shear viscosity remains relatively unchanged with filler incorporation the plastisol becomes increasingly pseudoplastic. The broad PSD within the S1 plastisol is capable of accepting considerable quantities of filler without a dramatic increase in high shear viscosity.

At low shear rates the viscosity does not rise continuously with filler incorporation. As the filler level is increased the low shear viscosity rises up to a maximum at 9% substitution, the viscosity then falls to a minimum, irrespective of GCC filler PS, see Figure 4.23.a, it then continues to rise with further substitution of filler. By considering the composite plot, presented in Figure 4.24.a, one can evaluate the effect of filler incorporation on the PSD within the S1 plastisol. The addition of 18% Polcarb causes a considerable reduction in PSD width, as clearly shown by considering the range of particle sizes between the 65% and 15% ogives, see Table 4.8.

**TABLE 4.8 - EFFECT OF FILLER INCORPORATION ON S1 PLASTISOL PSD WIDTH**

<table>
<thead>
<tr>
<th>Filler</th>
<th>65% Ogive d₆₅/μm</th>
<th>15% Ogive d₁₅/μm</th>
<th>PSD Width (d₆₅-d₁₅)/μm</th>
</tr>
</thead>
<tbody>
<tr>
<td>No Filler</td>
<td>6.0</td>
<td>0.3</td>
<td>5.7</td>
</tr>
<tr>
<td>18% Q300</td>
<td>4.8</td>
<td>0.6</td>
<td>4.2</td>
</tr>
<tr>
<td>18% Q60</td>
<td>3.0</td>
<td>0.6</td>
<td>2.4</td>
</tr>
<tr>
<td>18% Polcarb</td>
<td>2.0</td>
<td>0.8</td>
<td>1.2</td>
</tr>
</tbody>
</table>

The effect of filler incorporation at low shear rates can be readily explained by considering the change in PSD and plasticiser absorption, within the system. Introduction of a plasticiser absorbent filler such as Polcarb (106 g/100cc) increases the plasticiser demand within the plastisol from 64.26 g/100cc and reduces the PSD width. Both these factors cause an initial rise in low shear viscosity. As the
filler level is increased above 4.5%, by volume, the small filler particles start to fill the interstices within the open particle structure. The plasticiser displaced from these interstices contributes to the fall in plastisol viscosity. However, as the filler level is further increased above 13.5% the increase in plasticiser demand and reduction in PSD width outweigh any displacement of plasticiser and so plastisol viscosity starts to rise. The higher viscosity of the plastisols containing the smaller PS fillers is due to the higher plasticiser absorption of these fillers and the resultant reduction in PSD width. One can see from Table 4.8 that the PSD width falls from 4.2 μm to 1.2 μm, by reducing the GCC filler PS.

For the S1 plastisols the position of the minimum viscosity does not depend upon filler PS, as in the case of the E1 plastisol. For the E1 systems, the larger the size difference between the 17 μm secondary particles and the filler particles the more efficiently the particles packed together and the lower the filler level required to achieve the minimum. The finer PS fillers also pushed the position of the minimum to lower filler levels because the higher plasticiser demand of these systems causes a more rapid increase in viscosity with filler concentration. To be able to resolve the differences in packing efficiency which lead to changes in the position of the minimum viscosity it is necessary to have a size difference of at least an order of magnitude between the polymer particles and filler particles. For the S1 plastisol there is only a limited size difference, the average size of the filler particles is ≈ 2.0 μm for the paste polymer particles it is ≈ 1.3 μm and so the position of the minimum is independent of filler PS.

The importance of the relationship between particle packing efficiency and size ratio may also be demonstrated by comparing the position of the minimum for the S1 and E1 plastisols. One can see that, as stated previously, a greater size ratio enables the particles to pack more efficiently, only 6-13% filler is necessary for the E1 plastisol while 13.5% is necessary for the S1 plastisol.
The behaviour of the $T_{02}$ filled S1 plastisols shows that considerable care must be exercised when wishing to limit the effect of filler on plastisol viscosity. For the E1 plastisol, which is composed of 17 $\mu$m particles, adding a filler of $\approx 2.0$ $\mu$m, which is an order of magnitude smaller than the paste polymer particles, limits the effect of filler introduction. For an S1 plastisol, which has an average PS of 1.3 $\mu$m, one would expect the addition of $T_{02}$, which is composed of $\approx 0.3$ $\mu$m particles (ie an order of magnitude smaller), to limit the rise in viscosity because of the large size ratio which facilitates efficient packing. Such an effect is not observed for the incorporation of $T_{02}$. This filler causes a dramatic increase in low shear viscosity and pseudoplasticity. Such behaviour is not due to changes in particle packing but Brownian motion which becomes a significant factor and may dominate the rheology of suspensions, as PS is reduced below 0.3 $\mu$m.

4.2.2.3.b S2 Plastisol Filler Response

In the section considering the rheology of unfilled plastisols prepared from the S2 paste polymer I attributed the behaviour of this system to the broad distribution of non-porous secondary particles and not the interaction of the bimodal primary PSD. The Sedigraph failed to detect the presence of discrete independent 0.2 and 0.7 $\mu$m primary particles. I believe that the behaviour of a series of filled S2 plastisols, ageing studies and the low $K$ value (69) of the S2 paste polymer compared with that of the S1 paste polymer (73) provides evidence to cast doubt on the original proposed mechanism, described in Section 3.2.1.2.c. Both of the seeded emulsion plastisols were prepared from paste polymers which contain a bimodal primary PSD. In the S1 plastisol the "Newtonian" flow curve has been attributed to the bimodal primary PSD which was partially regenerated by the breakdown of secondary particles during plastisol preparation. The flow instabilities which lead to dilatancy are totally suppressed because the two distinct families of primary particles prevent the formation of hexagonal planes of particles which lead to dilatancy. I believe a similar mechanism controls the rheology of the S2 plastisol, although low shear rate viscosities are enhanced by structure formation and particle–particle
interactions while the high shear rate viscosity is suppressed by the reduction in the sizes of the primaries. The lower molecular mass (shown by a lower K value) and smaller size of the S2 primaries must make them more susceptible to solvation and dissolution in the plasticiser. Such particle-solvent interactions must lead to considerable structure development within the system and should explain the dramatic increase in S2 plastisol low shear viscosity with time.

During the discussion of the ageing phenomenon it was difficult to explain the behaviour of the S2 plastisol because the Sedigraph failed to detect a shift in PSD, which should occur if the S2 primaries partially dissolve or swell. I suspect this lack of resolution may be a consequence of particle-particle interactions which play such an important role in the behaviour of this system. These interactions may lead to the formation of a lightly flocculated structure within the Sedigraph sample cell, which would resist the sedimentation of particles, causing the instrument to suggest the presence of artificially high levels of small particles. The 0.2 µm primaries because of their susceptibility to Brownian motion and solvation would be particularly susceptible to this retardation of sedimentation. Without this structure development and particle solvation, which causes problems in PSA, there should be no difference in the filler response of the seeded emulsion plastisols. Both systems are based on the same design, they were manufactured from similar bimodal latices which contain 33% S primaries with a size ratio of 4 : 1. The only difference is the lower average PS and molecular mass of the S2 system.

The formation of structure within an S2 plastisol provides a framework for explaining the response of the dispersion to filler incorporation. We already know that the repulsive forces between filler particles are relatively weak, the introduction of these particles into an S2 plastisol must therefore reduce the structure contribution to viscosity. From Figure 4.23.b one can see that substituting 4.5% filler causes a fall in viscosity. However, higher levels cause a rapid increase in plastisol viscosity. This behaviour is as would be expected because the structure contribution to viscosity is relatively small and
so the high plasticiser absorption of the filler and reduction in PSD width, see Figure 4.24.b and Table 4.9, soon cause an increase in viscosity.

For the E2 plastisol, the low molecular mass shown by a K value of 69, small primary PS (0.15 μm), extremely high plastisol viscosity and hysteresis loops highlight the large contribution of structure development to plastisol rheology. It is because of this large contribution that the viscosity of an E2 plastisol containing 50% Q300 S, by volume, is lower than that of the unfilled plastisol.

TABLE 4.9 - EFFECT OF FILLER INCORPORATION ON S2 PLASTISOL PSD WIDTH
DATA TAKEN FROM FIGURE 4.24.b

<table>
<thead>
<tr>
<th>Filler</th>
<th>65% Ogive (μm)</th>
<th>25% Ogive (μm)</th>
<th>PSD Width (d50-d25)/μm</th>
</tr>
</thead>
<tbody>
<tr>
<td>No Filler</td>
<td>12.0</td>
<td>0.4</td>
<td>11.6</td>
</tr>
<tr>
<td>18% Q300</td>
<td>8.0</td>
<td>0.7</td>
<td>7.3</td>
</tr>
<tr>
<td>18% Q60</td>
<td>5.5</td>
<td>0.55</td>
<td>4.95</td>
</tr>
<tr>
<td>18% Polcarb</td>
<td>5.5</td>
<td>0.55</td>
<td>4.95</td>
</tr>
</tbody>
</table>

For the S2 plastisols the T.0% fillers behave in a similar manner to the GCC fillers. All fillers cause an initial reduction in plastisol low shear viscosity followed by a rapid increase, making the system more pseudoplastic. This increase in pseudoplasticity becomes more pronounced as the filler PS is reduced. Table 4.10 shows the amount of filler which is required to maintain S2 plastisol viscosity.
TABLE 4.10 - PERFORMANCE OF FILLERS IN S2 PLASTISOLS.

<table>
<thead>
<tr>
<th>Filler</th>
<th>Filler PS (µm)</th>
<th>Filler loading when filled plastisol n = unfilled plastisol n (phr)</th>
<th>Plasticiser Absorption (g/100cc)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Q300</td>
<td>2.9</td>
<td>30</td>
<td>66.5</td>
</tr>
<tr>
<td>Q60</td>
<td>2.0</td>
<td>16</td>
<td>80.6</td>
</tr>
<tr>
<td>Polcarb</td>
<td>1.1</td>
<td>4.5</td>
<td>106</td>
</tr>
<tr>
<td>RFC5</td>
<td>0.306</td>
<td>3.0</td>
<td>61.2</td>
</tr>
<tr>
<td>RTC60</td>
<td>0.275</td>
<td>2.0</td>
<td>70.1</td>
</tr>
</tbody>
</table>

From Table 4.10, it is obvious that as filler PS is reduced less filler is required to achieve the uncompounded plastisol viscosity. The smaller PS GCC fillers cause a more rapid increase in low shear viscosity because of their higher plasticiser absorption and reduction in PSD width, as shown in Table 4.9. One can see from Table 4.10 that although the plasticiser absorption of RFC5 and RTC60 is below that of Polcarb, both TiO₂ fillers require a lower loading to achieve the original viscosity. This must be due to their small PS which makes them susceptible to Brownian motion which causes a rise in low shear viscosity.

Having attributed the filler response of S2 and E2 plastisols to an initial reduction in structure development, it seemed reasonable to assume that these systems would respond in a different manner if the contribution of structure development to plastisol viscosity could be reduced. Such a reduction could be achieved by changing the affinity of the paste polymer for the plasticiser and the consequent particle-particle interactions by:

1. Increasing the molecular weight of the paste polymer while controlling the primary PSD,
2. changing the emulsifier and surfactant coatings, or
3. selecting a less active plasticiser.
Of the three possible techniques, since it is necessary to maintain the same PSD within the plastisol, if the contribution of structure development to filler response is to be isolated, it was decided to use a less active plasticiser. This should minimise any changes in PSD while reducing particle-particle interactions.

Figure 4.25.a confirms my assumption that the use of a less active plasticiser, such as DBS, instead of DIOP does not result in a significant change in the PSD within an S2 plastisol. It does however change the filler response. From Figure 4.25.b one can see that an S2 plastisol prepared from DBS does not experience a fall in low shear viscosity at 4.5% Polcarb substitution, as in the case of a DIOP plasticised S2 plastisol. This is probably a consequence of the reduced structural development within the plastisol. Filler addition does not cause as large a reduction in interparticle forces and so the plastisol does not experience an initial fall in low shear viscosity.
Fig. 4.23 – Seeded Emulsion Plastisol Filler Response

a, S1 Low Shear Viscosity

b, S2 Low Shear Viscosity

Filler
- △ Polcarb
- □ Q60
- □ Q300
Fig. 4.24 – Seeded Emulsion Plastisol Composite Plots

a, Effect of Filler on S1 Plastisol PSD

b, Effect of Filler on S2 Plastisol PSD
Fig. 4.25 – Evaluation of Structure Development (S2 100/50)

a, Limited Change in PSD

b, Reduced Interparticle Forces (DBS)
4.2.3 Effect of Stearate Coating GCC Fillers

Throughout the discussion of plastisol filler response considerable emphasis has been placed on the dominance of particle packing considerations. The size of PVC and filler particles has been presented as one of the main factors controlling rheology. Further evidence to support this belief comes from studies using coated GCC fillers. For a series of filled 100/50 plastisols, see Figures 4.12 and 4.13, the stearate coating has little if any effect on plastisol rheology even though plasticiser demand is significantly reduced. It is only when plasticiser levels are increased to 60 phr that the coating causes a drop in plastisol viscosity.
CHAPTER 5: SUMMARY, CONCLUSIONS AND RECOMMENDATIONS

5.1 SUMMARY OF PLASTISOL FLOW BEHAVIOUR

5.1.1 Microsuspension Systems

The rheology of plastisols prepared from microsuspension paste polymers is dominated by the broad unimodal distribution of primary particles centred around 1.0 μm. These particles are generated during plastisol preparation by the breakdown of the secondary particles which were only superficially agglomerated by the relatively low drying temperatures (of 50 - 60°C) employed during the spray drying process. During polymerisation, homogenisation conditions are carefully controlled in order to limit the size range of latex particles to 0.3 - 2.0 μm. The absence of particles smaller than 0.3 μm accounts for the lack of low shear pseudoplasticity in plastisols prepared from these resins, while the width of the distribution (d_{50} - d_{20} = 0.55 μm) ensures the lowest low shear viscosity of all the plastisols investigated. This low viscosity is achieved by the reduction of void volume due to the efficient packing of the continuous gradation of primary particle sizes and the suppression of solvation as a result of the high molecular mass (K value = 73). The minimal effect of solvation was shown by the limited ageing of the microsuspension plastisols and retention of the flow curve shape.

The spray drying experiments highlighted the need for careful control of drying temperatures. Once the temperature rose above 60°C, the secondary particles formed during this severe drying process resisted breakdown in the plasticiser. Their large size (8.0 μm diameter) combined with high porosity (0.4 cc/g) resulted in plastisols of extremely high viscosity and low shear dilatancy (starting at 0.5 S⁻¹). For commercial microsuspension plastisols, where a low shear viscosity is of paramount importance, medium drying temperatures should be employed to ensure substantial secondary particle breakdown.
The milling of these paste polymers is usually employed to limit the size of the secondary particles so that the surface finish of thin coatings does not suffer. However, it has been shown in this work that the milling process influences rheology through changes in the PSD within a plastisol. The M2 plastisol (unmilled), when prepared from paste polymers dried at 60°C, contains 30% secondary particles. At these levels they are present in sufficient quantities to suppress dilatancy without an increase in viscosity attributed to their high porosity. However, the milling process tends to weaken and rupture some of the secondary particles, these tend to break down in the plastisol reducing the concentration of secondary particles to 20%. At this lower level, they are not present in sufficient quantities and so the effect of the unimodal distribution of primaries dominates and the plastisol shows severe dilatancy in a 100/45 plastisol at 100 s⁻¹.

