Citation: Acham, Nicholas (1996). Non-aqueous Dispersions as a Basis for High-Solids Coatings. (Unpublished Doctoral thesis, City, University of London)

Non-aqueous Dispersions as a Basis for High-Solids Coatings

by

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Submitted for the degree of Doctor of Philosophy
at The City University, London
wholly carried out at the laboratories of The Paint Research Association, Teddington,
UK

October 1996

ABSTRACT

Plastisols constitute a large proportion of the coated steel strip market. A plastisol comprises a dispersion of polymer, generally poly(vinyl chloride) produced by aqueous emulsion or suspension polymerisation processes, that is subsequently dried and redispersed in an essentially non-volatile diluent plasticiser such as di(2-ethylhexyl) phthalate. Once applied, the plasticiser swells the polymer on heating so forming a tough and flexible coating. For environmental reasons, there is interest within industry in acrylic plastisols. However, acrylic plastisols gel prematurely at room temperature. The stability of vinyl plastisols is generally thought to be due to the presence of microcrystalline domains present in poly(vinyl chloride), and not present in amorphous acrylic polymers, retarding the swelling action of the plasticiser.

Improved plastisol stability was achieved using acrylic polymers of uniform particle size prepared by non-aqueous dispersion and aqueous emulsion polymerisation techniques with thermally reversible cross-links analogous to the microcrystalline domains present in poly(vinyl chloride). Thermally reversible cross-links were provided by hydrogen bonding and metal ion crosslinking. Novel procedures were developed for the non-aqueous dispersion polymerisation of mixtures of polar monomers and the preparation of polymers cross-linked by metal ions. Further improvements in acrylic plastisol stability were seen on application of the principle of osmotic deswelling. Plastisol stability was measured viscometrically.

Plastisols based on copolymers of methyl methacrylate and methacrylic acid or 2-hydroxyethyl methacrylate, and butylbenzyl phthalate showed improved stability compared to those based on poly(methyl methacrylate). This was attributed to hydrogen bonding. Polymers were prepared with high levels of methacrylic acid and 2-hydroxyethyl methacrylate, reaching 10% and 15% by weight respectively. Methyl methacrylate - methacrylic acid copolymers were also prepared with a range of particle sizes. It was observed that the stability of plastisols prepared from these polymers improved with increasing particle size. This was related to the surface to volume ratio of the polymer particles. Concentrating the methacrylic acid component into the surface region of a methyl methacrylate - methacrylic acid copolymer, using a variable composition seed and feed method of preparation, also rendered the polymer less susceptible to swelling by plasticiser. Improved stability was also seen with plastisols based on carboxylic acid containing polymers which had been neutralised with organometallic compounds such as diethyl zinc compared to unneutralised controls.

A theory for osmotic limitation of swelling of crosslinked polymers by strong solvents was presented. The mechanism relies on an osmotic force promoted by the presence of a low molecular weight polymer dissolved exclusively in the solvent phase tending to deswell the cross-linked polymer. The applicability of this theory to the problem of stabilising acrylic plastisols was tested. Plastisol stability was improved on addition of low molecular weight poly(butyl acrylate) and poly(methyl methacrylate) to the plasticiser phase. Experimental evidence suggested that there was some penetration of poly(butyl acrylate) into a 95:5 (wt) methyl methacrylate - methacrylic acid copolymer. Better exclusion of poly(butyl acrylate) from the cross-linked polymer could be achieved, and hence the osmotic deswelling increased, by increasing the molecular weight of the linear polymer.

ACKNOWLEDGEMENTS

Thanks must go to Dr. K. W. Allen for supervision of this work and to the management of the Paint Research Association for their support. Also to those colleagues who offered encouragement and guidance. Acknowledgement is due to my colleagues Dr. R. J. Kennedy, Mr. J. Watson and Miss. J. A. Crisp who carried out some of the viscometry and Mr. M. Taylor for helpful discussions with aspects of the mathematics of polymer solutions. Also to Prof. B. Vincent at Bristol University who through his role as project consultant provided the theoretical background to the concept of the osmotic limitation of swelling of cross-linked polymers.

This work was financially supported under the Environmental Protection Technology scheme of the Department of Environment and a consortium of the following industrial companies:

Akzo Coatings BV
Beckers Industrial Coatings
British Steel
Casco Nobel Industrial Coatings Ltd.
Coates Coatings Ltd.
Courtaulds Coatings
Cray Valley Products
DSM Resins BV
Harlow Chemical Co.
HPG Coatings
ICI Resins
Jotun

CONTENTS

COMMON ABBREVIATIONS AND SYMBOLS

a	Particle radius
	Cone radius
A	Hamaker constant
c_i	Concentration of all ions in solution
c_{md}	Concentration of monomer in particles
$C_{micelle}$	Micelle phase monomer concentration
C_w	Aqueous phase monomer concentration
d	Surface to surface distance between two spheres
	Thickness of viscous body under shear
F	Faraday constant
ΔG_{el}	Change in elastic Gibbs free energy
ΔG_m	Change in Gibbs free energy on mixing
ΔH_f	Enthalpy of fusion
k	Boltzmann constant
$k^i_{e,micelle}$	Rate coefficient for entry of i-mer into a micelle
k_p	Propagation constant
$k_{p,aq}$	Rate coefficient for aqueous phase propagation
k_t	Termination constant
K	Solute distribution coefficient
m_A	Molecular weight of bifunctional monomer A
m_B	Molecular weight of monomer B
m_1	Molecular weight of solvent
m_3	Molecular weight of dissolved species
M	Mass of polymer
Mn	Number average molecular weight
Mp	Peak molecular weight
Mw	Weight average molecular weight
n_A	Moles of bifunctional monomer A
n_B	Moles of monomer B
n_0	Total number of cells in lattice
N_c	Number of particles
n_1	Number of solvent molecules
n_2	Number of polymer chains
R	Gas constant
R_i	Rate of initiation
R_p	Rate of polymerisation

S	Entropy
T	Absolute temperature
	Torque
T_{mp}	Melting point
U	Velocity of upper surface of viscous body under shesr
v_1	Molar volume of solvent
V	Volume fraction of particles
V_A	Attractive potential energy
V_R	Potential free energy of electrostatic repulsion
V_0	Volume of unswollen polymer
VOC	Volatile organic content
x_A	Mole fraction of bifunctional monomer A
X	Number of crosslinks
y	Molar ratio of solvent to solute molecules
z	Counterion charge number
	Number degree of polymerisation at which an oligomer becomes surface active
	Cell coordination number
z_i	Charge number of all ions in solution
α	Partition coefficient of monomer between the polymer and diluent
	Cone angle
α_s	Linear deformation factor for x, y and z dimensions
ε_0	Permittivity of a vacuum
ε_r	Relative permittivity of a medium
χ_{12}	Flory-Huggins interaction parameter for solvent in polymer
χ_{13}	Flory-Huggins interaction parameter for solvent in dissolved species
δ	Adsorbed layer thickness
ϕ	Volume fraction of suspended phase
ϕ_1	Volume fraction of solvent
ϕ_2	Volume fraction of polymer
ϕ_2'	Volume fraction of polymer in more concentrated phase
ϕ_3	Volume concentration of dissolved species
ϕ_c	Critical packing fraction
γ	Shear strain
η	Shear viscosity
$[\eta]$	Intrinsic viscosity

η_s	Shear viscosity of medium
μ	Chemical potential
μ_1	Chemical potential of solvent in solution
μ_1^0	Chemical potential of pure solvent
μ_2	Chemical potential of polymer in solution
μ_2^0	Chemical potential of pure liquid polymer
ν_e	Effective number of chains in network
ν_i	ith chain
ρ_1	Density of solvent
ρ_3	Density of dissolved species
ρ_A	Density of bifunctional monomer A
ρ_B	Density of monomer B
τ	Shear stress
ψ	Potential at the particle surface
ω	Angular velocity

Abbreviations used for materials are given in Chapter 5.

CHAPTER 1-
INTRODUCTION

There has long been concern over the effects of air pollution on the environment and on human health. Of particular concern in recent years has been the elevated levels of ozone observed at ground level in Europe and America. The mean value for the concentration of ozone in the United Kingdom has doubled in the last one hundred years to about 30 parts per billion[1]. Peak values frequently exceed the guideline levels for health and vegetation exposure. Amongst air pollutants, the margin between those concentrations typically recorded and those at which detrimental effects on human health can be observed is lowest for ozone[2].

1.1 The formation and control of ozone

Ozone is present as a natural component of both the upper and lower atmospheres. In the upper atmosphere, it is formed by photochemical processes involving the absorption of ultra-violet solar radiation by oxygen or by lightning discharges[3]. However, in the lower atmosphere ozone is constantly formed and destroyed in a series of complex photochemical reactions involving naturally occurring oxygen and nitrogen oxides which results in zero net production. The natural background concentration of ozone found at ground level is due to migration of ozone from the upper atmosphere.

The source of the increased level of ozone seen in modern times is widely believed to stem from a series of photochemical reactions between nitrogen oxides and a group of compounds collectively known as volatile organic compounds (VOCs)[2].

It was estimated that man-made non-methane VOC emissions in Europe totalled some ten million tonnes in 1985 of which 53% originated from transport, principally road transport, and 34% from the use of organic solvents[4]. As the pollutants can travel great distances before reacting to form ozone, the source of the emissions can often be an urban or factory site in another country. It was, for example, estimated that in 1992 up to 40% of peak level ozone in the United Kingdom was due to pollutants of continental origin[2].

The nature of the problem required inter-governmental co-operation. In November 1991 the United Kingdom government signed the United Nations Economic Commission for Europe Convention on Long Range Transboundary Air Pollution which stipulates a reduction in the 1988 level of VOC emissions of 30% by 1999[1].

The need to meet these stringent emission levels placed new demands on industry, not least in the sector of paints and coatings.

1.2 Paints, coatings and volatile organic compounds

All objects suffer degradation at the surface; be it by oxidation from air, the results of ultra-violet radiation from the sun, moisture from the rain or abrasion or scratches from daily wear. By applying a surface coating, damage can be minimised. In addition coatings can be used in a decorative format. Thus the twin roles of surface coatings are to protect an object and to decorate it[5].

Surface coatings come in many forms such as paper, plastic and metal. Paint is considered the most versatile form as it can be applied to any material possessing any shape by a variety of methods[6]. Paint usually has three main components, namely pigment, resin and solvent.

Pigments come in the form of fine solid particles that are insoluble in the liquid phase of the paint. They can be either inorganic or organic in nature. Examples of the former include titanium dioxide, the iron oxides and carbon black, whilst for the latter the most important pigments are based on the chemistry of the azo group[6]. Their role is generally to provide colour and mechanical strength to the paint. Titanium dioxide has the added role of absorbing harmful ultra-violet radiation which leads to improved paint durability. Certain pigments such as zinc phosphate or zinc chromate have specialised roles as they impart enhanced resistance to corrosion of iron-based substrates.

Resins are responsible for forming the film and can be conveniently divided into two groups: thermoplastic and thermosetting. Thermoplastic resins are those that on heating start to flow more easily whilst remaining as a collection of individual molecules. Thermoset resins react chemically, on heating, forming a network of molecules cross-linked together. Once reacted, the resin cannot, unlike the thermoplastic resins, be softened again on heating. Classes of resin include acrylics, polyurethanes and silicones which can be designed to be either thermoplastic or thermosetting. Alkyd resins, however, tend to react by an oxidative mechanism at room temperature.

The role of the solvent is two-fold. Firstly it acts as the carrier of the resin and pigment allowing the paint to be applied to a surface. Secondly it permits control of the application conditions through adjustment of the paint viscosity and the rate of evaporation of the solvent that leads to film formation. Common organic solvents used in paints include the aliphatic hydrocarbons, the aromatic hydrocarbons, and a variety of ketones and esters.

In addition to the three main constituents described in the previous paragraphs, a variety of additives are included in typical paint formulations each fulfilling a particular function. Their roles may include adjusting the degree of gloss, improving the wettability of the paint on a particular substrate, controlling the paint rheology, or improving the rate of crosslinking for a resin such as an alkyd.

The environmental challenge for the paint industry is to reduce the use of organic solvents which in a typical solvent-borne paint can comprise more than 50% of the total weight. This has spurred the development of a raft of new technologies.

1.3 New technologies in the paint industry

Efforts by the paint industry to develop paints with reduced organic solvent content have been directed into four distinct areas. These are:

a) Waterborne coatings
b) Powder coatings
c) Radiation curable coatings
d) High solids coatings

The term 'coatings' has been used as the products associated with these particular technologies are distinct from the traditional concept of a paint containing pigment, resin and organic solvent and may involve different techniques of application. All of these alternative technologies have obvious advantages as well as disadvantages[4, 7].

1.3.1 Waterborne coatings

Use of water as an alternative 'solvent' to the traditional organic solvents brings instant cost advantages in the form of lower material costs and, given the lower fire risks, reductions in insurance premiums. Water is also inherently non-toxic and allows application of coatings using conventional techniques such as spraying.

The drawbacks are numerous. The high latent heat of water means that the stoving costs for a waterborne coating are about double those of an equivalent solvent-borne version. The range of application conditions is severely limited due to a dependence on atmospheric temperature and humidity. The high surface tension of water often leads to surface wetting problems with certain substrates such as plastics. Process plant must be made of materials resistant to corrosion, such as stainless steel, which increases capital costs. Microbial susceptibility poses a greater problem than for solvent-borne paints.

Many of the problems associated with waterborne coatings can be controlled with the use of additives. These include organic co-solvents used to assist film formation, biocides to render the coatings less susceptible to microbial degradation and pH regulators to reduce the rate of corrosion of reactors and storage vessels. Many of these materials can be classified as volatile organic compounds and some are considered even more toxic than typical organic solvents[8]. Thus, although use of waterborne coatings leads to a large reduction in the use of organic solvents, they can still, at the present time, contain a sizeable fraction of volatile organic compounds.

1.3.2 Powder coatings

Powder coatings are, by their very nature, solventless. They are prepared by blending the resin, pigments and additives, heating and extruding the mixture and finally grinding the product into a fine powder[4]. The powder can then be applied with an electrostatic gun. The transfer efficiency is very high with only about 30% by weight of the powder being lost on application. With an efficient recovery system, up to 97% by weight of the coating is used. This compares very favourably with conventional solvent-borne coatings where the transfer rate is only 25% by weight. On heating, the powder coating flows out to form a homogeneous film.

At present, powder coatings are only applied to metal substrates, though research is underway to extend this to fibreboard and plastics[7]. In addition, the mode of application can lead to the Faraday Cage effect which limits the range of shapes that can be coated. Thus shapes possessing deep recessed areas are not suitable. Film thicknesses of less than about 30 μm are difficult to obtain with satisfactory optical quality and film integrity. Colour matching also presents problems as the pigment is incorporated into the binder during the manufacturing process. Attempts to tint the powder will normally result in a film with a speckled appearance as the powder has only a limited ability to flow. Finally, cleaning the spray equipment is difficult and time consuming, particularly if the spray booth has a recovery system in use, and hence multiple colour changes are to be avoided.

1.3.3 Radiation curable coatings

These coatings are 'cured' with ultra-violet or electron beam radiation. The curing mechanism is polymerisation initiated either by a free radical or a cationic species. A typical formulation would comprise monomer and oligomer, a photoinitiator and optionally a dye or pigment. As the speed of cure is extremely fast, being in the order of seconds, these coatings have found wide-spread use in the printing industry. There is also considerable energy as well as space saving when using ultra-violet lamps in place of conventional ovens.

A major drawback is the poor exterior durability shown by these coatings. In addition, thick or heavily pigmented films are difficult to cure using ultra-violet radiation. Electron beam radiation can be used but is much more expensive both in capital and running costs. At present, only flat stock can be cured as the substrate must be in direct line-of-sight of the radiation source. Finally, the monomers have a tendency to sensitise workers if repeatedly in contact with the skin and lungs[4].

Although radiation curable coatings contain in principle zero per cent volatile organic compounds, some of the photoinitiators react to yield volatile degradation fragments. In addition, some photoinitiator packages require the use of volatile amines. The vapour pressure of the monomers must also be considered as contributing to the overall volatile organic content of these coatings.

1.3.4 High solids coatings

The definition of what constitutes a high solids coating varies, but generally the non-volatile fraction must be greater than 75% by volume. This brings with it certain advantages. High film thicknesses can be applied with fewer coats. Stoving costs are considerably reduced as there is less solvent to be removed from the applied films. Furthermore the application equipment needs little adaptation to deal with the higher viscosities generally encountered with this type of coating.

The problem of controlling the viscosity as the volume fraction of the resin increases can be addressed by the use as the binder of low molecular weight resins. However this often leads to poor film performance. One alternative has been to use non-volatile reactive solvents such as caprolactone polyols, glycidyl esters or acetoacetate derivatives[7]. Another route, which at present is only available to poly(vinyl chloride), is by way of the plastisol.

1.4 Plastisols

A plastisol comprises a dispersion of polymer, generally poly(vinyl chloride) produced by aqueous emulsion or suspension polymerisation processes, that is subsequently dried and redispersed in an essentially non-volatile diluent plasticiser such as di(2-ethylhexyl) phthalate. The rheology, or flow behaviour, of plastisols ranges in behaviour from fluid mixtures to heavy pastes which allows for a very wide range of applications. Once applied to the substrate, the application of heat renders the polymer soluble in the plasticiser forming a homogeneous solution which on cooling forms a dry flexible film.

Work on vinyl plastisols began in Germany at I.G. Farben as early as 1931 with commercial production following in 1938 [9]. Use was confined to the coating of fabrics and the production of sheet for shoe soles. The market for industrial coatings in Europe in 1991 was approximately 2.6 million tonnes of which the coating of steel strip, a process known as coil coating, accounted for 110 000 tonnes[4]. Plastisol coatings, which comprised 17% of the coil coating market in Europe in 1991, came second only to polyesters in market share[4].

A major drawback of using vinyl plastisols is the poor exterior durability shown by poly(vinyl chloride). This limits the applications of plastisols to those market segments where long-life is not a priority or where the coated item is for indoor use only. There are also concerns over the toxic nature of vinyl chloride monomer and possible emissions of toxic polychlorinated dibenzodioxins and dibenzofurans produced on incineration of poly(vinyl chloride)[10]. Manufacturers and users of conventional plastisols are now searching for alternative polymers.

Acrylic polymers are well known for their exterior durability and superior colour retention and do not pose as many problems in disposal, so the development of an acrylic plastisol should solve the problems inherent in using poly(vinyl chloride). A consequence of the improved exterior durability would be the extension of plastisol technology to the thin film market. At present, poly(vinyl chloride) plastisols are applied as thick films, normally several tens or even hundreds of microns thick, in order to extend their service lives.

Acrylic polymers dispersed in plasticiser do not, however, show the same degree of stability as poly(vinyl chloride) and increases in viscosity leading to eventual gelation occur easily and quickly. It is thought that the stability of poly(vinyl chloride) is due to the presence of microcrystalline domains within the particle structure which prevents excessive swelling of the polymer by the plasticiser[11]. On heating, these weak cross-links break down and the plastisol fuses. Acrylic polymers are, however, amorphous and are therefore unable to resist the solvating action of the plasticiser at room temperature.

This thesis describes the work conducted at the Paint Research Association on determining the technical feasibility of producing a commercial acrylic plastisol for application at coating thicknesses of 25-50 µm. This was to be achieved by limiting particle swelling through the incorporation of thermally reversible associations, covalent cross-linking or a combination of both mimicking the microcrystallinity of poly(vinyl chloride). Monodisperse polymer dispersions were to be prepared using both conventional emulsion as well as the less widely used non-aqueous dispersion polymerisation techniques. The work was supported by a group of industrial sponsors and by the Department of the Environment under the former Environmental Protection Technology scheme.

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CHAPTER 2-

ACRYLIC PLASTISOLS

Acrylic plastisols are dispersions of dried acrylic polymer, normally produced using aqueous suspension or emulsion polymerisation techniques, in plasticiser. On heating, the polymer dissolves in the plasticiser to form a homogeneous solution that on cooling forms a dry flexible material. Although it would be much easier to prepare the polymer directly in the plasticiser, the polymer would be soluble at the polymerisation temperature.

Mention of an acrylic plastisol was made as early as 1967[1]. It was based on poly(methyl methacrylate) prepared using a non-aqueous dispersion polymerisation technique. Numerous applications for acrylic plastisols have since been proposed and include use as an automotive undersealant, a noise damping coating, a fire retardant coating, a medical adhesive, a lining for thermoplastic closures, a printing ink, and as can and coil coatings[2, 3, 4, 5, 6, 7, 8, 9].

Commercialisation of acrylic plastisols has, however, met with only limited success due to the problem of premature gelation mentioned in Section 1.4. The only example of a commercially available acrylic polymer claimed to be suitable for formulation as a plastisol is offered by Röhm GmbH[10]. It is described in the company literature as being based on poly(alkyl methacrylates) for use in damping coatings, spot welding compounds, floor coatings and films. Member companies of the Paint Research Association have suggested that, from experience, this product cannot provide the basis for an industrial top-coat.

The literature on acrylic plastisols is mainly concerned with finding ways of improving their inherent instability. The following survey is divided into two main parts. The first part deals with the rheology of non-reactive, or thermoplastic, plastisols where the dispersed polymer phase is simply dissolved by the plasticiser diluent on application of heat. The second part is concerned with the rheology of reactive, or thermosetting, plastisols where not only is the disperse phase polymer dissolved by the plasticiser diluent, but there is also a chemical reaction between, for example, the polymer and the plasticiser. Non-reactive plastisols traditionally give soft coatings. However reactive plastisols, which contain active chemical groups, give much harder films due to the cross-linking reaction that takes place on the application of heat. Unless stated otherwise, all the disperse phase polymers mentioned in this chapter are produced by emulsion polymerisation.

2.1 The rheology of non-reactive plastisols

The rheology and stability of non-reactive, or thermoplastic, acrylic plastisols is dependent on many factors. Research has been focused on four areas in particular:

a) Plasticiser solvent power
b) Polymer particle size and distribution
c) Polymer particle morphology
d) Thermally reversible cross-links within the polymer particles.

2.1.1 Plasticiser solvent power

The solvent power of the plasticiser for the dispersed polymer can have a dramatic effect on the dispersion rheology. It is thought that increasing the solvent power of the plasticiser leads to partial swelling of the polymer surface[11, 12, 13]. The swollen surfaces then act to sterically stabilise the particles against their natural tendency to aggregate.

A change in solvent power can be brought about in several ways. By a careful choice of suitable polymer-plasticiser pairs, the affinity of the plasticiser for the polymer can be increased[11, 12, 14]. The temperature can be raised, increasing the plasticiser solvent power[12, 13]. Adulteration of the plasticiser with up to 10% by weight of a suitable organic solvent also has a similar effect[15]. The solvent, if sufficiently volatile, may sometimes be removed before application of the plastisol after only a relatively short period of time[16].

It is also reported that addition of a dissolved polymer into the plasticiser phase in combination with a suitable organic solvent can have a beneficial effect on the plastisol rheology[17]. The effect may originate from bridging interactions between adjacent polymer particles through the polymer chain.

2.1.2 Particle size and distribution

It has been observed that the swelling of dispersed particles in a strongly solvating plasticiser increases as the particle size decreases[18, 19]. Furthermore, if the polymer particles are too small, the plastisol can gel prematurely[19]. The reason for this dependence on particle size may be explained by the corresponding increase in the surface to volume ratio with decrease in particle diameter.

The blending of differing particle sizes is often used as a tool to tailor the rheology of a dispersion to a particular application. The shear thinning behaviour of some bimodal dispersions can be explained from the changes to the particle distribution[20]. At rest the heavier particles sediment under gravitational forces; however under shear the particles redistribute to give the optimum packing arrangement. Blending of dispersions of disparate particle size also allows increases in the volume concentration. By careful choice of the particle sizes, it is found that the smaller particles are able to fill the free volume created at the interstices of the larger particles. Tetramodal distributions of spherical particles can have volume packing fractions as high as 95% [20].

Blends of acrylic polymers prepared by suspension and emulsion polymerisation techniques have been proposed as suitable for replacing poly(vinyl chloride) in floor coverings[21, 22, 23]. The diameters of suspension and emulsion polymer aggregates are

50-200 μm and 5-100 μm respectively. The ratio of suspension to emulsion polymer ranges from 90:10 to 30:70 by weight. Typically 5-20 parts by weight of plasticiser are mixed with 10 parts by weight of polymer.

2.1.3 Particle morphology

It has been claimed that a core-shell particle morphology can provide a route to acrylic plastisols with improved stability[24, 25, 26]. The particles comprise a core material compatible with the plasticiser and a shell material incompatible with the plasticiser. The shell is able to provide protection to the core against solvation by the plasticiser at room temperature, but allows complete film formation at elevated temperatures. The particles are produced using a step-wise emulsion polymerisation technique. Table (2.1) compares the performance of a polymer with a core-shell morphology against more conventional polymers when dispersed in di(2-ethylhexyl) phthalate[24].

Table (2.1) Plastisols comprising 2 parts (wt) polymer and 3 parts (wt) di(2-ethylhexyl) phthalate heated at 150°C for 30 minutes[24].

Polymer type	Polymer composition[a]	Storage stability at 30°C (days)[b]	Compatibility[c]
Copolymer with core-shell morphology[d]	Core: 30/70 BA:MMA Shell: Poly(MMA)	>21	Compatible
Random copolymer	Copolymer 30/70 BA:MMA	0	Compatible
Homopolymer	Poly(MMA)	>21	Incompatible
Mixture of polymers	Mixture poly(MMA) + copolymer 30/70 BA:MMA	0	Compatible
Random copolymer	Copolymer 15/85 BA:MMA	5	Incompatible

[a] MMA methyl methacrylate

BA butyl acrylate

[b] Compositions are judged to be stable if the viscosity does not exceed 1000 Poise after storage at 30°C for three weeks

[c] Compatibility is tested by coating steel panels to a thickness of 5mm and heating the plastisol for 30 minutes at 100°C or 10 minutes at 180°C. If no exudation of plasticiser is visible after 7 days, the composition is deemed compatible

[d] Weight ratio of core to shell is 1:1

The results, summarised in Table (2.1), show that only the copolymer with the core-shell morphology is able to provide the proper balance between compatibility and storage stability.

Table (2.2) The effect of the time of addition of vinyl imidazole during emulsion polymerisations on ultimate plastisol shelf-life[25].

Polymer composition (% weight)	1	2	3	4
Methyl methacrylate	87.5	87.5	86.2	86.2
Butyl methacrylate	12.0	12.0	11.8	11.8
Vinyl imidazole	0.5	0.5	2.0	2.0
Feed time (hours)	3	3	3	3
Time to addition of vinyl imidazole (hours)	2	0	2	0
Plastisol composition (parts by weight)				
Dried polymer	20	20	20	20
Adipic acid polyester	-	-	30	30
Di-(2-ethylhexyl) phthalate	30	30	-	-
Trimethylolpropane trimethacrylate	-	-	5	5
Dicumyl peroxide	-	-	0.25	0.25
Chalk	-	-	45	45
Time to gel at room temperature (weeks)	2	1	1	0

It has been observed that copolymerisation involving nitrogen containing monomers often leads to improvements in the adhesion of coatings to difficult substrates[27]. The timing of the addition of the adhesion promoting monomer during the polymerisation process may also influence the final shelf-life of the plastisol[28, 27].

In Table (2.2), it can be seen that plastisol stability is noticeably improved on delaying the addition of vinyl imidazole to the final third of the feed[25]. In the case of a methyl methacrylate - butyl methacrylate copolymer containing 0.5% by weight vinyl imidazole, the shelf-life is doubled from one week to two. Other adhesion promoting monomers include N-vinyl-2-methyl imidazoline, dimethyl amino ethyl methacrylate and morpholino ethyl methacrylate.

2.1.4 Cross-linking

The stability of vinyl plastisols has, as has been explained in Section 1.4, been attributed to the presence of microcrystalline domains within the dispersed polymer particles[28]. It should thus be possible, by analogy, to improve the inherent instability of acrylic plastisols by designing polymers with transient or indeed some permanent cross-links.

Gels are the result of the formation of a three dimensional structure within the liquid. In the following two examples, the structure is held together through weak dipole-dipole interactions. Poly(acrylonitrile) in dimethylformamide is a thermally reversible gel[29]. The gel dissolves into a fluid on heating, but is able to reform on cooling. Equally, the reverse phenomenon may be seen as with poly(vinyl alcohol) in dimethylformamide[29]. In this case, gelation occurs on warming. Thus copolymerisation of suitable polar monomers may be a route to improving the stability of acrylic plastisols.

2.1.4.1 Copolymers containing acid and basic groups

A plastisol prepared from a 90:10 (wt) methyl methacrylate - methacrylic acid copolymer is claimed to show superior stability[30]. The shelf-life at 55°C of a plastisol comprising 100 parts by weight of this copolymer dispersed in 75 parts by weight di(2-ethylhexyl) phthalate and 25 parts by weight adiponitrile is 80 minutes. Likewise, copolymerisation of up to 10% by weight of an adhesion promoting monomer such as itaconic acid also leads to stable plastisols[31]. Thus a plastisol comprising 20 parts by weight of a 98:2 methyl methacrylate - itaconic acid copolymer dispersed in a mixture of benzyl octyl phthalate and chalk of weight ratio 30/50 increases in viscosity by only a factor of 3.5 over a three week period when stored at 30°C.

Further improvements to stability can be obtained by neutralising acid group containing polymers prior to dispersion into the plasticiser[32]. In one example, a pre-dried 95:5 (wt) methyl methacrylate - methacrylic acid copolymer, prepared by emulsion polymerisation, is held at room temperature for 24 hours over concentrated ammonium hydroxide. The polymer is then dried for 24 hours at room temperature over sodium hydroxide pellets. The enhanced stability may be due to the increased degree of polarisation of the ammonium salt over the undissociated acid. This would lead to dipole-dipole interactions between neighbouring groups in much the same way that two carboxylic acids can associate to form a dimer.

Neutralisation may also be carried out using a protective colloid or emulsifier containing chemical groups of an acidic or basic nature[33]. The polymer is required to have an acid or base number of greater than five. Shelf-lives of more than three days have been claimed. Suitable emulsifiers for acid group containing polymers are poly(amide-amines), poly(aminoimidazolines), poly(ether urethane-amines), poly(ethyleneimines) and stearylamine. Those for the basic group containing polymers include poly(acrylic acid), copolymers of acrylates or methacrylates containing acrylic or methacrylic acid, and stearic acid.

2.1.4.2 Copolymers containing metals

Improvements to plastisol stability are also seen on adding magnesium sulphate or zinc acetate to polymers, prepared by emulsion polymerisation, prior to or after isolation from the aqueous phase[34]. Although not explicitly stated in the literature, it must be assumed that the polymers contain acid groups or are esters. The enhanced stability can then be explained in terms of either neutralisation of the acid groups leading to ion pair formation or hydrolysis of the ester and subsequent ion pair formation[35]. Aggregation of ion pairs, into structures known as multiplets or even larger structures known as clusters, can take place[36].

The use of metal cations has been extended to include the effect of potassium hydroxide and aluminium hydroxide on a 82:15:3 (wt) methyl methacrylate - butadiene - methacrylic acid terpolymer prepared by emulsion polymerisation[37]. The cation source is added to the polymer dispersion before spray drying. The cross-linking reaction for mono- or divalent cations can be carried out at room temperature within a few minutes, however the trivalent ions require prolonged elevated temperatures. The physical properties of plastisols prepared from equal parts of the terpolymer and di(2-ethylhexyl) phthalate are summarised in Table (2.3).

The plastisols prepared from polymer neutralised with the metal cations all show significant improvements in stability. This does not appear to be a function of the valency of the metal. The water resistance also appears to be enhanced. Neutralisation with ammonium hydroxide is, however, not as effective. Only a minor improvement to plastisol stability is seen and the water resistance remains unchanged. Exudation of plasticiser does not occur to any great extent in any of the test specimens.

Table (2.3) The effect of neutralisation with metal cations of a 82:15:3 (wt) methyl methacrylate - butadiene - methacrylic acid terpolymer on plastisol stability[a]. Test panels are prepared by coating glass panels to 0.3mm and heating at 140°C for 20 minutes[37].

Composition (parts by weight)	1	2	3	4	5
MMA	82	82	82	82	82
Butadiene	15	15	15	15	15
MAA	3	3	3	3	3
KOH	2.0	-	-	-	-
Zinc acetate	-	6.4	-	-	-
$Al(OH)_3$	-	-	2.8	-	-
NH_4OH	-	-	-	1.3	-
Di-2-ethylhexyl phthalate	100	100	100	100	100
Initial viscosity (Poise)	178	193	175	371	168
14 days viscosity (40°C) / initial viscosity	1.4	1.3	1.3	5.0	5.3
Bleeding[b]	none	none	slight	none	none
Water resistance[c]	good	good	good	poor	poor

[a] > 99.9% by weight neutralisation

[b] Bleeding of coatings are evaluated visually after 30 days at 25°C and 60% relative humidity

[c] Water resistance is tested by dipping test panels into water at 23°C for 24 hours and visually inspecting them for signs of deterioration

Polyamino species are an alternative to metal cations[38]. Neutralisation of the polymer may be carried out prior to, during or after mixing with plasticiser. Two methods of addition are proposed if neutralisation takes place in the plasticiser. Either the reaction is allowed to take place at a low temperature after which the temperature is raised to ambient temperature. Alternatively the reaction can initially take place in the presence of a weakly gelling plasticiser before addition of the more strongly gelling plasticisers required for good compatibility. The polymers may be prepared using either emulsion or suspension polymerisation techniques. Table (2.4) shows comparative performances of plastisols prepared using a 42:40:15:3 (wt) styrene - acrylonitrile - butyl acrylate - acrylic acid emulsion copolymer neutralised with a range of metal cations and a diamine.

Table (2.4) Plastisols prepared from a 42:40:15:3 styrene - acrylonitrile - butyl acrylate - acrylic acid copolymer neutralised with a range of metal cations and a diamine[a] [38].

Basic compound	Shelf-life at 23°C (days)[b]
-	7
Zinc-(dimethyldithio)carbamate	21
Aluminium isopropoxide	30
Aluminium acetylacetonate	30
Magnesium ethoxide	30
Isophorodiamine	30
Zinc oxide	90

[a] Neutralisation is carried out by addition of 2g of metal cations or diamine to a dispersion of 40g of copolymer in 60g of butylbenzyl phthalate

[b] The plastisols are stored for eight days at 8°C and thereafter at 23°C. The time taken in days is measured for the initially fluid plastisols to become highly viscous

Disks prepared from the plastisols by heating the compositions at 100°C and 120°C for 20 minutes show increased hardness and strength. Applications include sealants for bottle covers, sound deadening coatings and sealants for cars, molded articles and synthetic leather.

It has been found advantageous to graft unsaturated carboxylic acids onto polymer particles which are then neutralised[39]. A recipe for the preparation of a typical graft copolymer is given in Box (2.1).

The viscosity of a plastisol comprising equal quantities of the dried polymer and tricresyl phosphate is 31 Poise. After seven days storage at 40°C, the viscosity remains unchanged. A similar ungrafted copolymer gels after only four days storage.

Box (2.1) Preparation of graft copolymer for plastisol compositions showing improved stability

The following ingredients, given in parts by weight, are heated together at 82°C for three hours:

Methyl methacrylate	100 parts
Distilled water	200 parts
Azobisisobutyronitrile	1.3 parts
Poly(sodium acrylate)	2 parts
Disodium hydrogen phosphate	6 parts

Addition of a solution comprising 2 parts methacrylic acid and 0.05 parts potassium persulphate is then made and heating continued for a further hour. On cooling, the dispersion is neutralised with barium hydroxide and filtered to yield 82 parts by weight of a graft copolymer of particle diameter 40μm.

2.1.4.3 Covalent cross-linking

Although introducing a degree of covalent cross-linking within polymer particles has not yet been considered as a route to stable acrylic plastisols, it has, however, been proposed as a means of improving the mechanical film properties, such as the hardness[40]. This can be achieved by reacting functional groups on the acrylic backbone such as hydroxyl, epoxide or vinyl with appropriate cross-linkers such as polyisocyanates, melamine resins or polyamines.

2.2 The rheology of reactive plastisols

The predominant routes to imparting reactivity, or thermosetting properties, to plastisols have been through introducing either (meth)acrylate, isocyanate or epoxy groups into the plasticiser. The plasticiser subsequently reacts with other suitable groups in the plasticiser phase or with groups copolymerised into the dispersed polymer.