The filler response of the microsuspension plastisols has been explained by comparing the effect of increasing the proportion of secondary particles with the effect of incorporating filler particles. When the proportion of secondary particles is increased, from 20% to 30% of the distribution, by changing the milling conditions, the high porosity of the secondary particles (0.4 cc/g) increases the plasticiser demand within the system. This is however balanced by the broadening of the distribution which facilitates more efficient packing and displaces plasticiser. As a result the plastisol low shear viscosity remains relatively unchanged. When the GCC fillers are incorporated into the plastisol, one can see from the composite plots that the increase in plasticiser demand, due to the filler particles, is not balanced by an increase in PSD width. The unfilled M1 plastisol has an almost identical PSD to the system containing 18% Polcarb. As a result the flow curve of the M1 plastisol remains relatively unchanged, it is merely shifted to a higher viscosity because of the increase in plasticiser demand within the system. For the M2 plastisol, filler incorporation causes a limited narrowing of the distribution and so there is a more pronounced effect on increasing high shear viscosity.
When compared with the seeded emulsion plastisols the microsuspension systems display a lower filler tolerance. This is a result of the efficient packing of the primary particles. Although this efficiency limits low shear viscosity it minimises the available space for incorporating the filler particles and so viscosity rises, unrestrained by a reduction in void volume.

The incorporation of T,0,2 does however change the shape of the flow curve because there is a change in PSD as well as plasticiser demand. Addition of 0.3 µm T,0,2 particles to a system primarily composed of ≈ 1.1 µm particles broadens the distribution and increases plasticiser demand. This results in a rapid increase in low shear viscosity and a limited fall in dilatancy due to the disruption of hexagonal particle plane formation.

5.1.2 Emulsion Systems

In direct contrast to the microsuspension systems the rheology of the emulsion plastisols is dominated by the secondary particles. For these paste polymers it is necessary to spray dry the latices under severe conditions (<70 - 80°C) in order to transform the narrow unimodal distribution of 0.15 µm primaries into secondary particles, otherwise plastisol viscosity would be too high to facilitate easy processing.

For the E1 plastisol a high drying temperature ensures that the primaries are thoroughly fused together and resist breakdown in the plasticiser. The E1 plastisols are therefore composed of a narrow distribution of 17.0 µm diameter secondary particles. Plastisol viscosity still tends to be high due to the high porosity of the secondaries (0.14 cc/g) and the high plasticiser absorption of the 0.15 µm primary particles. The small primary PS combined with a k value of 69 also caused a rapid increase in low shear rate viscosity upon ageing and a swelling of the 17.0 µm secondaries.

The dilatancy of the E1 plastisol and the microsuspension systems is due to the narrow unimodal nature of the distributions. The
discrepancy with Hoffmann's model \( ^{49} \) which predicts a discontinuity for these systems, is due to the width of the distribution. Commercial plastisols are seldom monodispersed. As the width of the distribution is increased it becomes more difficult to form Hoffman's hexagonal planes of particles which lead to the discontinuity and so the breakdown of ordered flow tends to occur over a range of shear rates and not at a discontinuity shear rate, resulting in dilatancy. The narrower distribution within the microsuspension plastisols (measured by the slope at 50% cumulative mass) compared with the El plastisols results in a more severe dilatancy (as the system approaches the model proposed by Hoffman).

For the larger PS systems (ie El compared with M1) dilatancy occurs at lower shear rates because more time is required for the cooperative movement of larger particles. This dependence of the onset of dilatancy on PS explains why Williams and Bergen's least-squares equation is not universally acceptable for the prediction of the onset of dilatancy as a function of reduced volume. The coefficients in their equation are valid for an extremely narrow distribution of 1.4 \( \mu m \) particles. It is however possible to accurately predict the onset of dilatancy for the M1 and El plastisols from the following least squares equations.

For M1 \( \log_{10} \beta_d = -2.5805 + 3.7532/a_m \)
Coefficient of determination \((r^2) = 0.9098\) \(\text{(5.1)}\)

For El \( \log_{10} \beta_d = -7.8109 + 6.8108/a_m \)
Coefficient of determination \((r^2) = 0.9796\) \(\text{(5.2)}\)

The acceptance of Hoffman's model enables the performance of filled El plastisols to be interpreted. Unlike the M1 plastisols, the introduction of the GCC filler particles into an El plastisol causes a dramatic change in the composite PSD which results in a change in the flow curve from a dilatant to a pseudoplastic shape. Low shear rate viscosity rises while high shear rate viscosity falls. This increase in low shear viscosity is due to the high plasticiser absorption of the
filler particles. An optimum filler level of ≈ 9.0% (depending upon filler PS) may be attributed to the balance between increasing plasticiser absorption and packing efficiency. At high shear rate there is no such conflict, the introduction of the ≈ 2.0 µm filler particles into the 17.0 µm paste polymer distribution suppresses dilatancy by the increase in PSD width which disrupts the formation of the hexagonal planes. At filler levels above 18%, high shear viscosity may start to rise again due to the high plasticiser absorption of the filler particles.

When TiO₂ filler is introduced, the flow curve is pushed to higher viscosities. There is no evidence of a change in packing efficiency because the size ratio between the filler and paste polymer particles is so large that the filler particles behave as a fluid towards the emulsion particles.

For the E2 plastisol, the drying temperature is not high enough to facilitate thorough fusion of the primary particles, as a result the plastisol is composed of a range of particle sizes. The larger particles tend to be intact secondary particles while the smaller particles tend to be fragments. A consequence of this partial regeneration of the primary PSD is the tendency to produce extremely high viscosity pseudoplastic plastisols. The broad distribution maintains the low shear viscosity while the high low shear viscosity is a consequence of the high plasticiser demand of the secondary particles and the small primary PS, which leads to considerable dissolution, swelling and structure development within the system. From the spray drying experiments it is obvious that careful control of the drying temperature is necessary to control primary particle regeneration within the plastisol. Too low a temperature results in the formation of secondary particle fragments which lead to high plastisol viscosity and pseudoplastic flow. An emulsion paste polymer dried at 80°C results in a dilatant 100/55 plastisol, a reduction in drying temperatures to 70°C results in such a high 100/55 plastisol viscosity that low shear viscosity can not be measured by a Rotovisko rheometer.
Filler effects are easily understood, there seems to be no evidence of changes in particle packing efficiency. Filler introduction initially causes a fall in pseudoplasticity. However, continued additions eventually cause an increase in low shear viscosity and pseudoplasticity. This effect is more pronounced for the larger PS GCC fillers because of their lower plasticiser absorption. The response of these systems is a consequence of the reduction in structure development in introducing filler particles.

For the TiO₂ filled system, the filler seems to have little effect on plastisol viscosity.

5.1.3 Seeded Emulsion Systems

The rheology of plastisols prepared from the S₁ seeded emulsion paste polymer is dominated by the primary particles. The bimodal nature of the distribution suppresses low shear viscosity by minimising void volume while dilatancy is prevented because it is not possible for such a distribution of particles to form hexagonal planes which is a precondition of dilatancy. The secondary particles are of low porosity (0.1 cc/g) and act as blending resin particles, being suspended in a dispersion of primaries. The medium drying temperatures employed ensure that the majority of the secondaries breakdown to liberate the bimodal primary PSD, which dominates rheology. However, spray drying experiments have shown that the plastisol becomes dilatant when drying temperatures are raised to ≈ 70°C because after such processing the distribution is composed of low porosity secondary particles. The narrow distribution of secondary particle sizes lead to dilatancy although viscosities are still restrained as these particles absorb relatively little plasticiser.

For the S₁ plastisol, the Sedigraph particle size analysis detected a bimodal primary PSD and a unimodal secondary PSD. The absence of particles smaller than 0.2 μm and the presence of a viscosity depressant ensures that S₁ plastisols do not exhibit pseudoplasticity at low shear rates. Filler incorporation imparted a rapid increase in low shear viscosity causing an increase in pseudoplasticity, although
compared with the microsuspension plastisols the filler tolerance was higher. The voids within the bimodal distribution of primaries were able to accommodate the filler particles and so retard the increase in viscosity. Like the E1 plastisol, the rise in low shear viscosity was not proportioned to filler level. There was a fall in viscosity at ~ 13.5% filler. For the seeded material the position of the minimum was independent of filler PS because the size ratio between the average size of the paste polymer particles and that of the filler particles was insufficient to influence changes in packing efficiency. When T,02 was incorporated into these plastisols there was a continuous increase in low shear viscosity and pseudoplasticity which may be expected as the small T,02 particles act by increasing the viscosity of the continuous phase.

For the S1 and S2 plastisols, although the PSD and mechanisms controlling plastisol viscosity were similar, the lower K value (<70) and smaller S primary size (<0.2 μm) of the S2 paste polymer lead to an increase in particle dissolution, particle-solvent and particle-particle interactions which resulted in structure development within the S2 plastisol. The resistance of this network to deformation played an important role in explaining the differences in rheological behaviour of the two systems.

The low shear pseudoplasticity imparted to an S2 plastisol is a direct result of the increased structure development within the system because additional energy is required to deform the plastisol. The ageing behaviour and filler response may also be explained by this structure development. The small primary PS and low K value lead to accelerated particle dissolution which causes the change in flow curve shape and dramatic increase in low shear viscosity, while changes in structure development account for the unusual filler response. When filler (GCC or T,02) is initially introduced into the plastisol, the low shear viscosity falls because of the lower interparticle forces attributed to the filler particles, it then rises as further filler is introduced, as the higher plasticiser absorption of the filler becomes the dominant factor controlling viscosity. This effect becomes more
pronounced with the smaller PS fillers as plasticiser absorption is increased and the reduction in structure development is less pronounced.

5.2. MATHEMATICAL RELATIONSHIPS BETWEEN PLASTISOL FLOW BEHAVIOUR AND PLASTISOL PARAMETERS

Throughout the preceding discussions the effect of PS and PSD on the flow behaviour of various filled and unfilled plastisols has been considered in a qualitative manner. To redress the balance, several quantitative relationships will now be presented. The first is based on the Chong et al equation\(^{72}\), which relates the relative viscosity, at 1 reciprocal second, to a polymer volume fraction parameter. Having confirmed the close relationship between plastisol viscosity and concentration, a mathematical model was developed which allows the plastisol flow curve to be generated from a knowledge of the plasticiser content and the PSD, characterised by standard deviation, mean size and Skewness.

5.2.1. Chong et al Equation

In 1971 Chong et al developed an empirical equation relating plastisol viscosity, at 1 reciprocal second, and polymer concentration:

\[
n = n_\infty \left[ 1 + \frac{0.75 \phi/\phi_\infty}{1 - \phi/\phi_\infty} \right]^2
\]  

(5.3)

where

- \( n \) = suspension viscosity
- \( n_\infty \) = suspending liquid viscosity
- \( \phi \) = polymer volume fraction
- \( \phi_\infty \) = polymer volume fraction at infinite viscosity
- \( \phi/\phi_\infty \) = reduced volume fraction (RVF)

The plastisols used in their study were composed of 1.0\( \mu \)m PVC paste polymer particles, and as such these systems are similar to the dispersions employed in my study. I therefore decided to evaluate the applicability of equation 5.3, to my plastisols.
Chong et al employed curve fitting techniques to determine \( \varphi_0 \). In my study I used the experimental data presented in Figure 5.1.a, which highlights the dependence of relative viscosity (nr) on volume fraction, \( \varphi_{\text{ref}} \) was defined as the volume fraction of polymer which would confer a specified viscosity. Figure 5.1.b shows the viscosity of the plastisols presented in Figure 5.1.a, as a function of RVF' (\( \varphi/\varphi_{\text{ref}} \)), where \( \varphi_{\text{ref}} \) corresponds to a volume fraction which would confer a relative viscosity of 283. Figure 5.1.c contains a similar set of results, in this case, \( \varphi_{\text{ref}} \) conferred a viscosity of 14641. One can see that as \( \varphi/\varphi_{\text{ref}} \) tends to \( \varphi/\varphi_{\text{ref}} \) the agreement with Chong et al's prediction improves. To quantify the point at which RVF' may be approximated to RVF, Figure 5.1.d was constructed. In this plot the average deviation from the Chong et al equation was plotted against the relative viscosity at which \( \varphi_{\text{ref}} \) was determined. The deviation data being extracted from a series of graphs similar to 5.1.b and 5.1.c. The horizontal deviation accounts for the difference between the RVF' of each of the plastisols and the RVF predicted by equation 5.3. The vertical deviation compares the actual viscosity of the plastisols with the predicted values. These discrepancies were expressed as \( \% \) values, according to:

\[
\% \text{ average horizontal deviation} = \left| \frac{\sum \text{exp RVF'} - \text{actual RVF}}{\text{actual RVF}} \right| \frac{1}{\text{number of observations}} \tag{5.4}
\]

\[
\% \text{ average vertical deviations} = \left| \frac{\sum \text{exp nr} - \text{actual nr}}{\text{actual nr}} \right| \frac{1}{\text{number of observations}} \tag{5.5}
\]

where \( \text{actual RVF} \cdot \varphi_0 = \text{value predicted by Chong et al equation} \)

The optimum relative viscosity for calculating \( \varphi_{\text{ref}} \) was taken as 10,000 as this gave a low vertical deviation and scatter of deviation. RVF' based on a nr of 10,000 were denoted by RVF*, due to the broad scatter of deviation, indicated by the scatter bands shown in Figure 5.1.d, the validity of specifying 10,000 as an exact value must be questioned. Values between 3,000 and 20,000 are equally valid.

The data for the E2 plastisols were not included in this study because the viscosity/volume fraction curve, Figure 5.1.a, did not follow
the same pattern as the other systems. The plastisol exhibited very high viscosities at low RVF and appeared to experience only a gradual increase in nr with volume fraction. The data did not collapse onto the master curve proposed by Chong et al. This E2 plastisol was composed 0.1μ primary particles, compared with the 1.0μ particles in Chong's study. It therefore seems reasonable to exclude this system from the study.

Care must be taken when determining eref because, as discovered in a paper due to Quemada, eref depends upon shear rate. In this study all measurements were made at 1 reciprocal second.

5.2.2. Flow Curve Modelling based on Polynomial Equations and Generalised Linear Interactive Modelling (GLIM)

Although equation 5.3 may be employed to predict viscosity, at a specified shear rate, what is desperately needed by the plastisol industry is a mathematical model which will enable the flow curve to be generated from PSD data. In order to establish such a model, it was first necessary to represent the flow curve by a mathematical expression and to characterise the PSD, within a plastisol, by several statistical parameters.

5.2.2.1. Characterisation of Flow Behaviour

The flow behaviour of the plastisols presented in Figures 3.1 and 3.2 was represented by curve fitting a second degree polynomial expression using a least squares technique. For the pseudoplastic systems (Figures 3.1.d, 3.2.a and 3.2.b) this was carried out over a range of shear rates (0.3 to 3,000 Pa.S). The viscosity was related to shear rate by an equation of the form:

\[
\log \eta_a = C_0 + C_1 \times \log \dot{\gamma} + C_2 \times (\log \dot{\gamma})^2
\]  

(5.6)

The initial fall in viscosity followed by a sharp rise in viscosity, with shear rate, for the dilatant systems (Figures 3.1.a, 3.1.b
and 3.1.c) was also represented by equations of this form. However, for these systems, certain assumptions were made, prior to curve fitting by the least squares technique, see Section 5.2.2.3.b.

Table 5.1 contains the polynomial coefficients which describe the pseudoplastic flow curves presented in Figures 3.1.d, 3.2.a and 3.2.b.

Table 5.1 - PSEUDOPLASTIC SYSTEMS: POLYNOMIAL COEFFICIENTS

<table>
<thead>
<tr>
<th>Polymer</th>
<th>DIOP phr</th>
<th>RVF</th>
<th>Coef C0</th>
<th>Coef C1</th>
<th>Coef C2</th>
<th>RMS Residuals</th>
</tr>
</thead>
<tbody>
<tr>
<td>S1</td>
<td>45</td>
<td>0.832</td>
<td>1.525</td>
<td>0.04459</td>
<td>-0.03177</td>
<td>0.05004</td>
</tr>
<tr>
<td></td>
<td>50</td>
<td>0.796</td>
<td>1.172</td>
<td>0.06206</td>
<td>-0.02525</td>
<td>0.04193</td>
</tr>
<tr>
<td></td>
<td>55</td>
<td>0.765</td>
<td>0.9843</td>
<td>0.04569</td>
<td>-0.02183</td>
<td>0.03205</td>
</tr>
<tr>
<td></td>
<td>60</td>
<td>0.735</td>
<td>0.7957</td>
<td>0.06155</td>
<td>-0.02465</td>
<td>0.01804</td>
</tr>
<tr>
<td>$v_{ref} = 0.732$</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>S2</td>
<td>45</td>
<td>0.843</td>
<td>1.472</td>
<td>-0.2423</td>
<td>0.04315</td>
<td>0.09291</td>
</tr>
<tr>
<td></td>
<td>50</td>
<td>0.807</td>
<td>1.330</td>
<td>-0.3044</td>
<td>0.05367</td>
<td>0.07387</td>
</tr>
<tr>
<td></td>
<td>55</td>
<td>0.776</td>
<td>0.9099</td>
<td>-0.1900</td>
<td>0.04468</td>
<td>0.05652</td>
</tr>
<tr>
<td></td>
<td>60</td>
<td>0.745</td>
<td>0.8230</td>
<td>-0.2241</td>
<td>0.04910</td>
<td>0.03611</td>
</tr>
<tr>
<td>$v_{ref} = 0.722$</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>E2</td>
<td>65</td>
<td>0.829</td>
<td>2.609</td>
<td>-0.8256</td>
<td>0.08352</td>
<td>0.03918</td>
</tr>
<tr>
<td></td>
<td>90</td>
<td>0.700</td>
<td>2.163</td>
<td>-1.025</td>
<td>0.1395</td>
<td>0.03992</td>
</tr>
<tr>
<td></td>
<td>100</td>
<td>0.658</td>
<td>1.982</td>
<td>-0.8215</td>
<td>0.08538</td>
<td>0.08538</td>
</tr>
<tr>
<td>$v_{ref} = 0.592$</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

To enable one to access the validity of employing the 2nd degree polynomial curve fitting technique, Figure 5.2.a was compiled. It contains the experimental data presented in Figures 3.1.d, 3.2.a and 3.2.b and the polynomial curves which were fitted through this data. As one can see from this figure and the RMS of the residuals the polynomial
expressions do accurately represent the pseudoplastic flow behaviour. In Section 5.2.2.3.a a graph will be presented which will enable the combined errors generated by the polynomial curve fitting and the GLIM model to be assessed.

5.2.2.2 Characterisation of Plastisol PSD.

Four statistical quantities were used to characterise the PSD of each plastisol, namely:

\[
\text{Standard Deviation (SD)} = \sqrt{\frac{\sum fx^2 - (\bar{fx})^2}{n - 1}} = \sigma \quad (5.7)
\]

\[
\text{Sample Mean (SM)} = \frac{\sum fx}{n} = \bar{x} \quad (5.8)
\]

\[
\text{Skewness (SK)} = \frac{\sum (x - \bar{x})^3}{n \sigma^3} \quad (5.9)
\]

\[
\text{Kurtosis (K)} = \frac{\sum (x - \bar{x})^4}{n \sigma^4} \quad (5.10)
\]

These parameters were extracted from the Sedigraph data presented in Figure 3.19. However, because the data was expressed as cumulative mass percent against the log of equivalent spherical diameter, the determination of the PSD parameters was a little complicated. In equations 5.7 to 5.10, \(x\) was transformed to log (equivalent spherical diameter \(X\) 100). The non-linear nature of the size axis was accounted for by taking the log of the diameter. Multiplying by 100, ensured that \(x\) was always larger than unity and so the higher powers in equations 5.7, 5.9 and 5.10 result in higher values. The class interval was taken as 1/15 of a decade i.e. 0.067. \(f\) was taken as the percentage of material in each class interval. \(n\) is the total percentage of material in all class intervals.

The statistical representation of the PSD is presented in Table 5.2. The validity of the Kurtosis value (which measures peakedness)
must be called into question as at least 200 data points should be evaluated. In this study 37 data points were considered.

Table 5.2. - FSD STATISTICS

<table>
<thead>
<tr>
<th>Polymer</th>
<th>Plastisol Behaviour</th>
<th>Standard Deviation (SD)</th>
<th>Sample Mean (SM)</th>
<th>Skewness (SK)</th>
<th>Kurtosis (K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>M1</td>
<td>Dilatant</td>
<td>0.434</td>
<td>2.22</td>
<td>2.10</td>
<td>6.51</td>
</tr>
<tr>
<td>M2</td>
<td>Dilatant</td>
<td>0.591</td>
<td>2.44</td>
<td>0.665</td>
<td>1.951</td>
</tr>
<tr>
<td>E1</td>
<td>Pseudoplastic</td>
<td>0.342</td>
<td>3.182</td>
<td>-1.803</td>
<td>6.246</td>
</tr>
<tr>
<td>E2</td>
<td>Pseudoplastic</td>
<td>0.750</td>
<td>2.76</td>
<td>-0.135</td>
<td>0.633</td>
</tr>
<tr>
<td>S1</td>
<td>Pseudoplastic</td>
<td>0.640</td>
<td>2.548</td>
<td>0.299</td>
<td>1.294</td>
</tr>
<tr>
<td>S2</td>
<td>Pseudoplastic</td>
<td>0.774</td>
<td>2.645</td>
<td>0.0301</td>
<td>0.555</td>
</tr>
</tbody>
</table>

* Units of RNO parameters: log (100 mm)

At this stage it became apparent that a distinction could be made between the pseudoplastic and dilatant systems on the basis of standard deviation. Systems with a SD below 0.620 exhibited dilatancy, the others pseudoplasticity. Further work is required to establish the role of DIOP concentration in this area, as dilatant systems may lose their dilatancy as polymer concentration falls, see Figure 3.1.a.
It may be possible to establish a relationship of the form shown above. Obviously further studies could enable the boundary between dilatant and pseudoplastic behaviour to be more closely characterised.

5.2.2.3 Mathematical Relationships between Polynomial Coefficients
(C₀, C₁ and C₂) and Plastisol Parameters (SD, SM, SK, K).

5.2.2.3.a Pseudoplastic Systems

To enable the flow curves represented by equation 5.6 to be generated from the PSD parameters, each of the coefficients were related to the RVF* and a particular PSD parameter, using General Linear Interactive Modelling (GLIM)**. Although each of the coefficients may be a function of RVF*, SD, SM, SK and K it is not possible to generate a GLIM model which would account for all possible relationships and interactions because as shown in Table 5.1 there are only three grades of material available for study. To obtain a more exact model one would need to construct a full fractional design*** in which each variable could be varied independently and to a strictly defined experimental design. However, it is possible to establish an equation which will relate each of the coefficients in equation 5.6 to RVF* and one of the PSD parameters.

(1) Evaluation of Coefficients contained in equation 5.6

Each of the coefficients contained in equation 5.6 was related to the RVF* and a parameter, using Loughborough Universities GLIM computer package, by an equation of the form:-

\[ C_i = A + Bx_1 + Cx_2 + Dx_1^2 + Ex_2^2 + Fx_1x_2 \] (5.11)

\[ \text{grand terms} \quad \text{linear terms} \quad \text{squared terms} \quad \text{interactive terms} \]

where, \( C_i \) = one of the coefficients in equation 5.6
\( x_1 = \text{RVF* in coded units} \)
$x_2$ = PSD parameter in coded units

A, B, C, D, E and F are constants

Appendix 11 contains the constants encountered in equation 5.11 for each of the coefficients expressed in equation 5.6.

It also contains the experimental data used to generate these constants and shows how the PSD parameters and RVF $^*$ are expressed in coded units.

The dependence of each of the coefficients in equation 5.6 on plastisol properties may be defined by the following equations.

\[
C_0 = 0.6670 + 0.3504 x_1 - 0.5088 x_2 \\
+ 0.06114 x_1^2 + 0.4658 x_2^2 + 0.06994 x_1 x_2
\]

where $x_1 = \frac{RVF^* - 0.7505}{0.0654}$

\[
x_2 = \text{Skewness} - 0.08/0.156
\]

\[
C_1 = -0.2778 - 0.05038 x_1 - 0.3757 x_2 \\
+ 0.06645 x_1^2 - 0.08300 x_2^2 + 0.04737 x_1 x_2
\]

For $x_1$, see equation 5.13

\[
x_2 = \frac{\text{SAMPLE MEAN} - 2.65}{0.0778}
\]

\[
C_2 = 0.06599 + 0.004947 x_1 + 0.05599 x_2 \\
- 0.01911 x_1^2 - 0.009613 x_2^2 - 0.008969 x_1 x_2
\]

For $x_1$, see equation 5.13

For $x_2$, see equation 5.16
The red lines in Figures 5.2.b, c and d correspond to equations 5.12, 5.15 and 5.17, respectively. As one can see these equations allow each of the coefficients to be defined by RVF* and a PSD parameter.

For the pseudoplastic systems it is therefore possible to generate the plastisol flow curve from the PSD and RVF* by converting these parameters to coded units and solving equations 5.12, 5.15 and 5.17. Having determined coefficient C0, C1 and C2 these parameters may then be inserted into equation 5.6 to generate the flow curve.

The validity of employing this statistical approach to predicting flow behaviour may be assessed by comparing the actual flow behaviour of a plastisol with the behaviour of the system predicted by the statistical approach.

For a series of pseudoplastic systems the actual polynomial coefficients determined by least squares curve fitting and the corresponding values predicted by the GLIM model are presented in Table 5.3.

<table>
<thead>
<tr>
<th>Polymer</th>
<th>RVF*</th>
<th>Coefficients</th>
<th>C2</th>
</tr>
</thead>
<tbody>
<tr>
<td>S1</td>
<td>0.832</td>
<td>1.526 (1.524)</td>
<td>0.04459</td>
</tr>
<tr>
<td>S1</td>
<td>0.765</td>
<td>0.9843 (0.9732)</td>
<td>0.04569</td>
</tr>
<tr>
<td>S2</td>
<td>0.843</td>
<td>1.472 (1.464)</td>
<td>-0.2423</td>
</tr>
<tr>
<td>S2</td>
<td>0.776</td>
<td>0.9099 (1.0146)</td>
<td>-0.1600</td>
</tr>
<tr>
<td>E2</td>
<td>0.829</td>
<td>2.609 (2.645)</td>
<td>-0.8256</td>
</tr>
<tr>
<td>E2</td>
<td>0.700</td>
<td>2.162 (2.093)</td>
<td>-1.026</td>
</tr>
</tbody>
</table>

Values in parenthesis predicted by GLIM model

Figure 5.2.f highlights the close agreement in the flow behaviour represented by equation 5.6 employing the fitted constants and the same equation using the predicted constants. There is very little difference between the predicted data represented by the red lines and the actual
data. Figure 5.2.e allows one to quantify the errors involved in predicting flow behaviour. The x axis represents the experimental observations while the y axis represents the predicted viscosity. As one can see there is an average error of 10% in predicting the flow behaviour of the pseudoplastic systems, (see figure 5.2.e)

5.2.2.3.b Dilatant Systems

A similar approach may be employed in predicting the behaviour of the dilatant systems (Figures 3.1.a, b and c). Figure 5.3.a shows the close agreement between the flow behaviour of such systems and the polynomial expressions representing dilatant behaviour, the only exception being the M1 0.817 system. At this point it must be emphasised that these polynomial expressions are only valid over a specified range of shear rates. In this case 0.3 to 3,000 S⁻¹. From Figure 5.3.b one can see that the E1 0.822 data, in particular, only extends the approximately 5.0 S⁻¹. To allow the coefficients in the polynomial expressions, for each of the systems, to be directly compared, imaginary data points were inserted, at shear rates between 10 and 3,000 S⁻¹, into the curve fitting program. This ensured that the polynomial expressions were all valid over the shear rate range (0.3 to 3,000 S⁻¹).

Table 5.4 contains the coefficients of the polynomial expressions represented by the solid lines presented in Figure 5.3.a.

**TABLE 5.4 - DILATANT SYSTEMS : POLYNOMIAL COEFFICIENTS**

<table>
<thead>
<tr>
<th>Polymer</th>
<th>D10P</th>
<th>RVF*</th>
<th>Coeff C₀</th>
<th>Coeff C₁</th>
<th>Coeff C₂</th>
<th>RMS Residuals</th>
</tr>
</thead>
<tbody>
<tr>
<td>M1</td>
<td>45</td>
<td>0.807</td>
<td>0.8876</td>
<td>-1.018</td>
<td>1.025</td>
<td>0.4109</td>
</tr>
<tr>
<td></td>
<td>50</td>
<td>0.772</td>
<td>0.7401</td>
<td>-0.5597</td>
<td>0.4598</td>
<td>0.2356</td>
</tr>
<tr>
<td></td>
<td>55</td>
<td>0.742</td>
<td>0.6733</td>
<td>-0.1916</td>
<td>0.1342</td>
<td>0.03519</td>
</tr>
<tr>
<td></td>
<td>60</td>
<td>0.713</td>
<td>0.5217</td>
<td>-0.1227</td>
<td>0.07466</td>
<td>0.01759</td>
</tr>
</tbody>
</table>

*ref = 0.755
Appendix 12 contains the coded data, from which the following equations, which relate these polynomial coefficients to the RVF" and PSD parameters, were derived:

\[ C_0' = 1.307 + 0.4702 x_1 - 0.01011 x_2 \]
\[ + 0.09110 x_1^2 - 0.1929 x_2^2 + 0.05905 x_1 x_2 \]

where \( x_1 = \text{RVF}" - 0.817 \)
\[ x_2 = SKMEAN - 2.701 \]
\[ 0.340 \]

\[ C_1' = -0.4591 - 0.2763 x_1 - 0.3315 x_2 \]
\[ - 0.1766 x_1^2 - 0.09445 x_2^2 - 0.5121 x_1 x_2 \]

For \( x_1 \) see equation 5.19
\[ x_2 = \text{SKEWNESS} - 0.1485 \]
\[ 1.389 \]

\[ C_2' = 0.5174 + 0.4842 x_1 + 0.3273 x_2 \]
\[ + 0.1764 x_1^2 + 0.07827 x_2^2 + 0.4267 x_1 x_2 \]

For \( x_1 \) see equation 5.19
\( x_2 " = " 5.22 \)

Figures 5.3.b, c and d contain the experimental data presented in Appendix 12. The red lines represent the above equations.
For the dilatant systems it is also necessary to quantify the magnitude of the dilatancy as equation 5.6 does not predict the position of the dilatancy maximum. This is achieved by evaluating log K factor, defined as:

\[
\log K \text{ factor} = \log \left( \frac{\text{viscosity maximum}}{\text{viscosity minimum}} \right) \tag{5.24}
\]

eg. For a 100/45 M1 plastisol, log K factor equals the log of the viscosity at point A divided by the viscosity at point B, in Figure 3.1.a.