2.2.1 Acrylate chemistry

The introduction of multifunctional (meth)acrylates and a suitable photoinitiator into the liquid phase of a plastisol allows the product to be cured photochemically[16, 32]. Suitable monomers include trimethylol propane triacrylate and trimethacrylate. In general, monomers possessing an ether linkage are to be avoided as they have a detrimental effect on overall plastisol stability. This may be due to their increased solvent power for the polymer. The tendency of ethers to form peroxides which could prematurely polymerise the remaining monomer may also be an explanation.

An alternative route to reactive plastisols is by using polymeric plasticisers containing (meth)acrylate terminal groups[41]. In Table (2.5) are examples of plastisols prepared by dispersing 25% by weight of poly(methyl methacrylate) in such a polymeric plasticiser. The plasticiser is the reaction product of one mole of a polyethylene glycol, two moles of a diisocyanate and two moles of 2-hydroxyethyl methacrylate. Shelf-lives in excess of five days at 40°C are obtained. The plastisols are cured by heating at 120°C for a few minutes.

Similar plastisols prepared using conventional plasticisers such as tricresyl phosphate, butyl benzyl phthalate and various chlorinated paraffins either do not exhibit the necessary stability or compatibility. The improved stability obtained on using these polymeric plasticisers may be attributed to their higher viscosity which would decrease the rate of plasticisation. This effect would be particularly pronounced at lower temperatures.

Table (2.5) The compatibility and stability of plastisols comprising 25% by weight poly(methyl methacrylate) in a polymeric plasticiser. The plasticisers are the reaction products of one mole of a polypropylene glycol, two moles of a diisocyanate and two moles of 2-hydroxyethyl methacrylate[41].

Diisocyanate	Mw of polypropylene glycol	Compatibility[a]	Stability at 40°C (days)[b]
Toluene diisocyanate	1025	compatible	> 5
Toluene diisocyanate	725	compatible	3
Isonate 181[c]	1025	compatible	> 5

[a] Compatibility is evaluated by heating the plastisols at 120°C for five minutes, allowing them to stand for 24 hours at room temperature and visually inspecting the samples for plasticiser exudation

[b] Definition of stability not given

[c] Modified di-p-isocyanato diphenyl methane (Upjohn)

2.2.2 Isocyanate chemistry

A thermosetting plastisol satisfying the twin demands of adequate storage stability and good adhesion required for sealing spot welds is obtained on addition to a thermoplastic plastisol of up to 35% by weight of commercially obtainable blocked polyisocyanate precursors and polyamines[42]. Examples of blocked polyisocyanate precursors include Desmocap 11, Desmocap 1280 and Desmodur BL 1100 (Bayer). The polyamines which may be used include Laromin C 260, Laromin A 372 and Laromin C 252 (BASF). A typical thermoplastic plastisol could be a methyl methacrylate - butyl methacrylate copolymer in di-(2-ethylhexyl) phthalate. Curing takes place on heating the compositions at 170°C for twenty minutes.

Alternatively, the precursor can be prepared from one mole of a polyol such as those based on polytetramethylene oxide of molecular weight 400-2000, two moles of a disocyanate such as meta-tetramethyl xylene diisocyanate, and two moles of a blocking agent such as methyl ethyl ketoxime[43]. Cure is effected with a diamine. Examples include isophorone diamine and cyclohexyl diamine. Addition of up to 25% by weight of the isocyanate and amine to a typical thermoplastic plastisol produces a reactive plastisol that is storage stable for more than three days at 40°C or two months at 25°C. Addition of a suitable catalyst such as dibutyl tin dilaurate allows cure to take place at 120°C over twenty minutes. Similar results are obtained on substituting the amine curing agent with a polyol[44]. In this case, conventional plasticisers are not used and the isocyanate and polyol comprise up to 70% by weight of the plastisol.

Another route to a stable reactive plastisol involves dispersing a polymer containing active hydrogen atoms into a plasticiser containing blocked isocyanate groups[45]. A suitable polymer is a methyl methacrylate - methacrylic acid copolymer. The blocked isocyanates can be prepared in a similiar manner as described previously. Examples are given comprising up to 80% by weight reactive plasticiser. Similarly, dispersion of a copolymer containing heterocyclic groups into a plasticiser mixture containing epoxy resins, as a route to improved adhesion, also leads to a reactive plastisol[19].

2.2.3 Epoxy chemistry

A thermosetting plastisol composition, for use in container closures in particular, comprises an acrylic particle with a core-shell structure[46]. The core comprises predominantly meth(acrylic) esters and the shell, an acrylic resin with a functional group containing monomer. The functional group could be a carboxyl, a hydroxyl, a methylol or an etherified methylol group. The concentration ranges from 7 to 330 millimoles per 100g of polymer. The acrylic polymer is dispersed in a medium comprising a mixture of conventional plasticiser and a suitable cross-linking agent at an approximate ratio of 100 parts polymer to 100 parts dispersing medium. The cross-linking agent could be a liquid epoxy compound, a polyamine, a polyamideamine, or a methylolated or ether methylolated amino resin. In the examples cited, the particle size is 1.0-1.5 microns and the number average molecular weight over 1 000 000 poly(styrene) equivalent. The pot life is considered to have been exceeded once the viscosity reaches 1000 Poise. Pot lives in excess of 28 days are claimed.

2.3 Summary

The vast majority of the available literature referring to acrylic plastisols concerns attempts at improving their inherent instability. Some progress has been made. Introduction of a core-shell particle morphology has resulted in shelf-lives at 30°C of up to three weeks[24]. However compositions are only considered unstable once their viscosity has reached 1000 Poise or has multiplied by a factor of 3.5.

Reactive plastisols based on blocked isocyanate precursors are able to be stored for up to two months at 25°C[43, 44]. The isocyanate precursors, being mostly polymeric in nature, are quite viscous and the range of applications for the plastisols is limited. The use of metal ions to neutralise copolymers containing acid groups is perhaps the most successful method. Shelf-lives of up to three months at room temperature are obtained using zinc oxide[38]. Over this period, the plastisols increase in viscosity from a fluid to highly viscous. The method, however, relies on storing the plastisol, initially, at 8°C for a week.

Most of the references to acrylic plastisols come from patents and the examples cited must be regarded as unsubstantiated in the absense of a satisfactory commercial product.

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CHAPTER 3-
THEORY OF ACRYLIC PLASTISOLS

The instability of acrylic plastisols at room temperature, described in Section 1.4, is thought to be due to the excessive swelling of the disperse polymer phase by diluent plasticiser. This leads to increases in the plastisol viscosity until the point of gelation is reached. In order to initiate a study into practical ways of preventing the problem of premature gelation, an appreciation of some of the theoretical aspects of acrylic plastisols is required.

As stated in the introduction to Chapter 2, the disperse polymer phase is generally prepared using aqueous suspension or emulsion polymerisation techniques. In this work, polymers were, as stated in Section 1.4, prepared using aqueous emulsion and non-aqueous dispersion polymerisation. Therefore, the requirements regarding the preparation and stabilisation of polymer dispersions in water and non-aqueous solvents must be considered. In order to assess practical stability, models of the rheology or flow behaviour of the polymer dispersions in plasticiser must also be available. Models describing the relationship between the viscosity and the volume fraction of the dispersed polymer phase, in particular, are needed. Finally, given the problem of premature gelation experienced by acrylic plastisols, the nature and strength of the polymer-plasticiser interactions needs to be understood. Models must account, in agreement with the aims of the work set out in Section 1.4, for the presence of thermally labile or covalent crosslinks within the polymer particles.

3.1 Polymer dispersions in aqueous and non-aqueous media

The polymer dispersions prepared as part of this study were synthesised using emulsion and non-aqueous dispersion polymerisation techniques. The two types of dispersion are quite distinct both in their mechanism for stabilising the polymer particles and their method of preparation.

3.1.1 The stabilisation of polymer dispersions in aqueous and non-aqueous media

Unstabilised polymer particles of similar chemical nature aggregate due to an attractive force known as the London dispersion force [1, 2]. The origin of this force resides in the fluctuations in the electron density distribution around each atom or molecule. This produces a fluctuating dipole moment which polarises a dipole in a neighbouring atom or molecule which interacts with the first one. The force of attraction observed between non-polar molecules has been explained on these grounds and the attractive potential energy (infinite separation defining zero potential energy) is proportional to the inverse sixth power of the distance. If the two atoms or molecules are further than about 10 nm, then by the time the electric field from one dipole has reached and polarised another, the first atom will have changed [3]. The poor correlation between the two atoms or molecules leads to a retarded and hence weaker attractive force, the relationship with distance changing to an inverse seventh power.

Between two particles, the attractive potential energy can be calculated by summing the contributions for the interactions of every atom or molecule in one particle with each atom or molecule in the other particle. This technique is known as 'pair-wise additivity'. For two spheres of radius *a* separated by a surface to surface distance of *d*, the attractive potential energy V_A is,

$$V_A = \frac{-A}{6}\left(\frac{2}{S^2-4} + \frac{2}{S^2} + \ln\left\{\frac{S^2-4}{S^2}\right\}\right) \qquad \text{Equation (3.1)}$$

where $S = 2 + d/a$ and A is the Hamaker constant. If $d \ll a$, then,

$$V_A \cong \frac{-Aa}{12d} \qquad \text{Equation (3.2)}$$

The Hamaker constant was originally based on the assumption that the particles were in vacuum, however a modification can be made to the constant when considering two particles in a fluid. The London force of attraction for macrobodies is long-range compared to the short-range interactions at contact distances due to permanent dipoles (Keesom interaction) [4].

Particle stability can be achieved by the provision of a repulsive energy to offset the attractive energy between particles. There must be a net repulsive energy significantly greater than the energy due to Brownian motion which has an average translational energy of 3/2kT [3]. In aqueous media, this can be brought about by the provision of a repulsive electrostatic force through ionisation of surface groups or by specific ion adsorption.

3.1.1.1 Electrostatic stabilisation

A description of the repulsive forces generated electrostatically is given in the Deryaguin-Landau-Verwey-Overbeek (DLVO) theory [5, 6]. The model used comprises a charged surface adjacent to which are adsorbed counterions (see Figure (3.1)). The plane through the centre of the hydrated ions is known as the *Outer Helmholz Plane*. The plane through the centre of adsorbed dehydrated ions (specific adsorption) is known as the *Inner Helmholtz Plane*. The layer between the surface and the *Outer Helmholtz Plane* is called the inner or Stern layer. Beyond this layer is a diffuse or Gouy-Chapman layer. Together they are known as the electrical double-layer model.

The electric field strength (potential gradient) decreases to zero with distance from the charged surface due to screening of the charge by intervening counterions. Thus there is a similar decrease to zero in the concentration of the counterions with distance. Ions with the same charge as that on the surface, known as coions, are repulsed from the surface. However their concentration increases as the force with which they are repulsed falls off with distance from the surface. The double layer, at equilibrium, is electrically neutral.

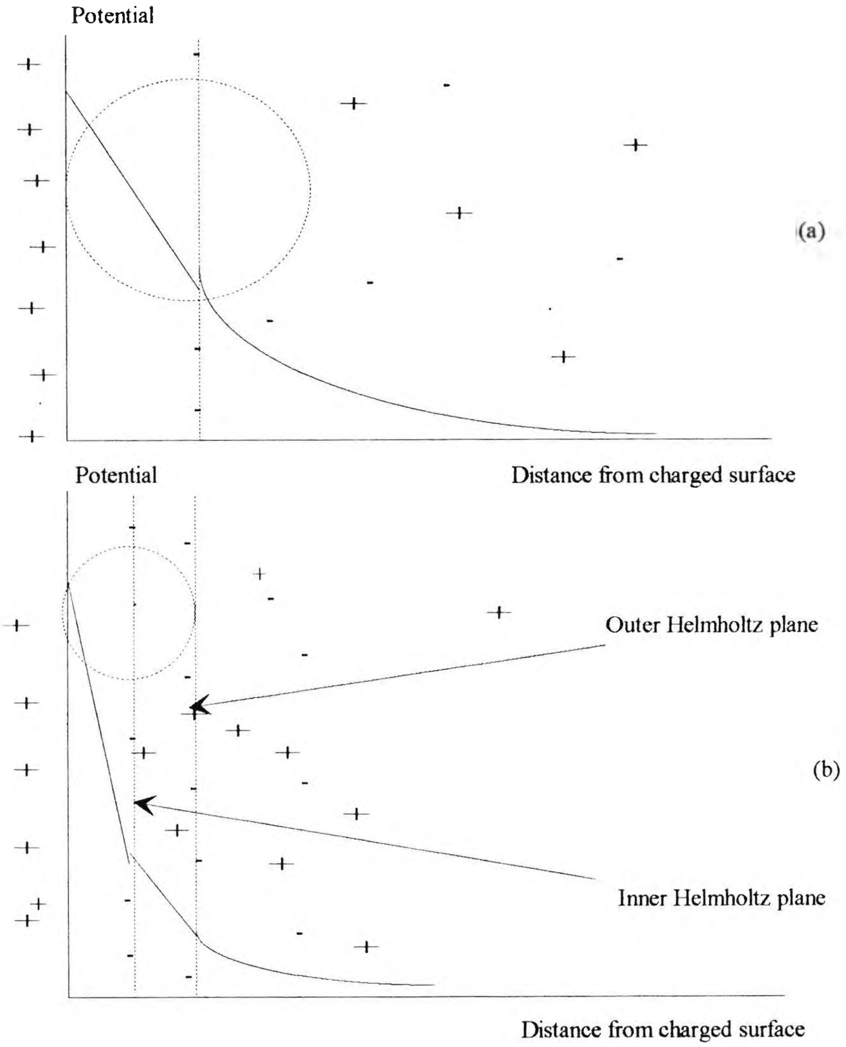

Figure (3.1) Schematic of double layer: (a) no specific adsorption; (b) some specific adsorption (adapted from a drawing in Lyklema, J. Colloidal Dispersions (Goodwin, J.W. (ed.)). Royal Society of Chemistry. London. 1982. Chapter 3, page 59).

The electrostatic force of repulsion between two charged stabilised particles is a consequence of the interaction of the two diffuse layers on close approach. A good approximation for the potential free energy of electrostatic repulsion V_R for two particles of radius a at a centre-to-centre distance of R treating the ions as volumeless point charges is,

$$V_R = 2\pi\varepsilon_r\varepsilon_0 a\left[\frac{4RT}{zF}\gamma\right]^2 \ln[1 + \exp(-\kappa H)] \qquad \text{Equation (3.3)}$$

where $\gamma = \tanh(zF\psi/4RT)$, $\kappa^2 = \dfrac{F^2 \sum c_i z_i}{\varepsilon_r \varepsilon_0 RT}$, $H = R - 2a$, ε_r is the relative permittivity of the medium, ε_0 is the permittivity of a vacuum, ψ is the potential at the particle surface, R is the gas constant, T is the absolute temperature, F is the Faraday constant, z is the charge number on the counterions and z_i and c_i are the charge numbers and concentrations of all the ions in solution [7]. As $\ln[1 + \exp(-\kappa H)]$ can be approximated by $\exp(-\kappa H)$, the potential free energy of electrostatic repulsion decays exponentially with distance from the particle surface. At a distance of $1/\kappa$, defined as the *thickness of the double layer,* the repulsive energy has dropped by a factor of 1/e [8].

Addition of the potential free energies of attraction and repulsion shows the dependence of the free energy as a function of the particle separation. This is represented graphically in Figure (3.2).

As the particles come together, a slight attractive force can sometimes be observed which is known as a secondary minimum. If the energy well is shallow, reversible flocculation may be observed where Brownian motion is able to disrupt the formation of particle clusters at the same rate as they are being formed. On closer approach, a large energy barrier is reached beyond which there is a large energy well known as the primary minimum. At this point, coagulation takes place. Thus, electrostatically stabilised particles are only thermodynamically metastable. The energy barrier can be reduced to the point where there is spontaneous coagulation by addition of suitable amounts of electrolyte [3]. Not shown in Figure (3.2), for reasons of clarity, is the force due to the interaction of the electron clouds around the atomic nuclei themselves which gives rise to a repulsive force on very close approach of the particles [9].

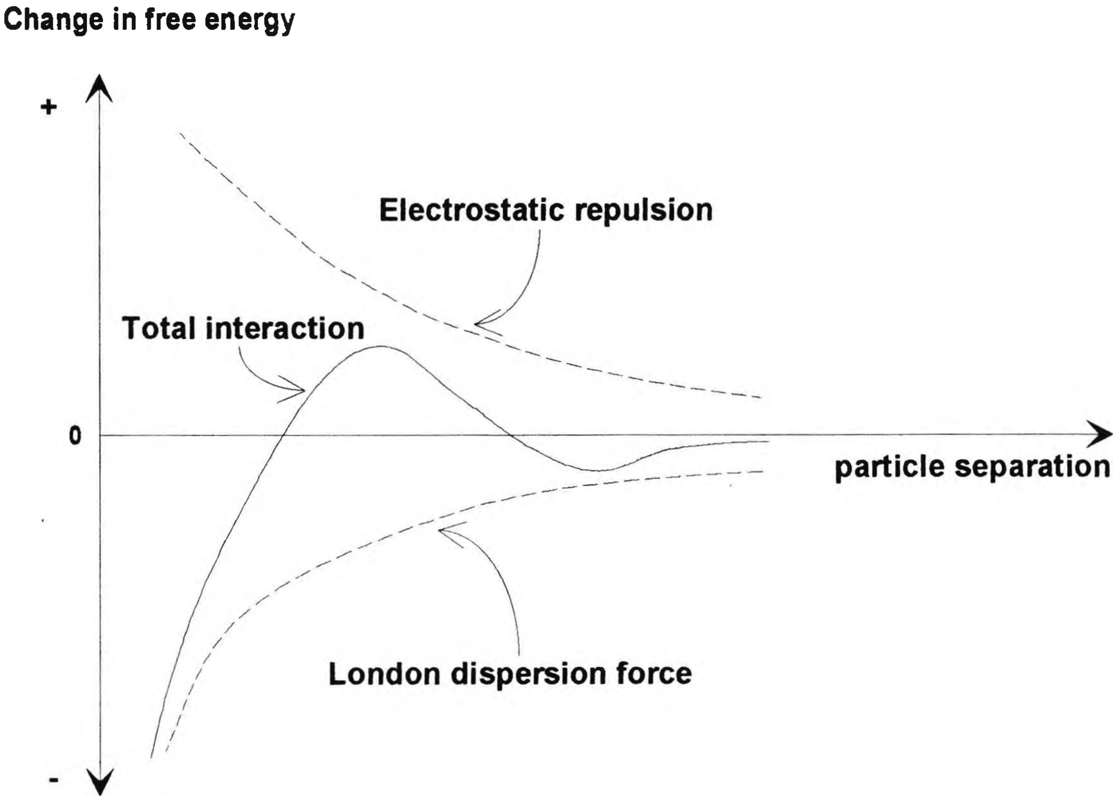

Figure (3.2) Typical change in free energy - distance of separation curve for electrostatic stabilisation.

Electrostatic stabilisation is not, however, as effective in non-aqueous media of low polarity as Equation (3.3) shows that the repulsive energy is proportional to the dielectric constant of the medium. Furthermore, due to the low level of dissociation in media of low polarity, the surface charge and potential is much reduced. As there is little screening of the surface charge, the repulsion energy-distance profile is very flat and concentrated dispersions (small interparticle distances) cannot be stabilised by charge [3]. However, it can be a source of colloidal stabilisation for very dilute dispersions. An alternative source of repulsive energy is generated through the physical interaction of opposing dissolved polymer chains attached to the particles. This form of stabilisation which can be used in aqueous and non-aqueous including non-polar media is known as steric or entropic stabilisation.

3.1.1.2 Steric stabilisation

The polymeric chains attached to the particle surface produce a solvated sheath of chain segments of thickness δ [3]. On approach of two such stabilised particles (see Figure (3.3)), the solvated sheaths overlap resulting in a localized increase in polymer concentration leading to an osmotic pressure from the solvent in the system (osmotic term). In addition, the number of possible configurations that the adsorbed polymer chains can adopt is reduced by the presence of the surface of the other particle (volume restriction term). The two terms can then be added together to give the total steric repulsion energy.

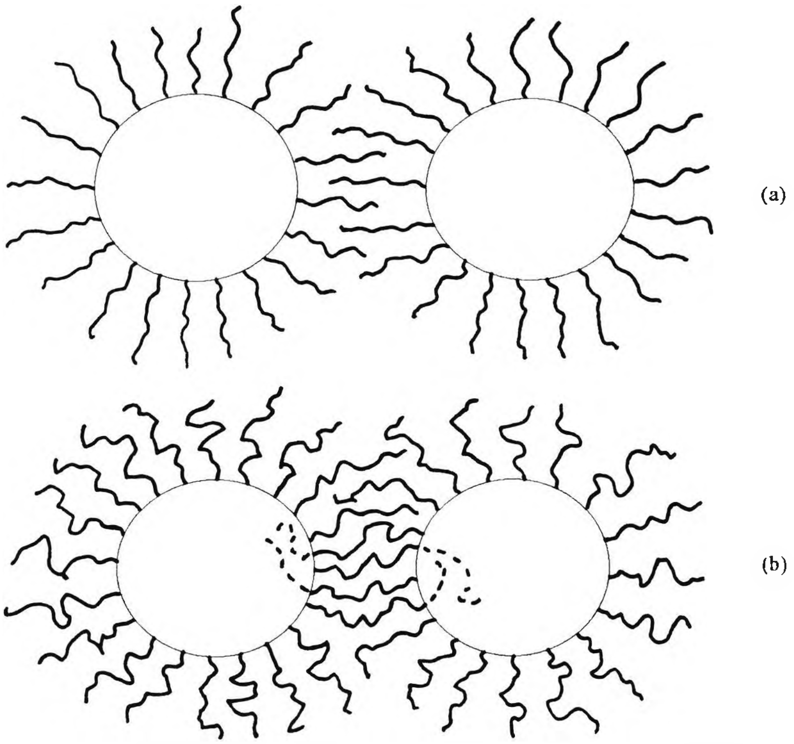

Figure (3.3) Schematic of two sterically stabilised particles: (a) osmotic factor due to high chain segment concentration between particles; (b) volume restriction factor due to exclusion of some chain conformations by presence of other particle (adapted from reference 7).

Calculation of the two terms involves application of a model for the polymer configuration in order to obtain a segment density distribution normal to the particle surface [10]. Most theories use the freely jointed chain which takes no account of the barriers to free rotation about bonds, details which determine the architecture of the molecule. The excluded volume must also be considered at a particle surface densely packed with polymer chains. Due to the use of such a primitive model for the chain configuration, these rather mathematically complex theories are not able to predict the actual chain dimensions but merely scale them to experimentally observed values.

A simpler approach is to start with the segment distribution function determined either experimentally or by assuming a mathematical form scaled to the measured barrier thickness. Nevertheless, neither approach yields a satisfactory quantitative theory of steric stabilisation.

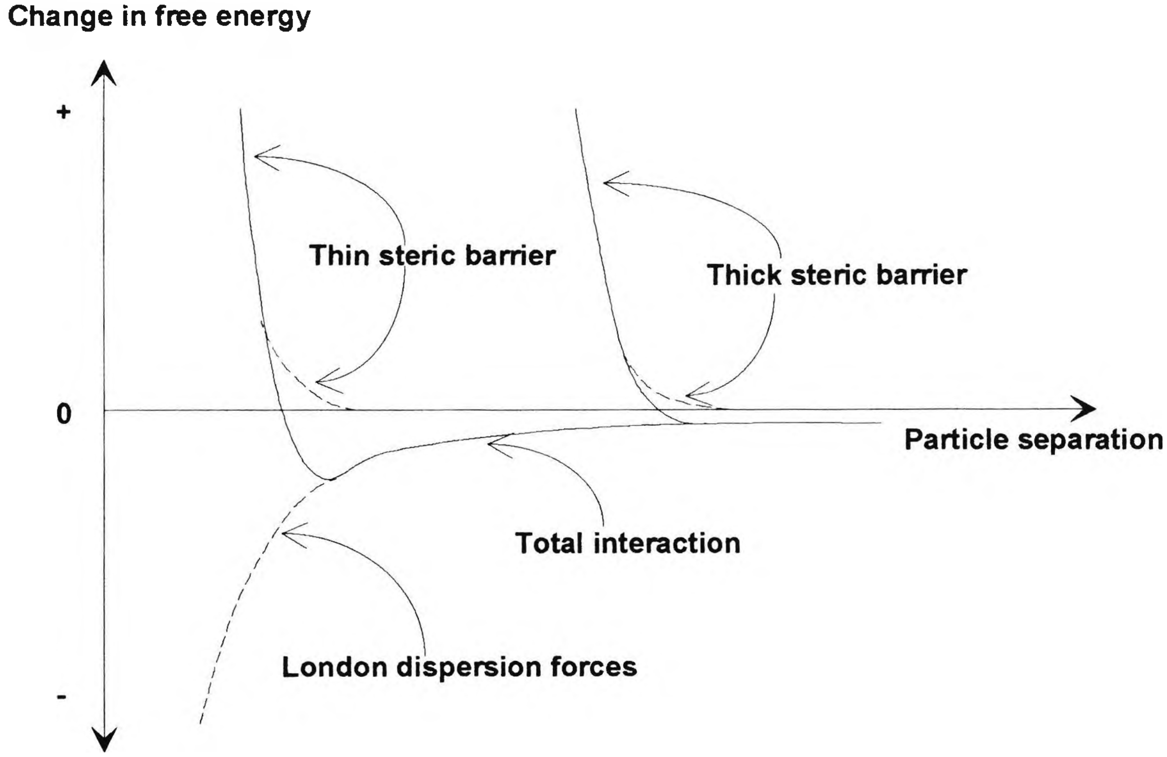

Figure (3.4) Typical change in free energy - distance of separation curve for steric stabilisation with both thin and thick barriers [11].

A typical free-distance curve for steric stabilisation is shown in Figure (3.4) for a thin and thick steric barrier [11]. Unlike electrostatically stabilised systems, the steric barrier is of a finite thickness beyond which the repulsive force falls to zero. For particles showing a high affinity for each other or possessing thin steric barriers, a slight attractive force or secondary minimum may be seen. Reversible flocculation may then be observed. Sterically stabilised particles show no primary minimum and so are thermodynamically stable. Flocculation can be induced by decreasing the solvency of the dispersion medium for the stabilising polymer [12]. This can be accomplished by raising or lowering the temperature or pressure or by careful addition of a non-solvent.

3.1.2 Aqueous emulsion and non-aqueous dispersion polymerisation

Aqueous emulsion and non-aqueous dispersion polymerisation both require the following components: monomer; diluent; stabilisers or surfactants; and initiator. A consideration of the role and requirements of the stabilisers, surfactants and initiators precedes descriptions of the mechanisms of aqueous emulsion and non-aqueous dispersion polymerisation.

3.1.2.1 Stabilisers, surfactants and initiators

Many polymers, including acrylics, are prepared by free radical addition polymerisation and require the presence of a free radical generating substance to initiate polymerisation. In both aqueous emulsion and non-aqueous dispersion polymerisation, the initiator is present in the diluent. Examples of common free radical initiators for aqueous emulsion polymerisation are ammonium or potassium persulphate. Examples for non-aqueous dispersion polymerisation include azobisisobutyronitrile and benzoyl peroxide. All generate radical fragments by a thermal dissociation mechanism.

As explained in Section 3.1.1, electrostatic stabilisation can be provided by ionisation of suitable surface groups or by the adsorption of specific ions to prevent coagulation of the polymer particles[8]. The latter method is frequently used for aqueous emulsion polymerisations. The specific ions are more commonly known as surfactants and possess a dual nature. One part of the molecule, comprising an aliphatic carbon chain, may be regarded as the anchor group which is adsorbed on the particle surface whilst the soluble ionic group extends into the aqueous environment. The driving force for adsorption of surfactants onto the particle surface is the rejection of the hydrophobic part of the molecule from the hydrogen-bonded structure of water[13]. Examples of surfactants include sodium lauryl sulphate and sodium dioctyl sulphosuccinate.

The steric stabilisers used in non-aqueous media, in place of surfactants, are also characterised by having a dual character. As there is no strong hydrophobic rejection of the anchor in non-aqueous media, the molecular weight of this group has to be sufficiently high to be insoluble in the medium[6]. The molecular weight of the soluble component, which defines the thickness of the steric barrier, must be sufficient to ensure that the secondary minimum is shallow enough for Brownian motion to separate interacting particles[14]. In practice, the molecular weight of the anchor group must not be significantly larger than the soluble group otherwise the stabiliser may precipitate out of the dispersion medium[15]. Thus the molecular weight of the soluble group being typically about 1500-2000, when poly(12-hydroxystearic acid) is employed, means that the molecular weight of the anchor group is normally in the same range[10].

Stabilisers exhibit a variety of geometries[10]. There is the so called comb stabiliser which possesses four or five soluble groups that are grafted onto the anchor backbone. Another is the stabiliser precursor which consists of a soluble group possessing a reactive end group that can subsequently react with the monomer during the course of the polymerisation. The advantage of using the latter is that the anchor group has the same composition as the particles and strongly associates with them.

Steric stabilisation in an aqueous medium is provided to some extent by non-ionic surfactants examples of which include polyoxyethylene (23)-lauryl ether and octyl phenoxy polyethoxyethanol. The adsorption mechanism is similar to that of ionic surfactants ie rejection of the hydrocarbon group to the particle interface.

3.1.2.2 The mechanism of aqueous emulsion polymerisation [16]

The model comprises water, monomer, a water soluble free radical initiator and a surfactant. At concentrations exceeding the critical micelle concentration (cmc), the surfactant is mainly present in an aggregated form or micelle, otherwise it is adsorbed in small amounts onto monomer droplets and dissolved molecularly. The monomer is mostly in the form of droplets with small amounts contained in the micelles (if present) and dissolved molecularly.

Aqueous emulsion polymerisation is characterised by three stages or intervals. During interval I, the rate of reaction increases primarily due to particle nucleation. Interval II commences on cessation of particle nucleation. The ratio of polymer and monomer in the now swollen particles remains approximately constant due to the balancing of the free energy of mixing (polymer wants to be infinitely dilute in monomer) and the surface energy. Thus as propagation continues, monomer migrates from the monomer droplets through the aqueous phase to the growing particles. The rate of reaction remains relatively constant during this interval. The rate of monomer diffusion is rarely rate determining. Interval III is the final stage of reaction and commences when, due to continued polymerisation, the monomer droplets eventually become exhausted and disappear. The concentration of monomer in the polymer particles will now start to decrease with time. The rate of reaction is now no longer constant.

In order to understand the particle nucleation process, the fate of free radicals produced in the aqueous phase must first be considered. They can either undergo aqueous phase termination, can enter an existing particle or create a new particle. Entry can occur when the propagating radical reaches a sufficient degree of polymerisation to become surface active. At this point the oligomer will tend to migrate to a particle surface. On further propagation, the oligomer crosses the water-particle surface interface irreversibly. Particle formation will cease when there are sufficient existing particles to capture all the oligomeric radicals produced. New particle formation can occur on entry of a surface active oligomeric radical into a micelle or by homonucleation.

The presence or not of micelles plays a dominant role in the mechanism of particle formation. Below the cmc, a charged radical produced from initiator decomposition propagates with monomer in the aqueous phase until it has attained a critical degree of polymerisation (greater than that required for it to become surface active) whereupon it forms a coiled structure excluding water. On becoming swollen with monomer, the transition to a precursor particle is complete. Further growth takes place through further propagation or through coagulation with other precursor particles. The latter mechanism is also known as homogeneous-coagulative nucleation. If persulphate is used as initiator, for example, charge stabilisation is achieved by the sulphate end group of the original collapsed chain, from other chains added to the particle due to coagulation and from capture of charged oligomeric radicals or termination products. Exit from the particles of free radicals can also occur. The only candidates that are sufficiently water soluble are monomeric radicals formed by transfer to monomer reactions with radical chain ends. The time taken for such a species to diffuse across a typical particle diameter is far shorter than the time required to propagate into a much less water soluble dimeric radical. Hence exit of monomeric radicals occurs to a significant extent. A useful qualitative treatment [16] excluding consideration of free radical exit, particle size polydispersity and particle coagulation gives the rate of particle formation in molar units $d(N_c/L)/dt$ as,

$$\frac{dN_c/L}{dt} = k_{p,aq} C_w \left[IM^{\bullet}{}_{jcrit} \right] \qquad \text{Equation (3.4)}$$

where $k_{p,aq}$ the is rate coefficient for aqueous phase propagation, C_w is the aqueous phase monomer concentration and $[IM^{\bullet}{}_{jcrit}]$ is the concentration of oligomeric radical of critical degree of polymerisation to collapse. It is also assumed that the timescale of particle formation (interval I) is less than that of reaching the steady state for radicals inside the polymer particles (taking account of radical entry and exit) and that all particles contain one free radical. This is a consequence of not taking account of compartmentalisation (isolation of radicals in individual particles) and free radical exit.

An alternative mechanism for particle formation in systems with zero or low concentrations of surfactant is *in situ* micellization. Surface active species that are formed as aqueous phase termination products can form micelles. This mechanism is considered to be uncommon as the concentration of suitable species such as distyrene sulphate is normally too far below the cmc.

A micellar entry theory for particle formation at above the cmc was first proposed by Harkins and developed quantitatively by Smith and Ewart [17, 18, 19, 20]. The model, however, assumed 100% initiator efficiency i.e. no aqueous phase termination, and does not account for compartmentalization and radical exit assuming instead that all the particles have a free radical. The model also predicts that the particle number falls to zero with the concentration of surfactant.

The modern theory of micellar entry is as follows. Propagation of an initiator free radical takes place in the aqueous phase until it reaches a degree of polymerisation at which it is surface active. Up to this point, aqueous phase termination is a competing reaction. The surface active radicals may either enter a micelle, aggregate with surfactant molecules or propagate further and form precursor particles by homonucleation. Homonucleation is, however, insignificant above the cmc. Monomer diffuses to the precursor particles where propagation is rapid because the concentration of monomer within the particles is higher than in the aqueous phase. Surfactant molecules are adsorbed onto their surfaces as they start to grow. Limited coagulation can take place as well as entry and exit of free radicals from the precursor particles. As the precursor particles continue to grow in size and number, they are able to capture all the new free radicals that would have formed new particles and particle nucleation ceases.

A semi-quantitative treatment of the mechanism that excludes coagulation, compartmentalization and size dependent parameters gives the following equation for the overall rate of particle formation [16],

$$\frac{dN_c/L}{dt} = k_{p,aq} C_w \left[IM^{\bullet}{}_{jcrit-1} \right] + \sum_{i=z}^{jcrit-1} k^{i}{}_{e,micelle}\, C_{micelle} \left[IM^{\bullet}{}_{i} \right] \qquad \text{Equation (3.5)}$$

where z is the number degree of polymerisation at which an oligomer becomes surface active, $C_{micelle}$ is the concentration of monomer in the micelle and $k^{i}_{e,micelle}$ is the rate coefficient for entry of a i-mer into a micelle. The first term on the right hand side is for homogeneous nucleation and the second for micellar nucleation.

As stated at the beginning of this sub-section, on cessation of particle nucleation, propagation within the particles continues with diffusion of monomer from the droplets through the aqueous phase to the growing particles. A consequence of the near constant rate of reaction during interval II is the narrowing of the polydispersity of the size distribution of the particles with time. Transfer to monomer and radical exit can take place as well as radical entry. Termination of two radicals residing in the same particle must also occur. Termination is very fast as one of the radicals is very short and mobile having just entered the particle as initiator derived radicals or as a result of transfer to monomer, exit and re-entry. The average number of radicals per particle is less than ½.

Interval III commences when all the monomer droplets have disappeared. As the weight fraction of the polymer in the particle increases, the viscosity also rises. As the particles grow, the rate of exit of monomeric radicals, produced by transfer to monomer, decreases. As radicals are resident in the particles for longer before encountering and terminating, termination is now between two radicals of moderate degrees of polymerisation. The number of radicals per polymer particle increases as more and more monomer is consumed and the termination rate decreases. This in turn leads to an acceleration in the rate of conversion known as the Trommsdorff effect. At very high conversions, the polymer becomes glassy and the propagation rate also decreases as the rate at which monomer can diffuse to the end of the now immobile growing polymer chains as opposed to the chemical reaction becomes rate determining. Termination is now by the reaction-diffusion mechanism where movement of the radical chain end is by propagation.