The log of the K factor may then be related to RVF" and a PSD parameter, as in the previous discussions, using the GLIM model.

Equation 5.25 relates the K factor to plastisol parameters.

\[
\log K \text{ factor} = 1.709 + 0.9138 \, x_1 + 0.8628 \, x_2 \\
- 0.03531 \, x_1^2 - 0.08067 \, x_2^2 + 0.5270 \, x_1 \, x_2 \tag{5.25}
\]

where 

\[
x_1 = \tan \left( 90 \, \text{RVF} \right) - 5.83 \tag{5.26} \\
x_2 = \text{SKEWNESS} - 0.1485 \tag{5.27} \frac{1.780}{2.574}
\]

Appendix 13 contains the data used to generate equation 5.25. Figure 5.3.e shows the close agreement between the experimental observations, defined in Appendix 13, and equation 5.25 generated to predict the K factor as a function of plastisol parameters.

As with the pseudoplastic systems, it is possible to compare the polynomial coefficients employed to define dilatant behaviour with the values predicted by the GLIM model, see Table 5.5.
TABLE 5.5 - COMPARISON OF FITTED AND PREDICTED COEFFICIENTS

<table>
<thead>
<tr>
<th>Polymer</th>
<th>RVF</th>
<th>$C_0'$</th>
<th>$C_1'$</th>
<th>$C_2'$</th>
</tr>
</thead>
<tbody>
<tr>
<td>M1</td>
<td>0.807</td>
<td>0.8876 (0.8842)</td>
<td>-1.018 (-0.9839)</td>
<td>1.025 (0.9921)</td>
</tr>
<tr>
<td>M1</td>
<td>0.713</td>
<td>0.5217 (0.5704)</td>
<td>-0.1227 (0.0557)</td>
<td>0.07466 (-0.0478)</td>
</tr>
<tr>
<td>M2</td>
<td>0.783</td>
<td>1.085 (1.0242)</td>
<td>-0.4901 (-0.4179)</td>
<td>0.3727 (0.3909)</td>
</tr>
<tr>
<td>M2</td>
<td>0.752</td>
<td>0.8840 (0.8969)</td>
<td>-0.2401 (-0.3209)</td>
<td>0.1313 (0.2198)</td>
</tr>
<tr>
<td>E1</td>
<td>0.921</td>
<td>1.909 (1.8709)</td>
<td>0.1355 (0.1009)</td>
<td>0.3430 (0.3949)</td>
</tr>
<tr>
<td>E2</td>
<td>0.822</td>
<td>0.9544 (0.9449)</td>
<td>-0.0955 (-0.1496)</td>
<td>0.1906 (0.2038)</td>
</tr>
</tbody>
</table>

Values in parenthesis predicted by GLIM model.

From Table 5.5, one can see that the GLIM model does not accurately predict the polynomial coefficients in all cases. For example for the M1 0.713 system the actual $C_2'$ coefficient is 0.07466 compared with -0.0478 predicted by the GLIM model (equation 5.23). These errors in prediction become more apparent when one combines the coefficients to regenerate the flow curve, Figure 5.3.g. The black lines are the fitted curves, the red lines were generated from the GLIM predicted coefficients. For the M1 0.713 system the GLIM model predicts pseudoplastic behaviour while the system clearly displays a limited dilatancy.

A measure of the errors generated by this technique is given in Figure 5.3.f which describes the relationship between the experimental observations and the values predicted by the GLIM model. According to this figure errors of approximately 40 percent are encountered in predicting the viscosity of the dilatant systems.

5.2.2.4 Limitations of Statistical Approach

The limitations of employing the statistical approach to predicting flow behaviour from plastisol parameters stem both from the
initial assumptions made in constructing the model and the availability of raw materials.

In the first instance it was assumed that flow behaviour may be represented by a second degree polynomial expression. For the pseudoplastic systems this appears to be valid. Figure 5.2.a shows the close correlation between the experimental observations and the equations generated to represent these values. However, for the dilatant systems the flow behaviour of the most concentrated M1 plastisol (M1 0.807, Figure 5.3.a) cannot be accurately represented by such an equation. The flow behaviour of this system manifest itself as a gradual reduction in viscosity with shear rate, up to approximately 30 reciprocal seconds, the viscosity then rises very rapidly, it cannot be represented by an parabola. The polynomial expression generated to represent this behaviour does not fit very accurately. One must therefore determine the plasticiser concentration at which the flow curve can no longer be accurately represented by a 2nd degree polynomial expression. The applicability of the approach is therefore constrained to a certain range of plasticiser levels.

It is assumed that the coefficients in the polynomial expression were related to the RVF" and a PSD parameter. It is however, likely that these coefficients are a function of all of the PSD parameters (SM, SK, SD, K), although certain parameters will have more of an effect than others.

For the pseudoplastic systems we can see that viscosity may be predicted by the statistical approach to within 10%. For the dilatant systems the error is larger, 40%. In this case the PSD parameter to which each coefficient was related may not have been the parameter having the dominant effect on that coefficient. To improve the predictive power of this approach a full factional design should be employed in which, the experimental window is closely defined, the effect of each PSD parameter on each coefficient and the interaction between the parameters could then be quantified. This would however necessitate the preparation of a large number of specially prepared paste polymers
thus allowing a PSD's to be generated which will allow a factorial design to be based on (SN, SK, SD and K). Such a process would be extremely difficult and expensive.

The predictive power of this model may still be improved, without employing the full factional design.

The data treatment employed so far may be repeated using all the different combinations of the PSD parameters to predict the coefficients in the 2nd degree polynomial. A plot similar to Figure 5.2.e could then be prepared for each particular combination of PSD parameters, and the combination giving the smallest error selected. The selection of the PSD parameters used in Figures 5.2 and 5.3 in the prediction of the polynomial coefficients was intuitive, this minimising of the errors by evaluating different combinations of PSD parameters would allow a systematic approach to be employed which should result in a more accurate predictive model.

It should be noted, at this point, that the predictive power of this model is limited to the experimental window considered. For example if the maximum sample mean considered was 2.760, then the behaviour of a material with a sample mean > 2.76 can not be predicted.
Fig. 5.1 – Effect of Concentration of the Dispersed Phase

a, Plastisol Viscosity ((1 S⁻¹)) / Volume Frac Plots

b, Relative Viscosity / RVF ((at 283)) Relationships
c, Relative Viscosity / RVF (\(14641\)) Relationships

d, Deviation from Chong et al Plot
Fig. 5.2 – Pseudoplastic Flow Behaviour

a, 2nd Degree Polynomial Curve Fitting

b, Prediction of Coeff C0 from Plastisol Props
Fig. 5.2 -

c, Prediction of Coeff C1 from Plastisol Props

\[
\begin{align*}
\text{REDUCED VOLUME FRACTION} & \quad \text{COEFFICIENT C1} \\
0.65 & \quad -1.2 \quad \ldots \quad 0.90 \\
0.70 & \quad -1.0 \quad \ldots \quad 0.90 \\
0.75 & \quad -0.8 \quad \ldots \quad 0.90 \\
0.80 & \quad -0.6 \quad \ldots \quad 0.90 \\
0.85 & \quad -0.4 \quad \ldots \quad 0.90 \\
0.90 & \quad -0.2 \quad \ldots \quad 0.90 \\
\end{align*}
\]

\begin{itemize}
\item \Delta \text{ SAMPLE MEAN } 3.548
\item \times \text{ SAMPLE MEAN } 2.645
\item \square \text{ SAMPLE MEAN } 2.760
\end{itemize}

\[\text{SAMPLE MEAN} \quad \Delta \quad 2.760 \quad \times \quad 2.645 \quad \square \quad 2.548\]

d, Prediction of Coeff C2 from Plastisol Props

\[
\begin{align*}
\text{REDUCED VOLUME FRACTION} & \quad \text{COEFFICIENT C2} \\
0.65 & \quad -0.10 \quad \ldots \quad 0.90 \\
0.70 & \quad 0.00 \quad \ldots \quad 0.90 \\
0.75 & \quad 0.05 \quad \ldots \quad 0.90 \\
0.80 & \quad 0.10 \quad \ldots \quad 0.90 \\
0.85 & \quad 0.15 \quad \ldots \quad 0.90 \\
0.90 & \quad 0.20 \quad \ldots \quad 0.90 \\
\end{align*}
\]

\begin{itemize}
\item \Delta \text{ SAMPLE MEAN } 2.760
\item \times \text{ SAMPLE MEAN } 2.645
\item \square \text{ SAMPLE MEAN } 2.548
\end{itemize}
e, Evaluation of Errors due to Statistical Design

f, Flow Curve Prediction

Note: red lines are predicted
Fig. 5.3 – Dilatant Flow Behaviour

a, 2nd Degree Polynomial Curve Fitting

b, Prediction of Coeff C0 from Plastisol Props
Fig. 5.3 -

c, Prediction of Coeff C1 from Plastisol Props

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d, Prediction of Coeff C2 from Plastisol Props
Fig. 5.3 –

e, Prediction of Dilatancy Mag from Plastisol Props

f, Evaluation of Errors due to Factorial Design
Fig. 5.3 -

g, Flow Curve Prediction

Note: red lines are predicted

LOG VISCOSITY

LOG SHEAR RATE

-1 -0.5 0 0.5 1 1.5 2 2.5 3

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5.3 CONCLUSION

5.3.1 Dominant Factors Controlling Rheology

5.3.1.1 Plasticiser Absortion and Packing Efficiency

From the preceding summaries one can see that, for the following systems, plastisol rheology and its response to filler inclusion may be explained by the increase in plasticiser demand within the system and a shift in PSD shown in the composite plots:

(1) For the microsuspension plastisols, rheology may be explained by a modified version of Hoffmans model in which ordered flow breaks down over a range of shear rates instead of at a critical discontinuity shear rate. Spray drying and milling conditions may be used to suppress dilatancy although an excessive proportion of porous secondary particles leads to an increase in viscosity and the return of dilatancy which moves to low shear rates. GCC filler addition causes only a limited shift in PSD, because the filler particles and paste polymer particles have a similar average diameter, and so the flow curve shape is retained, it is only shifted to higher viscosities.

(2) For emulsion plastisols severe drying conditions may lead to the formation of a narrow distribution of 17.0 μm diameter secondary particles. As a result of their large size, dilatancy occurs at very low shear rates. Ageing studies show that the small primary PS and low K value lead to the rapid swelling of the agglomerates which results in a rapid increase in low shear viscosity and the development of pseudoplasticity. Filler addition transforms the plastisol from a dilatant to a pseudoplastic dispersion. The rise in low shear viscosity and fall in high shear viscosity is a direct result of adding a second family of small, plasticiser absorbent particles. They increase plasticiser demand at low shear rates while easing the flow of particles at high shear rates. There is a minimum in low shear viscosity which depends
upon filler PS. It is a consequence of the balance between packing efficiency and plasticiser absorption.

(3) For seeded emulsion plastisols, prepared from high K value paste polymers with average primary sizes of 0.25 and 1.0 \( \mu \text{m} \), rheology is controlled by the efficient packing of primary particles and disruption of the hexagonal planes of particles which lead to dilatancy. The material therefore tends to be "Newtonian", even after protracted ageing times. Filler incorporation results in an increase in pseudoplasticity because of the increased demand for plasticiser. Packing considerations lead to a minimum viscosity at \( \approx 13.5\% \) filler, which does not depend upon filler PS as the PVC and filler particles are of similar average size.

5.3.1.2 Structure Development

By considering the behaviour of the seeded emulsion and emulsion plastisols one can see that structure development, particle-plasticiser and particle-particle interactions became significant factors in controlling plastisol rheology and filler response when the minimum PS falls below 0.2 \( \mu \text{m} \) and is accompanied by a lower molecular mass (\( K \) value = 70) and mild drying conditions.

For both these systems it has been shown, in this work, that structure development increases plastisol low shear viscosity, especially for the emulsion dispersion which contains 0.15 \( \mu \text{m} \) primaries. The change in interparticle forces upon filler introduction overrides the effect of changes in particle packing efficiency and plasticiser demand. When GCC filler is introduced into these systems the reduction in interparticle forces causes a fall in low shear viscosity and pseudoplasticity. However, continued addition of filler eventually causes a rise in low shear viscosity. This effect is more pronounced for the emulsion plastisols which contain smaller primaries and experience a greater degree of structure development.
5.3.2 New Techniques Applied to Plastisol Evaluation

5.3.2.1 Rheological Characterisation

The traditional problems encountered in obtaining consistent plastisol viscosity have been overcome by carefully controlling the humidity and temperature of filler and paste polymers prior to plastisol preparation, and the shear generated during mixing. Accurate viscosity measurements have been achieved, over an extended shear rate range, using the Rotovisko rheometer and a combination of coaxial cylinders. Care was taken to adhere strictly to a specified test schedule in order to ensure stable torque readings and control sample loss. A series of Severs rheometer dies allowed viscosity measurements to be made at extremely high shear rates.

5.3.2.2 Particle Size Analysis

The evaluation and comparison of numerous PSA techniques lead to the adoption of the Sedigraph Instrument for the analysis of the PSD within plastisols. The use of di butyl sebacate as the suspending medium arrested particle solvation and facilitated analysis in the PS range of 0.15 - 70 μm. This allowed plastisol rheology to be related to plastisol PSD. Experiments designed to measure changes in PSD with mixing conditions and filler content justified the development of "composite plots". It has been proved that it is indeed valid to combine the PSD of a filler dispersion with that within a virgin plastisol in order to represent the PSD within a filled system. By adopting the use of these composite plots it has been possible to investigate and account for the behaviour of filled plastisols.
5.3.2.3 Porosity Measurements

A mercury porosimetry technique, which is still under development at ICI, has been successfully applied to the examination of paste polymer intraparticle porosity. Preliminary results have shown that secondary particles formed from a bimodal latex have a lower intraparticle porosity than secondary particles generated from a unimodal latex. This behaviour would be expected as a unimodal distribution packs together less efficiently. Spray drying experiments confirm a relationship between increased secondary particle porosity and high plastisol viscosities. Until the development of this technique, it was not possible to characterise the porosity of the small fragile paste polymer particles and confirm that differences in secondary particle porosity may account for differences in plastisol rheology.

5.3.3 Mathematical Relationships between Plastisol Flow Behaviour and Plastisol Parameters

The adoption of the statistical approach has enabled plastisol flow behaviour to be predicted from plastisol parameters. For the pseudoplastic systems the technique is capable of predicting a flow curve to within 10%, for the dilatant systems the technique seems less reliable, incurring an error of = 40%. As will be outlined in Section 5.4, further work is required to improve the performance of the technique and assess the validity of employing this approach.