3.1.2.3 The mechanism of non-aqueous dispersion polymerisation [21]

The system for non-aqueous dispersion polymerisation comprises a non-aqueous diluent, monomer, a soluble free radical initiator and a stabiliser. All the components are soluble in the diluent. On heating, a polymer is formed that is insoluble in the diluent. Dispersion polymerisation may be regarded as a form of precipitation polymerisation modified by the presence of a polymeric stabiliser that prevents flocculation and aggregation of the precipitating polymer particles. The process is highly reproducible and controllable as heat and mass transfer between the polymeric and liquid phases can take place without restriction.

There is no comprehensive theory that predicts the number of particles formed in a dispersion polymerisation, however it is thought that, depending on the conditions, nucleation takes place either by self-nucleation or by an aggregative mechanism. Both mechanisms require production of free radicals by the breakdown of the initiator which then reacts with monomer to form growing oligomers with a reactive free radical end. In self-nucleation, the oligomers continue to grow until they reach a threshold molecular weight that is dependent on the solubility of the medium and collapse into a condensed state. As each oligomer behaves independently of the others, a new particle is formed from each.

In aggregative nucleation, growing oligomer chains start to associate reversibly with each other as their molecular weight and concentration increases. Small aggregates are unstable and break up again but beyond a certain size, become stable continuing to grow and will constitute new particle nuclei. The rate of nucleation is a function of the activation energy required to form a stable aggregate.

Experimental evidence from electron microscopy indicates that the rate of formation of particles falls off very quickly (within a few seconds or tens of seconds). This suggests capture of most of the oligomers being formed in the diluent phase by existing particles. The rate will be dependent on the number and size of the particles. Two theories have been proposed to explain this. In diffusion capture, a model proposed by Fitch and Tsai [22], an oligomer that reaches a particle by diffusion is irreversibly captured. The rate of capture is proportional to the surface area of the particles. The difference between this and the rate of initiation gives the rate of nucleation. The theory is formulated in such a way as to imply that the oligomers travel in straight lines rather than following a random walk path thus considerably underestimating the numbers captured. If the oligomers are captured irreversibly, then there would be far fewer particles than observed experimentally.

In equilibrium capture, the lower molecular weight oligomers are captured reversibly. They are also involved in the temporary formation of aggregates. Permanent removal of the oligomers takes place when the oligomer reaches the threshold degree of polymerisation while still captured and is therefore too insoluble to escape. Alternatively, oligomers are lost if they join aggregates that then become stable and grow. The fraction of oligomers that are captured or nucleate is a function of their equilibrium distribution just prior to the process of irreversible removal. Nucleation is controlled by the total surface area of the particles.

The presence of polymeric stabilisers enhances nucleation by association with the growing oligomers which increases the probability of forming nuclei and therefore reduces the likelihood of capture by existing particles. If the concentration of the stabiliser is depleted, then controlled agglomeration can take place. This occurs when the growing primary particles have insufficient stabiliser to effectively cover their surface and agglomerate to form larger but fewer particles. The assumption is made that the stabiliser is able to migrate from the old surface to the new. This is favoured by a loosely anchored stabiliser on a small particle at a low concentration (to limit the rate of collision and further agglomeration before redistribution of the stabiliser). A soft or monomer swollen particle would also ensure swift coalescence after collision.

Application of the theory to experiment suggests a number of points:

(a) Nucleation probably takes place by the aggregative mechanism;

(b) Increasing the solvency of the diluent reduces the rate of nucleation resulting in larger but fewer particles;

(c) The stabiliser is not depleted before the nucleation step has been completed but can become a factor during the later stages of particle growth;

(d) Capture of growing oligomers is the main factor in suppressing nucleation;

(e) Oligomer capture probably involves a gradual transition from the equilibrium to the diffusion capture mechanisms;

(f) The threshold degree of polymerisation (for aggregative nucleation) is so low (10-15) that nearly all the oligomers form nuclei or are captured before their radicals are terminated. Thus, in almost all cases, almost all polymerisation takes place within the particles.

Experimental evidence pointing to the locus of polymerisation being the interior of the particles includes the swelling of pre-formed polymer particles by monomer and the rate of polymerisation being independent of the particle size (therefore excluding the particle surface as the locus of polymerisation). Furthermore, the smooth spherical form of poly(methyl methacrylate) indicates growth of monomer-swollen particles. An exception is poly(vinyl chloride) whose particles have a rough granular surface suggesting deposition of polymer from solution.

A characteristic of dispersion polymerisation (and bulk polymerisation) is auto-acceleration (also known as the Trommsdorff effect) where the rate of polymerisation increases rapidly as more polymer is formed. This is due to the decrease in the termination rate as the viscosity within the particles increases. Diffusion of monomer to the radical chain ends is still possible so the chains continue to grow, but diffusion of the radical chains becomes more difficult as they continue to grow reducing the chance of termination by addition or disproportionation. There is an increase in the molecular weight as conversion proceeds. In the case of poly(methyl methacrylate), very high molecular weights can be achieved. However, at very high conversions, even monomer diffusion is inhibited and the propagation rate also falls. The result is the appearance of an overall peak rate of conversion. A general equation for the overall rate of polymerisation R_p has been given [23],

$$R_p = \alpha c_{md} k_p (VR_i/k_t)^{1/2} \qquad \text{Equation (3.6)}$$

where α is the partition coefficient of monomer between polymer and diluent, c_{md} is the concentration of monomer in the particles, k_p is the propagation constant, k_t is the termination rate constant, V is the volume of the volume fraction of the particles and R_i is the overall rate of initiation. The rate constants vary as the concentration of monomer in the particles changes. The rate is proportional to the square root of the initiator concentration and the volume of the particles.

In copolymerisation, the partition functions of the various monomers between the polymeric and diluent phases must be considered. In hydrocarbon diluents, the reactivity of polar monomers such as methacrylic acid is far greater than that of non-polar monomers such as the higher alkyl methacrylates. The compositions will not be homogeneous with the more polar monomers polymerising first giving an initial composition rich in polar monomer. As polymerisation proceeds, the composition will shift to a higher content of less polar monomer.

3.2 The rheology of solid-liquid dispersions

In order to understand the flow behaviour of plastisols, it may be useful to start with a simple model. The simplest is a suspension of non-interacting hard spheres, a practical example of which is a suspension of glass spheres in a liquid. The flow behaviour will be related to the concentration, normally expressed as the volume fraction, of the spheres. The change in behaviour of this simple model can then be predicted on adding steric stabilisers or surfactants which have the effect of changing the apparent volume fraction of the spheres.

Thus, after introducing some basic concepts in rheology, the behaviour of the hard sphere model will be examined. Then the effects of steric and electrostatic stabilisation will be considered in the light of the hard sphere model.

3.2.1 Some basic concepts in rheology

The term 'rheology', derived from the Greek word 'rheos' meaning flow, describes the study of the response of a body to an applied force, most often a shear force [24]. If the response or deformation of a body is recoverable on removal of an applied force, then the body is said to exhibit elastic behaviour. However, if the deformation is permanent, then the body shows viscous behaviour. If the body exhibits behaviour that is both elastic and viscous, then it is said to be viscoelastic.

In rheology, the applied force and corresponding deformation are respectively defined in terms of stress, or force per unit area measured in units of Pascals (Pa), Nm^{-2} or $dynes.cm^{-2}$ (Nm^{-2} = 10 $dynes.cm^{-2}$) and strain, which is the relative deformation [25].

Thus if a shear stress τ is applied to the surface of an elastic body at $y = d$ as shown in Figure (3.5), there is an instantaneous deformation of the body from ABCD to ABC'D'.

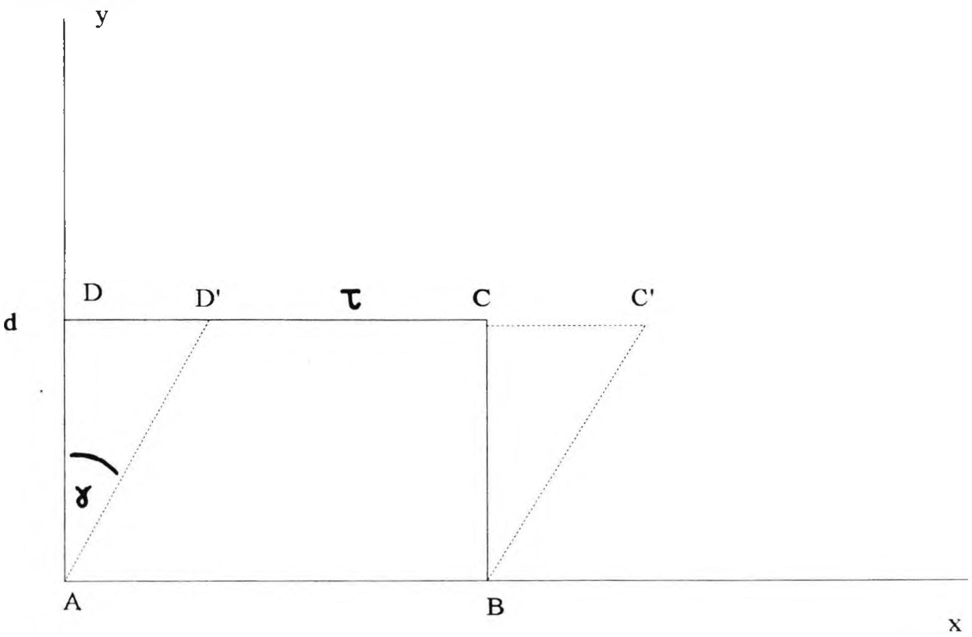

Figure (3.5) The effect of application of a shear stress τ to a block of Hookean material (shown in section) which deforms the section ABCD to ABC'D'.

There is no further movement once the deformed state has been reached however on release of the stress, the body recovers its original form. The strain, or relative deformation, is measured in terms of the angle γ. This model, which can be mechanically represented by a Hookean spring, is described mathematically by Equation (3.7),

$$\tau = G\gamma \qquad \text{Equation (3.7)}$$

where G is a constant known as the modulus of elasticity measured in Pascals. If a shear stress τ is applied to the surface of a viscous body at $y = d$ as shown in Figure (3.6), the upper plane of the body (or liquid) will move at relative velocity U and the intervening layers of the body between the top and bottom surfaces will move at the local velocity v_x the magnitudes indicated by the lengths of the arrows.

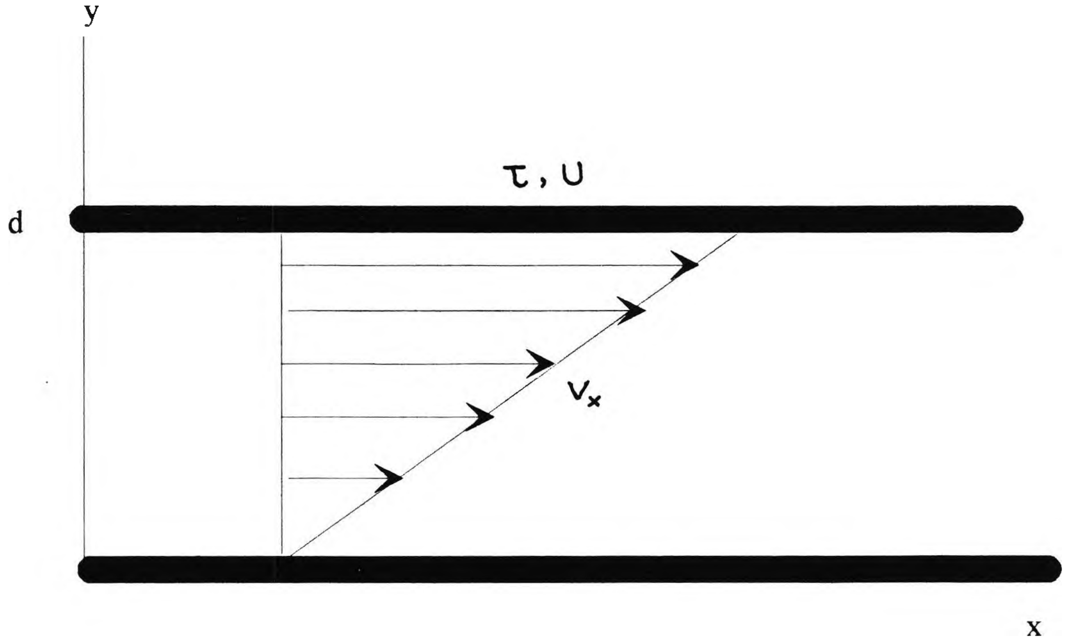

Figure (3.6) The effect of application of a shear stress τ to a Newtonian liquid (shown in section) which creates a velocity gradient U/d. Local velocities v_x.

This model, which can be mechanically represented by a dashpot or piston filled with a Newtonian liquid, is described mathematically by Equation (3.8),

$$\tau = \eta \frac{U}{d} \qquad \text{Equation (3.8)}$$

where U/d is the velocity gradient or shear rate usually denoted dγ/dt and expressed in reciprocal seconds, and η is a constant known as the shear viscosity which is measured in Poise (or 0.1 x Pa.s. or dyne.s.cm^{-2}). Viscoelastic behaviour can be modelled by combining the spring and dashpot models. Examples include the Maxwell body where a spring and dashpot are in series or the Kelvin body which comprises the two units in parallel[16].

Dilute solid-liquid suspensions exhibit viscous behaviour. However, as the concentration of suspended material increases, the behaviour of the suspension becomes increasingly viscoelastic. Eventually, at very high concentrations, the suspension will behave as an elastic solid [26]. The general shape of the shear viscosity versus shear rate curve for a concentrated solid-liquid suspension is shown in Figure (3.7) [27]. Initially, the viscosity remains constant as the shear rate is increased. This behaviour is described as Newtonian. As the shear rate is increased further, the viscosity decreases rapidly exhibiting shear thinning or pseudoplastic behaviour before reaching a second lower plateau. Finally, at very high shear rates, there can be an increase in viscosity. This is shear thickening or dilatant behaviour.

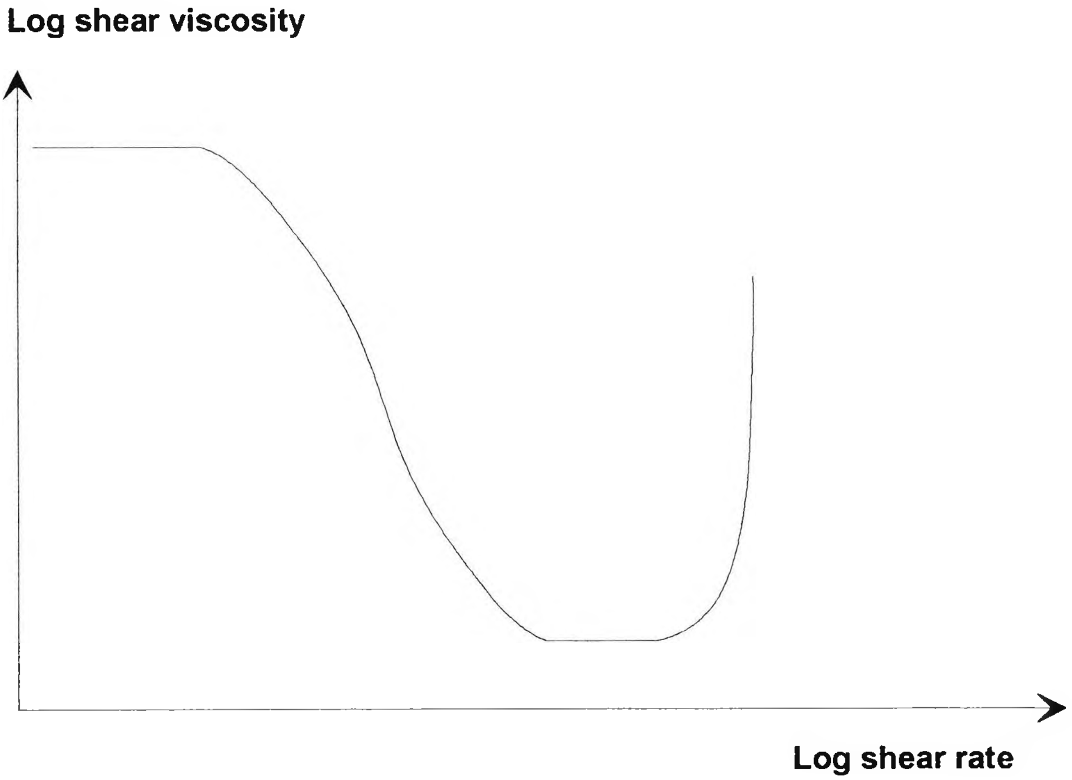

Figure (3.7) Schematic of the shear viscosity versus shear rate curve for a solid-liquid suspension[18].

In order to explain the behaviour illustrated in Figure (3.7), the forces acting on the solid particles must be considered[18]. Firstly, there are the hydrodynamic forces or viscous forces acting on the particles. These forces are proportional to the local velocity difference between the particle and the surrounding medium. Secondly, there is the Brownian randomising force. Finally, there are the forces arising from the interaction of particles such as electrostatic or steric repulsions or the attractive London dispersion forces.

Thus, when a concentrated suspension flows at very low shear rates, the particles move around interacting often with one other. As a result of the high resistance to free movement of the particles, the viscosity is high. Brownian motion dominates at these low values of shear rate and is able to restore the dispersion to its rest state and therefore the viscosity remains constant[18]. At higher shear rates, orientation of the particles is not restored by Brownian motion. However, the orientation assumed allows the particles to move past each other more freely and hence the viscosity falls. It is thought that the viscosity falls to a minimum value when the particles form into layers separated by layers of dispersion medium[28, 29]. At sufficiently high shear rates, the layers can be disrupted and the viscosity rises again[18].

3.2.2 The hard sphere model

The relationship between the concentration, or volume fraction, of a dilute suspension of uniform particles and the shear viscosity is expressed mathematically by the Einstein viscosity equation,

$$\frac{\eta}{\eta_s} = 1 + 2.5\phi \qquad \text{Equation (3.9)}$$

where η is the shear viscosity, η_s is the shear viscosity of the medium and ϕ is the volume fraction of the suspended phase[30, 31]. In order to simplify the theory, the suspension is assumed to be at infinite dilution where only single particle-medium interactions need to be considered and the need to consider Brownian forces may be put to one side. Furthermore, the particles are assumed to exert no long-range interparticle forces of attraction or repulsion on each other. In practise, despite being strictly valid only at infinite dilution, the relationship is found to be usable up to volume fractions of about 0.01 [32].

At higher concentrations, the effect of pairs of particles in close proximity must be considered. As this effect is a function of the square of the volume concentration, a correction term proportional to ϕ^2 must be added to Equation (3.9). Calculation of the coefficient involves consideration of not only hydrodynamic forces but also Brownian forces. The solution, for low shear rate conditions, has been given as 6.2 [33]. The amended expression is usable up to volume fractions of about 0.2 [34].

On raising the concentration further, three-way particle interactions become important. However, due to the mathematical complexity of the problem, only very approximate coefficients for the ϕ^3 term have been calculated. Even less is known about higher terms. Therefore, reliance is placed on a multitude of empirical and semi-empirical equations formulated to represent the behaviour of more concentrated dispersions.

The concept of free volume in relation to a suspension of particles was introduced by Robinson[35]. This was further developed by Mooney who considered the problem by adding spheres to an existing dispersion of identical spheres whilst maintaining the total amount of dispersion medium[36]. Krieger and Dougherty then arrived at a corrected form of the relationship derived by Mooney[37, 38]. This is shown as Equation (3.10),

$$\frac{\eta}{\eta_s} = \left(1 - \frac{\phi}{\phi_c}\right)^{-[\eta]\phi_c} \qquad \text{Equation (3.10)}$$

where $[\eta]$ is the intrinsic viscosity and ϕ_c is the critical packing fraction. The intrinsic viscosity is the limit of $(\eta-\eta_s)/\eta_s\phi$ as $\phi\rightarrow0$. The value is a characteristic of a given system and, as is the case in the Equation (3.9), equal to 2.5 for hard uncharged particles. The critical packing fraction is the volume fraction of the suspended phase at which the particles are in continuous three dimensional contact and unable to flow. A more recent derivation of Equation (3.10) was achieved using an averaging technique[39].

There are a host of other equations that have been proposed for concentrated suspensions, however Equation (3.10) is found to model results well over a range of shear rates[18]. This is accomplished by allowing the values for the intrinsic viscosity and critical packing fraction to vary with the shear rate. Thus shear thinning can be accounted for by a flow that brings about a more favourable orientation allowing the particles to glide past one another more easily.

3.2.3 Sterically and electrostatically stabilised particles

The rheology of sterically stabilised dispersions in non-aqueous media of low dielectric constant, where the adsorbed layer is small relative to the particle radius, resembles that of hard spheres[17]. The effective volume fraction is given by the volume occupied by the original particle and the contribution of the adsorbed layer according to Equation (3.11),

$$\phi_{eff} = \phi\left(1+\frac{\delta}{a}\right)^3 \qquad \text{Equation (3.11)}$$

where a is the particle radius and δ is the thickness of the adsorbed layer[40]. Viscoelasticity can, however, be seen at high concentrations when there is deformation or penetration of the adsorbed layers.

An important factor to consider for electrostatically stabilised systems, absent from non-aqueous dispersions, is the electrolyte concentration[17]. Varying the concentration has a dramatic effect on the rheology. At very high concentrations, where the interparticle coulombic forces are well screened, suspensions exhibit hard sphere behaviour. At very low concentrations, the suspensions are viscoelastic.

In addition, three phenomena associated with electrostatically stabilised suspensions, known as the electroviscous effects, have been identified which can influence the measured viscosity[41]. Application of a stress to a suspension deforms the diffuse part of the double layer around the particles. The result is an increase in the intrinsic viscosity of the suspension. This is the primary electroviscous effect. Electrostatic repulsive effects between particles increase the effective collision diameter. The effect is to alter the viscosity of the suspension by up to an order of magnitude. This is the secondary electroviscous effect. In the presence of absorbed polyelectrolytes, the thickness of the stabilising layer can expand and contract with electrolyte concentration or pH affecting the overall viscosity of the suspension. This is the tertiary electroviscous effect.

3.3 Polymer-plasticiser interactions

In order to identify criteria for preventing premature plastisol gelation, models describing the nature and strength of the polymer-plasticiser interactions need to be developed. The models must account for the presence of thermally labile or covalent crosslinks within the polymer particles.

The rigidity of hard thermoplastic polymers is attributed to attractive secondary valency forces between the macromolecules. The secondary valency forces take the form of van der Waals' forces and hydrogen bonding. Addition of a plasticiser neutralises the sites of secondary valency holding the polymeric chains together and separates them. This affords the chains an increased degree of molecular motion and the polymer becomes softer and more flexible[42]. The theoretical description of plasticisation falls within the framework of the thermodynamics of polymer solutions.

The first stage of the discussion considers the thermodynamics of solutions of non-crystalline and crystalline polymers. The theory is then extended to the case of a polymer with covalent crosslinks. Finally, a thermodynamic expression is derived predicting a novel route to controlling plastisol gelation by the osmotic limitation of polymer swelling.

3.3.1 The thermodynamics of polymer solutions: non-crystalline and crystalline polymers

When a polymer is dissolved in a solvent, there is an increase in entropy due to the large number of possible configurations that the macromolecules can now assume in solution[43]. A quantitative description of the behaviour of polymer solutions, based on a liquid lattice model, was developed by Flory and Huggins[44].

3.3.1.1 Derivation of the entropy of mixing

In order to calculate the total configurational entropy of a polymer solution, taking as the starting point pure solvent and a pure perfectly crystalline polymer, polymer molecules are added successively to a lattice consisting of $n_o = n_1 + yn_2$ cells where n_1 and n_2 are the numbers of solvent and solute molecules and y is the number of chain segments each of equal size to a solvent molecule (and unrelated to the size of the structural unit). y is therefore the molar ratio of solvent to solute molecules. Hence, each cell can accomodate either one solvent molecule or one chain segment. If i number of chains have already been added to the lattice, then there remain n_o - yi vacant cells in which to place the first segment of the i + 1 molecule. If z is the cell coordination number, which can range from six to twelve, then the second segment of this molecule can be placed in any one of the z adjacent cells except for those already occupied by segments from the previous i molecules. If the likelihood of one of the z cells, adjacent to the vacant cell to be occupied by the first segment, being occupied is f_i, then the expected number of available cells for the second segment will be $z(1 - f_i)$. For the third segment, the number of vacant cells will be $(z - 1)(1 - f_i)$ as one of the cells will already be occupied by the first segment. For each succeeding segment, the number of vacant cells can also be taken as $(z - 1)(1 - f_i)$ disregarding the comparatively few occasions on which a cell will be occupied by a segment apart from the preceeding one of the same chain. Hence the number of sets of y contiguous sites available to the molecule is,

$$v_{i+1} = (n_o - yi)z(z - 1)^{y-2}(1 - f_i)^{y-1} \qquad \text{Equation (3.12)}$$

The number of ways in which n_2 different molecules can be arranged in the lattice is,

$$\prod_{i=1}^{n2} v_i \qquad \text{Equation (3.13)}$$

However, if the molecules are identical and the order in which the n_2 are added to the lattice is unimportant,

$$\prod_{i=1}^{n2} v_i = n_2\,!\Omega$$

or

$$\Omega = \frac{1}{n_2\,!}\prod_{i=1}^{n2} v_i \qquad \text{Equation (3.14)}$$

where Ω is the number of ways in which n_2 sets of y consecutively adjacent cells can be chosen from the lattice. The average expectancy f_i of a cell chosen at random being occupied is equal to the fraction of all cells occupied by segments,

$$(1 - f_i) = (n_o - yi)/n_o \qquad \text{Equation (3.15)}$$

The value of f_i will be less than f_i due to the added restraint that the molecule whose segment occupies a cell cannot have an adjacent segment from the same chain in occupation of a neighbouring cell already ascertained to be vacant. Nevertheless, if Equation (3.15) is substituted for $(1 - f_i)$ in Equation (3.12) and z replaced by (z - 1),

$$\nu_{i+1} = (n_o - yi)^y[(z - 1)/n_o)]^{y-1} \qquad \text{Equation (3.16)}$$

As for large values of n_0,

$$\frac{(n_0 - yi)!}{(n_0 - y(i+1))!} \approx (n_0 - yi)^y$$

equation (3.16) may be approximated by,

$$\nu_{i+1} = \{(n_o - yi)!/[n_o - y(i + 1)]!\}[(z - 1)/n_o)]^{y-1} \qquad \text{Equation (3.17)}$$

Substitution of Equation (3.17) into Equation (3.14) yields Equation (3.18) by the following steps,

$$\nu_i = \{(n_o - y[i - 1])!/[n_o - yi]!\}[(z - 1)/n_o)]^{y-1}$$

hence,

$$\Omega = \frac{1}{n_2!}\cdot[(z - 1)/n_0]^{n_2(y-1)}\cdot\left\{\frac{n_0!}{(n_0 - y)!}\cdot\frac{(n_0 - y)!}{(n_0 - 2y)!}\cdot\frac{(n_0 - 2y)!}{(n_0 - 3y)!}\cdots\frac{(n_0 - y[n_2 - 1])!}{(n_0 - yn_2)!}\right\}$$

On cancelling terms,

$$\Omega = \frac{n_0!}{n_2!(n_0 - yn_2)!}\cdot[(z - 1)/n_0]^{n_2(y-1)} \qquad \text{Equation (3.18)}$$

The configurational entropy of mixing ordered pure polymer and solvent is given by Boltzmann's equation $S_c = k.\ln\Omega$ where k is the Boltzmann constant. The substitution of Equation (3.18) into the Boltzmann expression takes the following steps. By introduction of Stirling's approximation, Stirling: $N! \approx (2\pi N)^{½}.(N/e)^N$

or $\ln N! \approx N\ln N - N + \ln(2\pi N)^{½}$

which for large N reduces to $\ln N! \approx N\ln N - N$ Equation (3.19)

Taking natural logs of Equation (3.18),

$$\ln\Omega = \ln(n_0)! - \ln(n_0 - yn_2)! - \ln(n_2)! + n_2(y - 1)\ln[(z - 1)/n_0]$$

On substituting Equation (3.19) and collecting terms,

$$\ln\Omega \approx n_0\ln(n_0) - (n_0 - yn_2)\ln(n_0 - yn_2) - n_2\ln(n_2) + n_2(1 - y) + n_2(y - 1)\ln[(z - 1)/n_0]$$

On substituting $n_0 = (n_1 + yn_2)$ and $(n_0 - yn_2) = n_1$ in order to eliminate n_0, collecting multiples of log terms and using $-1 = \ln(1/e)$,

$$\ln\Omega \approx -n_1\ln\left[\frac{n_1}{n_1 + yn_2}\right] - n_2\ln\left[\frac{n_2}{n_1 + yn_2}\right] + n_2(y - 1)\ln[(z - 1)/e]$$

Hence,

$$S_c \approx -k\left\{n_1\ln\left[\frac{n_1}{n_1 + yn_2}\right] - n_2\ln\left[\frac{n_2}{n_1 + yn_2}\right] + n_2(y - 1)\ln[(z - 1)/e]\right\}$$

Equation (3.20)

The configurational entropy of mixing can be considered to occur in two steps: disorientation of the polymer molecules and then mixing of these disorientated molecules. The former is given when $n_1 = 0$,

$$\Delta S_{disorientation} \approx kn_2\{\ln y + (y - 1).\ln[(z - 1)/e]\}$$ Equation (3.21)

Assuming y is large, allowing the first term on the right to be discarded, the entropy of mixing of disorientated polymer molecules, obtained on subtraction of Equation (3.21) from Equation (3.20), is given by,

$$\Delta S_M \approx -k[n_1 \ln\phi_1 + n_2 \ln\phi_2] \qquad \text{Equation (3.22)}$$

where ϕ_1 and ϕ_2 are the volume fractions of the solvent and solute respectively. Contributions to the entropy from specific interactions between neighbouring segments has not been considered.

The foremost assumption implicit in this derivation is the use of the same lattice for solvent and solute. This assumes that the coordination number z is the same for both species which is unlikely. The limitation of this treatment is that it is only really of use for concentrated solutions. This comes out of the assumption that the segments of the i molecules added previously are randomly distributed (mean field theory [45]). They occur, in fact, in sequences of y consecutively adjacent cells. At high concentrations, the polymer chains will be intertwined and the assumption valid. However at low concentrations, the polymer chains will be isolated by large expanses of pure solvent and the distribution of chain segments will be non-random.

3.3.1.2 Derivation of the heat and free energy of mixing

Derivation of the heat of energy of mixing really involves calculation of the difference between the total energy of interaction between the solution and the pure liquid components. The forces of interaction between uncharged molecules decreases rapidly with distance such that consideration need only be addressed to interactions with first neighbour molecules. Three types of first neighbour interaction are possible between solvent molecules and polymer segments: those between two solvent molecules designated [1,1]; those between two polymer segments designated [2,2]; and those between a solvent molecule and a polymer segment designated [1,2]. Formation of a solution, which occurs by creation of interactions of the latter type at the expense of the two former, can therefore be summarised by the following stoichiometric equation,

$$1/2[1,1] + 1/2[2,2] = [1,2] \qquad \text{Equation (3.23)}$$

If the terms w_{12}, w_{11} and w_{22} are assigned to represent the energy associated with each interaction, the *change* in energy for formation of an [1,2] interaction using Equation (3.23) is,

$$\Delta w_{12} = w_{12} - (1/2)(w_{11} + w_{22}) \qquad \text{Equation (3.24)}$$

If for a particular arrangement of molecules there are p_{12} pairs of unlike contacts, then the heat of formation for that arrangement is,

$$\Delta H_M = \Delta w_{12} p_{12} \qquad \text{Equation (3.25)}$$

The probability that an adjacent site to a polymer segment is occupied by a solvent molecule is equal to the 'site fraction' which is defined as the number of sites adjacent to solvent molecules divided by the total number of sites adjacent to both solvent and polymer molecules. The total number of contacts between a polymer molecule and all its first order neighbours is z - 2 per chain segment plus two more for the terminal segments which makes a total of $(z - 2)y + 2$. Thus the 'site fraction ' is,

$$zn_1/\{zn_1 + [(z - 2)y + 2]n_2\} \qquad \text{Equation (3.26)}$$

which for large values of z approaches ϕ_1. Therefore, the probability that an adjacent site to a polymer segment is occupied by a solvent molecule is equal to ϕ_1. The total number of contacts between a polymer molecule and all its first order neighbours $(z - 2)y + 2$ which for large z can be approximated by zy. Therefore, the average value of

p_{12} for a solution of a given composition is $zyn_2\phi_1 \equiv zn_1\phi_2$. The heat of mixing pure solvent and polymer liquids is,

$$\Delta H_M = z\Delta w_{12}n_1\phi_2 \qquad \text{Equation (3.27)}$$

If Equation (3.27) is recast in another form,

$$\Delta H_M = kT\chi_{12}n_1\phi_2 \qquad \text{Equation (3.28)}$$

where,

$$\chi_{12} = z\Delta w_{12}/kT \qquad \text{Equation (3.29)}$$

χ_{12} is a dimensionless quantity known as the Flory - Huggins interaction parameter that represents the interaction energy per solvent molecule divided by kT. $kT\chi_{12}$ is therefore the difference in energy between a solvent molecule immersed in pure polymer ($\phi_2 \cong 1$) and one immersed in pure solvent.

Derivation of the configurational entropy is given in Section 3.3.1.1, however there is an additional contribution to the entropy as a result of the orienting influences on the solvent and polymer segments in solution which differ from those in the pure states as a result of first neighbour interactions. The entropy change refers to the process of converting pure solvent and pure polymer segments to an array of solvent - polymer segment pairs. This is called the standard state entropy change.

The standard state entropy change is, like the enthalpy change, proportional to the number of unlike pair contacts [1,2] created in solution. The change in energy for the formation of an unlike pair Δw_{12} can therefore be thought to comprise two parts, one representing the change in enthalpy, and one the product of the temperature and change in entropy. Therefore,

$$\Delta w_{12} = \Delta w_h - T\Delta w_s \qquad \text{Equation (3.30)}$$

The parameter χ_{12} will therefore comprise an entropy contribution (divided by k) as well as an enthalpy contribution (divided by kT) and therefore the term $kT\chi_{12}n_1\phi_2$ should be considered as a standard state free energy change rather than as solely a heat of mixing. The expression derived for ΔH_M is affected by the same constraint as the configurational change in entropy in that it is inapplicable for use in dilute polymer solutions (in practise, the expression is valid at concentration of polymer in excess of several percent for a molecular weight of 100 000). The probability that a particular site adjacent to a polymer segment is equal to the volume fraction of solvent assumes random mixing.

The total free energy change of mixing consists of the configurational entropy of mixing plus the standard state free energy change (discarding the '≈' from Equation (3.22)),

$$\Delta G_M = kT[n_1 \ln\phi_1 + n_2 \ln\phi_2 + \chi_{12}n_1\phi_2] \qquad \text{Equation (3.31)}$$

3.3.1.3 The chemical potential

More usually, Equation (3.31) is expressed in terms of the partial molar free energies, or chemical potentials μ, of the solvent and polymer. They are obtained by differentiating the free energy of mixing with respect to the number of solvent molecules or polymer chains bearing in mind that the volume fractions are a function of the number of solvent molecules or polymer chains, and multiplication of the result by Avogadro's number.

$\phi_1 = n_1 / (n_1 - yn_2)$ Equation (3.32a)

$\phi_2 = yn_2 / (n_1 - yn_2)$ Equation (3.32b)

Using the product rule,

$$\frac{d}{dx}(ab^{-1}) = a\frac{db^{-1}}{dx} + b^{-1}\frac{da}{dx} = -ab^{-2}\frac{db}{dx} + b^{-1}\frac{da}{dx} \quad \text{Equation (3.33)}$$

differentiation of ϕ_1 and ϕ_2 yields,

$$\frac{d\phi_1}{dn_1} = \frac{(n_1 + yn_2) - n_1}{(n_1 + yn_2)^2} = \frac{yn_2}{(n_1 + yn_2)^2} = \frac{\phi_1\phi_2}{n_1} = \frac{\phi_2{}^2}{yn_2} \quad \text{Equation (3.34a)}$$

$$\frac{d\phi_2}{dn_1} = \frac{-yn_2}{(n_1 + yn_2)^2} = \frac{-\phi_1\phi_2}{n_1} = \frac{-\phi_2{}^2}{yn_2} \quad \text{Equation (3.34b)}$$

Equation (3.34b) is obvious given that $\phi_1 + \phi_2 = 1$. If,

$$g = [n_1\ln\phi_1 + n_2\ln\phi_2 + \chi_{12}n_1\phi_2]$$

then,

$$\frac{dg}{dn_1} = n_1\frac{d(\ln\phi_1)}{dn_1} + \ln(\phi_1) + n_2\frac{d(\ln\phi_2)}{dn_1} + \chi_{12}\phi_2 + \chi_{12}n_1\frac{d\phi_2}{dn_1} \quad \text{Equation (3.35)}$$

Given d(lny)/dx = (1/y)dy/dx, Equation (3.35) can be rewritten,

$$\frac{dg}{dn_1} = \frac{n_1}{\phi_1)}\frac{d(\phi_1)}{dn_1} + \ln(\phi_1) + \frac{n_2}{\phi_2}\frac{d(\phi_2)}{dn_1} + \chi_{12}\phi_2 + \chi_{12}n_1\frac{d\phi_2}{dn_1} \quad \text{Equation (3.36)}$$

On substitution of $\frac{d\phi_1}{dn_1} = \frac{\phi_1\phi_2}{n_1}$ and $\frac{d\phi_2}{dn_1} = \frac{-\phi_1\phi_2}{n_1}$ *or* $\frac{-\phi_2{}^2}{yn_2}$, Equation (3.36) simplifies to,

$$\frac{dg}{dn_1} = \phi_2 + \ln(\phi_1) - \frac{\phi_2}{y} + \chi_{12}\phi_2 - \chi_{12}\phi_1\phi_2$$

and then,

$$dg/dn_1 = \phi_2(1 - 1/y) + \ln(1 - \phi_2) + \chi_{12}\phi_2^2 \qquad \text{Equation (3.37)}$$

Thus, the expression for the change in chemical potential on mixing for the solvent is given as,

$$\mu_1 - \mu_1^0 \quad = \quad RT\left[\ln \phi_1 + \left(1 - \frac{1}{y}\right)\phi_2 + \chi_{12}\phi_2^2\right] \qquad \text{Equation (3.38)}$$

where μ_1 is the chemical potential of the solvent in the solution, μ_1^0 is the chemical potential of the pure solvent. The chemical potential for the polymer is obtained in a similar manner and is given as,

$$\mu_2 - \mu_2^0 \quad = \quad RT\left[\ln \phi_2 + (1 - y)\phi_1 + \chi_{12} y \phi_1^2\right] \qquad \text{Equation (3.39)}$$

where μ_2 is the chemical potential of the polymer in the solution and μ_2^0 is the chemical potential of the pure liquid polymer.

From experiment, it is found that the constancy of the parameter χ_{12} with concentration in the free energy expression is confirmed with non-polar systems such as rubber in benzene but with systems where either the polymer segment or solvent contains dipoles, the parameter varies with concentration. Nevertheless, the expression does give a semi-quantitative approximation for the free energy and interaction parameter.

If the polymer and solvent are not completely miscible, separation into two phases will take place. The conditions for incomplete miscibility between the polymer and solvent can be defined by stipulating equality of the chemical potentials in the two phases. Equation (3.38) defines the chemical potential energy change of the solvent in terms of the volume fraction of polymer. As this equation has the quadratic form, there are two concentrations at which the above conditions are met. The curve of the chemical potential energy change of the solvent versus the volume fraction of the polymer must therefore pass through a minimum. Depending on the value assigned to χ_{12}, the curve can also pass through a maximum. For complete miscibility, the curve decreases with increase in the polymer composition. Therefore, the critical point at which phase separation occurs must be at the point at which the minimum, maximum and point of inflection in between first appear, or when they are coincident. The conditions for phase separation are,

$(d\mu_1/d\phi_2)_{T,P} = 0$ characteristic of a maximum or minimum

$(d^2\mu_1/d\phi_2^2)_{T,P} = 0$ characteristic of an inflection

Application of these conditions to Equation (3.38) and using d(lnx)/dx = 1/x yields,

$$1/(1 - \phi_2) - (1 - 1/y) - 2\chi_{12}\phi_2 = 0 \qquad \text{Equation (3.40a)}$$

$$1/(1 - \phi_2)^2 - 2\chi_{12} = 0 \qquad \text{Equation (3.40b)}$$

On substituting $2\chi_{12}\phi_2 = \phi_2/(1 - \phi_2)^2$ into Equation (3.40a) in order to eliminate χ_{12},

$$\phi_{2c} = 1/(1 + y^{1/2}) \qquad \text{Equation (3.41)}$$

where the subscript c denotes the moment of phase separation. On substitution of Equation (3.41) into the Equation (3.40b),

$$\chi_{12c} = (1 + y^{1/2})^2/2y$$

which for large y reduces to,

$$\chi_{12c} = 1/2 + 1/y^{1/2} \qquad \text{Equation (3.42)}$$

Thus χ_{12c} exceeds 1/2 by a small amount at finite chain lengths equalling 1/2 at infinite molecular weight.

For partially crystalline polymers, spontaneous transformation of crystalline polymer into a polymer solution requires that the sum of the free energy change of melting and solution be equal to zero or be negative [34]. This leads to the expression given in Equation (3.43),

$$\Delta H_f \frac{(T_{mp} - T)}{T_{mp}} \quad + \quad RT\left[\ln \phi_2 + (1-y)\phi_1 + x\chi_{12}\phi_1^2\right] \leq 0 \qquad \text{Equation (3.43)}$$

where ΔH_f is the enthalpy of fusion and T_{mp} is the melting point. The first term on the left hand side of the expression represents the free energy of fusion and the second term the free energy of mixing. The latter is obtained from Equation (3.39). It is assumed that the enthalpy of melting does not vary with temperature.

3.3.2 The thermodynamics of the swelling of elastomeric networks

A treatment of the thermodynamics of network swelling must start with the statistical thermodynamics of rubber elasticity [46].

3.3.2.1 The statistical theory of rubber elasticity

In a polymer network, the chains created by cross-linking will be arranged in a random configuration which can be described by a Gaussian function derived from the analysis of the configurations of a freely jointed chain [47]. In this model, the hypothetical chain consists of n linkages (where n is large) of length l that are able to rotate freely in any direction. If one end of the chain is at the origin of coordinates, the projection of the chain in one dimension, for example along the x-axis, is the product of the root mean square of the bond vector along the x-axis and the net number of chains in the positive or negative direction. The calculation of the probability for a particular value of x in either the positive or negative directions given small extensions of the polymer chain is,

$$W(x)\,dx = (\beta/\pi^{1/2})\exp(-\beta^2x^2)dx \qquad \text{Equation (3.44)}$$

where $\beta = \frac{\sqrt{3/2}}{n^{1/2}l}$. The most probable value of x is at x = 0. As x increases, the function W(x) decreases. For large values of n and for small extensions, W(x), W(y) and W(z) are independent of each other, thus,

$$\begin{aligned} W(x,y,z)\,dxdydz &= W(x)W(y)W(z)dxdydz \\ &= (\beta/\pi^{1/2})^3\exp(-\beta^2r^2)dxdydz \qquad \text{Equation (3.45)} \end{aligned}$$

where r is the magnitude of the vector between the two polymer chain ends ($r^2 = x^2 + y^2 + z^2$). W(x,y,z) represents the density of distribution of the free chain ends (i.e not the end fixed at the origin) or the probability per unit volume of finding the free chain end at x, y, z. Although limited to small extensions, in practise the Gaussian form is acceptable for use in the treatment of rubber elasticity and swelling. Bond angle restrictions are accommodated by altering the parameter β without changing the form of the distribution.

If a tetrafunctional polymer network is deformed, the coordinates describing the new spatial arrangement of the network junctions must change in proportion to the macroscopic deformation (an affine transformation). The deformation in the x, y and z dimensions can be expressed in terms of the deformation factors α_x, α_y and α_z. A polymer chain i with chain end components after deformation of x_i, y_i and z_i (the other chain end located at the origin) must have had components x_i/α_x, y_i/α_y and z_i/α_z before deformation. The number of chains with specified coordinates $\upsilon_i\ (x_i,y_i,z_i)$ after deformation is given by,

$$\upsilon_i\ (x_i,y_i,z_i) = \upsilon W(x_i/\alpha_x,y_i/\alpha_y,z_i/\alpha_z)\ dxdydz/\alpha_x\alpha_y\alpha_z$$

On substitution of Equation (3.45) and $r^2 = (x_i/\alpha_x)^2 + (\ y_i/\alpha_y)^2 + (z_i/\alpha_z)^2$,

$$\upsilon_i\ (x_i,y_i,z_i) = \upsilon(\beta/\pi^{1/2})^3\exp\{-\beta^2[(x_i/\alpha_x)^2 + (\ y_i/\alpha_y)^2 + (z_i/\alpha_z)^2]\}dxdydz/\alpha_x\alpha_y\alpha_z$$

Equation (3.46)

The deformation of the polymer network, when considered in isolation, takes place without a significant change in the internal energy of the system i.e. zero net change in the sum of the thermal energy added and work done to the system. Thus the elastic free energy ΔG_{el} can be equated by $-T\Delta S_{el}$ where ΔS_{el} is the entropy change accompanying deformation. This entropy change is obtained by calculating the configurational entropy change involved on formation of the deformed network and subtracting that involved on formation of the undeformed network ($\alpha_x = \alpha_y = \alpha_z = 1$). In order to perform the former calculation, the number of conformations that the chains can assume must be known. They are a function of the chain distribution given by Equation (3.46) and the number of combinations of pairs of cross-linked units.

The probability that a given chain has the spatial components x_i, y_i and z_i within the range dx, dy, dz is given by Equation (3.47),

$$\omega_i = W(x,y,z)\,dxdydz \qquad \text{Eqaution (3.47)}$$

The probability that each of the ν chains in the network has given spatial components is the product of ω_i. By grouping together those chains with the same coordinates (ν_i),

$$\prod_i \omega_i^{\nu_i}$$

Since all the chains are identical, the number of configurations Ω_1 is given by,

$$\Omega_1 = \nu! \prod_i \left(\frac{\omega_i^{\nu_i}}{\nu_i!} \right) \qquad \text{Equation (3.48)}$$

On taking natural logarithms and introducing Stirling's approximation for the factorials $\ln(N!) \approx N\ln(N) - N$,

$$\ln \Omega_1 = \nu \ln \nu - \nu + \sum [\nu_i \ln \omega_i - \ln \nu_i!]$$
$$\ln \Omega_1 = \nu \ln \nu - \nu + \sum [\nu_i \ln \omega_i - \nu_i \ln \nu_i + \nu_i]$$
As $\nu = \sum \nu_i$,
$$\ln \Omega_1 = \ln \nu \sum \nu_i + \sum [\nu_i (\ln \omega_i - \ln \nu_i)]$$

$$\ln \Omega_1 = \sum \nu_i \ln \left(\frac{\omega_i \nu}{\nu_i} \right) \qquad \text{Equation (3.49)}$$

On substitution of Equation (3.45) into Equation (3.47) and combining this new form of the equation with Equation (3.46),

$$\ln(\omega_i \upsilon / \upsilon_i) = \beta^2[x_i^2(1/\alpha_x^2 - 1) + y_i^2(1/\alpha_y^2 - 1) + z_i^2(1/\alpha_z^2 - 1)] + \ln(\alpha_x \alpha_y \alpha_z)$$

On substitution of this expression and Equation (3.46) into Equation (3.49), replacing the summations with integrations and omitting the subscript i,

$$\ln(\Omega_1) = \nu[(\beta^3 / \pi^{3/2}) / (\alpha_x \alpha_y \alpha_z)] \int \int \int_{-\infty}^{\infty} \exp\{-\beta^2 [(x / \alpha_x)^2 + (y / \alpha_y)^2 + (z / \alpha_z)^2$$
$$\times \{\beta^2 [x^2 (1 / \alpha_x{}^2 - 1) + y^2 (1 / \alpha_y{}^2 - 1) + z^2 (1 / \alpha_z{}^2 - 1)] + \ln(\alpha_x \alpha_y \alpha_z)\} dxdydz$$

Equation (3.50)

After integration,

$$\ln\Omega_1 = -\nu[(\alpha_x{}^2 + \alpha_y{}^2 + \alpha_z{}^2 - 3)/2 - \ln(\alpha_x\alpha_y\alpha_z)]$$ Equation (3.51)

The likelihood that one of the given ν units (same number of crosslink chains) chosen for cross-linking has a similar unit in the volume element δV adjacent to it is (ν - 1)δV/V where V is the total volume. The likelihood that another unit can be similarly paired from the remaining ν - 2 units is (ν - 3)δV/V, therefore the likelihood that all of the units are paired is,

$$\Omega_2 = (\nu - 1)(\nu - 3)\ldots(1)(\delta V/V)^{\upsilon/2} \approx (\upsilon/2)!(2\delta V/V)^{\upsilon/2}$$

If natural logarithms of the above expression are taken and V replaced with $\alpha_x\alpha_y\alpha_z V_0$ where V_0 is the volume of the undeformed sample,

$$\ln\Omega_2 = -(\upsilon/2)\ln(\alpha_x\alpha_y\alpha_z) + \text{constant}$$ Equation (3.52)

Substitution of Equation (3.51) and Equation (3.52) into Boltzmann's equation,

$$S = k \ln \Omega_1 + k \ln \Omega_2$$
$$S = \text{constant} - (k\upsilon_e/2)[\alpha_x{}^2 + \alpha_y{}^2 + \alpha_z{}^2 - 3 - \ln(\alpha_x\alpha_y\alpha_z)]$$

where ν has been replaced by υ_e the effective number of chains for an imperfect network (a finite network). The entropy change is obtained on subtracting the entropy of formation of an undeformed network ($\alpha_x = \alpha_y = \alpha_z = 1$),

$$\Delta S = -(k\upsilon_e/2)[\alpha_x^2 + \alpha_y^2 + \alpha_z^2 - 3 - \ln(\alpha_x\alpha_y\alpha_z)] \qquad \text{Equation (3.53)}$$

The parameter β does not appear in this final equation and therefore the corrections to this parameter for chains that are restricted do not affect the result for rubber elasticity.

3.3.2.2 Network swelling

If a good solvent is added to a polymer possessing covalent cross-links, then swelling occurs as the solvent mixes with the polymer to form a solution. As the polymer swells, the polymer chains between the network junctions are distorted and straightened out providing an elastic force in opposition to the mixing force. When the two forces balance each other, a state of equilibrium is then established. This case has been described theoretically by Flory and Rehner who considered the polymer network as being bound together at repeating points which are always the termini of four chains [48].

The free energy change on mixing a pure solvent with a pure amorphous unstrained polymeric network comprises the sum of two parts: the free energy of mixing; and the elastic free energy. The free energy of mixing is given by Equation (3.31) with $n_2 << n_1$ as the polymer comprises a network rather than individual molecules,

$$\Delta G_M = kT[n_1\ln\phi_1 + \chi_{12}n_1\phi_2] \qquad \text{Equation (3.54)}$$

The chemical potential with respect to the solvent is given by Equation (3.38) with $1/y \cong 0$,

$$\mu_1 - \mu_1^0 = RT\left[\ln(1-\phi_2) + \phi_2 + \chi_{12}\phi_2^2\right] \qquad \text{Equation (3.55)}$$

As the deformation of the polymer network, when considered in isolation, takes place without a significant change in the internal energy of the system, the elastic free energy ΔG_{el} can be equated by $-T\Delta S_{el}$. Assuming an isotropic deformation i.e. linear displacement of the network junctions on deformation, $\alpha_x = \alpha_y = \alpha_z = \alpha_s$ where α_s is the linear defomation factor,

$$\Delta G_{el} = \frac{(kTv_e)}{2}\left(3\alpha_s^2 - 3 - \ln\alpha_s^3\right) \qquad \text{Equation (3.56)}$$

The chemical potential with respect to the solvent is obtained as given by,

$$\mu_1 - \mu_1{}^0 = N\left(\frac{d\Delta G_{el}}{d\alpha_s}\right)_{T,P}\left(\frac{d\alpha_s}{dn_1}\right)_{T,P} \qquad \text{Equation (3.57)}$$

where N is the Avogadro number. $\alpha_s{}^3 = V/V_0$ where V_0 and V are the volumes of the relaxed and swollen networks respectively. Assuming that there was no volume change on mixing,

$$\alpha_s{}^3 = V/V_0 = 1/\phi_2 = (V_0 + n_1v_1/N)/V_0$$

where v_1 is the molar volume of the solvent. Thus,

$$\left(\frac{d\alpha_s}{dn_1}\right)_{T,P} = \frac{v_1}{3\alpha_s{}^2V_0N} \qquad \text{Equation (3.58)}$$

Given that,

$$\left(\frac{d\Delta G_{el}}{d\alpha_s}\right)_{T,P} = \left(\frac{kTv_e}{2}\right)\left(6\alpha_s - \frac{3}{\alpha_s}\right) \qquad \text{Equation (3.59)}$$

By substituting Equation (3.58) and Equation (3.59) into Equation (3.57),

$$\mu_1 - \mu_1{}^0 = RT\left(\frac{\nu_e}{2}\right)\left(6\alpha_s - \frac{3}{\alpha_s}\right)\left(\frac{v_1}{3\alpha_s{}^2 V_0 N}\right) = RT\frac{v_1 \nu_e}{V_0 N}\left(\frac{1}{\alpha_s} - \frac{1}{2\alpha_s{}^3}\right)$$

and then by substituting for α_s, the expression for the chemical potential is,

$$\mu_1 - \mu_1{}^0 = RT\frac{v_1 \nu_e}{V_0}\left(\phi_2{}^{\frac{1}{3}} - \frac{\phi_2}{2}\right) \qquad \text{Equation (3.60)}$$

with ν_e expressed in moles. The overall change in chemical potential for the swelling of a polymer network is then given by,

$$\mu_1 - \mu_1{}^0 = RT\left[\ln(1 - \phi_2) + \phi_2 + \chi_{12}\phi_2{}^2 + \frac{v_1 \nu_e}{V_0}\left(\phi_2{}^{\frac{1}{3}} - \frac{\phi_2}{2}\right)\right] \qquad \text{Equation (3.61)}$$

The activity of the solvent a_1 is given by the relationship $\ln a_1 = (\mu_1 - \mu_1{}^0)/RT$. Equilibrium swelling is given when the activity of the solvent within the swollen network μ_1 equates to that outside $\mu_1{}^0$ i.e.,

$$-\left(\ln\phi_1 + \phi_2 + \chi_{12}\phi_2^2\right) = v_1\left(\frac{\nu_e}{V_0}\right)\left(\phi_2^{\frac{1}{3}} - \frac{\phi_2}{2}\right) \qquad \text{Equation (3.62)}$$

3.3.3 The thermodynamics of the osmotic limitation of swelling

A novel method for controlling the degree of swelling of crosslinked polymer particles by plasticiser that leads to the premature gelation seen with acrylic plastisols is described. The method is applicable to polymers with chemical or thermally reversible crosslinks.

The swelling of crosslinked polymer particles in solvent can be controlled by addition of a compound, such as a linear polymer, that is exclusively soluble in the solvent phase. The volume of solvent diffusing into the polymer phase is a function of the concentration of the solvent-soluble compound. The theoretical treatment is based on the Flory-Huggins and Flory-Rehner theories introduced in Sections 3.3.1 and 3.3.2 respectively[49].

The concept of the osmotic limitation of swelling of crosslinked polymers in solutions of linear polymer has, however, been described before[50 51 52 53 54 55 56 57]. Theoretical treatments, using both classical Flory-Rehner and scaling theories that, in contrast to the following theory, account for partitioning of the linear polymer into the solvent and crosslinked polymer phase, have been derived for linear polymers compatible and incompatible with the crosslinked polymers. An example of the former that has been studied includes poly(styrene) with styrene - divinyl benzene copolymers whilst for the latter, poly(methyl methacrylate) with crosslinked poly(styrene) [42, 43]. The effect on swelling equilibria of solutions of poly(ethylene glycol) on poly(N-isopropylacrylamide), which is associatively crosslinked, has also been studied[44, 45]. A theoretical treatment encompassing polyelectrolyte networks has been published[47]. The crosslinked polymer has, until now, been studied in bulk rather than as dispersed and stabilised submicron sized particles.

The change in chemical potential of the solvent on swelling a crosslinked polymer is given above in Equation (3.61). If the term ln(1 - ϕ_2) is expanded (i.e. into the infinite series -ϕ_2 - $(\phi_2)^2/2$ - $(\phi_2)^3/3$), all terms beyond the ϕ_2^2 term can be ignored for small values of ϕ_2 and Equation (3.61) reduces to,

$$\mu_1 - \mu_1^0 = RT\left[\left(-\tfrac{1}{2} + \chi_{12}\right)\phi_2^{\ 2} + \frac{v_1 \, v_e}{V_0}\left(\phi_2^{1/3} - \phi_2/2\right)\right] \qquad \text{Equation (3.63)}$$

The change in chemical potential of the solvent in a solution of the solvent-soluble compound described above using the same approximation as in Equation (3.63) is,

$$\mu_1 - \mu_1^0 \quad = \quad RT\left[-\frac{\phi_3}{y} - (\tfrac{1}{2} - \chi_{13})\phi_3^{\,2}\right] \qquad \text{Equation (3.64)}$$

where ϕ_3 is the volume fraction of the solvent-soluble compound and χ_{13} is the Flory-Huggins interaction parameter for the solvent in the solvent-soluble compound.

The equilibrium condition is given by equating Equation (3.63) with Equation (3.64). This expression is given as Equation (3.65),

$$RT\left[-\left(\frac{\rho_3}{\rho_1}\right)\left(\frac{m_1}{m_3}\right)\phi_3 - (\tfrac{1}{2} - \chi_{13})\phi_3^{\,2}\right] = RT\left[(-\tfrac{1}{2} + \chi_{12})\phi_2^{\,2} + \frac{\nu_1 \nu_e}{V_0}\left(\phi_2^{\,1/3} - \frac{\phi_2}{2}\right)\right]$$

Equation (3.65)

where $1/y$ has been replaced by $(\rho_3/\rho_1)(m_1/m_3)$. ρ_1, ρ_3, m_1 and m_3 are the density and molecular weights of respectively the solvent and the solvent-soluble compound. On rearrangement,

$$m_3 = \left(\frac{\rho_3}{\rho_1}\right)\left(\frac{m_1}{B}\right)\phi_3 \qquad \text{Equation (3.66)}$$

where $B = -(-\tfrac{1}{2} + \chi_{12})\phi_2^{\,2} - (\tfrac{1}{2} - \chi_{13})\phi_3^{\,2} - \nu_1\left(\frac{\nu_e}{V_0}\right)\left(\phi_2^{\,1/3} - \frac{\phi_2}{2}\right)$

The term υ_e/V_0 represents the density of effective chains or cross-linking units in the polymer network. The relationship between υ_e and the number of cross-links depends on whether the cross-link being considered is covalent or reversible. For a network comprising n_A moles of tetrafunctional monomer A such as divinyl benzene (of molecular weight m_A) and n_B moles of bifunctional monomer B such as methyl methacrylate (of molecular weight m_B) where every A molecule is assumed to form a crosslink,

$$\frac{\nu_e}{V_0} = \frac{n_A \rho_B}{M} = \frac{n_A \rho_B}{n_A m_A + n_B m_B} \qquad \text{Equation (3.67)}$$

In Equation (3.67), ρ_A is the density of monomer A and M the mass of the polymer. The density of the polymer is assumed to be dominated by ρ_B. Substitution of the mole fraction $x_A = n_A/(n_A + n_B)$ to eliminate n_B leads to Equation (3.68)

$$\frac{v_e}{V_0} = \frac{\rho_B}{m_A + \left(\frac{1}{x_A} - 1\right) m_B} \qquad \text{Equation (3.68)}$$

If $m_A = m_B$, then Equation (3.68) simplifies to the following expression,

$$\frac{v_e}{V_0} = \frac{x_A \rho_B}{m_B} \qquad \text{Equation (3.69)}$$

For a polymer where monomer A is, for example, methacrylic acid, the polymer would contain, via extensive hydrogen bonding, thermally reversible crosslinks. As each hydrogen bond requires two methacrylic acid molecules, the expression for υ_e/V_0 is half the value given for covalent crosslinks.

Equation (3.66) has been plotted in Figure (3.8) for various values of ϕ_2 for hydrogen bond type cross-linking. The values for the other parameters are given below:

$m_1 = 400$ (the molecular weight of dioctyl phthalate, a common plasticiser, is 390)

$m_B = 100$ (methyl methacrylate)

$\rho_1 = \rho_3 = \rho_B = 1$ g cm^{-3}

$\chi_{12} = 0.1$ $\chi_{13} = 0.4$

$x_A = 0.01$

Each curve represents the maximum molecular weight that the low molecular weight polymer can assume for a given degree of swelling. It would appear, from this example, that 10-20% by volume of a low molecular weight polymer dissolved in the plasticiser has a significant effect on the degree of swelling. The volume fraction of low molecular weight polymer required for a given degree of swelling decreases as the molecular weight decreases.

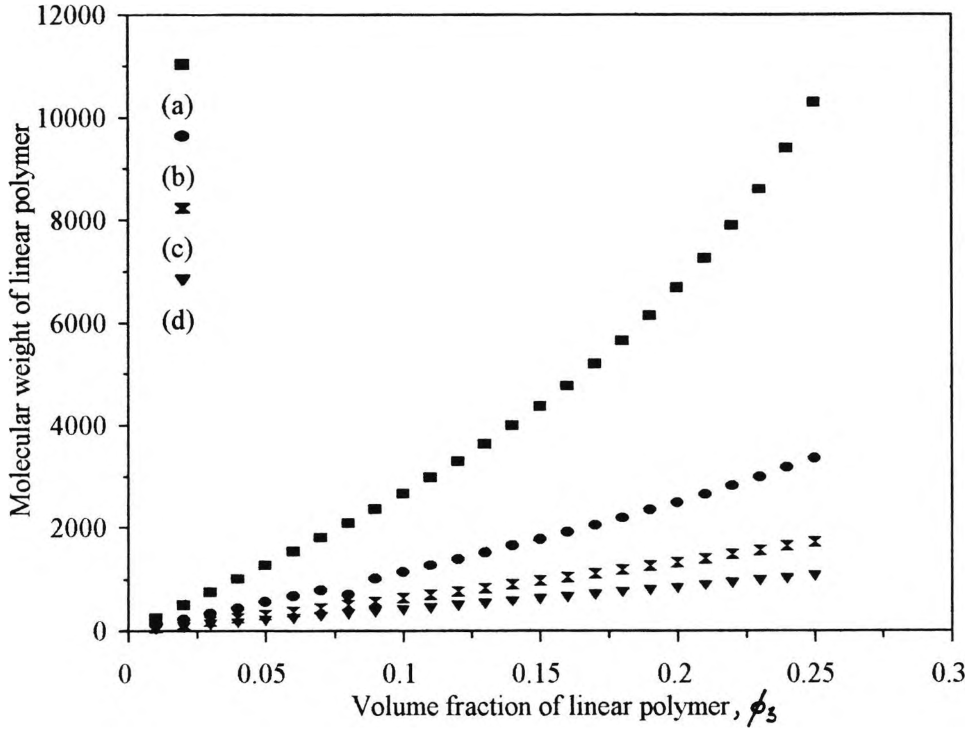

Figure (3.8) Theoretical volume fraction of linear polymer in solvent as a function of its molecular weight at (a) $\phi_2 = 0.2$; (b) $\phi_2 = 0.3$; (c) $\phi_2 = 0.4$; (d) $\phi_2 = 0.5$. Curves calculated from Equation (3.65) for thermally reversible crosslinks.

3.4 Summary

A number of conclusions can be drawn from consideration of the preceding theory relating to acrylic plastisols.

Electrostatically stabilised polymers which are dried and redispersed in a plasticiser of low polarity are expected to show poor dispersion stability because, as stated in Section 3.1.1.1, the electrostatic repulsive force is proportional to the dielectric constant of the medium. However, if the dielectric constant is moderately high and given the lack of electrolytes, the double layer could extend quite far into the plasticiser. This would imply an increased effective particle radius, or phase volume, and consequent increase in viscosity. There is evidence, for poly(vinyl chloride), that the surface of the polymer particles can be partially swollen by even weak plasticisers providing an elastic or steric barrier to flocculation[58]. This would also increase the effective particle volume. Sterically stabilised polymer particles should, provided the stabiliser is soluble, show good dispersion stability in plasticiser.

It can be seen, from Section 3.2.1, that there is, for solid-liquid suspensions, an exponential relationship between viscosity and dispersed polymer volume fraction. Thus, as commercial plastisols contain at least 50% by volume dispersed polymer, only a small percentage increase in the particle volume, as a result of swelling of the polymer by the plasticiser, can be permitted before the plastisol becomes too intractable for application. In addition, the primary and secondary electroviscous effects, described in Section 3.2.2, will increase the apparent viscosity of plastisols prepared with electrostatically stabilised polymer dispersions.

From Section 3.3.1, it can be seen that in order for a polymer to be insoluble in a solvent at room temperature but dissolve at elevated temperatures, it must possess thermally reversible crosslinks. Examples of thermally reversible crosslinks are found in crystalline polymers. Solutions of highly crystalline polymers may, however, precipitate out again. Applied to the case of a plastisol film, plasticiser exudation may be seen if the film is stored above its glass transition temperature. This is because the energy barrier to intramolecular bond rotation is sufficiently reduced to allow segmental motion to take place. Thus the thermally reversible crosslinks may reform in the coating leading to a two phase system [59, 60].

The case for polymers with covalent crosslinking was considered in Section 3.3.2. At high levels of crosslinking, the polymer will be insoluble in the solvent. At lower levels, the polymer will swell. Covalently crosslinking polymers can therefore only limit, and not arrest, swelling of the polymer by solvent. The rate of swelling may also be reduced.

The mechanism based on the osmotic limitation of swelling, described in Section 3.3.3, can, theoretically, prevent swelling of the polymer phase by solvent altogether at low levels of both covalent and thermally reversible crosslinking. This may be the best route to a stable acrylic plastisol.

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CHAPTER 4-

TASKS AND OBJECTIVES

A plastisol comprises a dispersion of polymer, generally poly(vinyl chloride) produced by aqueous emulsion or suspension polymerisation processes, that is subsequently dried and then redispersed in an essentially non-volatile diluent plasticiser such as di(2-ethylhexyl) phthalate. The plastisol can vary in consistency from a paste to a fluid, maintaining its initial state for months. On heating, the plasticiser begins to solvate and swell the dispersed polymer phase. The viscosity increases and the plastisol will eventually gel and fuse into a homogeneous mass.

Plastisols prepared from acrylic polymers do not, however, show the same degree of stability as those from poly(vinyl chloride) and increases in viscosity leading to gelation occur easily and quickly. It is thought that the stability of poly(vinyl chloride) is due to the presence of microcrystalline domains within the particle structure which prevents excessive swelling of the polymer by the plasticiser[1]. On heating, these weak crosslinks break down and the plastisol fuses. Acrylic polymers are, however, amorphous and therefore do not resist the solvating action of the plasticiser at room temperature.

The objective of the work was the preparation of a prototype acrylic plastisol with improved viscosity stability, which would be suitable for commercial development by industry. The plastisol could comprise up to 5% by weight organic solvent. As discussed in Section 1.4, the strategy for restricting particle swelling involved introducing thermally reversible crosslinks into acrylic polymer particles, which would be analogous to the microcrystallinity found in poly(vinyl chloride).

Thermally reversible crosslinks can be introduced into a polymer by randomly copolymerising a monomer, such as methacrylic acid, that can associate with itself through hydrogen bonds. These hydrogen bonds, which can be disrupted on heating, act as crosslinks making the polymer more rigid and inflexible.

For purposes of comparison, polymers were also prepared with covalent crosslinks. Typically, this can be achieved by polymerisation of a tetrafunctional monomer such as ethylene glycol dimethacryate or divinyl benzene, or copolymerisation of bifunctional monomers such as methyl methacrylate.

The applicability of the theory of osmotic limitation of swelling to the problem of acrylic plastisol stability was also tested.

4.1 Project tasks

The project can be divided into four separate tasks:

(a) The preparation of polymers with thermally reversible and covalent crosslinks

(b) The preparation of plastisols based on polymers prepared in (a) and assessment of their stability

(c) The preparation of coatings using plastisols prepared in (b) and assessment of their stability

(d) The experimental verification of the osmotic limitation of swelling mechanism

4.1.1 The preparation of polymers with thermally reversible crosslinks

The first task was the preparation of a range of polymers with thermally reversible crosslinks. The polymers were prepared using aqueous emulsion and non-aqueous dispersion polymerisation techniques.

Aqueous emulsion polymerisation was initiated using potassium or ammonium persulphate, and the polymer particles were stabilised principally using the anionic surfactant Aerosol OT (the sodium salt of dioctylsulphosuccinate). The non-ionic surfactant, Brij 35 (polyoxyethylene (23)-lauryl ether), was also used in some preparations.

For the non-aqueous dispersion polymerisations, the free radical initiator 2,2'-azobis-2-methylbutyronitrile (AIBN) was used. The steric stabilisers used in non-aqueous dispersion polymerisation are not commercially easily available and were therefore synthesised. Prepared in the comb stabiliser form, they were based principally on 12-hydroxystearic acid, though some were also prepared from lauryl methacrylate.

All the polymers prepared by aqueous emulsion and non-aqueous dispersion polymerisation were copolymers based on methyl methacrylate in combination with other acrylic monomers. Thermally reversible crosslinks were introduced into these polymers in a variety of ways:

(a) Hydrogen bonding
Copolymers of methyl methacrylate with methacrylic acid,
2-hydroxyethyl methacrylate or acrylic acid

(b) Dipole-dipole interactions
Copolymers of methyl methacrylate with methacrylonitrile

(c) Acid-base interactions
Terpolymers of methyl methacrylate, methacrylic acid and
2-(dimethylamino)ethyl methacrylate

(d) Metal crosslinks
Neutralisation of methyl methacrylate - methacrylic acid
copolymers with butyl lithium, diethyl zinc or diisobutyl
aluminium hydride

Some polymers with covalent crosslinks were also prepared in order to allow comparisons to be made with those with thermally reversible crosslinks. The method of preparation differed for aqueous emulsion and non-aqueous dispersion polymerisation. Three routes were used to prepare polymers using the non-aqueous dispersion polymerisation technique:

(a) Terpolymer of methyl methacrylate, methacrylic acid and glycidyl methacrylate with ring opening reaction between glycidyl and acid groups

(b) Copolymer of methyl methacrylate and urethane diacrylate

(c) Polymeric steric stabilisers possessing reactive groups pendant to the polymer backbone

Covalently crosslinked copolymers prepared using the aqueous emulsion polymerisation technique were based on methyl methacrylate and ethylene glycol dimethacrylate.

Diameters and size distributions of the polymer particles were obtained using scanning electron microscopy and photon correlation spectroscopy. Particle diameters were typically 0.20 microns. However, a range of 2% methacrylic acid copolymers of particle diameter up to 2.00 microns was prepared using non-aqueous dispersion polymerisation in order to investigate the effect of particle size on plastisol stability. In general, the polymer particles were monodisperse ie of uniform size.

Average molecular weights were determined using gel permeation chromatography. Typical number average molecular weights for the polymers prepared using the non-aqueous dispersion polymerisation technique were in the range 20 000-40 000 poly(styrene) equivalent; though the effect of increasing this to 250 000 was investigated. The value for polymers produced using aqueous emulsion polymerisation was nearer 150 000.

4.1.2 The preparation of plastisols and assessment of their stability

The second task was the preparation and evaluation of the stability of plastisols prepared using the polymers with thermally reversible or covalent crosslinks. The plastisols were prepared by redispersing approximately 10% w/w dried polymer into a range of commercially available diester plasticisers. A more detailed description is contained in Section 5.2.6. The stability was estimated by measuring the viscosity of dilute plastisols over 17 hours with a cone and plate viscometer.

4.1.3 The preparation of plastisol films and assessment of their stability

The third task was the preparation and evaluation of the properties of plastisol coatings. The plastisols, comprising 50% w/w dried polymer, were applied to clean glass panels using a draw-down bar which gave a wet film thickness of 75 microns. The plastisols were then heated at 130°C for 30 minutes in a vented oven. Particular attention was paid to the film integrity and any signs of plasticiser exudation. Further details are given in Section 5.2.9.