5.4 RECOMMENDATIONS FOR FURTHER STUDY

Having established a framework in which the rheology of filled and unfilled plastisols has been related to particle size distributions and particle morphology, I feel that the understanding of plastisol rheology may be further expanded by exploring the following avenues:

(1) The use of several plasticisers of differing activities should allow the resultant changes in PSD and structure development within filled and unfilled plastisols to be evaluated.

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(ii) Once the mercury porosimetry technique has been fully developed, at ICI, the measurement of secondary particle porosity, on paste polymer samples prepared at differing spray drying temperatures, should allow the role of secondary particle porosity in plastisol rheology to be more fully understood.

(iii) The filler performance of the spray dried samples should be more fully explored so that the use of the composite plots in predicting changes in rheology could be further evaluated.

(iv) Ageing studies on the spray dried samples using various plasticisers and the evaluation of secondary particle porosity should allow the ageing phenomenon to be more fully understood.

(v) Although the selection of emulsifiers and surfactants is largely controlled by the polymerisation conditions, end uses and patent considerations, the commercially sensitive nature of these materials has excluded them from this study. I am sure that a research programme considering their effect on plastisol rheology would be extremely useful.

(vi) Further work is required to evaluate the validity of employing the statistical approach, outlined, to predicting flow behaviour. A factional design may aid the evaluation of relationships and interactions. It may be necessary to employ a model other than the 2nd degree polynomial.
The models developed in this study have several limitations. When considering the dilatant systems it was not possible to model the high shear rate shear thinning. This was because a 2nd degree polynomial equation was employed. Higher degree polynomials allow the high shear rate shear thinning to be considered. However, experiments have shown that the greater number of coefficients required in the model makes the manipulation of the model extremely difficult and reduces the predictive power, especially at either end of the shear rate axes. There are also problems in choosing an optimum relative viscosity for the evaluation of ref. Strictly speaking the exact value depends upon the paste polymer being considered, this should be determined by experimentation. However a value of 10,000 may be employed if an error of approximately 5% is acceptable.

The predictive power of this statistical approach is limited to the experimental region, predictions outside this region may be subject to gross errors. A more rigorous and fundamental approach employing a range of specially prepared paste polymers, as opposed to commercial materials, would enable a model with greater predictive power to be developed. Although, this model may be less applicable to commercial plastisols.
APPENDIX 1 - FORMULATION OF THE MIX DESCRIBED IN TABLE 2.5

The mix design is based on a 100/50 plastisol and a 40% by weight calcium carbonate dispersion. The volumes of solids to liquids in each component are:

For 100/50 Plastisol:

- Solids: 100 grams, 100/1.4 = 71.43 cm³
- Liquids: 50 grams, 50/0.98 = 51.02 cm³

For GCC Dispersion (40% solids):

- Solids: 40 grams, 40/2.65 = 15.09 cm³
- Liquids: 60 grams, 60/0.98 = 61.22 cm³

To maintain the same solids to liquid volume ratio while increasing the level of GCC, the ratios of PVC, DIOP and GCC filler paste must be adjusted. Calculations based on the volume of each component are shown in Table 6.1, these were converted back to weights in Table 6.2 by taking each component's density into account.
CHAPTER 6: APPENDICES

APPENDIX 1 - FORMULATION OF THE MIX DESCRIBED IN TABLE 2.5

The mix design is based on a 100/50 plastisol and a 40% by weight calcium carbonate dispersion. The volumes of solids to liquids in each component are:

For 100/50 Plastisol:

Solids: 100 grams, 100/1.4 = 71.43 cm³
Liquids: 50 grams, 50/0.98 = 51.02 cm³

For GCC Dispersion (40% solids):

Solids: 40 grams, 40/2.65 = 15.09 cm³
Liquids: 60 grams, 60/0.98 = 61.22 cm³

To maintain the same solids to liquid volume ratio while increasing the level of GCC, the ratios of PVC, DIOP and GCC filler paste must be adjusted. Calculations based on the VOLUME of each component are shown in Table 6.1, these were converted back to weights in Table 6.2 by taking each component's density into account.
### TABLE 6.1 - BY VOLUME

<table>
<thead>
<tr>
<th>% FILLER IN SOLIDS (by volume)</th>
<th>CODE</th>
<th>0</th>
<th>4.5</th>
<th>9</th>
<th>13.5</th>
<th>17.61 (18%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PASTE POLYMER</td>
<td>A</td>
<td>71.43</td>
<td>68.22</td>
<td>65.00</td>
<td>61.79</td>
<td>58.85</td>
</tr>
<tr>
<td>(100% - % filler) x 71.43/100</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>FILLER in filler paste</td>
<td>B</td>
<td></td>
<td>3.21</td>
<td>6.43</td>
<td>9.64</td>
<td>12.58</td>
</tr>
<tr>
<td>(% filler x 71.43)/100</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>DIOP in filler paste</td>
<td>C</td>
<td></td>
<td>13.02</td>
<td>25.09</td>
<td>39.11</td>
<td>51.00</td>
</tr>
<tr>
<td>B x 61.22/15.09</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>FILLER PASTE B + C</td>
<td>D</td>
<td></td>
<td>16.23</td>
<td>32.52</td>
<td>48.75</td>
<td>63.60</td>
</tr>
<tr>
<td>DIOP to be added</td>
<td>E</td>
<td></td>
<td>51.02</td>
<td>38.00</td>
<td>24.93</td>
<td>11.91</td>
</tr>
<tr>
<td>51.02 - C</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>for 0%, DIOP to be added</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>added = 51.02 cm²</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

### TABLE 6.2 - BY WEIGHT (PBW)

- Volumes in Table 6.1 were converted to the weights in Table 6.2 by multiplying the volumes of each material by its density.

**Mix Formula:**

<table>
<thead>
<tr>
<th>% FILLER IN SOLIDS (By Volume)</th>
<th>0</th>
<th>4.5</th>
<th>9.0</th>
<th>13.5</th>
<th>18.0</th>
</tr>
</thead>
<tbody>
<tr>
<td>PASTE POLYMER</td>
<td>A x 1.4</td>
<td>100</td>
<td>95.51</td>
<td>91.00</td>
<td>86.51</td>
</tr>
<tr>
<td>GCC FILLER PASTE</td>
<td>D x 1.29</td>
<td></td>
<td>20.97</td>
<td>42.02</td>
<td>62.99</td>
</tr>
<tr>
<td>DIOP</td>
<td>E x 0.98</td>
<td>50.00</td>
<td>37.24</td>
<td>24.43</td>
<td>11.67</td>
</tr>
</tbody>
</table>
APPENDIX 2 - FORMULATION OF THE MIX DESCRIBED IN TABLE 2.6

The mix design is based on a 100/50 plastisol. The volume of solids to liquids is:

Solids : 100 grams, 100/1.4 = 71.43 cm³
Liquids : 50 grams, 50/0.98 = 51.02 cm³

To maintain the same solids to liquid volume ratio while increasing the level of GCC, the ratio of PVC to GCC must be adjusted, see Tables 6.3 and 6.4

TABLE 6.3 - BY VOLUME

<table>
<thead>
<tr>
<th>% FILLER IN SOLIDS (By Volume)</th>
<th>CODE</th>
<th>0</th>
<th>4.5</th>
<th>9.0</th>
<th>13.5</th>
<th>18.0</th>
</tr>
</thead>
<tbody>
<tr>
<td>PASTE POLYMER (100%-%filler)x71.42/100</td>
<td>A</td>
<td>71.43</td>
<td>68.22</td>
<td>65.00</td>
<td>61.79</td>
<td>58.55</td>
</tr>
<tr>
<td>FILLER %filler x 71.42/100</td>
<td>B</td>
<td>-</td>
<td>3.21</td>
<td>6.43</td>
<td>9.64</td>
<td>12.88</td>
</tr>
<tr>
<td>DIOP</td>
<td>C</td>
<td>51.02</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

TABLE 6.4 - BY WEIGHT

<table>
<thead>
<tr>
<th>% FILLER IN SOLIDS (By Volume)</th>
<th>0</th>
<th>4.5</th>
<th>9.0</th>
<th>13.5</th>
<th>18.0</th>
</tr>
</thead>
<tbody>
<tr>
<td>PASTE POLYMER A x 1.4</td>
<td>100</td>
<td>95.51</td>
<td>91.00</td>
<td>86.51</td>
<td>82.39</td>
</tr>
<tr>
<td>FILLER B x 2.65</td>
<td>-</td>
<td>8.51</td>
<td>17.04</td>
<td>25.55</td>
<td>33.34</td>
</tr>
<tr>
<td>DIOP C x 0.98</td>
<td>50</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
APPENDIX 3 - FORMULATION OF THE MIX DESCRIBED IN TABLE 2.7

The mix design is based on a 100/50 plastisol and a 40% by weight titanium dioxide dispersion. The volumes of solids to liquids in each component are:

For 100/50 Plastisol:

Solids: 100 grams, \( \frac{100}{1.4} = 71.43 \text{ cm}^3 \)
Liquids: 50 grams, \( \frac{50}{0.98} = 51.02 \text{ cm}^3 \)

For TiO₂ Dispersion (40% solids):

Solids: 40 grams, \( \frac{40}{4.05} = 9.877 \text{ cm}^3 \)
Liquids: 60 grams, \( \frac{60}{0.98} = 61.224 \text{ cm}^3 \)

To maintain the same solids to liquid volume ratio while increasing the level of titanium dioxide, the ratios of PVC, DIOP and TiO₂ filler pastes must be adjusted. Calculations based on the VOLUME of each component are shown in Table 6.5, these were converted back to weights in Table 6.6 by taking each component's density into account.
### TABLE 6.5 - BY VOLUME

<table>
<thead>
<tr>
<th>% FILLER IN SOLIDS (by volume)</th>
<th>CODE</th>
<th>0</th>
<th>1</th>
<th>2</th>
<th>4</th>
</tr>
</thead>
<tbody>
<tr>
<td>PASTE POLYMER (100% - %filler) x 71.43</td>
<td>A</td>
<td>71.43</td>
<td>70.72</td>
<td>70.00</td>
<td>68.57</td>
</tr>
<tr>
<td>FILLER in filler paste (%filler x 71.43)</td>
<td>B</td>
<td></td>
<td>0.743</td>
<td>1.429</td>
<td>2.857</td>
</tr>
<tr>
<td>DIOP in filler paste B x 61.22</td>
<td>C</td>
<td></td>
<td>4.427</td>
<td>8.857</td>
<td>17.71</td>
</tr>
<tr>
<td>FILLER PASTE B + C</td>
<td>D</td>
<td></td>
<td>5.142</td>
<td>10.286</td>
<td>20.57</td>
</tr>
<tr>
<td>DICP to be added 51.02 - C</td>
<td>E</td>
<td>51.02</td>
<td>46.59</td>
<td>42.17</td>
<td>33.31</td>
</tr>
</tbody>
</table>

### Mix Formula:

% FILLER IN SOLIDS (by volume) | 0 | 1 | 2 | 4 |
<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>PASTE POLYMER A x 1.4</td>
<td>100</td>
<td>99.01</td>
<td>98.00</td>
<td>95.99</td>
</tr>
<tr>
<td>T.C2 PASTE POLYMER D x 1.379</td>
<td>7.09</td>
<td>14.19</td>
<td>28.38</td>
<td></td>
</tr>
<tr>
<td>DIOP E x 0.98</td>
<td>51.02</td>
<td>45.66</td>
<td>41.33</td>
<td>32.64</td>
</tr>
</tbody>
</table>

---

TABLE 6.6 - BY WEIGHT (PBW)

Volumes in Table 6.5 were converted to the weights in Table 6.6 by multiplying the volume material by its density.
APPENDIX 4 - FORMULATION OF THE MIX DESCRIBED IN TABLE 2.8

The mix design is based on a 100/50 plastisol and a 50% by weight Spheriglass dispersion. The volumes of solids to liquid in each component are:

For 100/50 Plastisol:
- Solids: 100 grams, 100/1.4 = 71.43 cm³
- Liquids: 50 grams, 50/0.98 = 51.02 cm³

For Spheriglass Dispersion (50% solids):
- Solids: 50 grams, 50/2.47 = 20.24 cm³
- Liquids: 50 grams, 50/0.98 = 51.02 cm³

To maintain the same solids to liquid volume ratio while increasing the level of Spheriglass, the ratios of PVC, DIOP and Spheriglass filler paste must be adjusted. Calculations based on the VOLUME of each component are shown in Table 6.7, these were converted back to weights in Table 6.3 by taking each component's density into account.

**TABLE 6.7 - BY VOLUME**

<table>
<thead>
<tr>
<th>% FILLER IN SOLIDS (by volume)</th>
<th>CODE</th>
<th>0</th>
<th>7</th>
<th>14</th>
<th>21</th>
<th>28</th>
</tr>
</thead>
<tbody>
<tr>
<td>PASTE POLYMER (% - % filler)×71.43/100</td>
<td>A</td>
<td>71.43</td>
<td>66.43</td>
<td>61.42</td>
<td>55.43</td>
<td>51.43</td>
</tr>
<tr>
<td>FILLER in filler paste (%filler × 71.43)/100</td>
<td>B</td>
<td>_</td>
<td>5.00</td>
<td>10.00</td>
<td>15.00</td>
<td>20.00</td>
</tr>
<tr>
<td>DICP in filler paste B × 51.02/20.24</td>
<td>C</td>
<td>_</td>
<td>12.60</td>
<td>25.21</td>
<td>37.80</td>
<td>50.42</td>
</tr>
<tr>
<td>FILLER PASTE B + C</td>
<td>D</td>
<td>_</td>
<td>17.60</td>
<td>35.21</td>
<td>52.80</td>
<td>70.42</td>
</tr>
<tr>
<td>DICP to be added 51.02 - C</td>
<td>E</td>
<td>51.02</td>
<td>38.42</td>
<td>25.81</td>
<td>13.22</td>
<td>0.60</td>
</tr>
</tbody>
</table>
TABLE 6.8 - BY WEIGHT

- Volumes in Table 6.7 were converted to the weights in Table 6.8 by multiplying the volume of each material by its density.