4.1.4 The experimental verification of osmotic limitation of swelling mechanism

Poly(methyl methacrylate) and poly(butyl acrylate) solution polymers of varying molecular weight were prepared. They played the role of the solvent-soluble compounds insoluble in the dispersed polymer phase required by the theory described in Section 3.3.3. The number average molecular weights were in the range 3 500-7 000 poly(styrene) equivalent. The polymerisations were carried out using 2,2'-azobis-2-methylbutyronitrile (AIBN) either in butylbenzyl phthalate with octyl mercaptan as the free radical moderator; or in isopropanol, a good chain transfer solvent.

The effect, on plastisol stability, of adding up to 20% w/w of the solution polymers into the plasticiser phase was assessed in the manner described in Section 4.1.3.

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CHAPTER 5-

EXPERIMENTAL METHODS AND MATERIALS

This chapter provides information on the purity and sources of the materials and outlines the experimental techniques used during the course of the project.

5.1 Materials

The materials can be broadly divided into the following four groups: monomers; solvents; initiators, moderators, surfactants, and organometallic compounds; and plasticisers. Information on the purity and the source as well as the common abbreviations or trademarks is provided in Tables (5.1) to (5.4). All the materials were used as received.

Table (5.1) Monomers

Material	Abbreviation	Purity /%	Supplier
Acrylic acid	AA	99	Aldrich
Allyl methacrylate	AMA	98	Aldrich
Butyl acrylate	BA	99+	Aldrich
2-(Dimethylamino)ethyl methacrylate	DMAEM	98	Aldrich
Divinyl benzene	DVB	55 (mixture)	Aldrich
Ethylene glycol dimethacrylate	EGDM	98	Aldrich
Glycidyl methacrylate	GMA	97	Aldrich
2-Hydroxyethyl methacrylate	HEMA	97	Aldrich
12-Hydroxystearic acid	-	technical	Cray Valley Products
Isophorone diisocyanate	IPDI	98 (mixture)	Aldrich
Lauryl methacrylate	LMA	96	Aldrich
Methacrylic acid	MAc	Technical	ICI Paints
Methacrylonitrile	MAN	99	Aldrich
Methyl methacrylate	MMA	technical	Cray Valley Products
3-Sulphopropyl methacrylate, potassium salt	3-SPM, K	98	Aldrich

Table (5.2) Solvents

Material	Abbreviation or Trademark	Purity /%	Supplier
Butyl acetate	-	98	BDH
Dimethyl sulphoxide	DMSO	99+	Aldrich
Ethyl acetate	-	99	BDH
n-Hexane	-	95	BDH
Isoparaffin bp 85-95°C	Isopar B	-	Exxon Chemicals
Isoparaffin bp 204-254°C	Isopar M	-	Exxon Chemicals
2-propanol	-	99+	Aldrich
n-Propanol	-	99	BDH
Aliphatic solvent bp 162-197°C	Shellsol D40	-	Shell Chemicals
Toluene	-	99	BDH
Xylene	-	99	BDH

Table (5.3) Initiators, moderators, surfactants, organometallic compounds and other materials

Material	Abbreviation or Trademark	Purity	Supplier
Aluminium isopropoxide	-	98	Aldrich
Aluminium tri-(sec-butoxide)	-	97	Aldrich
Ammonium persulphate	-	98	Aldrich
2,2'-azobis-2-methylbutyronitrile	AIBN Vazo 67	98	Janssen Chimica Du Pont
Barium hydroxide monohydrate	-	99	Aldrich
Benzoyl peroxide	-	70[a]	Aldrich
n-Butylamine	-	99	BDH
tert-Butyl catechol	-	97	Wardblenkinsop
Butyl lithium, 1.6 M in hexanes	-	-	Aldrich
Calcium hydride, -40 mesh	-	95+	Aldrich
Dibutyltin dilaurate	DBTDL	98	Aldrich
Chromium III octoate solution	Cordova AMC - 2	-	Cordova Chemicals
Diethyl zinc, 1.0 m in hexanes	-	-	Aldrich
Diisobutyl aluminium hydride, 1.0 M in hexanes	DIBAL - H	-	Aldrich
Dimethyl laurylamine	-	97	Aldrich
Hydroxyethylcellulose	Natrosol GR R726	-	Hercules
Methane sulphonic acid	-	70[b]	Aldich
1-Octyl mercaptan	-	97	Aldrich
Polyoxyethylene 23-lauryl ether	Brij 35	-	Sigma
Potassium persulphate	-	99+	Aldrich
Sodium bicarbonate	-	99	May and Baker
Sodium dioctylsulphosuccinate	Aerosol OT	96	Aldrich
Sodium ethoxide, 21% in denatured ethanol	-	96	Aldrich
Sodium hydroxide	-	98	Rhône - Poulenc
Zinc oxide	-	99	BDH

[a] Remainder is water

[b] Technical grade

Table (5.4) Plasticisers

Abbreviation or trademark	Material	Supplier
Acronal LR 8820	Soft resin	BASF
BBP	Butylbenzyl phthalate	Harcros Chemicals
Cymel 303	Hexamethoxymethyl melamine	Dyno Cyanamid
DIDA (Reomol)	Diisodecyl adipate	Ciba-Geigy Industrial Chemicals
-	Dilinear 7, 9 phthalate	BP Chemicals
DOP (Bisoflex)	Di-2-ethylhexyl phthalate	BP Chemicals
DOS	Di-2-ethylhexyl sebacate	Croda Surfactants
Palamoll 652[a]	-	BASF
Paraplex WP1	Polymeric	Rohm and Haas
Reoplex 1102	Polyester	Ciba-Geigy
Reoplex GL	Polyester	Ciba-Geigy
TXP (Reomol)	Trixylenyl phosphate	Ciba-Geigy Industrial Chemicals
Ultramol III	Polyadipate	Bayer
Uraplast RA 11	Polyadipate	DSM
Uraplast W 10[b]	-	DSM
Witamol 600 Stab	Polyester	Hüls

[a] A polymeric plasticiser derived from adipic acid and polyfunctional alcohols

[b] A linear saturated polymer based on orthophthalic acid

The plasticisers listed in Table (5.4) are principally monomeric esters or linear polyesters. The phthalates are by far the most widely used, commercially, as they provide a broad range of properties at low cost. Butylbenzyl phthalate is used to plasticise acrylics. Adipates and sebacates are generally used with poly(vinyl chloride) in low temperature applications, but also impart hand and drape to sheeting and coated fabrics. Phosphate plasticisers provide flame retardency to vinyl polymers. Linear polyesters are used for their lower volatility and reduced tendency to migrate. However, they are less efficient, have high viscosities and are more expensive[1].

5.2 Experimental methods

Listed below are the experimental methods that were employed in order to prepare and characterise the various materials used throughout the course of the work:

(a) Acid content determination

(b) Non-volatile content determination

(c) Molecular weight determination

(d) Particle size measurement

(e) pH measurement

(f) Assessment of plastisol stability

(g) Glass transition temperature measurement

(h) Gel content measurement

(i) Preparation of plastisol films

Detailed descriptions of each method now follow.

5.2.1 Acid content determination

Approximately 2 g of sample was weighed and dissolved in a mixture of toluene and ethanol. The solution was then titrated against 0.1 M potassium hydroxide using phenolphthalein as the indicator. The acid value is the number of milligrams of potassium hydroxide required to neutralize the free acids in 1 g of dried sample. Measurements were carried out in duplicate following the international standard ISO 3682-1983 (E): Binders for paints and varnishes - Determination of acid value - Titrimetric method[2].

5.2.2 Non-volatile content determination

Duplicate samples of approximately 2 g of the test material were weighed into small aluminium dishes and placed in a vented oven at a pre-set temperature for a pre-determined period of time. Test conditions varied according to the nature of the test material. For the steric stabilisers, they were 105°C for 3 hours and for the polymers prepared using an aqueous emulsion polymerisation technique, 30°C overnight. The results are expressed as the percentage residual mass of material after heating under the specified conditions. The test procedure was carried out according to BS 3900:Part B2:1970: Determination of volatile matter and non-volatile matter[3].

A different method was required for the polymers prepared by non-aqueous dispersion polymerisation due to their tendency to dry quickly. Two 2ml samples of the non-aqueous dispersion were pipetted into small pre-weighed vials, sealed and weighed. Two further 2ml aliquots of the non-aqueous dispersion were then pipetted into two small pre-weighed aluminium dishes and the samples allowed to dry to constant weight at room temperature or in a vented oven at a low temperature. The percentage non-volatile content can then be calculated from the weights of 2ml samples of the non-aqueous dispersion in their original and dried states.

5.2.3 Molecular weight determination by gel permeation chromatography

Polymer molecular weights, in equivalent poly(styrene), were determined by ICI Paints division, ICI Chemicals and Polymers Limited (now Zeneca), International Paint Limited and Cray Valley Products using gel permeation chromatography. This is a liquid chromatographic method that separates molecules according to their size.

5.2.3.1 Principle and theory

The sample solution is introduced onto the column, filled with a rigid and porous packing, and is carried by a solvent mobile phase through the column. The solvent can permeate as well as surround the packing. During a chromatographic run, molecules which are too large to penetrate the pores of the packing remain in the mobile solvent phase surrounding the packing and elute first from the column at the point of total exclusion. Small molecules which can permeate into all the pores of the packing elute last at the point of total permeation. Intermediate sized molecules will permeate the pores to some extent spending a fraction of their time within the pores and a fraction outside. The degree of permeation is a function of the solute molecular size.

The selective degree of permeation of solute molecules into the column packing can be viewed as a repeated exchange of the solute between the stagnant solvent in the pores of the packing and the mobile bulk solvent. The solute molecules are in thermodynamic equilibrium and the distribution of the molecules between the two phases is driven by entropic differences [4]. For a dilute solution at equilibrium,

$$\Delta G^0 = - RT \ln(K) \qquad \text{Equation (5.1)}$$

$$\Delta G^0 = \Delta H^0 - T\Delta S^0 \qquad \text{Equation (5.2)}$$

where ΔG^0, ΔH^0 and ΔS^0 are the standard free energy, enthalpy and entropic differences respectively for the solute between the two phases at constant temperature and pressure, K is the solute distribution coefficient, R the gas constant and T the absolute temperature. The solute distribution coefficient is defined as the concentration of the solute in the pores divided by that outside. K is zero for molecules excluded from penetrating the pores and one for those able to penetrate fully. Values in excess of one suggest the role of some sort of other mechanism such as adsorption.

The mobility of the solute molecules is restricted within the pores of the packing relative to that in the mobile bulk phase and hence separation is an entropy-controlled process. Adsorption and absorption effects are absent and hence the enthalpic term is zero. Therefore,

$$K = \exp(\Delta S^0/R) \qquad \text{Equation (5.3)}$$

As there is a loss in entropy as the solute molecules enter the pores, ΔS^0 is negative and K is therefore less than one and the solute elutes before the solvent. Equation (5.3) also shows that solute retention is, in principal, independent of temperature. In fact, there is only a small temperature effect in that the size of the solute molecules changes with temperature which in turn affects ΔS^0. The problem is minimised in good solvents. However, even small shifts in the calibration curve will have a significant impact on molecular weight values calculated from this curve. Changes in temperature will also have an effect on peak broadening.

There are various theories that attempt to model the mechanism of size separation in gel permeation chromatography. The models try to explain the mechanism in terms of the size and shape of the solute molecules and the pores. The differences in theoretical approach are a result of the various conformations that a solute molecule can adopt. The random coil model is generally used for synthetic polymers whilst for biopolymers, the rigid rod and sphere models are considered more appropriate [5]. Chain conformation has an effect on the relationship between the size and molecular weight of the solute molecule. Thus, from geometry, for rod shaped macromolecules, the length is proportional to the molecular weight; and for solid spherical macromolecules, the radius is proportional to the cube root of the molecular weight. For polymers adopting a random coil structure,

$$R_g \propto M^{\alpha} \qquad \text{Equation (5.4)}$$

where R_g is the radius of gyration and $\alpha \approx 0.5$ [6]. The value of α varies slightly for different polymer - solvent systems at different temperatures. The impact of a slight variation of α between 0.5 and 0.6 can lead to large errors in molecular weight requiring careful calibration of gel permeation chromatography equipment. Calibration should be carried out under the same conditions using standards with the same polymer structure as the samples.

As most polymer samples consist of a distribution of molecular weights, the molecular size of a sample is described in terms of an average weight. One form of average is the number-average molecular weight Mn which is defined as the mass of the sample in grams $\Sigma\ W_i$ or $\Sigma\ N_i M_i$ divided by the total number of chains present N or $\Sigma\ N_i$ where

W_i and N_i are the weight and number of molecules of molecular weight M_i and i is an incrementing index over all molecular weights present. To summarise,

$$Mn = \frac{\sum N_i M_i}{\sum N_i} = \frac{\sum W_i}{\sum (W_i / M_i)} \qquad \text{Equation (5.5)}$$

Another type of average is the weight average molecular weight Mw which is defined according to the following equation,

$$Mw = \frac{\sum N_i M_i^2}{\sum N_i M_i} = \frac{\sum W_i M_i}{\sum (W_i)} \qquad \text{Equation (5.6)}$$

The value of Mw is always larger than Mn except for a mondisperse sample where they are identical. The ratio Mw/Mn is a measure of the breadth of the molecular weight distribution and is known as the polydispersity. For step polymerisation, the value of the polydispersity approaches two. For a cross-linked polymer, the value is very large.

5.2.3.2 General methods of calibration

Calibration can be carried out using narrow or broad molecular weight distribution (MWD) standards. With a set of narrow MWD standards, the peak retention times of each can be related to the stated molecular weights. Use of this calibration method, however, is rather limited by the range of standards. Poly(styrene) is the most common standard used with a very wide range of molecular weights available. Only a small number of other polymers are obtainable and then only with a narrower molecular weight range. Molecular weights of samples without a suitable range of calibration standards and hence calibrated using poly(styrene) are often quoted in equivalent poly(styrene) values.

An alternative to this is to use the universal calibration method which relies on the concept of separation of molecules of different size according to their hydrodynamic volume V_h [7]. This is based on the following equation,

$$[\eta] \propto V_h/M \qquad \text{Equation (5.7)}$$

where $[\eta]$ and M have been previously defined (see Chapter 3) [8]. This equation assumes that the polymer molecule is a random spherical coil of beads each of which offers hydrodynamic resistance but connected by a string that does not. By rearrangement of Equation (5.7), $[\eta].M$ is proportional to V_h. A plot of $\log[\eta].M$ against retention time gives a single curve for a variety of different polymer types. The empirical relationship,

$$[\eta] = \mathbf{K}M^{\mathbf{a}} \qquad \text{Equation (5.8)}$$

where **K** and **a** are constants that vary with polymer type, solvent and temperature, relates the intrinsic viscosity with molecular weight [9]. **K** and **a** are known as Mark-Houwink constants and values can be obtained from the literature or determined experimentally. The intrinsic viscosity is experimentally measurable. To use this method, all that is required is a set of narrow MWD standards and the Mark-Houwink constants for the standards and the sample. In the absence of **K** and **a** values for the sample, they can be calculated using a single narrow MWD standard of the sample.

When using broad MWD standards, the data can be treated in two ways. The integral method tries to relate the molecular weight at a particular weight fraction from the known MWD curve of the standard to the retention time at the same given weight fraction from the MWD curve of the standard determined using gel permeation chromatography. Obtaining the complete MWD of the standard is an extremely laborious task involving polymer fractionation. An alternative way of obtaining the necessary MWD data is to generate a theoretical curve from a molecular weight average and the molecular weight of the repeat unit assuming a Gaussian distribution. Baseline choice and integration limits can greatly affect the reliability of this method of calibration. A linear calibration i.e. a linear relationship between log(molecular weight) and retention time, can be attempted when the number and weight average molecular weights of the standard is known by an iterative curve fitting procedure.

The most common type of detector used to measure the concentration of each species eluting from the separation column measures the differential refractive index i.e. the difference in refractive index between the sample stream and a reference which is normally the pure solvent. Thus, although the output from such a detector is a voltage, this is proportional to the weight concentration $\Delta W_i/\Delta V$. A typical raw gel permeation chromatography trace is shown in Figure (5.1) with millivolts on the y-axis and the retention time in minutes on the x-axis.

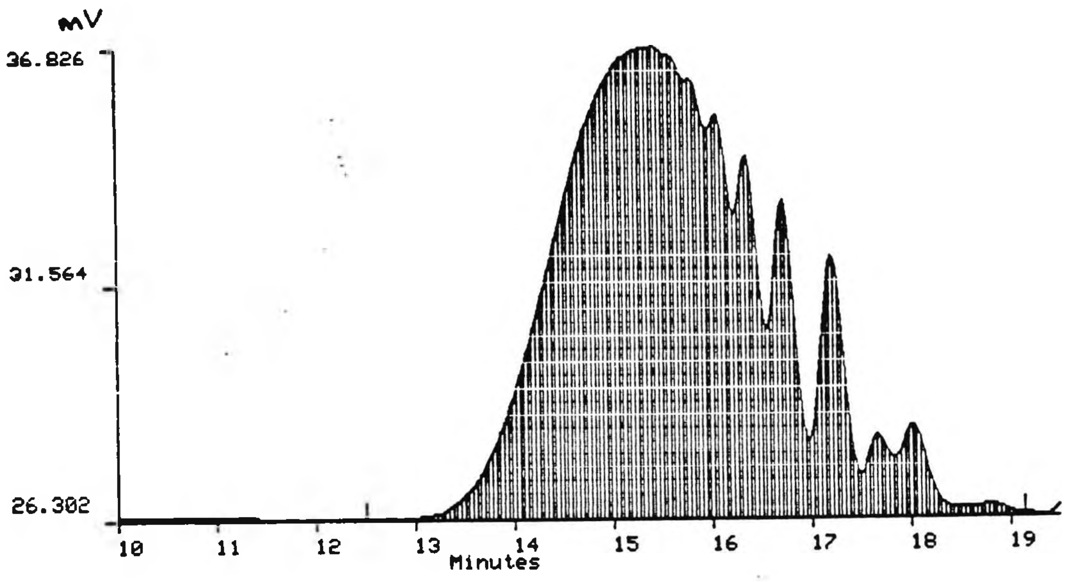

Figure (5.1) Gel permeation chromatography of poly(12-hydroxystearic acid) (batch 2335/162). Detector response (mv) versus retention time (minutes). Conditions: see ICI Paints below.

The Mn and Mw can be calculated manually by drawing at least eight and for broad distributions twenty vertical lines onto the chromatogram at equally spaced intervals and measuring their heights in millimetres to ± 0.25 mm [10]. The appropriate M_i can be read off a molecular weight calibration curve generated separately. The cumulative weight fraction MWD, obtained by integrating the area under the curve in Figure (5.1) at a series of retention times and dividing by the total area, is shown in Figure (5.2).

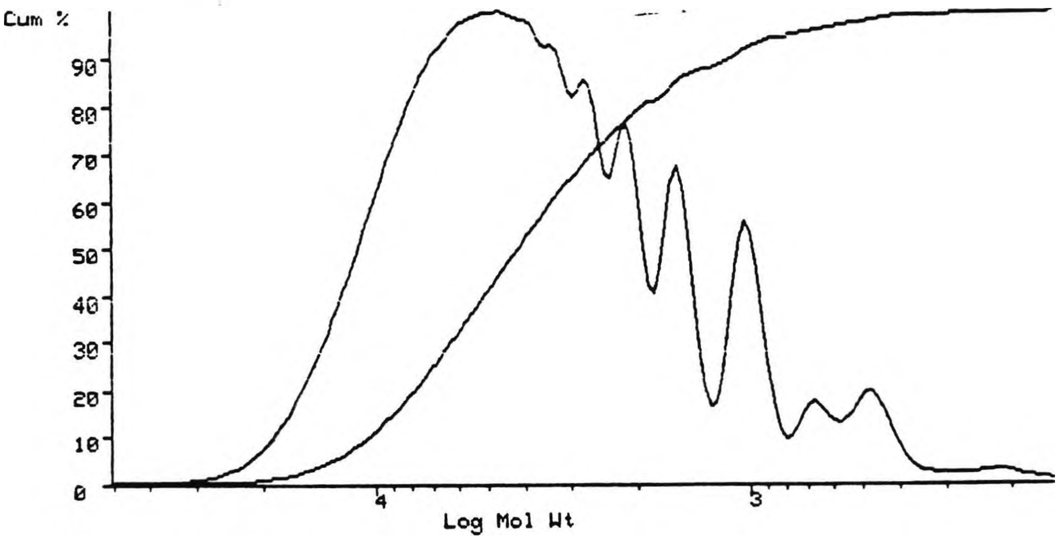

Figure (5.2) Gel permeation chromatography of poly(12-hydroxystearic acid) in Figure (5.1). Original data replotted in terms of percentage cumulative weight fraction versus log molecular weight and differential weight fraction versus log molecular weight.

The retention times have been converted to the log of the molecular weight. Differentiation of this curve gives the differential weight fraction MWD also shown in Figure (5.2) where ΔW/ΔlogM is plotted against log M. The curves in Figure (5.1) and

Figure (5.2) show a remarkable similarity in shape. This is due to the linear relationship between the log of the molecular weights and the retention times for the standards. The differential weight fraction X_i can be defined mathematically as follows,

$$X_i = \frac{\Delta W_i}{\Delta \log M_i} = \frac{\Delta W_i}{\Delta V} \frac{\Delta V}{\Delta \log M_i} \qquad \text{Equation (5.9)}$$

where $\Delta W_i/\Delta V$ is the weight concentration of solute, proportional to the detector output, and $\Delta \log M_i/\Delta V$ is the gradient of the calibration curve. For a linear calibration curve, the gradient is a constant and Equation (5.9) reduces to,

$$X_i = \frac{\Delta W_i}{\Delta \log M_i} \propto \frac{\Delta W_i}{\Delta V} \qquad \text{Equation (5.10)}$$

Further representative traces are given in Appendix A (at end of this chapter) for a stabiliser precursor based on poly(12-hydroxystearic acid), a comb stabiliser, poly(butyl acrylate) and copolymers prepared by non-aqueous dispersion and emulsion polymerisation.

5.2.3.3 Experimental procedures

The apparatus and experimental procedure used to obtain average molecular weights was as follows:

(1) ICI Paints

All the apparatus was from Waters Associates and comprised a 510 pump, a 410 differential refractive index detector and a 712 WISP autosampler. This was controlled by a DEC Pro 380 computor with Waters V4 software. The columns, arranged in series, comprised two 30cm Polymer Laboratories PLgel Mixed D containing a 5µm poly(styrene - divinyl benzene) gel. The columns were maintained at 40°C. The solvent, tetrahydrofuran, was pumped at 1ml/min. The samples were prepared at a concentration of 30mg/ml in tetrahydrofuran and left to stand for four hours at room temperature. They were then filtered through a 0.45µm poly(tetrafluoroethylene) filter and 100µl aliquots injected onto the first column. Calibration was carried out using a series of ten narrow MWD poly(styrene) standards of molecular weight range 580 - 480 000.

(2) ICI Chemicals and Polymers Limited

The apparatus comprised a differential refractive index detector. The column set, obtained from Waters Associates comprised the following in series: two Ultrastyragel Linear (part number 10681); Ultrastyragel 500Å (part number 10571); and Ultrastyragel 100Å (part number 10570). All the columns were packed with poly(styrene - divinyl benzene) gels. The solvent, tetrahydrofuran, was pumped at a rate of 1ml/min. The injection volume was 100µl. Calibration was carried out using poly(styrene) standards.

(3) International Paint Limited

All the apparatus was from Waters Associates and comprised a 510 pump, a 410 differential refractive index detector and a 712B WISP autosampler. The software was based on Drew Scientific GPC (1990). The columns, arranged in series, comprised two 300 x 7mm internal. diameter Polymer Laboratories PLgel 10^4Å and 10^3Å containing a poly(styrene - divinyl benzene) gel. The columns were maintained at 40°C and the detector at 35°C. The solvent, unstabilised tetrahydrofuran, was pumped at 1ml/min. The samples were prepared at a concentration of 2%w/v solids in tetrahydrofuran and left overnight. They were then filtered through a 0.45µm poly(tetrafluoroethylene) filter and 100µl aliquots injected onto the first column. The samples were prepared as received. Calibration was carried out using a series of five Polymer Laboratories narrow MWD poly(styrene) standards of molecular weights 2.96k, 9.2k, 30.3k, 68k and 220k. The calibrants were prepared as one solution in tetrahydrofuran at a concentration of 1% w/v per calibrant. The solution was injected immediately after preparation as a 50µl aliquot. Dibutyl phthalate was used in the calibration and sample solutions as an internal marker. Two injections of each sample were made successively followed by a single calibration solution injection. Data was collected at 1Hz over 26 minutes and was processed with manual setting of the baseline and integration limits.

(4) Cray Valley Products

The apparatus was from Perkin Elmer and comprised a LC10 pump and a LC77 differential refractive index detector. The column was a 300 x 4.6mm Polymer Laboratories PLgel 10µm MB packed with a poly(styrene - divinyl benzene) gel. The column was maintained at 20-25°C. The solvent, tetrahydrofuran, was pumped at 1.5ml/min. The samples were prepared at a concentration of 1% w/w. There was an on-line 0.5µm filter. The sample injection volume was 100µl. Xylene was added to the samples and calibrants to determine the solvent peak position. Calibration was carried out using a series of four logarithmically placed narrow MWD poly(styrene) standards of molecular weight range 1k - 2000k.

5.2.4 Particle size measurement

Polymer particle diameters were measured using both scanning electron microscopy and photon correlation spectroscopy [11]. For electron microscopy, it was found necessary to gold coat the dried samples at -20°C using an Emscope SC 500 sputter coater. In this way, overheating the samples was avoided. Photographs were taken using an ISI 100A scanning electron microscope operating at an accelerating voltage of 20 kV at magnifications of approximately x 15 000-45 000. Representative micrographs of polymers prepared by both non-aqueous dispersion and aqueous emulsion polymerisation can be found in Appendix B (at the end of this chapter). They include polymer dispersions with stabilisers based on both poly(12-hydroxystearic acid) and poly(lauryl methacrylate) (see chapter 7) and those prepared using both the single and two stage method of preparation (see chapter 6).

The polymer dispersions were shaken vigorously prior to removal of a small sample for viewing. Although only one or sometimes two micrographs (each at different magnifications) were taken of each sample, the homogeneity of the samples was verified by visual inspection under the electron microscope. If the sample size distribution was monodisperse, then only a few measurements were made. For those samples exhibiting a broader distribution, a larger number of measurements were made. A method has been described known as *truncated multiple traversing* which considerably reduces the number of particles that must be measured [12]. At least ten particles must be measured in each class that has influence on the distribution and many micrographs of the same sample are required for best results.

Formal particle size distributions were not determined as there were insufficient particles and micrographs to make the distribution statistically significant. For those samples that appeared reasonably monodisperse (see micrographs of batches 13.11, 17.28-17.30 and 17.2 in Appendix B), then only a few particles were measured. Where there was obviously a significant distribution (see micrographs for batch 22.42 in Appendix B), a particle size range was established by measuring several of the largest and smallest particles.

Photon correlation spectroscopy was carried out on a Coulter Nanosizer at ICI Paints. (the original traces are no longer available). This technique is used to measure particles of less than a few microns suspended in a liquid.

When a coherent light (electromagnetic) source is focussed on a dilute suspension, the suspended particles scatter the light. This is because the oscillating electric field in the light beam induces an oscillating electric dipole in polarisable particles. The oscillating dipoles then scatter the light. As the scattered electric field is a function of particle position, the intensity of the scattered light, which is proportional to the square of the electric field, has a time dependency due to random or Brownian motion. Information on the dynamics of the particles (their translational diffusion coefficient) is contained in the fluctuations in intensity and is described by the autocorrelation function,

$$\langle I(0)I(\tau)\rangle = \lim_{T\to\infty}\frac{1}{T}\int_0^T I(t)I(t-\tau)dt \qquad \text{Equation (5.11)}$$

where the intensity I has different values at time t and (t - τ). T is the total experimental duration. This is the function for an analogue signal.

There is a high degree of correlation between the intensities taken at short times as the particles have not moved very far over this period and the autocorrelation function is equal to $\langle I^2\rangle$. Over longer periods, all correlation is lost and the auto correlation function equals $\langle I\rangle^2$, the square of the *average* intensity. The autocorrelation function decays exponentially with time as a function of the diffusion coefficient D. For a suspension of rigid monodisperse compact particles, the photon autocorrelation function C(τ) is,

$$C(\tau) = \langle n(0)n(\tau)\rangle = \langle n\rangle^2[1 + b\exp(-\Gamma\tau)] \qquad \text{Equation (5.12)}$$

where $\Gamma = Dq^2$ and $q = \frac{4\pi n_r}{\lambda_0}\sin\frac{\theta}{2}$. n is the number of pulses or photons per unit time and the baseline $\langle n\rangle^2$ is proportional to the square of the average intensity. n_r is the refractive index of the medium, λ_0 is the wavelength of the light in a vacuum, θ the scattered angle from the incident beam and b is a constant. Γ is known as the *linewidth* defined as the half-width at half-maximum of the scattered light.

In order to calculate the diffusion coefficient and ultimately the particle size from the photon autocorrelation, the function is first normalised with the baseline and then 1 subtracted to leave the function b exp(-Γτ). This is then fitted using a least squares technique to determine the values of b and Γ. The relationship between the diffusion coefficient and the particle diameter d is given for a sphere by the Stokes-Einstein equation,

$$D = \frac{kT}{3\pi \eta d} \qquad \text{Equation (5.13)}$$

where η is the viscosity of the medium, k is the Boltzmann constant and T the absolute temperature. In contrast to electron microscopy, the diameter given in Equation (5.13) is the z-average diameter and generally higher than those obtainable from microscopy. This is due to a sheath of solvent molecules, ionic surfactants or steric stabilisers that may have been attached to the particle surfaces. The difference in particle diameters is particularly noticeable for very small particles.

Whereas a monodisperse sample has only a single exponential decay function, the interpretation of data for polydisperse samples is much more difficult as information on the size distribution must be obtained by deconvolution of the sum of all the single exponentials contributing to the measured autocorrelation function. The measured autocorrelation function $| g^{(1)} (\tau) |$ after baseline normalisation and subtraction of unity is given by,

$$\left|g^{(1)}\ \tau\right| = \int_0^\infty G(\Gamma)\ \exp(-\Gamma\tau)\, d\Gamma \qquad \text{Equation (5.14)}$$

where G(Γ) represents the distribution of linewidths resulting from the distribution of particle sizes.

A typical instrument comprises a source optics and laser, a focussing lens that reduces the typical laser beam diameter of 1mm to about 100µm, a sample cell assembly, a photomultiplier tube and a correlator. The Nanosizer, marketed by Coulter Electronics (no longer available) has an applicable size range of 0.04-3 µm [13]. Results are obtained as a mean equivalent spherical diameter and a polydispersity index which ranges from 1 to 9 where 1 indicates monodispersity and 9 polydispersity. The Nanosizer obtains four values of the correlation coefficient and carries out a linear least squares fit of the logarithm of the function to obtain the particle diameter. The polydispersity index is obtained from the deviation of the linear regression from the actual curve.

Experimental parameters are the temperature of the sample, the refractive index and the viscosity of the medium.

The samples analysed with this instrument were non-aqueous dispersions. The medium chosen for dilution of the original samples was n-hexane. The final concentration was such that there was sufficient transmission of light as indicated on an analogue meter. The concentration is low in order to avoid multiple scattering. As the diffusion coefficient is a function of concentration, it is possible to run a series of experiments at different concentrations and extrapolate back to zero. The count rate should be less than 10 MHz. To avoid interference from contaminating dust particles, the dilute samples ought to be filtered. As light scattering experiments are adversely affected by the presence of aggregations of polymer particles, problems handling the rapidly drying polymer dispersions may have influenced the results.

5.2.5 pH measurement

Measurement of the pH of the polymers prepared by emulsion polymerisation was carried out using an EIL 7055 pH meter and EIL hydrogen electrode, both manufactured by Electronic Instruments Limited.

5.2.6 Assessment of plastisol stability

Plastisol stability was assessed by measuring the viscosity of the test sample with time on a Carrimed CS 100 controlled stress rheometer using a cone and plate geometry. The liquid sample is placed between a rotating cone and stationary plate as shown in Figure (5.3).

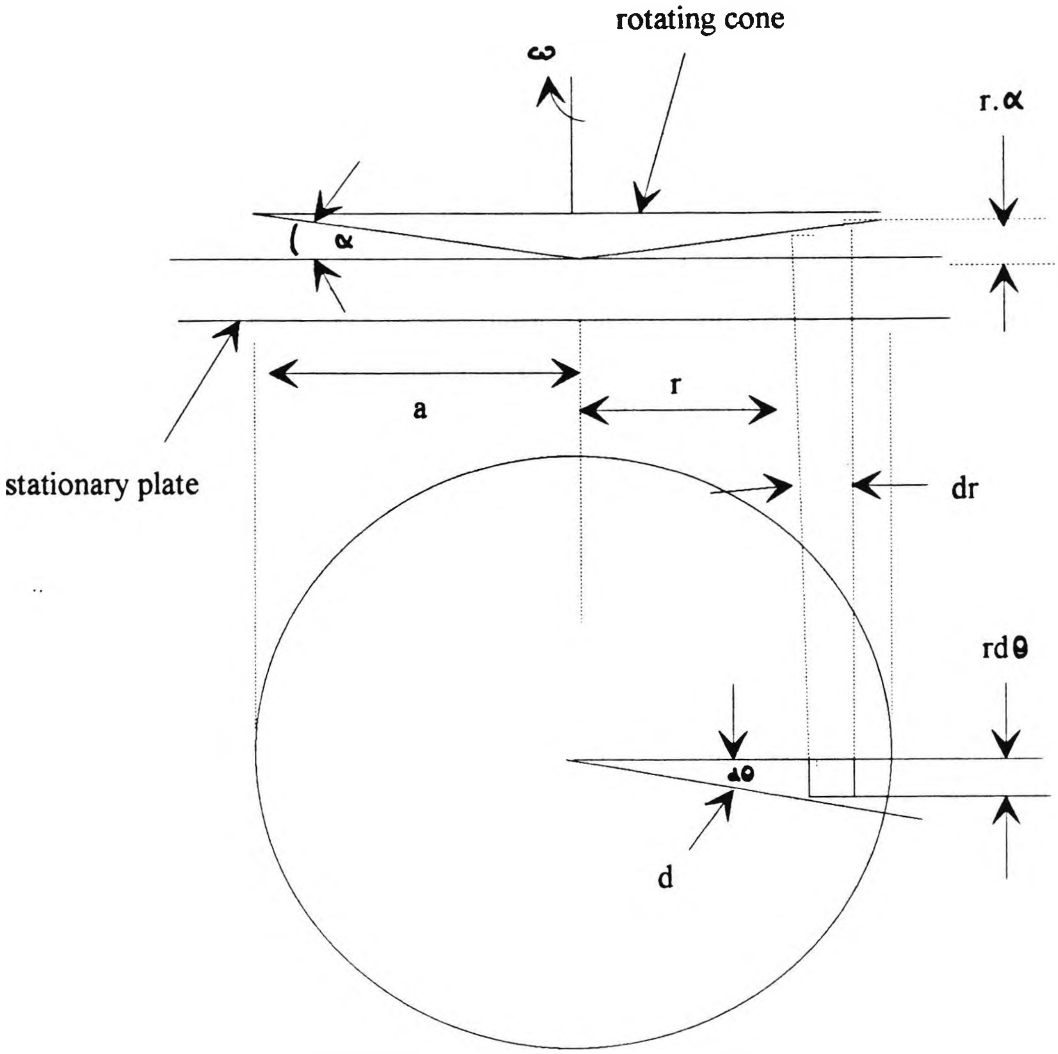

Figure (5.3) The cone and plate viscometer geometry (adapted from Patton, T.C., Paint Flow and Pigment Dispersion. Wiley. New York. 1979. 2nd Edition. Page 55).

The velocity of the surface of the liquid in contact with the cone can be expressed as r ω where r is an arbitrary distance measured perpendicular from the axis of the cone and ω the angular velocity in radians per second. The thickness of the sample or distance between the cone and plate at any point is given by r.tanα where α is the angle of the cone, or for small angles rα. Thus the velocity profile or shear rate is given by the following equation,

$$\frac{d\gamma}{dt} = \frac{r\omega}{r.\tan\alpha} = \frac{\omega}{\tan\alpha} \approx \frac{\omega}{\alpha}$$ Equation (5.15)

For a given angular velocity, the shear rate increases with a smaller cone angle. The shear rate is independent of the radius and is therefore uniform throughout the entire sample. A linear velocity profile can only be assumed for small cone angles when the surfaces of the cone and plate are nearly parallel to one another. As the shear rate is a constant, the shear stress must also be a constant. The shear stress, which is the force acting on the layer of the liquid adjacent to the rotating cone divided by the area on the cone surface can be calculated by considering a small area r.dθ by dr. The area is then given by the following double integral,

$$\textit{Cone surface area} = \int_0^{2\pi} d\theta \int_0^a r.dr \qquad \text{Equation (5.16)}$$

where a is the radius of the cone. The force can be given by T/r where T is the torque measured in Newton metres. Thus the equation for the shear stress τ is,

$$\tau = \frac{T}{\int_0^{2\pi} d\theta \int_0^a r^2.dr} = \frac{3T}{2\pi a^3} \qquad \text{Equation (5.17)}$$

For a given torque, the shear stress increases the smaller the cone radius. The expression for the viscosity η is,

$$\eta = \frac{\tau}{d\gamma / dt} = \frac{\alpha 3T}{\omega 2\pi a^3} \qquad \text{Equation (5.18)}$$

All cone and plate viscometers allow the cone to be moved away from the plate to allow for sample changing and in order to fit different sized cones. In order to avoid errors in contacting the cone tip (which might become worn) with the plate (which might become indented), the cones used with the Carrimed instrument were truncated. The gap between the cone and the plate was set such that the virtual tip was in contact with the plate. With cones possessing a small angle of 0.5° or 1°, setting this gap accurately becomes problematical. Thermal expansion also contributes to a greater extent when trying to set a small gap.

Viscosity measurements are made on the Carrimed CS100 controlled stress rheometer by choosing a torque, and hence stress, and then measuring the angular displacement or shear rate. The maximum torque about the cone axis is 10^2 Nm (100 000 dyne cm) and the maximum angular velocity allowed is 50 radians per second. The rheometer was fitted with a 4cm/2° stainless steel cone. The cone size was chosen to be sufficiently sensitive to detect subtle changes in dispersion rheology without requiring too large a sample volume. The maximum shear rate and shear stress obtainable with this cone were 1 444 s^{-1} and 5 968 dynes.cm^{-2} respectively. The plate temperature was controlled at 25°C by a Peltier system.

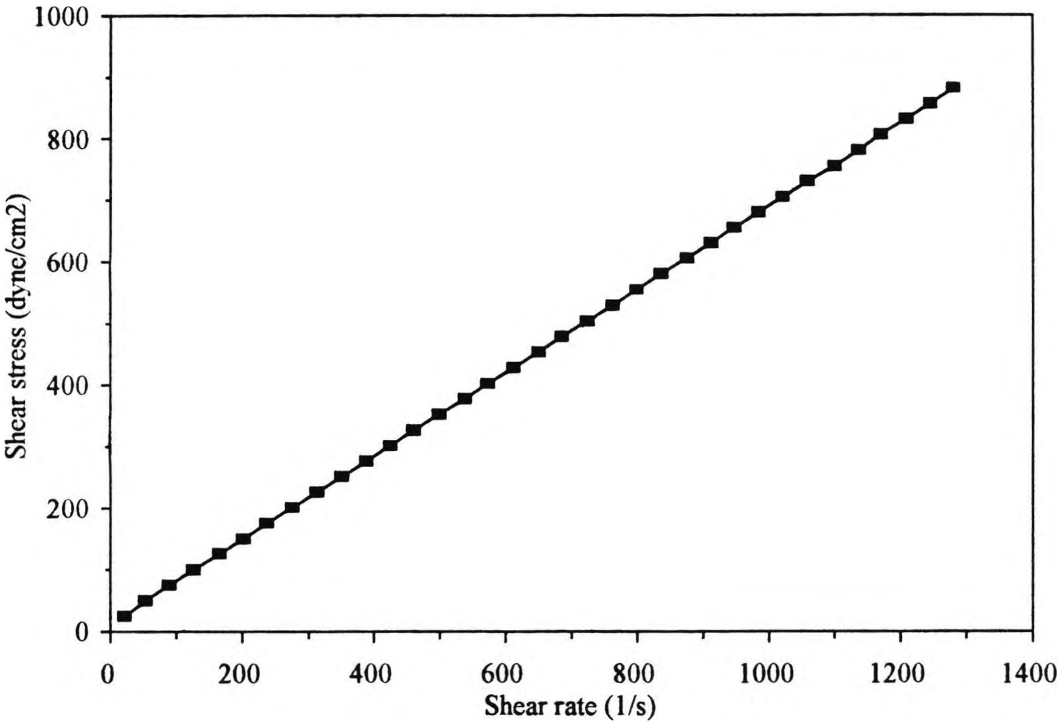

Figure (5.4) Flow curve of a 95:5 methyl methacrylate-methacrylic acid copolymer (batch 21.16) 100% neutralised with diethyl zinc (prepared by non-aqueous dispersion polymerisation) dispersed in butylbenzyl phthalate at a 10:90 weight ratio. Second cycle at time zero.

The experimental procedure for measuring the plastisol viscosity comprised carrying out two shear stress cycles an hour for up to 17 hours. Each cycle consisted of a period during which the stress was steadily increased from zero, held at a constant value and then steadily reduced to zero. A typical result for the upward part of the cycle is shown in Figure (5.4). This sort of figure is known as a flow curve. The viscosity of the sample was calculated as the gradient of the upward sweep of the second shear stress cycle.

The instrument was calibrated with a 23.5 Centipoise (at 25°C) standard viscosity oil on a weekly basis. The standard was calibrated using a capillary viscometer itself calibrated against traceable standards. The error in the viscosity using the rheometer was about 5%.

Test samples were prepared from plasticisers and the dried polymers on a 2g scale using an automatic muller. Polymers were dried in a vented oven overnight at 30°C, broken up into lumps using a mortar and pestle and sieved through a 500μm mesh. Due to the exponential relationship between the relative viscosity of the plastisol and the volume fraction of the dispersed polymer phase, described in Section 3.2.2, they were prepared dilute, typically comprising 10% w/w dried polymer. In this way, limited particle swelling could be accomodated without the risk of the plastisol gelling immediately. Differences in plastisol stability could then be more easily discerned. Weighing errors associated with preparation of the test plastisols amounted to a total error of about 5% in the weight fraction of dried polymer in plasticiser for plastisols with 10% w/w dried polymer.

The results are expressed as relative viscosities, the measured viscosity divided by the plasticiser viscosity, thus discounting the effect of the plasticiser viscosity.

5.2.7 Glass transition temperature measurement

Glass transition temperatures (Tg) of a number of plastisols were measured, under the guidance of Dr. Mike Richardson at the National Physical Laboratory (Teddington) using differential scanning calorimetry (DSC). Thermal analysis, which includes DSC, is defined by the International Confederation of Thermal Analysis as a 'term covering a group of techniques in which a physical property of a substance and/or its reaction product(s) is measured as a function of temperature' [14]. In DSC, the physical property being measured is the change in energy of the test sample that is often seen as the temperature is raised. In the case of polymers, the DSC traces are generally characterised by a series of events marking changes in the physical state such as those at the crystallisation, melting, curing or glass transition point.

Experiments were carried out on a Perkin-Elmer DSC2 which uses a technique known as power compensation whereby the difference in power required to keep both the sample and a reference at the programmed temperature is measured. The procedure involved weighing out approximately 20 ± 0.01 mg of sample into a small aluminium pan and placing it into a well fitted with a heater. An identical empty pan was placed into a similar well fitted with a separate heater as a reference. The two pans were then heated from 260°K to 400°K at the rate of 20°K min^{-1}. Assuming that the pans are identical, the difference in power required to maintain the two pans at the same temperature is related to the heat capacity of the test sample. As a polymer is heated below the glass transition, the heat capacity increases in a linear fashion. After the glass transition, the heat capacity of the polymer continues to increase linearly with temperature but at a different rate. The intersection of the two curves denotes the glass transition. A typical DSC trace of temperature in degrees Kelvin versus heat capacity in units of J/g/degree is shown in Figure (5.5).

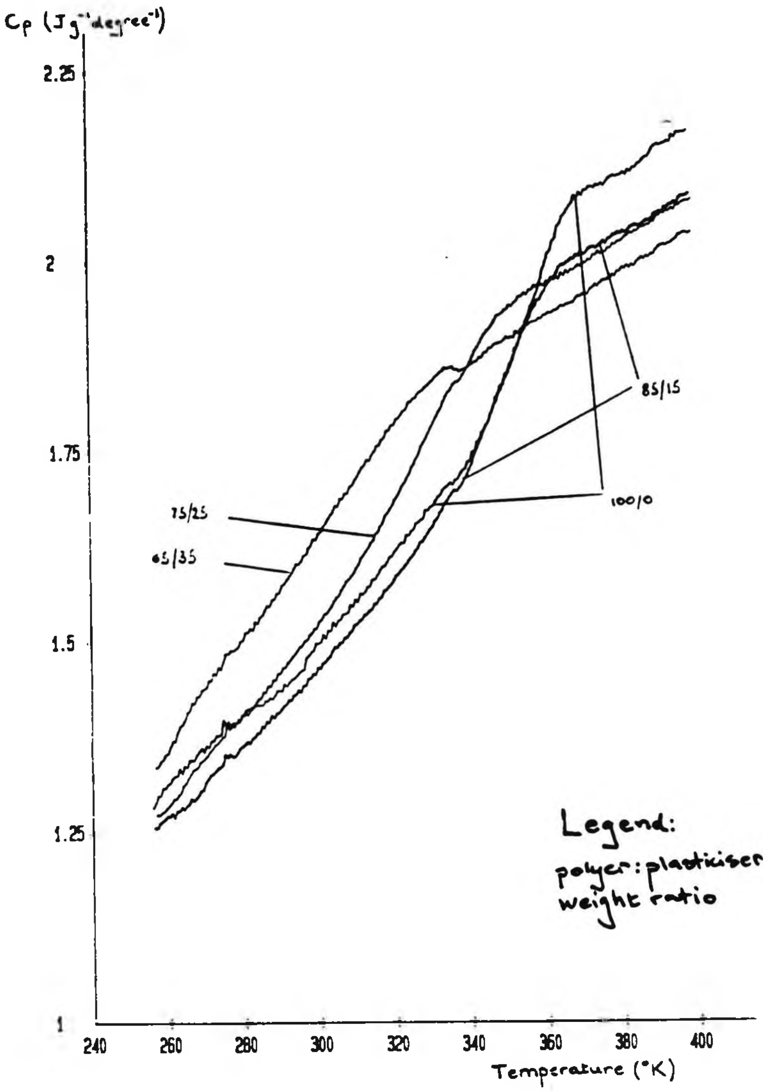

Figure (5.5) A DSC traces for plastisols comprising 92.5:7.5 methyl methacrylate-methacrylic acid copolymer (prepared by non-aqueous dispersion polymerisation) dispersed in butylbenzyl phthalate at various weight ratios. Temperature (°K) versus specific heat capacity at constant pressure Cp ($J.g^{-1}.deg^{-1}$) .

The temperature was calibrated by heating samples of mercury, gallium and indium standards through their melting points in tenth of a degree steps. Calibration of the heat capacity was carried out using a sapphire standard. The advantage of sapphire over the more common indium standard is that the calibration can be carried out over any temperature range and that only the displacement in heat capacity need be measured. With indium, the calibration test temperature range includes the melting point and the enthalpy change must therefore be calculated.

All the samples were subjected to an identical heating cycle prior to the test cycle in order to reduce differences between the samples that might arise due to their particular thermal histories and also to improve thermal contact between the sample and the base of the aluminium pans. In order to further reduce variations in glass transition temperature measurements due to differences in heating rate, a method of measurement was adopted based on the definition of Tg as the point of intersection of the enthalpy curves for the glassy and liquid states [15]. The heat capacities of the glassy and liquid phases (c_g and c_l) can be given in terms of the following linear equations,

$$c_g = a + bT \qquad \text{Equation (5.19a)}$$

$$c_l = A + BT \qquad \text{Equation (5.19b)}$$

where a, A, b and B are constants and T is the temperature in degrees Kelvin. The constants can be calculated using the method of least squares. Integration of equations (5.19) to give the enthalpies (H) in the form of the indefinite integrals,

$$H_g\,(T) = aT + \tfrac{1}{2}bT^2 + P \qquad \text{Equation (5.20a)}$$

$$H_l\,(T) = AT + \tfrac{1}{2}BT^2 + Q \qquad \text{Equation (5.20b)}$$

where P and Q are integration constants. By substitution of a temperature in the glassy phase T_1 into Equation (5.20a) and a temperature in the liquid phase T_2 into Equation (5.20b), and subtracting to give $H_l\,(T_2) - H_g\,(T_1)$, Q-P is obtained. The glass transition temperature can then be calculated by solution of the quadratic equation $H_g\,(Tg) = H_l\,(Tg)$. The values are routinely reproducible to ±1°K and independent of heating but not cooling rate [7]. Variation of the cooling rate allows the preparation of different glasses. Quenching of a liquid polymer results in a glass with a higher free volume and glass transition temperature than one allowed to cool more slowly to a relatively more stable state. However, it has been shown that for most polymers processed in the temperature range 50-500°K min^{-1}, the spread of Tg is restricted to about 3-4°K [7].

This method of Tg calculation can be described graphically [16]. In Figure (5.6), the Tg is the point at which the area (A + C) = area B. This equates to the perpendicular D-E being moved left or right such that the area under the theoretical curve F-D-E-G is the same as that under the experimental curve F-G.

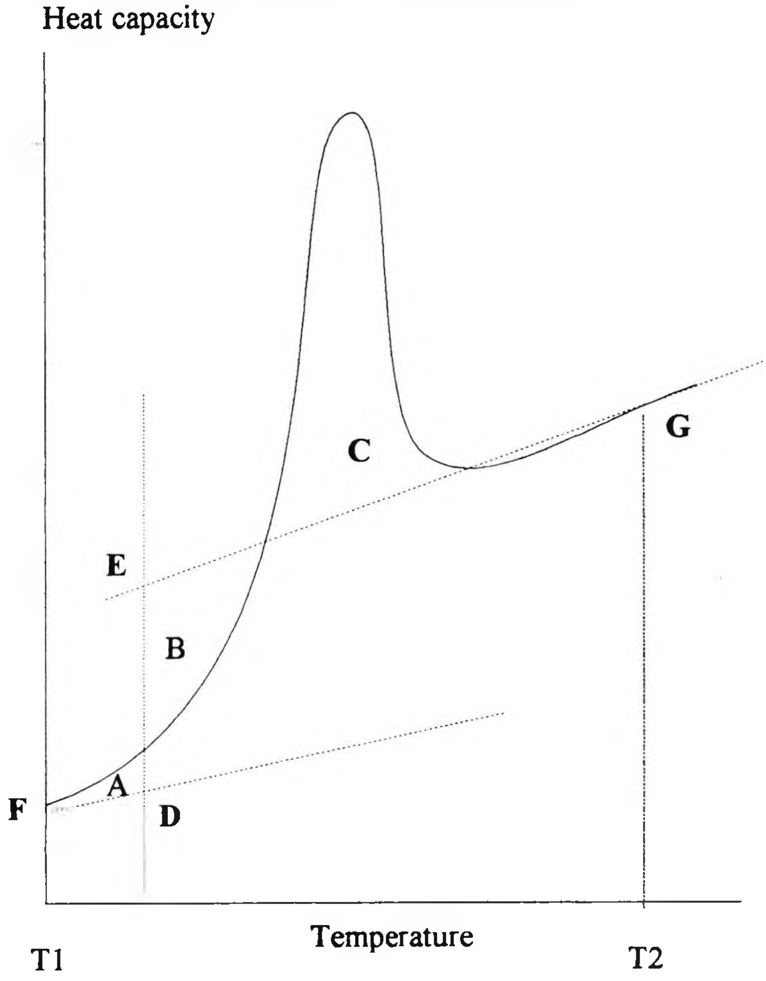

Figure (5.6) Graphical construction showing how Tg is defined when the area (A + C) = area B (adapted from reference 13).

5.2.8 Gel content measurement

The gel content, or the degree of crosslinking, of the covalently crosslinked polymers was determined using three methods. Different methods were applied to the polymer when in its original form to already dried. Both methods suitable for the undried polymers relied on dissolving the un-crosslinked fraction in a solvent and then separating it from the crosslinked portion with a centrifuge. Details of one method are described in Box (5.1).

Box (5.1) Centrifuge method for determining the gel content of crosslinked polymers[17]

(1) Approximately 2 grams of the test dispersion or latex were weighed into a suitable container.

(2) The sample was thinned with 50 ml of the dispersion or latex solvent.

(3) 50 ml of methyl ethyl ketone was added to the diluted sample.

(4) Two 10 ml samples were then pipetted into two pre - weighed centrifuge tubes.

(5) The samples were centrifuged at 3 000 rpm for 45 minutes and the supernatent decanted.

(6) Fresh quantities of methyl ethyl ketone were added to the sample and the sample teased with a glass rod and step (5) repeated.

(7) Step (6) was repeated after which the sample tubes were dried in an oven at 150°C to constant weight.

(8) The final weight was compared to the original non - volatile weight and the gel content expressed as a percentage of the original weight.

The alternative method is identical to that given in Box (5.1) with the additional step between steps (3) and (4) of ballmilling a 20 ml sample for 2-3 days. Due to the problem of incompatibility between an aqueous phase and added methyl ethyl ketone, the latter method was found to be better suited for the polymers prepared by emulsion polymerisation.

A method based on the Soxhlet extraction technique was found to be effective for the dried polymer. This is described in Box (5.2). It was found necessary to fuse the sample in order to prevent loss of particulate material through the pores of the filter paper.

Box (5.2) Soxhlet extraction technique for determining the gel content of crosslinked polymers

(1) The polymer powder was heated into a fused mass.

(2) Filter papers (Whatman 542) were pre-dried in an oven and the sample carefully weighed onto the paper.

(3) The papers were then folded up and placed into the extraction apparatus.

(4) The sample was then extracted with methyl ethyl ketone for a number of hours and the sample removed, dried and weighed.

(5) The gel content was expressed as a percentage of the original non-volatile weight

5.2.9 Preparation of plastisol coatings

Plastisols were prepared by dispersing pre-dried polymer into plasticiser on an automatic muller at the ratio of 50:50 by weight. This is considered the minimum amount of polymer required for acceptable coating properties. The plastisols were coated onto clean glass panels using a number seven K-bar (RK Chemical) which gave a wet film thickness of 75 microns. The coating was heated at 130°C for thirty minutes in a vented oven. The appearance of the plastisol before and after heating was noted.

Appendix A Gel permeation chromatography traces

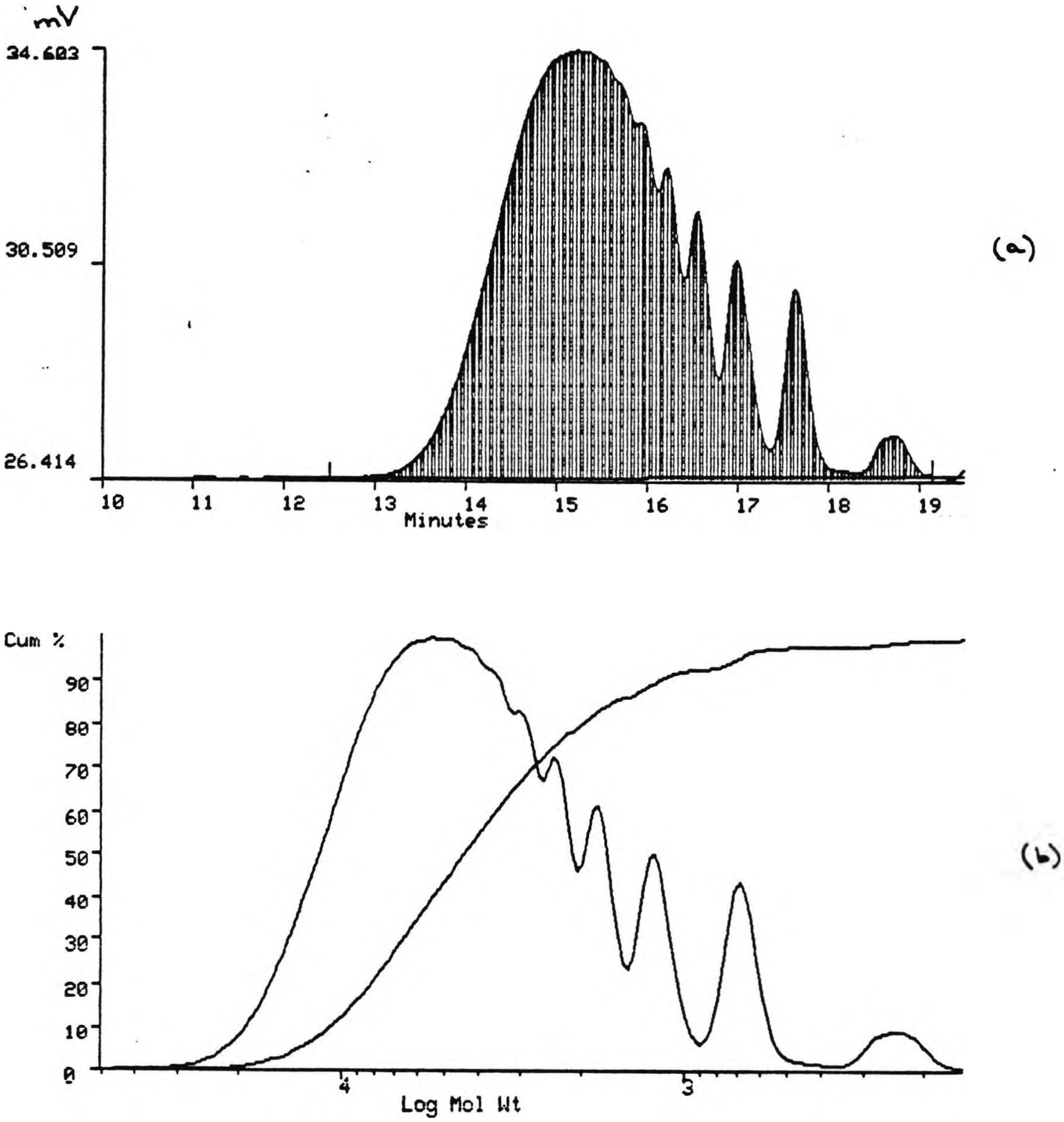

Figure (5A.1) Stabiliser precursor (batch 2335/163): (a) Detector response (mV) versus retention time (minutes); (b) Original data replotted in terms of percentage cumulative weight fraction versus log molecular weight and differential weight fraction versus log molecular weight. Conditions: see ICI paints.

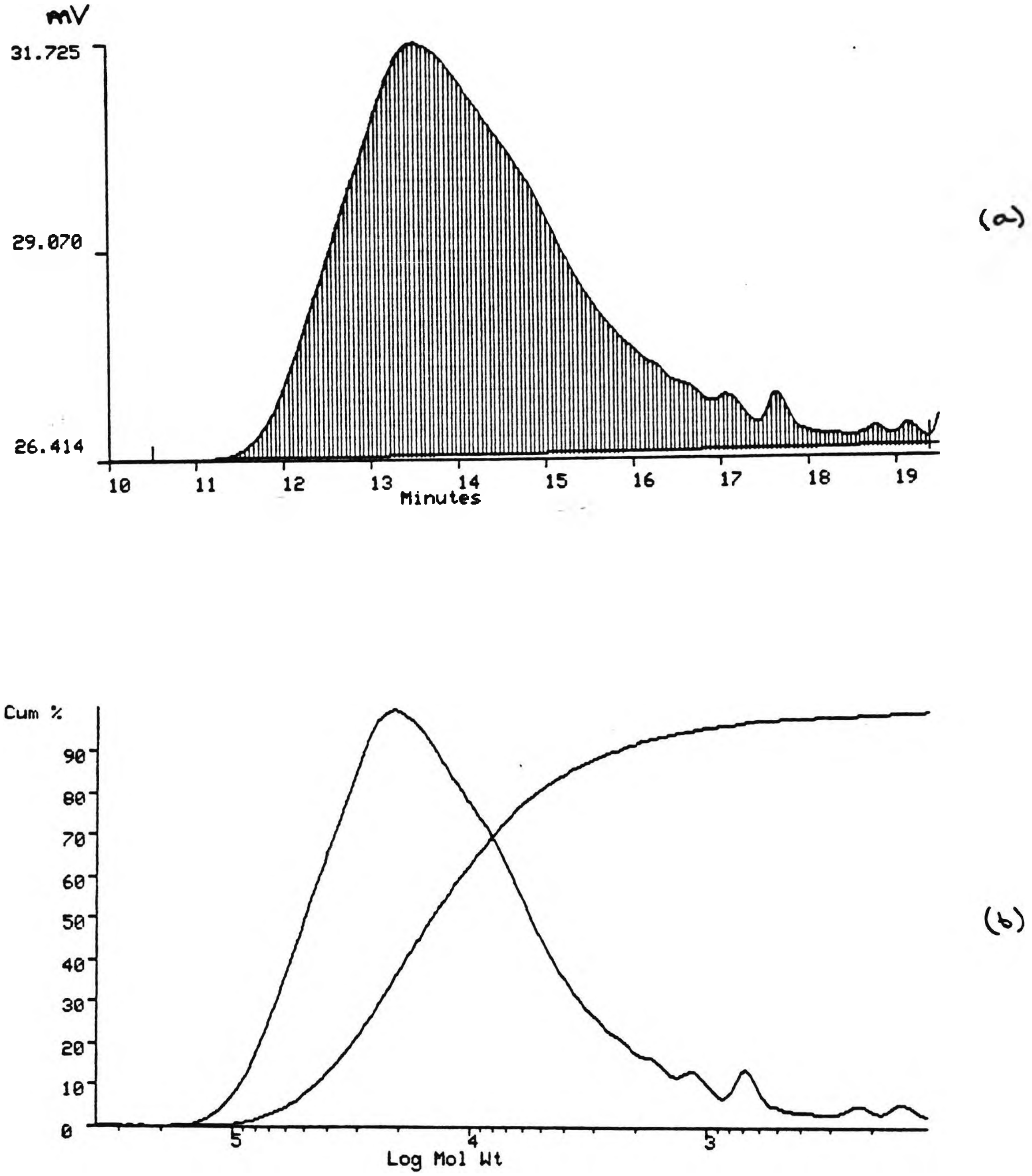

Figure (5A.2) Comb stabiliser (batch 2335/165): (a) Detector response (mV) versus retention time (minutes); (b) Original data replotted in terms of percentage cumulative weight fraction versus log molecular weight and differential weight fraction versus log molecular weight. Conditions: see ICI paints.

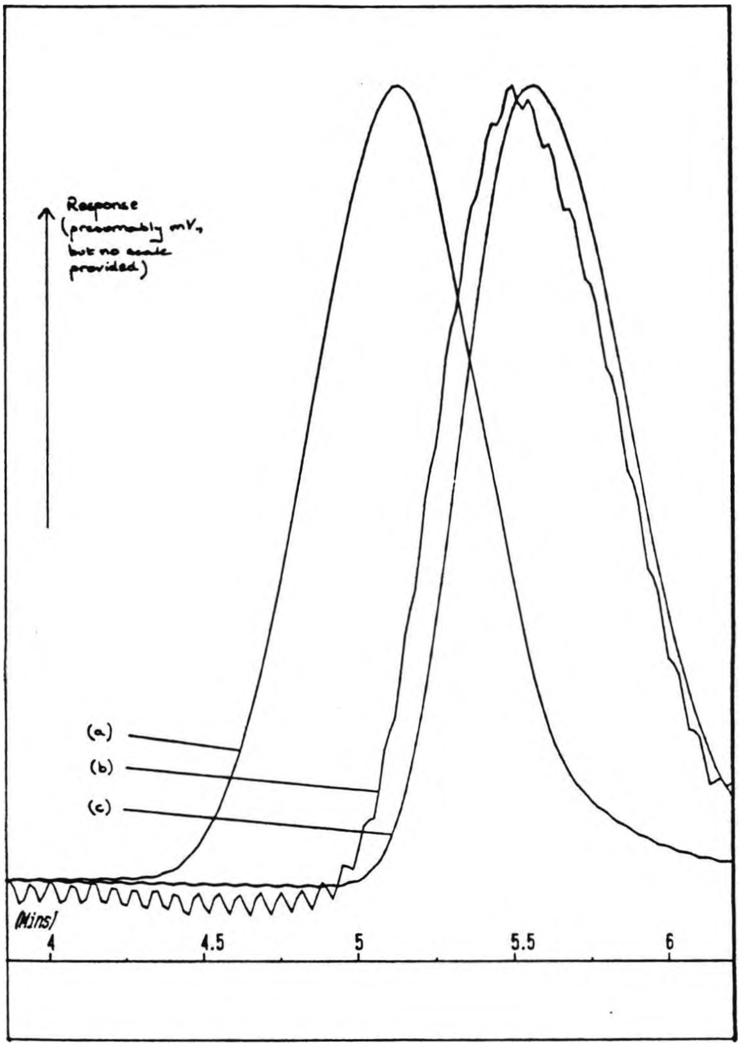

Figure (5A.3) Response versus time (minutes). (a) 92.5:7.5 methyl methacrylate-methacrylic acid copolymer prepared by non-aqueous dispersion polymerisation (batch 6.10); (b) poly(butyl acrylate) (batch 2366/23); (c) poly(butyl acrylate) (batch 2366/30). Conditions: see Cray Valley Products.

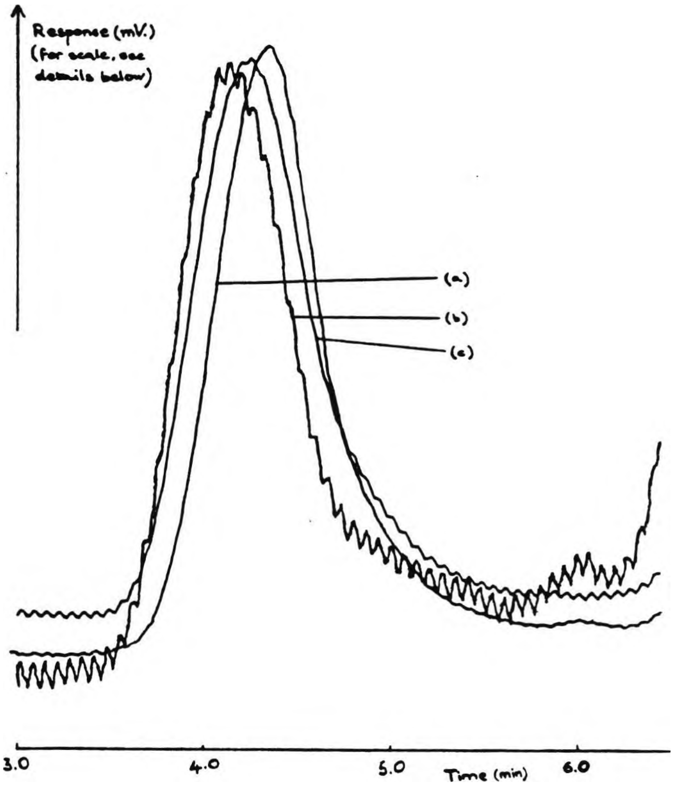

Figure (5A.4) Response versus time (minutes). (a) 92.5:7.5 methyl methacrylate-methacrylic acid copolymer prepared by non-aqueous dispersion polymerisation. 18mV full scale (batch 14.3); (b) as for (a) 8mV full scale (batch 14.4); (c) as for (a) but prepared by aqueous emulsion polymerisation. 13mV full scale. Conditions: see Cray Valley Products.

Appendix B Scanning electron micrographs

Figure (5B.1) shows a polymer prepared by aqueous emulsion polymerisation. Figures (5B2) and (5B.3) are of polymers prepared by a seed and feed non-aqueous dispersion polymerisation method. Those in figures (5B.4) and (5B.5) were also prepared by non-aqueous dispersion polymerisation but in a single stage.

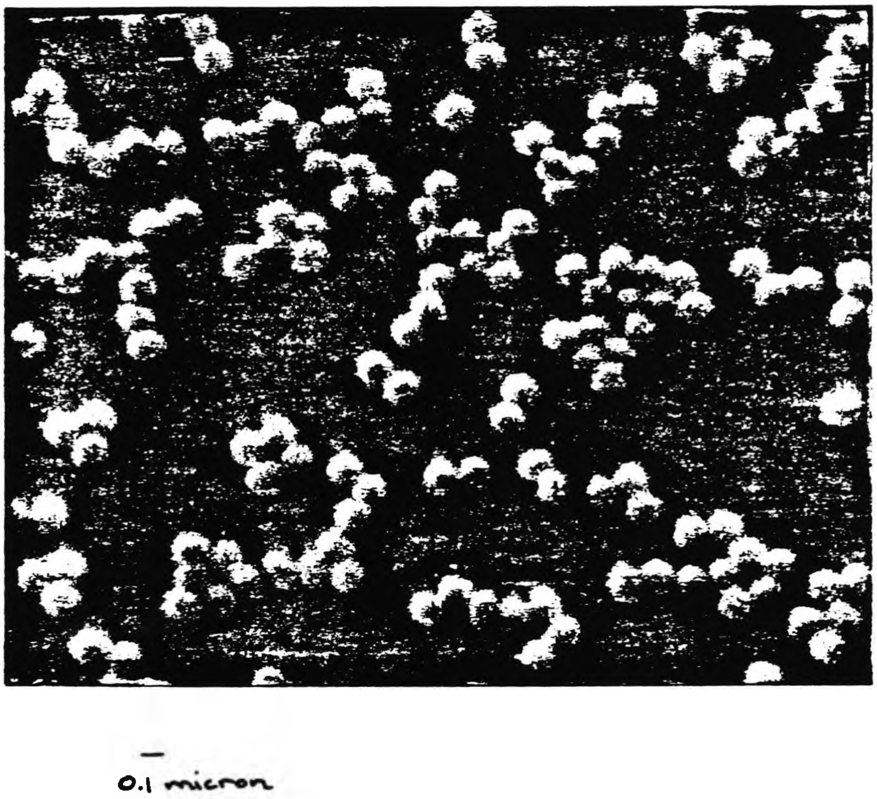

Figure (5B.1) 95:5 methyl methacrylate-ethylene glycol dimethacrylate copolymer (batch 13.11) x23 000.

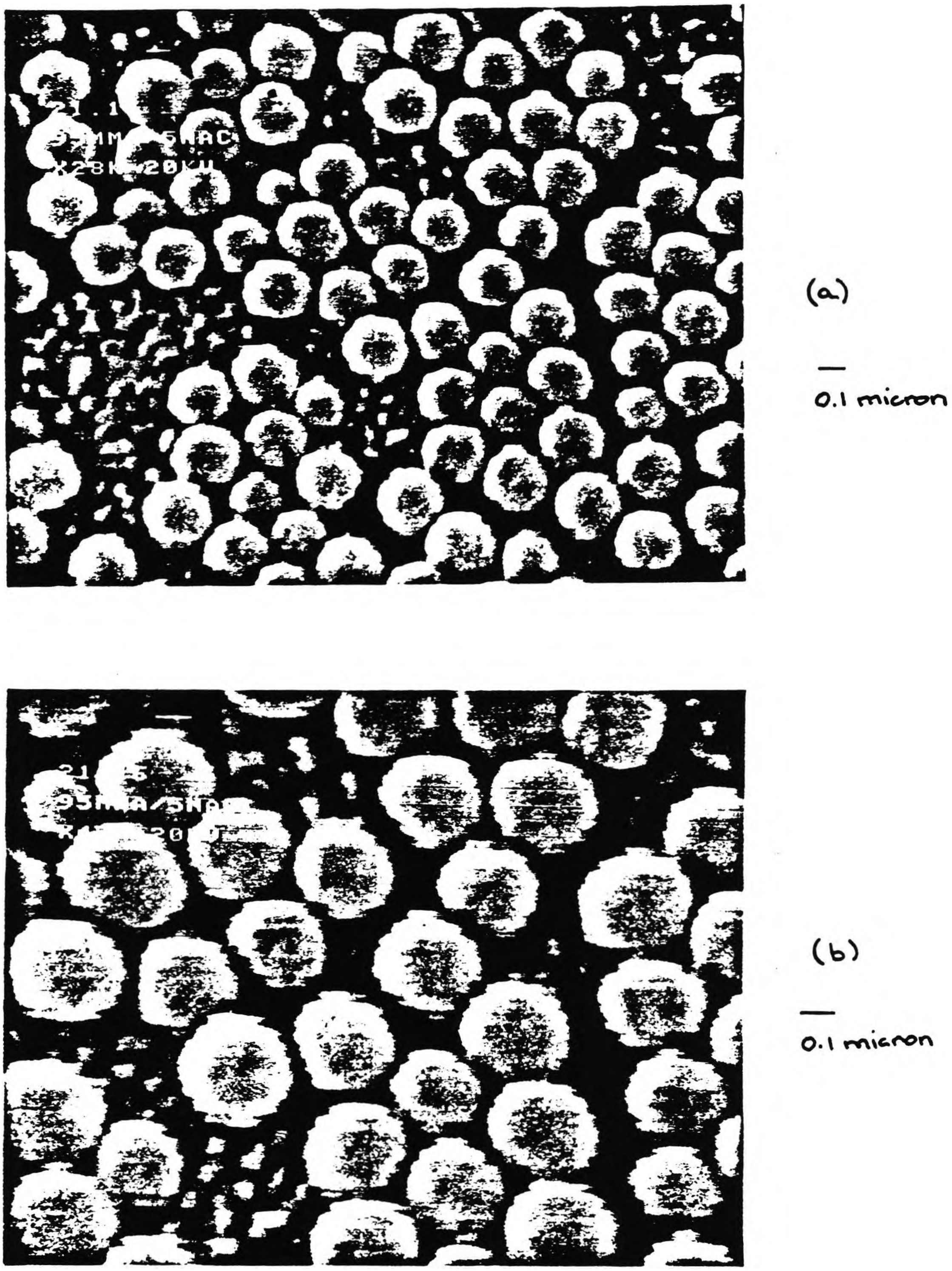

Figure (5B.2) 95:5 methyl methacrylate-methacrylic acid copolymer with poly(12-hydroxystearic acid) stabiliser (batch 21.16): (a) x28 000; (b) x47 000.