Mix Formula:

<table>
<thead>
<tr>
<th>% FILLER IN SOLIDS (By Volume)</th>
<th>0</th>
<th>7</th>
<th>14</th>
<th>21</th>
<th>28</th>
</tr>
</thead>
<tbody>
<tr>
<td>PASTE POLYMER</td>
<td>A x 1.4</td>
<td>100</td>
<td>93.00</td>
<td>86.00</td>
<td>79.00</td>
</tr>
<tr>
<td>SPHERICLASS FILLER PASTE</td>
<td>D x 1.381</td>
<td>_</td>
<td>24.31</td>
<td>48.63</td>
<td>72.92</td>
</tr>
<tr>
<td>DICP</td>
<td>E x 0.78</td>
<td>50.00</td>
<td>37.65</td>
<td>25.29</td>
<td>12.96</td>
</tr>
</tbody>
</table>
APPENDIX 5 - CALCULATION OF APPARENT VISCOSITY AND SHEAR RATE FROM ROTOVISKO READINGS (S) AND (N)

Viscosity \( n \) = \( \frac{G \cdot S}{N} \) (A5.1) Shear Rate \( \gamma \) = \( \frac{m \cdot N}{N} \) (A5.2)

where \( S \) = torque reading  
\( N \) = speed (rpm)

For MV2

\( G = 417.1 \) (for 50 scale), 4171 (for 500 scale)  
\( m = 0.9 \)

For SV2

\( G = 4226.0 \) (for 50 scale), 42260 (for 500 scale)

Thus using the SV2 system, a torque of 17.5 on the 50 scale at a speed of 5.66 rpm can be evaluated as follows:

\[ n = \frac{4226 \times 17.5}{5.66} = 13066 \text{ mPa.S} = 13.06 \text{ Pa.S} \]

\[ \gamma = 0.89 \times 5.66 = 5.037 \text{ s}^{-1} \]
At this point it should be emphasised that the viscosity obtained by equation (A5.1) and the rate of shear obtained by equation (A5.2) will be an "apparent" apparent viscosity and an apparent rate of shear, since these terms have been derived from the Newtonian expression for rate of shear at the inner cylinder.

For Newtonian fluids, the shear rate at the inner cylinder wall, $\gamma_N$, may be obtained from equation (A5.3),

$$\gamma_{(\text{Newtonian})} = \frac{2\Omega}{1-(\frac{r_1}{r_2})^2}$$

(A5.3)

where $\Omega$ = angular velocity

$r_1$ = bob radius

$r_2$ = cup radius

For non-Newtonian fluids, the shear rate not only depends upon the position in the cylinder gap, but on the properties of the fluid.

Since the flow curve of the materials studied in this thesis tend to be non-Newtonian a better approximation of shear rate (explicit formula) is obtained using equation (A5.4), based on the work of Kreiger and Elrod,

$$\dot{\gamma} = \frac{\Omega}{K} \left[ 1 + K + \frac{1}{n'} \right] \left( \frac{1}{n'} \right)^{\frac{1}{2}}$$

(A5.4)

where $K = \ln \frac{r_2}{r_1}$

$$n' = \frac{d \ln \tau}{d \ln \Omega} \quad \tau = \text{shear stress on the bob}$$

$$n'' = \frac{d \ln n'}{d \ln \Omega}$$

(Equation A5.4 is presented in the notation employed at Warren Spring Laboratory)
This is a general expression for rate of shear for all fluids in a coaxial cylinder viscometer. Inspection shows that \( \frac{d \ln \tau}{d \ln \Omega} \) is unity for Newtonian fluids but will take on values other than unity for non-Newtonian samples.

Figure 5.1.a shows the flow curve of a plastisol encountered in the course of my work. This system exhibits pseudoplasticity, Newtonian flow, and dilatant behaviour, depending upon shear rate. The viscosity and shear rate were calculated assuming Newtonian flow. To consider the errors encountered in making such an assumption, the shear rate was calculated using equation A5.4, which contains a correction for non-Newtonian flow. The ratio of shear stress determined by equation A5.3 to shear stress determined by equation A5.4 was then plotted against shear rate determined by equation A5.3, see Figure A5.1.

By studying Figure A5.1 one can see that the errors generated by employing equation A5.3 (assuming Newtonian flow) increase as the system deviates from Newtonian flow. At 0.18 \( \text{s}^{-1} \) the plastisol is clearly pseudoplastic, employing equation A5.3 results in an error of approximately 13% in predicting shear rate. However at approximately 10.0 \( \text{s}^{-1} \) the error is less than 1%. From Figure A5.1.a one can see that the system behaves as a Newtonian fluid at this shear rate. The agreement between the shear rate generated by each of the sets of concentric cylinders is also very close at this point, deviating from each other by less than 1%. If the overlap had occurred at a non-Newtonian portion of the curve the agreement would undoubtedly decrease.

Since the plastisols employed in this study do not obey the power law relationship, \( n \) depending upon shear rate, the shear rate exponent in the "power law" \( \dot{\gamma} \) has to be determined at each shear rate considered in the study, if equation A5.4 is to be employed. This complicates the use of equation A5.4, especially since small errors in evaluating \( n' \) have a pronounced effect on \( \dot{\gamma} \), as shown by the scatter in Figure A5.1.b. It was therefore decided to use equation A5.3 throughout this thesis, the plastisol behaviour being considered on a comparative basis. For any particular system it should however be appreciated that
the adoption of this procedure means that the shear rate and, apparent viscosity are subject to error, as the calculation of apparent viscosity is based on the Newtonian shear rate calculation:

Apparent viscosity = shear stress \( \tau \) / shear rate \( \dot{\gamma} \) (Newtonian)

where \( \tau = \frac{M}{2\pi r^2 h} \) (A5.5)

\( M = \) torque applied to inner cylinder \( (N \cdot cm) \),
\( r = \) inner cylinder radius \( (cm) \),
\( h = \) inner cylinder height \( (cm) \)

Note: for concentric cylinder geometrics, \( \tau \) depends upon the above relationship, it is not influenced by fluid properties.

For the concentric cylinder geometry the mathematical treatment of the viscometer data requires that the torque to be measured is solely created by the resistance of the liquid sample being sheared in the well-defined coaxial cylinder gap. However, all rotors have bottom and top end faces and an additional torque may arise between these end faces and the cup. To minimize these end effects the top and bottom end faces are recessed. In the bottom recess air is trapped when the rotor and the cup filled with the sample are brought together. The entrapped air bubble covers approximately 90% of the rotor bottom end face. When the rotor rotates, the air cushion at the bottom surface prevents the sample from being sheared underneath the rotor and eliminates the normal torque contribution of the rotor bottom end face only the small rim around the recess adds a tiny torque which is taken into account in the evaluation of the "G" constant.

The recess at the top of the rotor allows any surplus of the sample to spill over so that again the rotor - when rotating shears only air.

The bottom end face effect may be evaluated by measuring the angular velocity and torque at several values of \( h \), the depth of immersion. The data are plotted as torque/angular velocity \( (M/\Omega) \) against \( h \) and the plot is extrapolated to a value of zero for \( M/\Omega \).
Equation A5.5 then becomes,

\[ \tau = \pi R^2 (h + \rho) \]

Such a procedure was not adopted as this was taken into account in the "A" factor and plastisols were evaluated on a comparative basis, see figure 2.4. (120)
Fig. A5.1 – Non–Newtonian Flow in Concentric Cylinders

a, M1 100/50 + 18% 0.300 (see Fig. 4.6.c)

b, Errors due to Newtonian Flow Assumption
APPENDIX 6 - CALCULATION OF SEVERS RHEOMETER DIE CONSTANTS

1 mm DIE

actual internal diameter of die = 1.14 mm

\[ r = 0.057 \quad r^2 = 1.056 \times 10^{-4} \quad r^3 = 1.85 \times 10^{-4} \]

height of the cylindrical die tube = 3.16 cm

\[ \text{Viscosity} = \frac{10^3 \pi \times 1.056 \times 10^{-5} (P \times 5.895)}{8 \times 3.16 D} \times \rho \]

\[ = 9.05 \times 10^{-3} \times \frac{P_0}{D} \]

The constant of 5.895 was introduced to convert the pressure reading on the Severs rheometer, from psi to kPa.

shear rate = \[ \frac{4D}{\pi} \times 1.85 \times 10^{-4} \rho = 6382 \frac{D}{\rho} \]

1.5 mm DIE

actual internal diameter of die = 1.59 mm

\[ r = 0.0795 \quad r^2 = 3.99 \times 10^{-5} \quad r^3 = 5.025 \times 10^{-4} \]

height of the cylindrical die tube = 3.16 cm

\[ \text{Viscosity} = \frac{10^3 \pi \times 3.99 \times 10^{-5} (P \times 5.895)}{8 \times 3.16 D} \times \rho \]

\[ = 0.0342 \frac{P_0}{D} \]

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Shear rate = \( \frac{4D \times 5.025 \times 10^{-4}}{\pi} \rho = 2534 \frac{D}{\rho} \)

2 mm DIE

Actual internal diameter of die = 2.13 mm

- \( r = 0.1065 \) \( r^2 = 1.29 \times 10^{-4} \)
- \( r^3 = 1.21 \times 10^{-3} \)

Height of the cylindrical die tube = 3.16 cm

Viscosity = \( \frac{10^3 \pi \times 1.29 \times 10^{-4} \times \rho \times 6.286 \rho}{8 \times 3.16 \Delta D} \)

= 0.111 \( \frac{Pa_s}{D} \)

Shear rate = \( \frac{4D \times 1.21 \times 10^{-3}}{\pi} = 1053 \frac{D}{\rho} \)

Summary - Severs constants

<table>
<thead>
<tr>
<th>Die</th>
<th>Shear rate(s(^{-1}))</th>
<th>Viscosity (PaS)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.0 mm</td>
<td>6882 ( \frac{D}{\rho} )</td>
<td>9.05 \times 10^{-3} ( \frac{Pa_s}{D} )</td>
</tr>
<tr>
<td>1.5 mm</td>
<td>2534 ( \frac{D}{\rho} )</td>
<td>0.0342 ( \frac{Pa_s}{D} )</td>
</tr>
<tr>
<td>2.0 mm</td>
<td>1053 ( \frac{D}{\rho} )</td>
<td>0.111 ( \frac{Pa_s}{D} )</td>
</tr>
</tbody>
</table>
The above calculations were extracted from ISO 4573, they assume Newtonian flow and take no account of the end effect or wall slip. The purpose of the next section is evaluate the validity of complying with this standard. Although throughout this thesis the use of the Severs Rheometer Complied with ISO 4573.

The ISO standard employs $P_{\text{expt}}$ and $Q_{\text{expt}}$ in the calculation of shear stress and shear rate, where,

\[
P_{\text{expt}} = P_{c} + P_{e}
\]

\[
Q_{\text{expt}} = Q_{o} + Q_{s}
\]

In these equations,

$P_{\text{expt}}$ = pressure drop along the capillary length $L$, due to the experiment. (Pa)

$P_{e}$ = pressure drop due to end effect, i.e. the pressure required to generate the flow profile.

$P_{c}$ = pressure drop employed in calculating the true shear stress at the well.

$Q_{\text{expt}}$ = flow rate, measured directly during the experiment (cm$^3$/s).

$Q_{s}$ = flow rate due to plug-type flow.

$Q_{o}$ = flow rate employed in calculating the true shear rate at the wall.

Experimental shear rate $\frac{\gamma_{\text{expt}}}{R^2}$ (A6.3)

Experimental shear stress $\frac{R P_{\text{expt}}}{2 L}$ (A6.4)

Experimental viscosity $\frac{1}{\mu_{\text{expt}}}$ (A6.5)

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However, if the non-Newtonian flow, end effect and wall slip are taken into account the true viscosity at the wall may be calculated as follows:

Shear stress at the wall \( \tau_W = \frac{R\tau_0}{2L} \) \( \text{(A6.6)} \)

Newtonian shear rate at the wall \( \gamma_n = \frac{Q_0}{\pi R^2} \) \( \text{(A6.7)} \)

True wall shear rate \( \dot{\gamma}_w = \gamma_n \left( \frac{3n'+1}{4n'} \right) \) \( \text{(Rabinowitch equation) A6.8} \).

where \( n' \) is the flow behaviour index

true viscosity at the wall \( \frac{\tau_W}{\gamma_w} \)

\( R = \) die radius  
\( L = \) die length  
\( n' = \) flow behaviour index

**Evaluation of End Effect**

The end effect may be evaluated using a series of dies of the same radius but differing lengths. One then generates a series of graphs relating \( P_{\text{expt}} \) to die length at selected flow rates:

![Graph showing \( P_{\text{expt}} \) vs. \( L \) with different flow rates: \( Q' < Q'' < Q''' \). The graph also indicates the location of \( 2\gamma_w \).]
The intercept reveals $P_e$ for each flow rate. It is then possible to generate $P_o$ and using this value evaluate $\tau_W$. 

Note: $P_o = P_{\text{expt}} - P_e$

Evaluation of Wall Slip\(^{22}\)

Having evaluated and effect and determined the true shear stress at the wall, it is possible to quantify wall slip by constructing a plot of true shear stress at the wall against experimental shear rate, for a series of dies of various radius.

The experimental shear rate is then plotted against the reciprocal of the die radius at selected shear stresses.
\[ 32 \tau_{\text{expt}} = 32 \tau_0 + 4 \pi \gamma S \]

\[ \pi D^2 \quad \pi D^2 \quad R \]

The true Newtonian shear rate can then be taken as the intercept of this plot for a given shear stress.

The non-Newtonian flow behaviour may be accounted for using the Rabinowitch equation (A6.8), which allow the true wall shear rate to be generated from the Newtonian shear rate.

If one considers a plot of shear stress against shear rate it becomes apparent that wall slip and end effect act in opposite directions.

\[ \tau_{\text{expt}} \rightarrow \tau_{\text{expt}} \]
\[ \tau_{\text{w}} \rightarrow \tau_{\text{w}} \]

If one considers the situation in which there is an end effect but no wall slip, then \( \tau_{\text{expt}} \) is calculated from \( P_{\text{expt}} \) which contains a component pressure \( P_e \), due to end effect. It is therefore higher than \( \tau_w \) which is based on \( P_0 \). The effect of wall slip is to displace an experimental shear stress, experimental shear rate relationship to higher shear stresses. If one now considers the opposite situation in which there is wall slip but no end effect. The inclusion of a flow rate component due to slip in the calculation of \( \dot{\gamma}_{\text{expt}} \) results in \( \dot{\gamma}_{\text{expt}} \) being higher than \( \dot{\gamma}_w \). This results in the \( \dot{\gamma}_{\text{expt}}/\dot{\gamma}_{\text{expt}} \) plot being displaced to higher shear rates. From this discussion it thus becomes
obvious that wall slip and end effect may under certain circumstances cancel each other out.

To accurately characterise the rheological behaviour of the plastisols considered in this study the above procedures should be adopted. Dies of various length being employed to quantify end effect, dies of various radius being used to evaluate wall slips. The Robinowitch equation allowing the true shear rate at the wall to be calculated from the "Newtonian" shear rate at the wall, by employing the flow behaviour index $n'$.

From the preceding discussion one can see that the evaluation of the true shear stress and shear rate at the wall is quite involved. In addition the flow behaviour index $n'$ would have to be evaluated over a whole range of shear rates, if the flow curve is to be accurately quantified. This would be tedious and time consuming, unless a computer program was developed. Such an approach was not employed in this work as the results presented are comparative as opposed to absolute values. An indication of the magnitude of the end effect and wall slip for a plastisol considered in my work may be taken from Figure 2.2. Although to accurately measure the effect $F_e$ and $Q_s$ should be evaluated.

In Figure 2.2.a the flow curves using three different dies superimpose, suggesting that either wall slip and end effect or negligible or that they are of similar magnitude and therefore cancel each other out. The latter suggestion seems unlikely as each of the different dies generate the same data over a range of shear rates, where the magnitude of wall slip and end effect should vary. In addition the Severs flow curves generated in Figure 2.2.b for a much higher viscosity system also agree quite closely, the viscosity data for the 2$\text{mm}$ and 1.5$\text{mm}$ diameter dies almost superimpose. These observation imply that wall slip and end effect are not significant factors in the behaviour of these plastisols. Any discrepancy between the viscosity data generated from different dies is small compared with the gross difference in the behaviour of plastisols varying in plasticiser content, filler level etc.
APPENDIX 7 - TEST VARIABLES FOR SEDIGRAPH 5000ET

Calcium Carbonates
Sample Density ($\rho$) = 2.65 g/cm$^3$
Liquid Density ($\rho_0$) = 0.9951 g/cm$^3$
Liquid Viscosity (n) = 0.7679 centipoise
Cell temperature = 32°C
Sedimenting system: Sodium pyrophosphate solution
(0.98 g/litre) + propan-2-ol.
Dispersing procedure: mix 1.75 g calcium carbonate with
1.25 g propan-2-ol, subject to ultrasound for 30 secs, then add
40 g Sodium pyrophosphate solution and subject
to ultrasound for a further 30 seconds.

Rate (start μm) = $\frac{211.80 (\rho-\rho_0) \times \text{multiplier}}{n}$
Rate (50 μm) = $\frac{211.80 (2.6-0.9651) \times (1)}{0.7679}$ = 443
Running Time = $\frac{41250}{443}$ = 93 minutes

Spheriglass 5000CP03
Sample Density ($\rho$) = 2.47 g/cm$^3$
Liquid Density ($\rho_0$) = 0.78276 g/cm$^3$
Liquid Density (n) = 1.82 centipoise
Cell temperature = 28°C
Sedimenting system: Propan-2-ol
Dispersing Procedure: mix 2.00 g Spheriglass 5000 CP03 with 40 g propan-2-ol,
subject to ultrasound for 60 seconds

Rate (80 μm) = $\frac{211.80 (2.47-0.78275) \times 2.55}{1.82}$ = 503
Running time = $\frac{41250}{503}$ = 82 minutes
**Paste Polymers (all except E2)**

Sample Density (ρ) = 1.4 g/cm³
Liquid Density (ρ₀) = 0.9414 g/cm³
Liquid Viscosity (n) = 6.83 centipoise
Cell temperature = 33°C
Sedimenting system = Dibutyl Sebacate (DBS)

Dispersing procedure: dilute plastisol 14 : 1 with DBS under gentle agitation provided by Sedigraph stirrer

Rate (70 μm) = \( \frac{211.80 (1.4-0.9414) \times 1.96}{6.83} = 28 \) 6.83
Running time = \( \frac{41250}{28} = 24 \text{ hours} \)

---

The same sample preparation was adopted but the sedimenting fluid viscosity and density were slightly different as a 100/90 plastisol was tested compared with a 100/45 plastisol for the other paste polymers.

**Rate Calculations**

Sample Density (ρ) = 1.4 g/cm³
Liquid Density (ρ₀) = 0.9386 g/cm³
Liquid Viscosity (n) = 7.01 centipoise
Cell temperature = 33°C
Rate (70 μm) = \( \frac{211.80 (1.4-0.9386) \times 1.96}{7.01} = 27 \) 7.01

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APPENDIX 8 - PLASTICISER LEVEL CALCULATIONS

Volume Ratio present in GCC dispersion:

Weight of each component

<table>
<thead>
<tr>
<th>Component</th>
<th>Weight</th>
<th>Density</th>
</tr>
</thead>
<tbody>
<tr>
<td>GCC</td>
<td>242.1g</td>
<td>2.65 g/cm³</td>
</tr>
<tr>
<td>DIOP</td>
<td>209.6g</td>
<td>0.98 g/cm³</td>
</tr>
</tbody>
</table>

Volume of each component

<table>
<thead>
<tr>
<th>Component</th>
<th>Volume</th>
</tr>
</thead>
<tbody>
<tr>
<td>GCC</td>
<td>242.1 / 2.65 = 91.36 cm³</td>
</tr>
<tr>
<td>DIOP</td>
<td>209.6 / 0.98 = 213.9 cm³</td>
</tr>
</tbody>
</table>

Assuming constant volume ratio, the weight of each component in an equivalent TiO₂ dispersion:

<table>
<thead>
<tr>
<th>Component</th>
<th>Weight</th>
</tr>
</thead>
<tbody>
<tr>
<td>TiO₂</td>
<td>91.36 x 4.05 = 370.0g</td>
</tr>
<tr>
<td>DIOP</td>
<td>213.9 x 0.98 = 209.6g</td>
</tr>
</tbody>
</table>
### APPENDIX 9 - GRAPH 3.18.a DATA

### TABLE 6.9 - CALCULATION OF \( \sigma_n \) FOR FIGURE 3.18.a

<table>
<thead>
<tr>
<th>Paste Polymer</th>
<th>Oil Absorption g/100g</th>
<th>PVC Volume (cm³)</th>
<th>DIOP Volume (cm³)</th>
<th>( \sigma_n = \frac{\text{PVC Volume}}{\text{PVC Vol+DIOP Vol}} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>M1</td>
<td>34.9</td>
<td>71.43</td>
<td>25.61</td>
<td>0.667</td>
</tr>
<tr>
<td>M2</td>
<td>32.6</td>
<td>71.43</td>
<td>33.27</td>
<td>0.582</td>
</tr>
<tr>
<td>S1</td>
<td>24.25</td>
<td>71.43</td>
<td>24.74</td>
<td>0.743</td>
</tr>
<tr>
<td>S2</td>
<td>22.7</td>
<td>71.43</td>
<td>23.16</td>
<td>0.755</td>
</tr>
<tr>
<td>E1</td>
<td>41.2</td>
<td>71.43</td>
<td>42.04</td>
<td>0.630</td>
</tr>
<tr>
<td>E2</td>
<td>26.8</td>
<td>71.43</td>
<td>27.35</td>
<td>0.723</td>
</tr>
</tbody>
</table>
TABLE 6.10 - CALCULATION OF RELATIVE SOLIDS VOLUME, VISCOSITY DATA, AT 1.017 S⁻¹, EXTRACTED FROM FIGURES 3.1 AND 3.2

<table>
<thead>
<tr>
<th>Paste Polymer</th>
<th>DICP (phr)</th>
<th>( \sigma )</th>
<th>( \sigma / \alpha )</th>
<th>Viscosity Pa·S</th>
</tr>
</thead>
<tbody>
<tr>
<td>M1</td>
<td>45</td>
<td>0.609</td>
<td>0.913</td>
<td>15.14</td>
</tr>
<tr>
<td></td>
<td>50</td>
<td>0.583</td>
<td>0.874</td>
<td>7.33</td>
</tr>
<tr>
<td></td>
<td>55</td>
<td>0.560</td>
<td>0.840</td>
<td>4.98</td>
</tr>
<tr>
<td></td>
<td>60</td>
<td>0.533</td>
<td>0.807</td>
<td>3.40</td>
</tr>
<tr>
<td>M2</td>
<td>45</td>
<td>0.609</td>
<td>0.893</td>
<td>20.12</td>
</tr>
<tr>
<td></td>
<td>50</td>
<td>0.583</td>
<td>0.855</td>
<td>9.97</td>
</tr>
<tr>
<td></td>
<td>55</td>
<td>0.550</td>
<td>0.821</td>
<td>6.09</td>
</tr>
<tr>
<td></td>
<td>60</td>
<td>0.538</td>
<td>0.789</td>
<td>4.06</td>
</tr>
<tr>
<td>S1</td>
<td>45</td>
<td>0.609</td>
<td>0.820</td>
<td>33.77</td>
</tr>
<tr>
<td></td>
<td>50</td>
<td>0.583</td>
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<td>60</td>
<td>0.538</td>
<td>0.724</td>
<td>6.46</td>
</tr>
<tr>
<td>S2</td>
<td>45</td>
<td>0.609</td>
<td>0.807</td>
<td>29.59</td>
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<td>0.583</td>
<td>0.772</td>
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<td>8.31</td>
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<td>0.538</td>
<td>0.713</td>
<td>6.82</td>
</tr>
<tr>
<td>E1</td>
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<td>0.889</td>
<td>98.02</td>
</tr>
<tr>
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<td>0.538</td>
<td>0.854</td>
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<td>0.824</td>
<td>15.32</td>
</tr>
<tr>
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<td>0.500</td>
<td>0.794</td>
<td>8.67</td>
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<tr>
<td>E2</td>
<td>90</td>
<td>0.427</td>
<td>0.605</td>
<td>148.1</td>
</tr>
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</table>
APPENDIX 10

TABLE 6.11 - GRAPH 3.18.b DATA

<table>
<thead>
<tr>
<th>Paste Polymer</th>
<th>DICP phr</th>
<th>$\sigma/\sigma*$</th>
<th>$1/(\sigma/\sigma*)$</th>
<th>Discontinuity Shear Rate ($S^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>M1</td>
<td>45</td>
<td>0.913</td>
<td>1.095</td>
<td>35</td>
</tr>
<tr>
<td></td>
<td>50</td>
<td>0.874</td>
<td>1.144</td>
<td>50</td>
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<tr>
<td></td>
<td>55</td>
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<td>1.190</td>
<td>80</td>
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<td>60</td>
<td>0.807</td>
<td>1.240</td>
<td>120</td>
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<td>E1</td>
<td>55</td>
<td>0.889</td>
<td>1.125</td>
<td>0.70</td>
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<td>70</td>
<td>0.794</td>
<td>1.260</td>
<td>6.00</td>
</tr>
</tbody>
</table>

* Values taken from Appendix 9
+ Values taken from Figure 3.1.a and 3.1.c., respectively.
## APPENDIX II - PSEUDOPOLYMER SYSTEMS: GLIM DATA

### COEFFICIENT $C_0$ PREDICTION

<table>
<thead>
<tr>
<th>Polymer</th>
<th>Coded Units</th>
<th>Normal Units</th>
<th>Coefficient $C_0$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$x_1$</td>
<td>$x_2$</td>
<td>RVF&quot;</td>
</tr>
<tr>
<td>S1</td>
<td>-0.237</td>
<td>1.4038</td>
<td>0.735</td>
</tr>
<tr>
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<td>0.222</td>
<td>1.4038</td>
<td>0.765</td>
</tr>
<tr>
<td></td>
<td>0.695</td>
<td>1.4038</td>
<td>0.796</td>
</tr>
<tr>
<td></td>
<td>1.246</td>
<td>1.4038</td>
<td>0.832</td>
</tr>
<tr>
<td>S2</td>
<td>-0.0841</td>
<td>-0.3199</td>
<td>0.745</td>
</tr>
<tr>
<td></td>
<td>0.3898</td>
<td>-0.3199</td>
<td>0.776</td>
</tr>
<tr>
<td></td>
<td>0.864</td>
<td>-0.3199</td>
<td>0.807</td>
</tr>
<tr>
<td></td>
<td>1.414</td>
<td>-0.3199</td>
<td>0.843</td>
</tr>
<tr>
<td>E2</td>
<td>-1.414</td>
<td>-1.378</td>
<td>0.658</td>
</tr>
<tr>
<td></td>
<td>-0.772</td>
<td>-1.378</td>
<td>0.700</td>
</tr>
<tr>
<td></td>
<td>1.199</td>
<td>-1.378</td>
<td>0.829</td>
</tr>
</tbody>
</table>

RVF" (coded) = RVF" - $0.7505 = x_1$

SK (coded) = SK - 0.08 = $x_2$

$A = 0.6670$
$B = 0.3504$
$C = -0.5088$
$D = 0.06114$
$E = 0.4658$
$F = 0.06994$
COEFFICIENT C1 PREDICTION

<table>
<thead>
<tr>
<th>Polymer</th>
<th>Coded Units</th>
<th>Normals Units</th>
<th>Coefficient Co</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$x_1$</td>
<td>$x_2$</td>
<td>RVF$^*$</td>
</tr>
<tr>
<td>S1</td>
<td>- 0.237</td>
<td>- 1.311</td>
<td>0.735</td>
</tr>
<tr>
<td></td>
<td>0.222</td>
<td>- 1.311</td>
<td>0.765</td>
</tr>
<tr>
<td></td>
<td>0.696</td>
<td>- 1.311</td>
<td>0.796</td>
</tr>
<tr>
<td></td>
<td>1.246</td>
<td>- 1.311</td>
<td>0.832</td>
</tr>
<tr>
<td>S2</td>
<td>- 0.0841</td>
<td>- 0.0643</td>
<td>0.745</td>
</tr>
<tr>
<td></td>
<td>0.3898</td>
<td>- 0.0643</td>
<td>0.776</td>
</tr>
<tr>
<td></td>
<td>0.864</td>
<td>- 0.0643</td>
<td>0.807</td>
</tr>
<tr>
<td></td>
<td>1.414</td>
<td>- 0.0643</td>
<td>0.843</td>
</tr>
<tr>
<td>E2</td>
<td>- 1.414</td>
<td>1.414</td>
<td>0.658</td>
</tr>
<tr>
<td></td>
<td>- 0.772</td>
<td>1.414</td>
<td>0.700</td>
</tr>
<tr>
<td></td>
<td>1.199</td>
<td>1.414</td>
<td>0.829</td>
</tr>
</tbody>
</table>

\[
RVF^* \text{ (coded)} = RVF^* - 0.7505 = x_1 \\
0.0654
\]

Sample mean (coded) = \[
\frac{SM - 2.65}{0.0778} = x_2
\]

A = - 0.2778
B = - 0.05038
C = - 0.3757
D = 0.06645
E = - 0.08300
F = 0.04737

-342-
## COEFFICIENT C2 PREDICTION

<table>
<thead>
<tr>
<th>Polymer</th>
<th>Coded Units</th>
<th>Normals Units</th>
<th>Coefficient C0</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>x₁</td>
<td>x₂</td>
<td>RVF&quot;</td>
</tr>
<tr>
<td>S1</td>
<td>0.237</td>
<td>-1.311</td>
<td>0.735</td>
</tr>
<tr>
<td></td>
<td>0.222</td>
<td>-1.311</td>
<td>0.765</td>
</tr>
<tr>
<td></td>
<td>0.696</td>
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</tr>
<tr>
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<td>1.246</td>
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<td>0.832</td>
</tr>
<tr>
<td>S2</td>
<td>0.0841</td>
<td>-0.0643</td>
<td>0.745</td>
</tr>
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<td>0.3898</td>
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<td>0.776</td>
</tr>
<tr>
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<td>0.807</td>
</tr>
<tr>
<td></td>
<td>1.414</td>
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<td>0.843</td>
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<tr>
<td>E2</td>
<td>-1.414</td>
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</tr>
<tr>
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</tr>
<tr>
<td></td>
<td>1.199</td>
<td>1.414</td>
<td>0.829</td>
</tr>
</tbody>
</table>

\[
RVF'' \text{ (coded)} = RVF'' - 0.7505 = x_1 \\
\text{Sample Mean (coded)} = SM - 2.65 = x_2 \\
\]

\[
A = 0.06599 \\
B = 0.004947 \\
C = 0.05599 \\
D = -0.01911 \\
E = -0.009613 \\
F = -0.008969
\]
### APPENDIX 12 -- DILATANT SYSTEMS : GLIM DATA