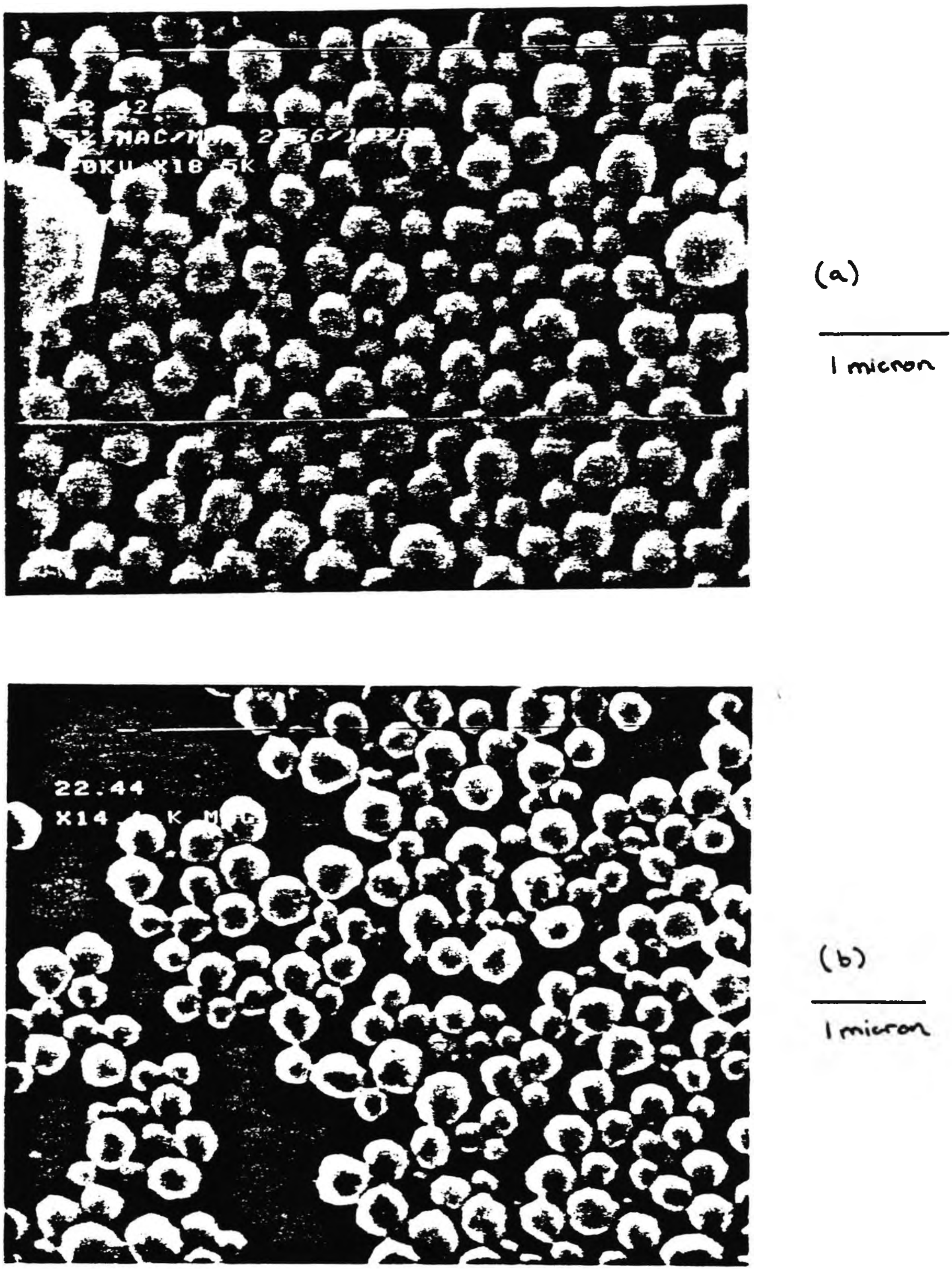

Figure (5B.3) Methyl methacrylate-methacrylic acid copolymers with poly(lauryl methacrylate) stabiliser: (a) 95:5 methyl methacrylate-methacrylic acid (batch 22.42) x18 500; (b) 92.5:7.5 methyl methacrylate-methacrylic acid (batch 22.44) x14 100.

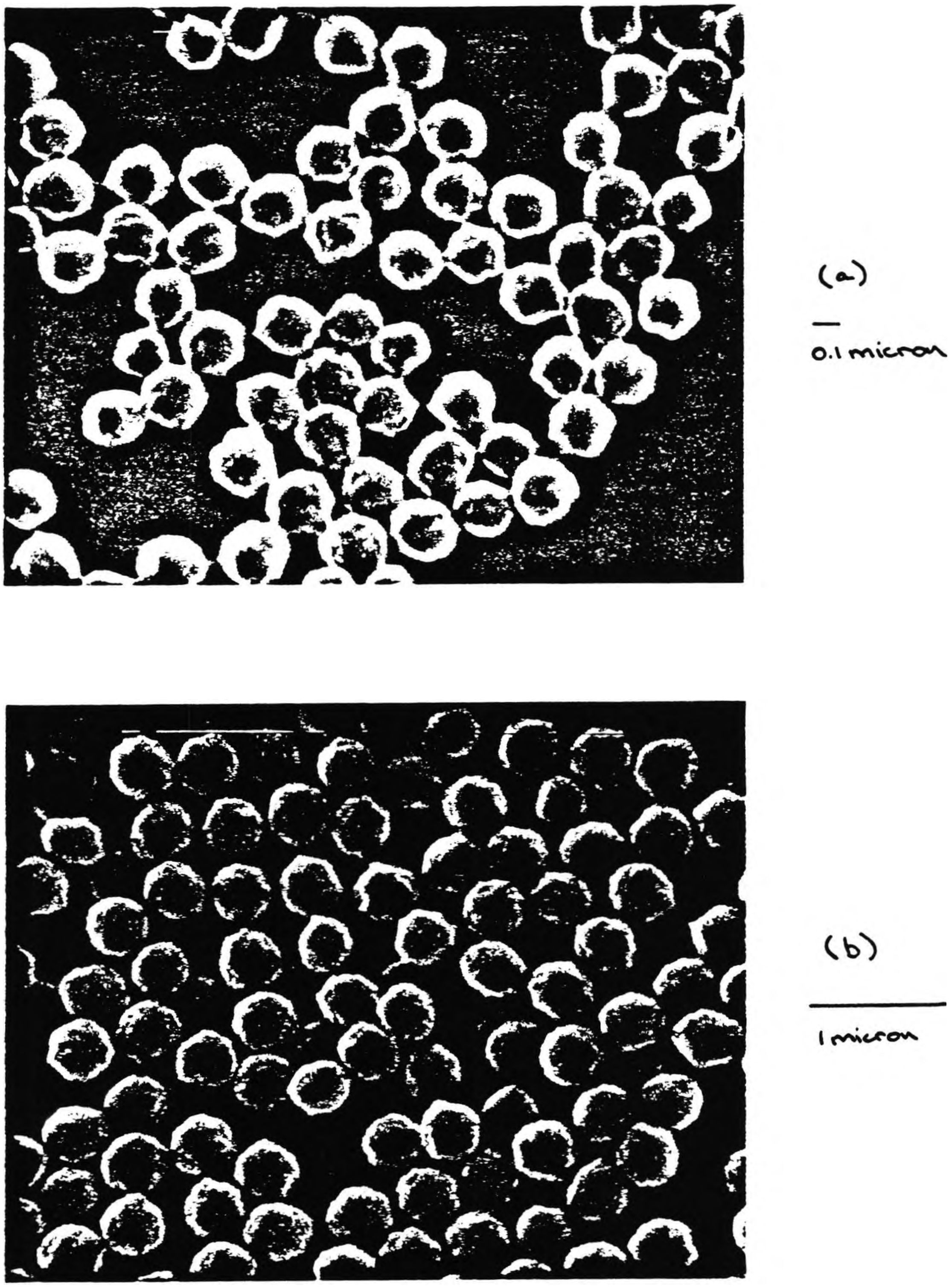

Figure (5B.4) 95:2 methyl methacrylate-methacrylic acid copolymers with poly(12-hydroxystearic acid) stabiliser: (a) batch 17.28 x28 000; (b) batch 17.30 x19 400.

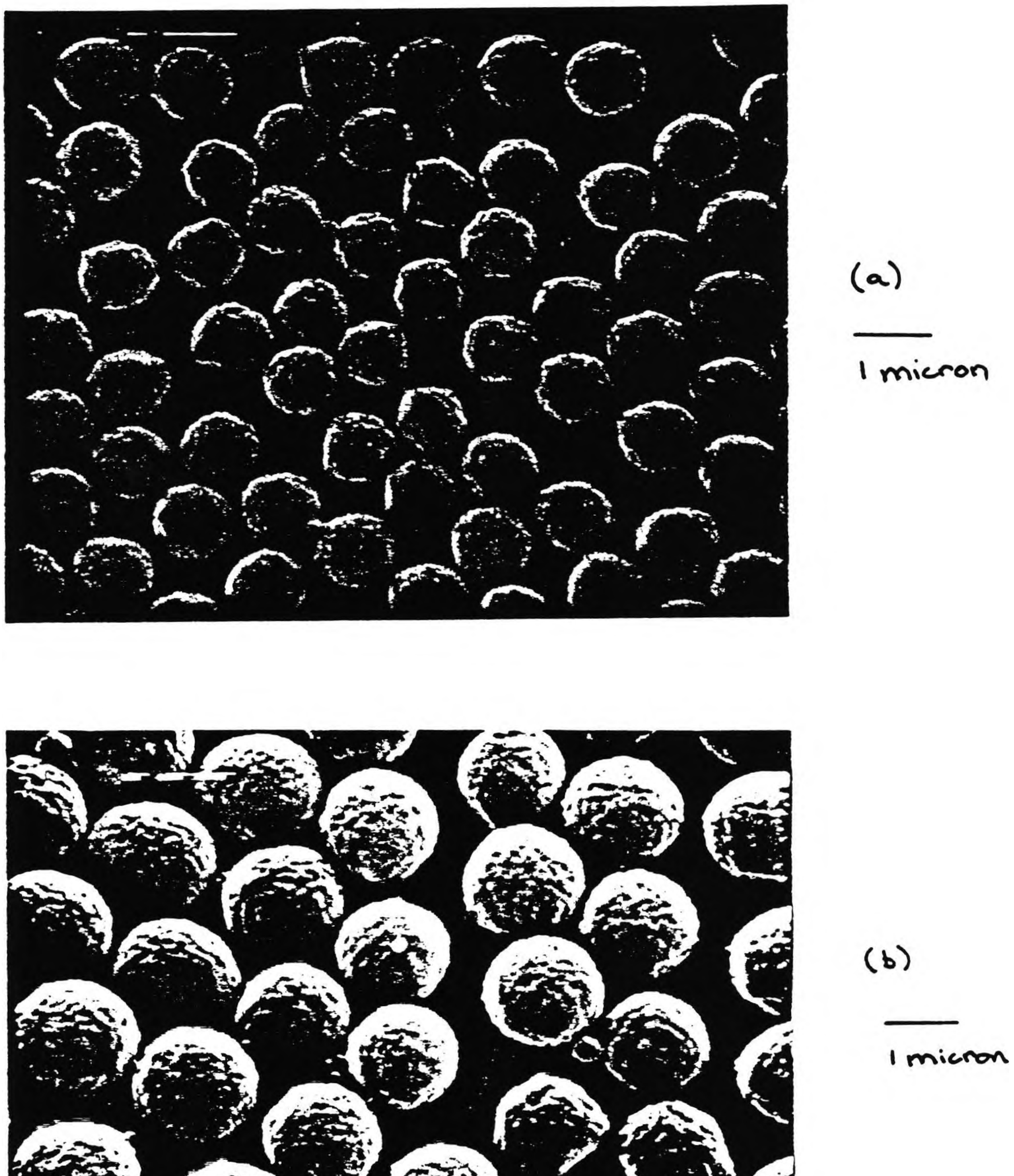

Figure (5B.5) 95:2 methyl methacrylate-methacrylic acid copolymers with poly(12-hydroxystearic acid) stabiliser: (a) batch 17.29 x9 300; (b) batch 17.2 x8 800.

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CHAPTER 6-

TRANSIENTLY CROSSLINKED POLYMERS I: HYDROGEN BONDS AND DIPOLE-DIPOLE INTERACTIONS

Polymers were prepared with thermally reversible crosslinks. The effect of the crosslinks on the rate of swelling of the polymers, when formulated as plastisols, was measured viscometrically. The theory of the action of a solvent on polymers with thermally reversible crosslinks is described in Section 3.3.1. The crosslinks consisted of hydrogen bonds and dipole-dipole interactions. As described in Section 4.1.1, these crosslinks were provided by the monomers methacrylic acid, acrylic acid, 2-hydroxyethyl methacrylate and methacrylonitrile. The polymers, all comprising methyl methacrylate and one of the monomers listed above, were prepared using non-aqueous dispersion and aqueous emulsion polymerisation techniques.

The polymers were then dried and redispersed into a range of commercially available plasticisers. The stability of these simple plastisols was assessed in the liquid form and as an applied coating. Liquid stability was determined, as described in Section 5.2.6, by measuring the change in viscosity over time. Coating stability was assessed on the basis of visual examination for plasticiser exudation and mechanical integrity.

Each step is described in detail in the following sections under the headings:

(a) The preparation of polymers using non-aqueous dispersion polymerisation
(b) The preparation of polymers using aqueous emulsion polymerisation
(c) Plastisol stability
(d) Plastisol glass transition temperatures
(e) Plastisol films

6.1 The preparation of polymers using non-aqueous dispersion polymerisation

The nature of non-aqueous dispersion polymerisation is described in Section 3.1.2. The preparation of polymers by the non-aqueous dispersion polymerisation route requires, as explained in Section 3.1.2, steric stabilisers. The unavailablity of suitable commercial steric stabilisers required their in-house preparation. Comb type stabilisers were prepared based on 12-hydroxystearic acid following an established method[1].

6.1.1 Preparation of steric stabilisers based on 12-hydroxystearic acid

The preparation of the comb stabilisers was a multi-step operation involving the following steps:

(a) Acid initiated condensation polymerisation of 12-hydroxystearic acid

(b) Reaction of poly(12-hydroxystearic acid) with glycidyl methacrylate via ring opening mechanism to form stabiliser precursor

(c) Reaction of the precursor with acrylic monomers by a free radical polymerisation mechanism to form the comb stabiliser

Poly(12-hydroxystearic acid) functioned as the part of the stabiliser soluble in the medium used for the non-aqueous dispersion polymerisations. Thus, it was responsible for providing steric stabilisation. The acrylic polymer was the insoluble part of the stabiliser anchoring the molecule to the polymer particles formed by non-aqueous dispersion polymerisation.

Commercially available 12-hydroxystearic acid contains 8-15 % by weight stearic and palmitic acids which act as chain terminators limiting the molecular weight. A typical recipe for the condensation polymerisation of 12-hydroxystearic acid, step (a) above, is given in Box (6.1). The reaction was monitored by periodic acid value determinations, described in Section 5.2.1, to give a molecular weight of about 2000. This corresponded to an acid value of about 35 mg(KOH)/g.

Box (6.1) Condensation polymerisation of 12-hydroxystearic acid (batch number 2335/162)

The following materials were heated at 185°C for 3.25 hours in a 2 L reaction flask fitted with a condenser and Dean-Stark separator. The rate of reaction was monitored by periodically determining the acid value, decribed in Section 5.2.1, of the mixture. The number average molecular weight (Mn) was measured according to the method described in Section 5.2.3. The non-volatile fraction was determined according to the method described in Section 5.2.2.

900 g	12-hydroxystearic acid
90 g	xylene
1 g	methane sulphonic acid

Final acid value	33.7 mg(KOH)/g
Theoretical molecular weight	1650-1660
Experimental Mn	2441
Non-volatiles	86.2 %

The actual theoretical molecular weight of 1650-1660 was calculated from the formula weight and the experimental acid value of the polyester. The acid value for one mole of 12-hydroxystearic acid (56100 mg) was divided by the formula weight (300) to calculate the acid value (per gram) which was 187 mg(KOH)/g. Dividing this value by the experimentally obtained value and multiplying by the formula weight of the monoester yielded the theoretical molecular weight of 1650. By assuming loss of one mole of water from each mole of monoester and using this lower value of the formula weight (282), the upper limit of 1660 was obtained. The experimental and predicted molecular weights do not coincide as the former is a number weighted average of all chain lengths whilst the latter assumes that there is no chain length distribution.

The stabiliser precursor, as described in step (b) above, was formed as the glycidyl methacrylate adduct of poly(12-hydroxystearic acid) by the base catalysed ring opening reaction of the epoxide ring of the methacrylate and the remaining acid groups on the polyester. A slight excess of glycidyl methacrylate was used. A typical recipe is given in Box (6.2). The precursor possessed a reactive methacrylate end group where there had been residual carboxylic acid groups.

Box (6.2) Preparation of stabiliser precursor based on poly(12-hydroxystearic acid) (batch number 2335/163)

The following reaction mixture was held at 120°C for 4 hours. The rate of reaction was monitored by periodically determining the acid value of the mixture. The acid value and non-volatile fraction were measured according to the methods described in Section 5.2.

500.0 g	poly(12-hydroxystearic acid) (2335/162)
140.3 g	xylene
0.7 g	tert-butyl catechol
55.1 g	glycidyl methacrylate
1.5 g	dimethyl laurylamine

Acid value	1.08 mg(KOH)/g
Non-volatiles	67.2 %

Details of the batches of poly(12-hydroxystearic acid) and stabiliser precursor employed in the preparation of the non-aqueous dispersion polymers described in this chapter are summarised in Table (6.1). The molecular weights (weight average (Mw), number average (Mn) and peak (Mp)), acid values and non-volatile content determinations were conducted according to the methods described in Section 5.2. The molecular weight polydispersities for all the batches of poly(12-hydroxystearic acid) were about two, the value predicted from theory for stepwise polymerisations[2]. Those for the batches of stabiliser precursor were similar.

Table (6.1) Poly(12-hydroxystearic acid) and stabiliser precursor batches. Component weights given in grams.

	Poly(12-hydroxystearic acid)			Stabiliser precursor		
Batch number	2335/15	2335/162	2366/81	2335/26	2335/163	2366/83
12-hydroxystearic acid	900	900	900	-	-	-
Xylene	90	90	90	150.00	140.3	140.0
Methanesulphonic acid	5	1	1	-	-	-
2335/15	-	-	-	850.00	-	-
2335/162	-	-	-	-	500.0	-
2366/81	-	-	-	-	-	500.0
Glycidyl methacrylate	-	-	-	88.75	55.1	52.9
t-butyl catechol	-	-	-	0.50	0.7	0.7
Dimethyl laurylamine	-	-	-	1.50	1.5	1.5
Reaction temperature (°C)	190	185	180	120	120	120
Reaction time (hours)	4.7	3.25	4	14.5	4	9.5
Molecular weight[a]						
Mw	4713	5086	5440	5252	5335	5553 5348i
Mn	2226	2441	2645	2665	2424	2331 2892i
Mp	4592	4672	5144	5298	5484	6036 4520i
Acid value (mg(KOH)/g)	33.00	33.7	31.8	0.0856	1.08	0
Polydispersity (Mw/Mn)	2.12	2.08	2.07	1.97	2.20	2.38 1.85
Final solids (%)	85.68	86.2	86.8	82.94	67.2	67.9

[a] ICI Paints division and International Paint Limited (i)

The final step, step (c), was the conversion of the stabiliser precursor into a comb type stabiliser by free radical solution polymerisation of the methacrylate end group with other acrylic monomers. The final molecule comprised equal amounts by weight of both poly(12-hydroxystearic acid) and acrylic polymer and appeared as a clear solution of copolymer entirely free of precipitated insoluble material. A typical recipe is given in Box (6.3).

Box (6.3) Preparation of a 50:49:1 by weight stabiliser precursor - methyl methacrylate - methacrylic acid comb stabiliser (batch number 2336/165)

The mixture of stabiliser precursor, monomers and initiator (2,2'-azobis-2-methylbutyronitrile) was fed into the refluxing solvent over two hours and then held at reflux for a further 1-1.5 hours. At this point two further additions of the initiator were made at 1-1.5 hour intervals to ensure complete conversion. The non-volatile content of the final product was determined according to the method described in Section 5.2.2.

373.50 g	ethyl acetate
186.21 g	butyl acetate

250.00 g	precursor (2335/163)
164.64 g	methyl methacrylate
3.36 g	methacrylic acid
6.00 g	2,2'-azobis-2-methylbutyronitrile

2 x 1.50 g	2,2'-azobis-2-methylbutyronitrile

Non-volatiles	34.1 %

Details of the batches of comb stabiliser employed in the preparation of the non-aqueous dispersion polymers described in this chapter are summarised in Table (6.2). The molecular weights (weight average (Mw), number average (Mn) and peak (Mp)) and non-volatile content determinations were conducted according to the methods described in Section 5.2. The molecular weights were typical for comb stabilisers which are, using gel permeation chromatography, in the range Mw = 20 000-35 000 and Mn = 6 000-15 000 [1].

Table (6.2) Comb stabilisers. Component weights in grams

Batch numbers	2335/58	2335/165	2366/87	2335/77
Ethyl acetate	93.20	372.50	372.50	93.20
Butyl acetate	46.60	186.21	186.21	46.60
2335/26	60.24	-	-	60.24
2335/163	-	250.00	-	-
2366/83	-	-	250.00	-
Methyl methacrylate	49.00	164.64	166.36	45.00
Methacrylic acid	1.00	3.36	3.39	-
2-hydroxyethyl methacrylate	-	-	-	5.00
2,2'-azobis-2-methylbutyronitrile	2.50	9.00	9.00	2.50
Acrylic polymer composition (% wt)	98 MMA 2 MAc	98 MMA 2 MAc	98 MMA 2 MAc	90 MMA 10 HEMA
Reaction temperature (°C)	87	<102	90.5	95
Reaction time (hours)	6	6	6	7.5
Molecular weight[a]				
Mw	-	19655	24744	-
Mn	-	4302	3061	-
Mp	-	20959	21854	-
Polydispersity (Mw/Mn)		4.57	8.08	
Final solids (%)	38.2	34.1	34.7	39.8

[a] ICI Paints division

6.1.2 Non-aqueous dispersion polymerisation

Using the stabilisers prepared in Section 6.1.1, a variety of polymers were produced employing two methods. The first, known as the one-shot method, involved charging all the ingredients needed for the polymerisation into the reaction vessel and heating them to the required temperature[3]. The other employed a seed and feed technique[4]. Use of a standard seed stage fixed the initial number of particles produced leading to better control of the final particle size.

6.1.2.1 The one-shot method[3]

Using this simple method, a series of 98:2 (wt) methyl methacrylate - methacrylic acid copolymers of particle size 0.27-2.00 microns was prepared. The particle size was controlled by varying the total amount of monomer. The greater the monomer concentration, the greater the solubility of the reaction mixture for the precipitating polymer. The increased solvency required the aggregation of a greater number of oligomers for nucleation to take place thus reducing the subsequent number of primary particles. As there were fewer particles competing for the available monomer, the particles were able to grow to a larger size.

Details of the method of polymer preparation are described in Box (6.4). In order to suppress the inhibiting effect of oxygen, the early stage of the reactions was carried out under nitrogen. Once the solvent mixture had started to reflux, the nitrogen purge was no longer required. 1-Octyl mercaptan was used as a free radical scavenger to control molecular weight. For ease of handling, it was prepared as a 10% w/w solution in Isopar M (an isoparaffin of boiling point range 204-254°C).

Details concerning the final polymers are given in Table (6.3). The non-volatile content was determined in order to indicate the extent of conversion. In some cases, conversions in excess of 100% are suggested. This is probably due to loss of diluent through the glass joints and seals during the course of the polymerisation. Polymer particle diameters, measured under a scanning electron microscope, are also included in the table. Both the non-volatile content and the polymer particle diameters were determined according to the methods described in Section 5.2.

Box (6.4) One-shot preparations of 98:2 by weight methyl methacrylate - methacrylic acid copolymers of particle size 0.27-2.00 microns prepared by non-aqueous dispersion polymerisation

The following mixture was added to the reaction flask and heated under nitrogen to the refluxing temperature. After four hours of refluxing, two additions of initiator (2,2'-azobis-2-methylbutyronitrile) were made at one hour intervals to ensure complete conversion.

Monomer mix (% w/w)	30.00-39.50
Solvent weight ratio (n-hexane:Shellsol D40)	85:15
Comb stabiliser (% w/w monomer)	7.5
2,2'-Azobis-2-methylbutyronitrile (% w/w)	0.08
1-Octyl mercaptan (10% w/w in Isopar M) (% w/w)	0.07
2,2'-Azobis-2-methylbutyronitrile (% w/w)	2 x 0.04

The nature of the polymer particle surface, when viewed under a scanning electron microscope, resembled, in all cases, a raspberry. The implication is that the particles comprised a number of smaller species that had agglomerated but had not completely lost their individual structures. Under the conditions of high solvency in a one-shot preparation, the stabiliser could have rapidly desorbed from the particle surface leading to particle aggregation. As polymerisation proceeded, there would be a rapid drop in the monomer content and hence the solvency. Consequently, the aggregates would become too rigid to coalesce uniformly. An alternative explanation is that as the monomer concentration decreases, a new crop of particles could have formed which was then swept up by the existing particles resulting in particles with a rough surface. In contrast, the polymers prepared using a seed and feed technique appeared to possess smooth surfaces. Using the seed and feed method of polymerisation usually avoids the risk of formation of a second crop of particles.

Table (6.3) 98:2 (wt) methyl methacrylate - methacrylic acid non-aqueous dispersion copolymers of particle size 0.27-2.00 microns prepared using the one-shot method

Batch number	17.28	17.30	17.27	17.29	17.35	17.31	17.2	17.32
Total monomer (% w/w)	30.00	32.50	35.00	37.50	38.00	38.50	39.60	39.50
Particle diameter (μm)[a]	0.27	0.43	0.76	1.00	1.33	1.70	1.60	2.00
Theoretical non-volatiles (% w/w)	32.25	34.94	37.93	40.31	40.85	41.39	42.58	42.46
Experimental non-volatiles (% w/w)	33.0	35.6	39.3	40.3	39.7	40.6	43.0	40.9

[a] Electron microscope

6.1.2.2 The seed and feed method

The first stage of the seed and feed method of non-aqueous dispersion polymerisation comprised preparation of fine poly(methyl methacrylate) seed particles. The seed monomer constituted 5% by weight of the total monomer charge. Larger particles were then grown from the seed particles by careful metering of the remaining monomer mixture.

A typical small scale formulation, in this case a 95:5 (wt) methyl methacrylate - methacrylic acid copolymer, is given in Box (6.5). The solvent mixture was typically toluene, Isopar B, Shellsol D40 and n-hexane in the weight ratio 6:14:15:65 but this was later simplified to an 85:15 by weight mixture of n-hexane and Shellsol D40.

Monomer generally made up about 50% of the total weight. The stabiliser concentration, split between the seed and the two halves of the feed approximately in proportion to the growth in particle area, totalled 4.9-8.4% by weight of the monomer concentration. The free radical initiator, 2,2'-azobis-2-methylbutyronitrile, was employed at 2% of the total weight and the free radical scavenger, a 10% w/w solution of 1-octyl mercaptan in Isopar M, at a level of 0.1% by weight active.

For polymers comprising large amounts of polar monomers, such as methacrylic acid, acrylic acid and 2-hydroxyethyl methacrylate, an addition of 2% by weight n-propanol was necessary just before commencement of the feed stage in order to increase the overall solvent strength. This prevented precipitation of less soluble polar copolymers, which could form a second crop of particles mopping up the remaining stabiliser and flocculating the polymer. Increased amounts of stabiliser were also required. In contrast, a previous investigation into the single-stage preparation of poly(methyl methacrylate) found that at monomer concentrations in the range 8.5-34% w/w, the polymer dispersions coagulated or flocculated before the reaction had gone to completion[3]. This was partly attributed to the low solvency conditions.

Particular care was also taken to ensure that the monomer feed was adequately diluted by the returning reflux to avoid localised concentrations of monomer in the reactor and consequent risk of coagulam formation. In a similar manner to the one-shot experiments, all the polymerisations were conducted under nitrogen in order to reduce the inhibiting effect of oxygen.

Box (6.5) The preparation of a 95:5 by weight methyl methacrylate - methacrylic acid copolymer by a seed and feed non-aqueous dispersion polymerisation procedure (batch number 6.2)

The following reactants were charged into the reactor and refluxed under nitrogen.

Seed Stage:	Methyl methacrylate	2.68	g
	2,2'-Azobis-2-methylbutyronitrile	0.12	g
	Comb stabiliser (34.0% w/w solution)	1.25	g
	Toluene	3.00	g
	Isopar B	7.32	g
	Shellsol D40	7.74	g
	n-Hexane	33.55	g

After 20 minutes, 0.40g of a 10% w/w solution of 1-octyl mercaptan in Isopar M was added. The two monomer feeds were then metered into the reactor in successive hours.

1st monomer feed (added over one hour):

Methyl methacrylate	28.35	g
Methacrylic acid	1.56	g
2,2'-Azobis-2-methylbutyronitrile	0.06	g
1-Octyl mercaptan (10% w/w solution)	0.45	g
Comb stabiliser (34.0% w/w solution)	7.75	g

2nd monomer feed (added over one hour): identical to first monomer feed except contained only 1.80 g of comb stabiliser

Refluxing was continued for a further 30 minutes after the feed was finished to ensure complete conversion of monomer.

Final non-volatile content	52.8%
Particle diameter	0.370 μm (photon correlation spectroscopy)

The results of the characterisation of a range of methyl methacrylate - methacrylic acid copolymers prepared according to the method described in Box (6.5) are summarised in Table (6.4). The standard seed stage was used in all cases with the exception of batch 8.6. In this case, 25% by weight of the total monomer was charged. The higher molecular weight polymers were prepared by first reducing by half (batch 14.3) and then reducing to zero (batch 14.4) the amount of 1-octyl mercaptan used. Due to increased chain entanglement, a higher molecular weight polymer ought to have a reduced rate of velocity of dissolution in plasticiser[5]. Two copolymers, chosen for extended evaluation, were scaled-up. A methyl methacrylate homopolymer (batch 20.2) and a 92.5:7.5 (wt) methyl methacylate - methacrylic acid copolymer (batch 16.15) were scaled-up respectively by a factor of four and eight.

Molecular weights and particle diameters were measured according to the methods described in Section 5.2. In some cases, the particle diameters were measured both with scanning electron microscopy and photon correlation spectroscopy. The dispersity index, obtained from photon correlation spectroscopy measurements, gives a measure of the distribution of particle sizes. The values range from 1 which indicates monodispersity to 9 which indicates polydispersity.

The number average molecular weights of the polymers in Table (6.4) are approximately 20 000-50 000 rising to almost 250 000 in the absence of mercaptan. In general, the polydispersities were above the value of two predicted for random polymerisation. However, as this assumes a constant rate of initiation and random termination or transfer, the implication is that the rate of polymerisation varied throughout the reaction[6]. Polydispersity appeared to decrease on reducing the level of 1-octyl mercaptan.

Table (6.4) Methyl methacrylate - methacrylic acid (MAc) copolymers prepared using a seed and feed non-aqueous dispersion procedure

Batch number	% weight MAc	Mw[a]	Mn[a]	Mp[a]	Polydispersity (Mw/Mn)	Particle diameter (μm)[b]	Dispersity index
6.9	0	107300	23200	80400	4.63	0.19-0.48	
						0.266p	5
20.2	0	-	-	-	-	0.10	-
8.6	2.00	116672c	49920c	120292c	2.34	0.29-0.38	-
		119570c	56094c	121824c	2.13		
6.8	3.49	121000	23100	80400	5.24	0.14	
						0.352p	7
6.2	4.99	108000c	43677c	103377c	2.47	0.20	
						0.370p	4
6.4	7.49	-	-	-	-	0.20	-
6.10	7.49	102700	21800	86400	4.71	0.19	
		110602c	41746c	108733c	2.65	0.268p	3
		83402c	33799c	56836c	2.47		
16.15	7.48	-	-	-	-	0.14	-
14.3	7.48	169992c	120341c	141508c	1.41	0.33	-
14.4	7.48	277288c	243193c	270808c	1.14	0.22	-
6.6	9.99	121200	26300	86400	4.61	0.20	
						0.364p	3

[a] ICI Resins and Cray Valley Products (c)

[b] Electron microscope and photon correlation spectroscopy (p)

The particle size measurements determined using microscopy indicated that most of the dispersions were reasonably monodisperse (see Section 5.2.4 and Appendix B of same chapter). As predicted in Section 5.2.4, the values obtained from light scattering were higher than those obtained from microscopy. As light scattering experiments are adversely affected by the presence of aggregations of polymer particles, problems handling the rapidly drying polymers may have influenced the results.

A limited series of methyl methacylate - methacrylic acid copolymers with a core-shell morphology, as described in Section 2.1.3, were prepared. The core comprised methyl methacrylate homopolymer and the shell, methyl methacylate - methacrylic acid copolymer. The ratio between core and shell was 3:1 by weight. The polymers were prepared using the seed and feed technique, the core as the seed and the shell as the feed. Further details concerning these polymers are given in Table (6.5).

Table (6.5) Methyl methacrylate - methacrylic acid (MAc) copolymers prepared by non-aqueous dispersion polymerisation with a core-shell morphology

Batch number	% weight MAc	Core (3 parts by weight)	Shell (1 part by weight) % weight MAc	Particle diameter (μm)[a]
22.51	7.50	MMA	35.94	0.28
22.52	1.87	MMA	7.49	0.35
22.53	5.00	MMA	20.00	0.35

[a] Electron microscope

Copolymers were also prepared, in the same manner to the methyl methacrylate - methacrylic acid copolymers summarised in Table (6.4), with methyl methacrylate and respectively 2-hydroxyethyl methacrylate and acrylic acid as alternatives to methacrylic acid. Details are given in Table (6.6). The stabiliser containing 2-hydroxyethyl methacrylate (2335/77) was used in the preparation of batches 9.6 and 9.7. Batch 9.4 was prepared from the stabiliser precursor 2335/26 (see Section 3.1.2.1). The molecular weights were similar to those given in Table (6.4).

Table (6.6) Methyl methacrylate - 2-hydroxyethyl methacrylate (HEMA) and methyl methacrylate - acrylic acid (AA) copolymers prepared by non-aqueous dispersion polymerisation.