#### COEFFICIENT Co PREDICTION

<table>
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<th>Normals Units</th>
<th>Coefficient Co</th>
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<td>$x_1$</td>
<td>$x_2$</td>
<td>$RVF^*$</td>
</tr>
<tr>
<td>S1</td>
<td>- 1.413</td>
<td>- 1.415</td>
<td>0.713</td>
</tr>
<tr>
<td></td>
<td>- 1.019</td>
<td>- 1.415</td>
<td>0.742</td>
</tr>
<tr>
<td></td>
<td>- 0.611</td>
<td>- 1.415</td>
<td>0.772</td>
</tr>
<tr>
<td></td>
<td>- 0.136</td>
<td>- 1.415</td>
<td>0.807</td>
</tr>
<tr>
<td>X2</td>
<td>- 1.291</td>
<td>- 0.768</td>
<td>0.722</td>
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<td></td>
<td>- 0.883</td>
<td>- 0.768</td>
<td>0.752</td>
</tr>
<tr>
<td></td>
<td>- 0.462</td>
<td>- 0.768</td>
<td>0.783</td>
</tr>
<tr>
<td></td>
<td>0</td>
<td>- 0.768</td>
<td>0.817</td>
</tr>
<tr>
<td>E2</td>
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<td>0.822</td>
</tr>
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<td>0.503</td>
<td>1.415</td>
<td>0.854</td>
</tr>
<tr>
<td></td>
<td>0.924</td>
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</tr>
<tr>
<td></td>
<td>1.413</td>
<td>1.415</td>
<td>0.921</td>
</tr>
</tbody>
</table>

$RVF^*$ (coded) = $RVF^* - 0.817 \over 0.0736 = x_1$

Sample Mean (coded) = $xM - 2.701 \over 0.340 = x_2$

\[
\begin{align*}
A &= 1.307 \\
B &= 0.4702 \\
C &= -0.01011 \\
D &= 0.09110 \\
E &= -0.1929 \\
F &= 0.05905
\end{align*}
\]
### Coefficient C1 Prediction

<table>
<thead>
<tr>
<th>Polymer</th>
<th>Coded Units</th>
<th>Normal Units</th>
<th>Coefficient Co</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$X_1$</td>
<td>$X_2$</td>
<td>RVF$^*$</td>
</tr>
<tr>
<td>S1</td>
<td>-1.413</td>
<td>1.414</td>
<td>0.713</td>
</tr>
<tr>
<td></td>
<td>-1.019</td>
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</tr>
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<td>-0.611</td>
<td>1.414</td>
<td>0.772</td>
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<td>-0.136</td>
<td>1.414</td>
<td>0.807</td>
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<tr>
<td>S2</td>
<td>-1.2911</td>
<td>0.374</td>
<td>0.722</td>
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<tr>
<td></td>
<td>-0.883</td>
<td>0.374</td>
<td>0.752</td>
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<td>-0.462</td>
<td>0.374</td>
<td>0.783</td>
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<tr>
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<td>0</td>
<td>0.374</td>
<td>0.817</td>
</tr>
<tr>
<td>E2</td>
<td>0.0679</td>
<td>-1.414</td>
<td>0.822</td>
</tr>
<tr>
<td></td>
<td>0.503</td>
<td>-1.414</td>
<td>0.854</td>
</tr>
<tr>
<td></td>
<td>0.924</td>
<td>-1.414</td>
<td>0.885</td>
</tr>
<tr>
<td></td>
<td>1.413</td>
<td>-1.414</td>
<td>0.921</td>
</tr>
</tbody>
</table>

RVF$^*$ (coded) = $\frac{RVF^* - 0.817}{0.0736} = x_1$

SKWNESS (coded) = $\frac{SK - 0.1485}{1.380} = x_2$

A = -0.4591
B = -0.2763
C = -0.3315
D = -0.1766
E = -0.09445
F = -0.5121
## COEFFICIENT C2 PREDICTION

<table>
<thead>
<tr>
<th>Polymer</th>
<th>Coded Units</th>
<th>Normals Units</th>
<th>Coefficient C0</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>x₁</td>
<td>x₂</td>
<td>RVF&quot;</td>
</tr>
<tr>
<td>S1</td>
<td>- 1.413</td>
<td>1.414</td>
<td>0.713</td>
</tr>
<tr>
<td></td>
<td>- 1.019</td>
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<td>0.742</td>
</tr>
<tr>
<td></td>
<td>- 0.611</td>
<td>1.414</td>
<td>0.772</td>
</tr>
<tr>
<td></td>
<td>- 0.136</td>
<td>1.414</td>
<td>0.807</td>
</tr>
<tr>
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<td>0.722</td>
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<td>0.752</td>
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<td>0.783</td>
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<tr>
<td>E2</td>
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<td>0.822</td>
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<td></td>
<td>0.503</td>
<td>- 1.414</td>
<td>0.854</td>
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<td>0.924</td>
<td>- 1.414</td>
<td>0.885</td>
</tr>
<tr>
<td></td>
<td>1.413</td>
<td>- 1.414</td>
<td>0.921</td>
</tr>
</tbody>
</table>

\[
\text{RVF" (coded)} = \frac{\text{RVF"} - 0.817}{0.0736} = x_1
\]

\[
\text{SKEWNESS (coded)} = \frac{\text{SK} - 0.1485}{1.380} = x_2
\]

A = 0.5174
B = 0.4842
C = 0.3273
D = 0.1764
E = 0.07627
F = 0.4267
### APPENDIX 13 - K FACTOR PREDICTIONS : GLIM DATA

<table>
<thead>
<tr>
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<th>Coded Units</th>
<th>Normal Units</th>
<th>K factor</th>
</tr>
</thead>
<tbody>
<tr>
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<td>tan 90 RVF* Skewness x₁ x₂</td>
<td></td>
<td></td>
</tr>
<tr>
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<td></td>
<td>1.22</td>
</tr>
<tr>
<td></td>
<td>- 1.142 1.414 2.89 2.10</td>
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</tr>
<tr>
<td></td>
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</tr>
<tr>
<td></td>
<td>- 1.414 1.414 2.19 2.10</td>
<td></td>
<td>0.41</td>
</tr>
<tr>
<td>M2</td>
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<tr>
<td></td>
<td>- 1.076 0.376 3.06 0.665</td>
<td></td>
<td>0.79</td>
</tr>
<tr>
<td></td>
<td>- 1.251 0.376 2.61 0.665</td>
<td></td>
<td>0.55</td>
</tr>
<tr>
<td></td>
<td>- 1.379 0.376 2.28 0.665</td>
<td></td>
<td>0.36</td>
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<td>0.50</td>
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<tr>
<td></td>
<td>0.117 - 1.414 6.13 - 1.803</td>
<td></td>
<td>0.32</td>
</tr>
<tr>
<td></td>
<td>- 0.462 - 1.414 4.64 - 1.803</td>
<td></td>
<td>0.25</td>
</tr>
<tr>
<td></td>
<td>- 0.820 - 1.414 3.72 - 1.803</td>
<td></td>
<td>0.18</td>
</tr>
</tbody>
</table>

\[
\text{tan 90 RVF (coded)} = \frac{\text{tan 90 RVF}}{2.574} - 5.83
\]

\[
\text{Skewness (coded)} = \frac{\text{Skewness}}{1.380} - 0.1485
\]

A = 1.709
B = 0.9138
C = 0.8628
D = -0.03531
E = -0.0606
F = 0.5270

-347-
FLOW PROPERTIES OF FLUIDS

The coefficient of viscosity of Newtonian fluids is a constant irrespective of the shear stresses involved, and is independent of time, by definition. Many real materials particularly polymer melts and solutions and suspensions of particles in liquids such as PVC pastes, do not, however exhibit the simple characteristics of a Newtonian fluid. Today three broad classes of flow behaviour are recognised.

(a) Time-independent fluids: fluids in which the rate of shear at a given point is some function of shearing stress at the point and nothing else.

(b) Time-dependent fluids: more complex systems in which shear stress–shear rate relationships depend on how the fluid has been sheared and on its previous history.

(c) Elasticoviscous fluids: systems which are predominantly viscous but which exhibit partial recovery after deformation. This class could be considered as a special sub-class of (b) but is normally treated separately.

Time-independent Fluids.

Time-independent fluids are defined mathematically by equation;

\[ \gamma = f (\tau) \]
or graphically by a curve of shear stress plotted against shear rate. All sorts of curves are possible and may occur. However four basic types are indicated below.

![Diagram showing different types of flow curves: Newtonian, Bingham, and Pseudoplastic.](image)

For a Newtonian fluid,

\[ \gamma = \frac{\tau}{\mu} \]

\( \gamma \) = shear rate  
\( \tau \) = shear stress  
\( \mu \) = coefficient of viscosity

The Bingham body is an idealised material which is considered to have an internal structure which collapses above a yield stress \( \tau_y \), above which the shear rate increases linearly with shear stress.

\[ \gamma = \frac{1}{\mu} (\tau - \tau_y) \quad \text{when } \tau > \tau_y \]

For pseudoplastic materials the shear rate increases at a more than linear rate with increase in shear. A consequence of the shape of a pseudoplastic flow curve (plot of \( \tau \) against \( \gamma \)) is that there is no constant of proportionality. Therefore, instead of talking about the coefficient of viscosity, which we use for Newtonian liquids, it is more common to refer to the "apparent viscosity", \( \mu_a \), defined as shear stress/shear rate. Such an apparent viscosity decreases with rate of shear for pseudoplastics, is independent of rate of shear for
Newtonian fluids and increases with rate of shear for dilatant fluids. This is highlighted below:

Skelland has summarised the equations which have been proposed to describe pseudoplastic behaviour. The most widely used equation being the power law equation (also known as the Oswald-de Waele equation).

\[ \tau = K \gamma^n \]

where \( K \) = consistency index
\( n \) = flow behaviour index

In the logarithmic form

\[ \log \tau = \log K + n \log \gamma \]

This means that log-log plots of \( \tau \) versus \( \gamma \) will yield a straight line (for a power law material - over a limited range of shear rates)
Once again the power law equation is the most useful empirical equation to describe dilatancy, but in this case \( n \) is greater than 1. Considerable deviation from such a relationship can, however, occur and there are PVC plastisols which appear dilatant over one shear rate but pseudoplastic over another.

Appendix 5 and 6 describe the techniques which may be emphasised to characterise these time-independent fluids.

Time-dependent Fluids

There are a number of fluids whose flow properties, such as \( \mu_s \), change with the time of shearing. Most formal studies on time-dependent behaviour have been concerned with reversible effects such as thixotropy and rheopexy.

Thixotropy is that property of a body by virtue of which \( \mu_s \) is temporarily reduced by previous deformation. This means that the viscosity depends upon the time of stirring as compared with the pseudoplastic material which depends on the rate of shear. Thixotropy may be demonstrated using a rotary viscometer. The sample is stirred for a fixed period of time, for example one minute, at a low shear rate and the torque measured at some time during this period. The speed is then increased stepwise without stopping the machine and the torque measured at the new shear rate. This is then repeated over several increased stirring rates. A curved plot will result. Without stopping the viscometer, measurements are then made at a series of decreasing stirring rates and the torque measured. In the time interval between making the measurements when increasing the speeds and making the measurements at decreasing speeds the viscosity will have dropped and the resulting curve will be below the curve made when making measurements in the sequence of increasing speeds.
The loop shown above is a characteristic thixotropic hysteresis loop, the magnitude of which depends upon time for which the material was sheared at each speed, the number of speeds employed and the maximum shear rate employed as well as on the flow characteristics of the material. It is therefore not possible to give a single measurement of thixotropy.

Today the word “rheop” is more commonly used to denote the solidification of a thixotropic system under the influence of gentle movement.
Elasticoviscous Fluids

A number of materials exist which show properties intermediate to those of classical solids and liquids, when placed under stress the deformation is not instantaneous and is sometimes only partially reversible. Such materials are said to be viscoelastic.

The measurement of both elastic and viscous responses of viscoelastic substances subjected to defined shear rates is technically difficult when absolute values are required. Only very sophisticated and consequently very expensive instruments can give "absolute" answers.

Viscoelasticity may be quantified using a Couette type sensor system. Such a system may have its outer cylinder driven with an oscillating speed, i.e. the speed changes sinusoidally with time around either a mean zero speed or this oscillation is superimposed on any non-zero rotational speed value. This means a harmonic oscillatory input of strain with a certain frequency, and amplitude. On the inner cylinder the harmonic output of the resulting stress is measured having the same frequency, but a different amplitude and a phase lag between input and output. This difference depends on the elastic component in the shear-rate shear stress response of the sample tested in this special sensor system. The mathematical treatment of the data measured and recorded allows one to determine the storage modulus $G'$ and the loss modulus $G''$. $G'$ is a measure of the energy stored and recovered per cycle while $G''$ is a measure of the energy lost as heat per cycle.
CHAPTER 7: REFERENCES


15. ICI Ltd., British Patent 1 415 195.


35 M. J. MOONEY, Colloid Sci., 6, 162 (1951).


57 J. T. LAZOR, Mod. Plast., 42 (9), 149 (1965).
60 A. EINSTEIN, Ann. Phys., 17, 459 (1905), ibid. 19, 289 (1906), ibid 34, 591 (1911).
64 S. FORRVK, Plastvarlden, 18 (3), 58 (1968).
68 G. C. FURNAS, Industrial Engineering Chemistry, 23 (10), 1052 (1931).
79 F. PONIZIL, Kunststoffe, 64, 53 (Feb 1974).
83 Kanegafuchi, British Patent, 1 162 980.
84 Dynamit Nobel Aktiengesellschaft, British Patent 1 108 786.
90 L. UNDERDAL, S. LANGE, O. PALMGREN and N. P. THORSHAW, Plast and Rubb. Instut. Internat. Conf. on PVC Processing, 6/7 April 1978

-357-
91 YU. A. MERINO, A. A. TRAPEZNIKOV and V. V. GUZEEV, Colloid Journal of the USSR, 44 (6), 948 (1982).
92 British Standard for PSD measurement by Microscopy.
95 ECC International Central Laboratories, St. Austell, Cornwall, England.
96 Tioxide Central Laboratories, Stockton - on - Tees, Cleveland, England.
97 Potters Industries Inc., UK Distributors, Croxton and Garry, Curtis Road, Dorking, Surrey, England.
100 Brookfield Viscometer Manual, c/o Baird and Tatlock, PO Box 1, Romford, England.
101 Rotovisko Manual, c/o MSE, Manor Royal, Crawley, Sussex, England
102 IEC, 4575
103 Haake Calibration Fluid, UK Distributors: MSE, Manor Royal, Crawley, Sussex, England
104 J MUELLER, W STAUFFER, K XASER, Chima 27 (2), 82 (1973)
109 Operators Manual (MDP 7025), c/o Malvern Instruments Limited, Spring Lane, Malvern, Worcestershire, England
110 Sedigraph 5000 ET Instruction Manual, c/o Coulter Electronics Limited, Northwell Drive, Luton, Beds., England
111 Operators Manual (2200/3300); c/o Malvern Instruments Limited, Spring Lane, Malvern, Worcestershire, England
112 ICI Private Communication
113 J.A. DAVIDSON, Powder Technol., 23, 233 (1979)
114 J.A. DAVIDSON, Powder Technol., 23, 239 (1979)
117. DAVIES O.L. and GOLDSMITH P.L., Statistical Methods in Research and Production, Oliver and Boyd, Edinburgh
120 Introduction to Practical Viscometry, Gebhard Schramm, Haake GmbH, West Germany 1981
123 GREEN H. and WALTMANN R.N., Thixatropy, Colloid Chemistry, 6, 328, (1946)

-359-