Batch number	% weight comonomer	Mw[a]	Mn[a]	Mp[a]	Polydispersity (Mw/Mn)	Particle diameter (µm)[b]
9.4	5.01 HEMA	140542c	81991c	126525c	1.71	0.15
9.6	9.99 HEMA	138100	22500	97700	6.14	0.08 - 0.31
9.7	14.85 HEMA	123486c	62830c	120292c	1.96	0.19
17.5	7.50 AA	-	-	-	-	0.25 - 0.41

[a] ICI Resins and Cray Valley Products (c)

[b] Electron microscope

6.2 The preparation of polymers using aqueous emulsion polymerisation

After the preparation of a range of polymers using non-aqueous dispersion polymerisation, described in Section 6.1, the next step, as explained in the introduction to this chapter, was the preparation of an equivalent range of polymers using aqueous emulsion polymerisation. The procedure for aqueous emulsion polymerisation relied on a seed and feed technique similar to that described in Section 6.1.2.2. The theory of aqueous emulsion polymerisation is explained in Section 3.1.2. A simple formulation, based on the anionic surfactant Aerosol OT (sodium dioctylsulphosuccinate) and the free radical dissociative initiator ammonium persulphate, was adopted. The seed stage monomer wholly comprised methyl methacrylate and constituted 12.5% by weight of the total monomer charge.

Box (6.6) Preparation of a 98:2 by weight methyl methacrylate - methacrylic acid copolymer using an aqueous emulsion polymerisation technique (batch number 13.3)

Distilled water was initially heated to 75°C, whereupon an initial charge of 5 g of methyl methacrylate was added containing dissolved surfactant. Heating was continued until at 80°C the initiator was added in the form of a solution in 5 g of distilled water. After about 15 minutes, a blue seed latex was formed and the remaining monomer and surfactant was fed in as 5 ml aliquots over 2 hours. After the final addition, a further addition of initiator solution was made and heating continued for 30 minutes.

Seed stage:		
	Distilled water	59.6 g
	Methyl methacrylate	5.0 g
	Aerosol OT	0.042 g
	Ammonium persulphate	0.064 g
Feed stage:		
	Methyl methacrylate	34.2 g
	Methacrylic acid	0.8 g
	Aerosol OT	0.294 g
Post-addition:		
	Distilled water	1.0 g
	Ammonium persulphate	0.013 g

% Conversion	98.2
Particle diameter (μm)	0.13
pH	2.5

A typical small scale formulation for a 98:2 (wt) methyl methacrylate - methacrylic acid copolymer is given in Box (6.6). The percentage conversion was calculated by comparison of the theoretical and experimentally determined non-volatile contents.

The experimental non-volatile content, the particle diameter and the pH of the polymer was determined according to the methods described in Section 5.2. The pH of the polymer was allowed to drop from near neutral to acid conditions over the course of the reaction. This change is due to the production of bisulphate anions, a dissociation product of persulphate, which are then able to ionise to hydrogen ions and sulphate ions[7].

Details on a range of polymers, prepared in a similar manner to the method described in Box (6.6), based on methyl methacrylate copolymerised with respectively methacrylic acid, 2-hydroxyethyl methacrylate and methacrylonitile are given in Table (6.7).

Amongst the polymers listed in Table (6.7) are two prepared using mixed surfactants. In addition to Aerosol OT the non-ionic surfactant Brij 35, a polyoxyethylene 23-lauryl ether, was included at levels equal to (batch 15.2) and double (batch 15.4) the concentration of the anionic surfactant. It was expected that the stability of polymers with a moderate degree of steric stabilisation would be superior to those with only electrostatic stabilisation when formulated as plastisols.

The polymer particle diameters were typically 0.10-0.15 microns unless specially formulated. Larger particles were also prepared. In Table (6.7), batch 15.16 (with a particle diameter of 0.46 microns) was prepared using a surfactant-free seed stage and only very small quantities (about a tenth of the usual amount) of surfactant during the feed stage. Stabilisation was almost entirely provided by the sulphate end groups derived from the persulphate initiator[7]. Batch 15.19 (with a particle diameter of 0.35 microns) also had a surfactant-free seed stage but a feed stage containing the usual amount of surfactant. However, the seed stage also included about 0.05% w/w Natrosol GR R726, an hydroxyethylcellulose. Hydroxyethylcellulose is known to graft onto the polymer backbone and, through associative bonding and flocculation, produce larger particles[8].

Table (6.7) Polymers based on methyl methacrylate copolymerised with respectively methacrylic acid (MAc), 2-hydroxyethyl methacrylate (HEMA) and methacrylonitrile (MAN) prepared by aqueous emulsion polymerisation

Batch number	Composition (by weight)	% Conversion	Particle diameter (μm)	pH
13.1[a]	100 MMA	89.5	0.15	2.5 - 3.0
13.3	98:2 MMA/MAc	98.2	0.13	2.5
15.19	98:2 MMA/MAc	92.5	0.35	2.0 - 2.5
15.16	98:2 MMA/MAc	91.9	0.46	2.0 - 2.5
13.4	95:5 MMA/MAc	94.2	0.17	2.5 - 3.0
13.5[b]	92.5:7.5 MMA/MAc	92.4	0.15	2.0
15.2	92.5:7.5 MMA/MAc	95.0	0.15	2.0 - 2.5
15.4	92.5:7.5 MMA/MAc	95.3	0.15	2.0 - 2.5
13.6	90:10 MMA/MAc	93.8	0.15	2.5 - 3.0
13.7	90:10 MMA/HEMA	93.8	0.15	2.5 - 3.0
13.8	85:15 MMA/HEMA	93.4	0.13	2.5 - 3.0
16.12	95:5 MMA/MAN	95.1	0.15	2.0
16.13	92.5:7.5 MMA/MAN	94.6	0.15	2.0

[a] Mw 192,613 Mn 146,647 Mp 172,788 Mw/Mn = 1.31 (Courtaulds)

[b] Mw 208,201 Mn 164,134 Mp 181,634 Mw/Mn = 1.27 (Courtaulds)

The molecular weights of the polymers were comparable to those produced by non-aqueous dispersion polymerisation free of the free radical scavenger 1-octyl mercaptan described in Section 6.1.2.2.

6.3 Plastisol stability

Acrylic plastisols, as explained in Section 1.4, gel prematurely because of excessive swelling of the polymeric phase by the plasticiser. Thermodynamic theory, introduced in Section 3.3.1, suggests that plastisols prepared from polymers with thermally reversible crosslinks are more resistant to gelling. Polymers were prepared, as described in Sections 6.1 and 6.2, with thermally reversible crosslinks by non-aqueous dispersion and aqueous emulsion polymerisation. The polymers were then formulated as plastisols and their susceptibility to gelation tested. By measuring the change in viscosity of the plastisols over time, the likelihood of early gelation could be predicted.

Typical commercial plastisols have a polymer to plasticiser ratio of about 50:50 by weight. Due to the exponential relationship between viscosity and dispersed polymer volume fraction described in Section 3.2.2, only a small degree of swelling of the polymer by the plasticiser is needed, at this ratio, before the plastisol gels. Therefore, in order to observe any trends in the stability of plastisols prepared with different polymers, only relatively dilute plastisols were tested. The method, including isolation of the polymer particles, is described in detail in Section 5.2.6.

Several series of tests were carried out, each assessing one of a number of parameters concerned with the stability of the plastisols. The results from each series are presented in the succeeding sections under the following headings:

(a) The effect of the plasticiser
(b) The effect of varying the acid content of polymers prepared by non-aqueous dispersion polymerisation
(c) The effect of varying the acid content of polymers prepared by aqueous emulsion polymerisation
(d) The effect of varying the weight fraction of polymer
(e) The effect of varying the 2-hydroxyethyl methacrylate content of the polymers

(f) The effect of varying the methacrylonitrile content of the polymers
(g) The effect of varying the particle diameter of the polymers
(h) The effect of varying the molecular weight of the polymers
(i) The effect of polymers with a core-shell morphology

Although the tests measured changes in viscosity, the results are presented as changes in the relative viscosity where the relative viscosity is the measured viscosity divided by the plasticiser viscosity. This allows direct comparison to be made between plastisols prepared with different plasticisers. The viscosities of the principal commercial plasticisers that appear in the remainder of this thesis are presented in Table (6.8).

Table (6.8) Plasticiser viscosities at 25°C.

Plasticiser	Viscosity (Poise)
Di (2-ethylhexyl) sebacate (DOS)	0.1834
Diisodecyl adipate (DIDA)	02088
Butylbenzyl phthalate (BBP)	0.4230
Di (2-ethylhexyl) phthalate (DOP)	0.6041
Trixylenyl phosphate (TXP)	1.168

The experimental data required for calculating the plasticiser viscosities was, as described in Section 5.2.6, obtained on a programmable cone and plate viscometer. The viscosities were calculated from the upward sweep of a single shear stress cycle using Equation (3.2). The cycle comprised steadily increasing the stress to 230 dyne.cm^{-2} over two minutes, holding for 30 seconds and then decreasing the stress to zero at the same rate.

6.3.1 The effect of the plasticiser

The solvent strength of the plasticisers in Table (6.8) was assessed by measuring the change in viscosity of plastisols comprising 2 parts (wt) of a 92.5:7.5 (wt) methyl methacrylate - methacrylic acid copolymer (batch 6.4) and 8 parts (wt) plasticiser. The viscosities were obtained according to the method described in Section 5.2.6. The viscometer was programmed to complete two shear stress cycles every hour for 16 hours. The experimental conditions for both cycles comprised steadily increasing the shear stress to 1 000 dyne.cm^{-2} over one minute, holding this stress for twenty seconds and then decreasing the stress at the same rate.

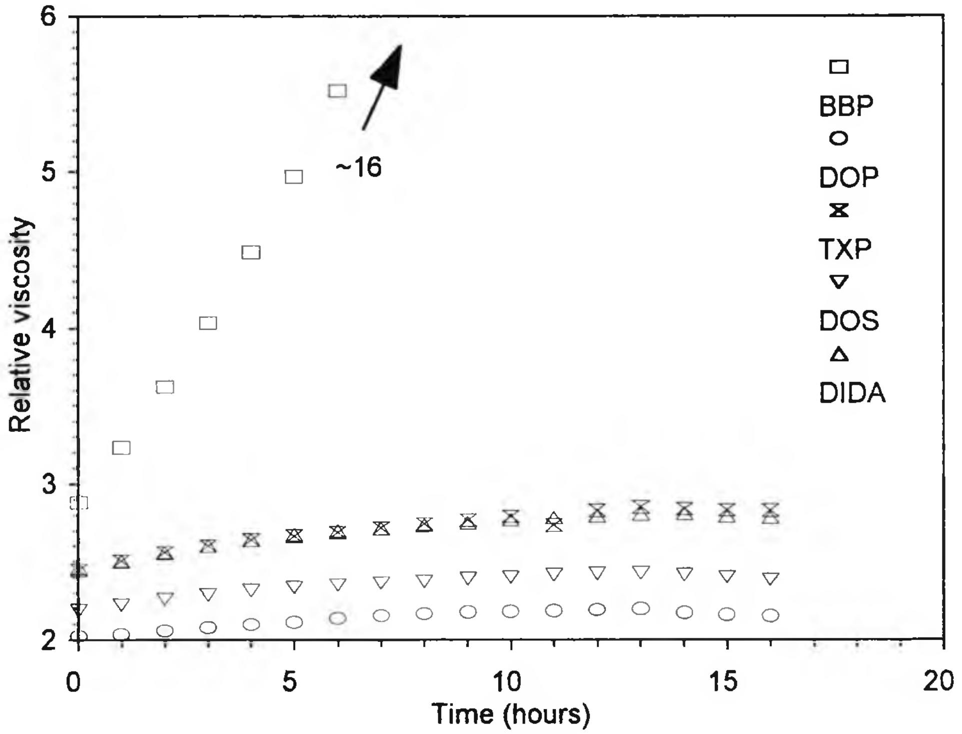

Figure (6.1) The change in viscosity over time of plastisols prepared with 2 parts (wt) of a 92.5:7.5 (wt) methyl methacrylate - methacrylic acid copolymer (batch 6.4) and 8 parts (wt) plasticiser at 25°C.

The results, depicted in Figure (6.1) showed that only the plastisol based on butylbenzyl phthalate exhibited any dramatic change, increasing in viscosity approximately five-fold. The remaining plastisols, comprising those prepared from di(2-ethylhexyl) phthalate, trixylenyl phthalate, di(2-ethylhexyl) sebacate and diisodecyl adipate, showed very little change in viscosity over time from their original values. On the basis of these results, butylbenzyl phthalate was chosen as the plasticiser for the majority of the subsequent plastisol stability experiments. Despite the problems that a powerful and fast acting plasticiser would present in terms of plastisol storage stability, it would be able to highlight differences between the test plastisols more clearly.

6.3.2 The effect of varying the acid content of polymers prepared by non-aqueous dispersion polymerisation

Plastisols were prepared from butylbenzyl phthalate and a range of methyl methacrylate - methacrylic acid copolymers. The methacrylic acid content of the polymers, previously prepared by non-aqueous dispersion polymerisation, was in the range 0-10% of the total polymer weight. A 92.5:7.5 (wt) methyl methacrylate - acrylic acid copolymer was also prepared. All the plastisols had a polymer - plasticiser ratio of 10:90 by weight.

The plastisol viscosities were measured over 17 hours. Two shear stress cycles were carried out every hour. For the plastisol based on the methyl methacrylate - acrylic acid copolymer, the first cycle comprised increasing the stress to 200 dyne.cm^{-2} over two minutes, holding for ten seconds and then decreasing the stress to zero over one minute. The second cycle was identical except the limiting stress was 1 000 dyne.cm^{-2}. The experimental conditions for the remaining plastisols comprised, for both shear stress cycles, increasing the stress to 3 000 dyne.cm^{-2} over one minute for the first five to six hours and for the remainder of the experiment 5 900 dyne.cm^{-2}, holding this stress for twenty seconds and then decreasing the stress at the same rate.

The results are depicted in Figure (6.2). The plastisol based on poly(methyl methacrylate) rose rapidly in viscosity reaching a constant relative viscosity of about

27 after about ten hours. At this point, the plastisol had changed in nature from an initial opaque and fluid dispersion to a clear polymer solution. As the percentage of methacrylic acid in the polymer increased to 5% by weight, the rate of increase in plastisol viscosity decreased until at levels of 7.5% and more, the viscosity rise was negligible over the duration of the experiment. The methyl methacrylate - acrylic acid copolymer did not show the same degree of stability in butylbenzyl phthalate as its methacrylic acid analogue. The relative viscosity of the plastisol rose steeply reaching a constant value of about 40 after 10 hours.

On closer examination of Figure (6.2), it appears that the polymer containing 3.5% by weight methacrylic acid is less stable in butylbenzyl phthalate than that containing only 2%. However, the particle diameter of the latter was twice that of the former. If the rate of particle swelling was directly proportional to the surface to volume ratio, the reduced rate of swelling expected from a larger particle might more than offset the increased rate of swelling of a polymer with 1.5% less methacrylic acid. This is discussed in detail in Section 6.3.7.

The poor stability shown by the methyl methacrylate - acrylic acid copolymer in butylbenzyl phthalate and the apparent improved stability of polymers containing methacrylic acid could be explained in terms of changes in the polymer glass transition temperatures. These changes in glass transition temperature could in turn be explained in terms of the presence of thermally reversible crosslinks, introduced theoretically in Section 3.3.1, which make the polymer chains less flexible.

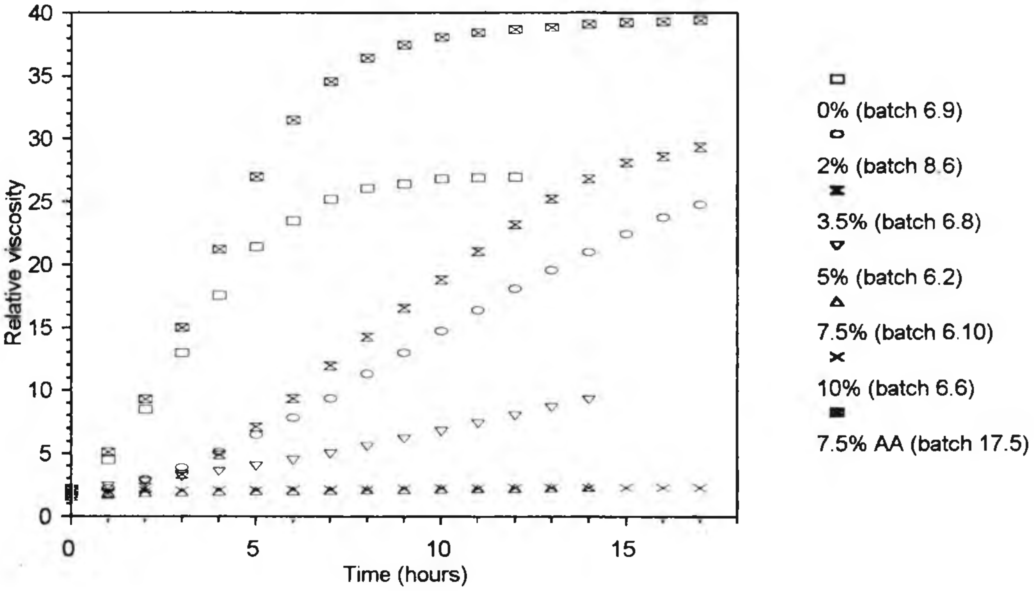

Figure (6.2) The change in viscosity over time of plastisols prepared from 1 part (wt) of methyl methacrylate - methacrylic acid or methyl methacrylate - acrylic acid (AA) copolymers, previously prepared by non-aqueous dispersion polymerisation, and 9 parts (wt) butylbenzyl phthalate at 25°C. The methacrylic acid comprised 0-10% (wt) of the copolymer.

Literature values of the glass transition temperature of poly(methyl methacrylate), poly(methacrylic acid) and poly(acrylic acid) are 378°K, 501°K and 379°K respectively[9]. A popular equation for predicting the glass transition temperature of a random copolymer where the comonomer properties differ markedly is,

$$\frac{1}{T_g} = \frac{w_1}{T_g(1)} + \frac{w_2}{T_g(2)} \qquad \text{Equation (6.1)}$$

where Tg is the glass transition temperature of the copolymer, Tg(1) and Tg(2) are the glass transition temperatures of the pure homopolymers, and w_1 and w_2 are the weight fractions of the two comonomers [10] [11]. This relationship yields a convex curve when Tg is plotted against w_1 or w_2. Using this equation, the glass transition temperature of a 92.5:7.5 by weight methyl methacrylate - methacylic acid copolymer would be 385°K (7°K above poly(methyl methacrylate)) whilst that for an equivalent methyl methacrylate - acrylic acid copolymer would be 378°K (not greatly different from poly(methyl methacrylate)) [12]. Thus the improvement in stability witnessed with methyl methacrylate - methacrylic acid copolymers could be related to the increase in glass transition temperature. The consequent decrease in polymer chain flexibility would reduce the rate of plasticiser diffusion[13].

6.3.3 The effect of varying the acid content of polymers prepared by aqueous emulsion polymerisation

Plastisols were prepared comparable to those described in Section 6.3.2 but based on methyl methacrylate - methacrylic acid copolymers obtained by aqueous emulsion polymerisation. Similar viscosity stability over time for these plastisols was observed. The results are shown in Figure (6.3).

The viscometer was programmed to carry out two shear stress cycles an hour for 17 hours. For batch 13.1, both cycles, for the first four hours, comprised increasing the shear stress to 1 000 dyne.cm^{-2} over one minute, holding for twenty seconds and then decreasing the stress at the same rate. For the remainder of the experiment, the limiting stress was 5 900 dyne.cm^{-2}. The procedure for batch 15.2 was identical to that of batch 17.5 given in Section 6.3.2. The procedure for the remaining plastisols involved increasing the stress to some limiting value over one minute, holding for twenty seconds and then decreasing the stress to zero at the same rate. For the plastisols based on batches 13.3, 13.4, 13.5, 13.6 and 15.4, the limiting stresses were 3 000, 2 000, 1 000, 1 000 and 1 500 dyne.cm^{-2} respectively.

Plastisols prepared with poly(methyl methacrylate) (batch 13.1) and the polymer with 2% (wt) methacrylic acid (batch 13.3), not shown in Figure (6.3), rose rapidly in viscosity to 57 and 84 Poise respectively. The polymer had, by this stage, completely dissolved in the plasticiser. These values are significantly higher than the equivalent plastisols decribed in Section 6.3.2 based on polymers prepared by non-aqueous dispersion polymerisation. A plausible explanation may lie in the great difference in molecular weights between the two types of polymer.

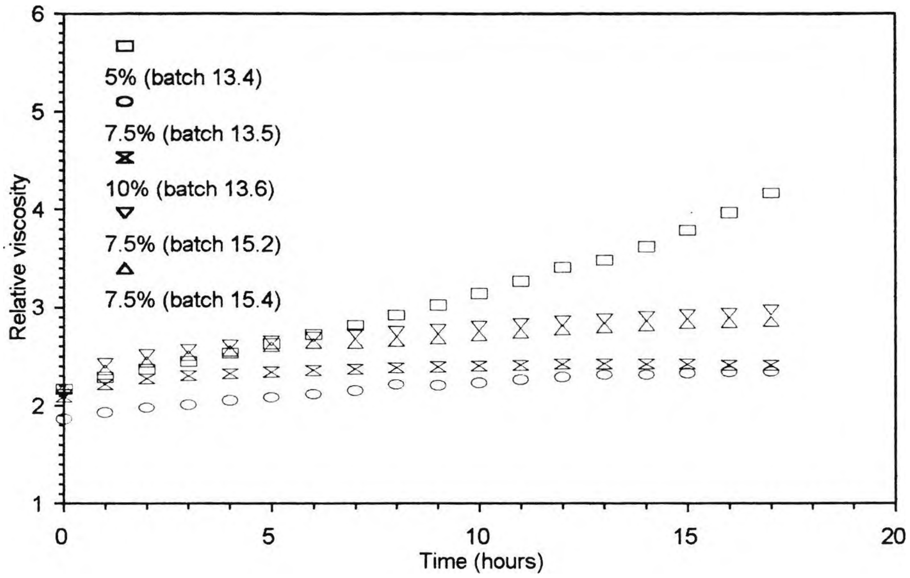

Figure (6.3) The change in viscosity over time of plastisols prepared from 1 part (wt) of methyl methacrylate - methacrylic acid copolymers, previously prepared by aqueous emulsion polymerisation, and 9 parts (wt) butylbenzyl phthalate at 25°C. The methacrylic acid comprised 5-10% (wt) of the copolymer.

As the methacrylic acid content of the polymer rose, so the plastisol viscosity stability improved. The rise in viscosity became negligible over the timescale of the experiment at a methacrylic acid level of 7.5% (wt) copolymer. Consequently, any advantage gained using a non-ionic surfactant (Brij 35), which provides steric stabilisation better suited to the plasticiser environment, in combination with the anionic surfactant (Aerosol OT) could not be perceived (batches 15.2 and 15.4).

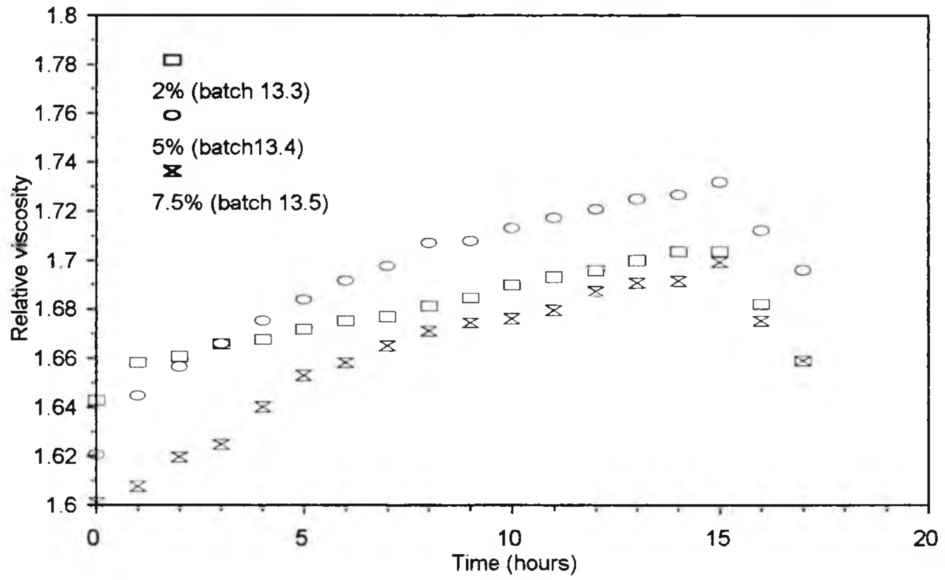

Figure (6.4) The change in viscosity over time of plastisols prepared from 1 part (wt) of methyl methacrylate - methacrylic acid copolymers, previously prepared by aqueous emulsion polymerisation, and 9 parts (wt) trixylenyl phosphate at 25°C. The methacrylic acid comprised 2-7.5% (wt) of the copolymer.

Plastisols formulated with trixylenyl phosphate, a less powerful plasticiser than butylbenzyl phthalate, and the methyl methacrylate - methacrylic acid copolymers showed little rise in viscosity over 15 hours. The results are shown in Figure (6.4). The experimental procedure involved increasing the stress to some limiting value over one minute, holding for 20 seconds and then decreasing the stress to zero at the same rate. The limiting stresses were 2 500 dyne.cm^{-2} for the plastisol based on the polymer containing 2% (wt) methacrylic acid (batch 13.3) and 2 000 dyne.cm^{-2} for those based on the polymers containing 5% (wt) and 7.5% (wt) methacrylic acid (batches 13.4 and 13.5).

6.3.4 The effect of varying the weight fraction of polymer

Plastisols were prepared at polymer - plasticiser ratios of 10:90, 20:80 and 30:70 by weight. The polymer was a 90:10 (wt) methyl methacrylate - methacrylic acid copolymer prepared by non-aqueous dispersion polymerisation (batch 6.6). The plasticiser was butylbenzyl phthalate. The viscosities of the plastisols were measured over 17 hours. The results are shown in Figure (6.5).

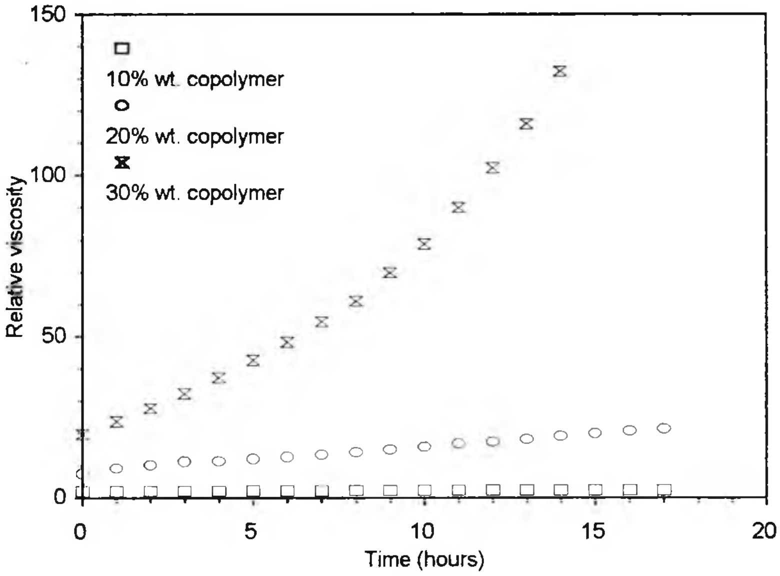

Figure (6.5) The change in viscosity over time of plastisols prepared from a 90:10 methyl methacrylate - methacrylic acid copolymer, previously prepared by non-aqueous dispersion polymerisation, and butylbenzyl phthalate at 25°C. The polymer - plasticiser ratio was in the range 10-30:90-70 (wt).

The viscometer was programmed to carry out two shear stress cycles every hour. Each cycle involved steadily increasing the stress to 5 900 dyne.cm^{-2} over one minute, holding it for twenty seconds and then reducing it to zero at the same rate. The procedure was identical for all three plastisols except for the first six hours of the experiment with the plastisol containing 10% (wt) polymer when the limiting stress was only 3 000 dyne.cm^{-2}.

The results show that, despite the apparent stability shown as a dilute plastisol, the plastisol viscosity stability, with this polymer, is insufficient at more realistic polymer weight fractions. The plastisol containing 30% (wt) polymer increased rapidly in relative viscosity from about 20 to 130 after 14 hours. In contrast at 20% (wt) polymer, the increase was much more modest but still doubled over a period of 17 hours. At 10% (wt) polymer, the increase was negligible. Due to the exponential relationship between viscosity and disperse phase volume fraction, described in Section 3.2.2, plastisols with moderate volume fractions of disperse phase polymer are susceptible to gelling should the polymer swell to even a low degree.

6.3.5 The effect of varying the 2-hydroxyethyl methacrylate content of the polymers

Viscosities were measured of a range of plastisols based on butylbenzyl phthalate and methyl methacrylate - 2-hydroxyethyl methacrylate copolymers. The polymers were previously prepared by aqueous emulsion and non-aqueous dispersion polymerisation. The proportion of 2-hydroxyethyl methacrylate was in the range 5-15% (wt) polymer. The polymer - plasticiser ratio was 10:90 by weight. The results are shown in Figure (6.6).

The viscometer was programmed to carry out two shear stress cycles an hour for 17 hours. The procedure comprised increasing the shear stress to some limiting stress over one minute, holding this stress for twenty seconds and then decreasing the stress to zero over one minute. The limiting stress was 3 000 dyne.cm^{-2} for the plastisols based on the polymers prepared by non-aqueous dispersion polymerisation and 2 000 dyne.cm^{-2} for those based on polymers prepared by aqueous emulsion polymerisation.

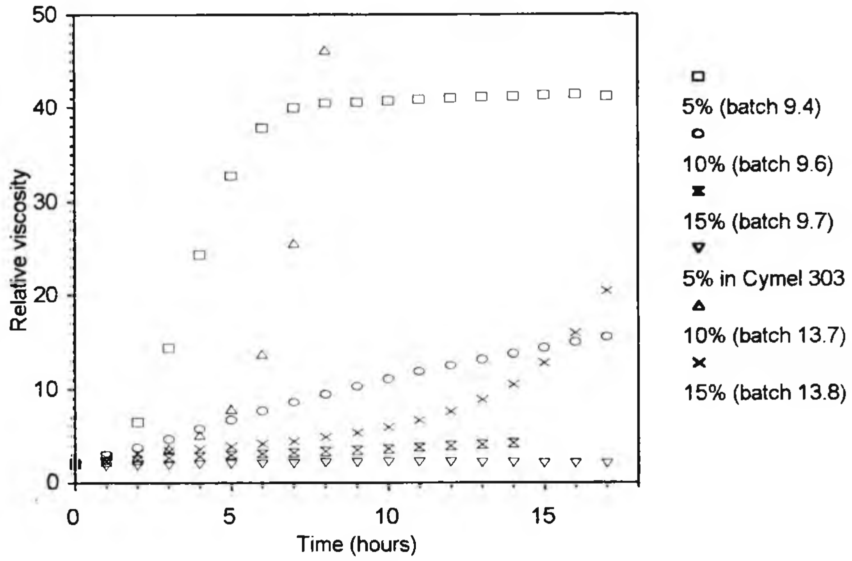

Figure (6.6) The change in viscosity over time of plastisols prepared from 1 part (wt) of methyl methacrylate - 2-hydroxyethyl methacrylate copolymers, previously prepared by aqueous emulsion (batches 13.7 and 13.8) and non-aqueous dispersion (batches 9.4, 9.6 and 9.7) polymerisation, and 9 parts (wt) butylbenzyl phthalate at 25°C. The 2-hydroxyethyl methacrylate comprised 5-15% (wt) of the copolymer.

The plastisols based on polymers prepared by non-aqueous dispersion polymerisation with 10 and 15 % (wt) 2-hydroxyethyl methacrylate (batches 9.6 and 9.7 respectively) showed improved stability over poly(methyl methacrylate). The polymer with only 5% (wt) 2-hydroxyethyl methacrylate (batch 9.4) appeared to impart no improvement in plastisol stability. The effectiveness of 2-hydroxyethyl methacrylate appeared to be half that of methacrylic acid mole for mole. Glass transition temperatures of 328°K and 359 °K are given for poly(2-hydroxyethyl methacrylate) [10]. Using Equation (6.1) given in Section 6.3.2, the glass transition temperatures of the copolymers with 5%, 10% and 15% by weight 2-hydroxyethyl methacrylate are 376°K, 372°K and 369°K respectively. All the values are less than that for poly(methyl methacrylate) and therefore the improvements in plastisol stability provided by these copolymers cannot be explained solely in terms of the glass transition temperature.

The plastisols based on the polymers prepared by aqueous emulsion polymerisation showed a lower degree of stability than those prepared by non-aqueous dispersion polymerisation. The plastisol based on the polymer with 10% 2-hydroxyethyl methacrylate (batch 13.7) had already reached a viscosity of 160 Poise, after 17 hours. Increasing the content of 2-hydroxyethyl methacrylate in the polymer to 15% (wt) (batch 13.8) produced a more stable plastisol. A plausible explanation for these results may be a lower than expected degree of copolymerisation with methyl methacrylate than that during the non-aqueous dispersion polymerisations. This would be due to the relatively high degree of solubility in water of 2-hydroxyethyl methacrylate.

Thermosetting plastisols could be produced by dispersing acid or hydroxy-group containing polymers in a urea-formaldehyde or a melamine-formaldehyde resin[14]. On gelling, the films would be harder and likely to suffer fewer problems due to incompatibility and subsequent exudation of plasticiser. Viscosity measurements were made of plastisols based on 2-hydroxyethyl methacrylate containing polymers, obtained by non-aqueous dispersion polymerisation, and hexamethoxymethyl melamine (Cymel 303). It appeared that increasing the proportion of 2-hydroxyethyl methacrylate increased the solubility of the polymer in the resin.

The result for a plastisol containing the 95:5 (wt) methyl methacrylate - 2-hydroxyethyl methacrylate copolymer is shown in Figure (6.6). The polymer - plasticiser ratio was 10:90 by weight. The viscometer was programmed to carry out two shear stress cycles an hour using a 2cm/1° cone. The procedure involved increasing the stress to 38 000 dyne.cm^{-2} over one minute, holding for twenty seconds and then decreasing the stress to zero over one minute. Although the relative viscosity appeared to be relatively stable rising from 1.67 to 2.02 over 17 hours, the actual viscosity was too high to be practical. The measured viscosity of Cymel 303 was 34.48 Poise, therefore its use as a plasticiser is severely limited. Further experimentation was discontinued as, according to the supplier, this was the lowest viscosity 100% melamine-formaldehyde resin available.

6.3.6 The effect of varying the methacrylonitrile content of the polymers

The viscosities of two plastisols based on methyl methacrylate - methacrylonitrile copolymers prepared by aqueous emulsion polymerisation, and butylbenzyl phthalate were measured over 17 hours. The polymer - plasticiser ratio was 10:90 by weight. The viscometer was programmed to carry out two shear stress cycles every hour. The procedure comprised increasing the stress up to a limiting value over two minutes, holding this stress for ten seconds and then decreasing the stress at twice the initial rate. The limiting stresses for the plastisol with the 95:5 (wt) methyl methacrylate - methacrylonitrile copolymer (batch 16.12) were 200 $dyne.cm^{-2}$ for the first cycle and 1 000 $dyne.cm^{-2}$ for the second. The limiting stresses for the plastisol with the 92.5:7.5 (wt) methyl methacrylate - methacrylonitrile copolymer (batch 16.13) were 200 $dyne.cm^{-2}$ and 3 000 $dyne.cm^{-2}$ respectively. The results are shown in Figure (6.7).

Both plastisols increased rapidly in viscosity from less than 5 Poise to a limiting value of about 60-70 Poise after just two hours. There was no improvement in stability on poly(methyl methacrylate). In fact, it appeared that copolymerising methacrylonitrile increased the affinity of the plasticiser for the polymer. The glass transition temperature of poly(methacrylonitrile) is 393°K and that of a methyl methacrylate - methacrylonitrile copolymer would be little different from poly(methyl methacrylate)[15]. Thus, this result supports the hypothesis of an increase in glass transition temperature and polymer chain rigidity leading to a decrease in plasticiser diffusion rate introduced in Section 6.3.2.

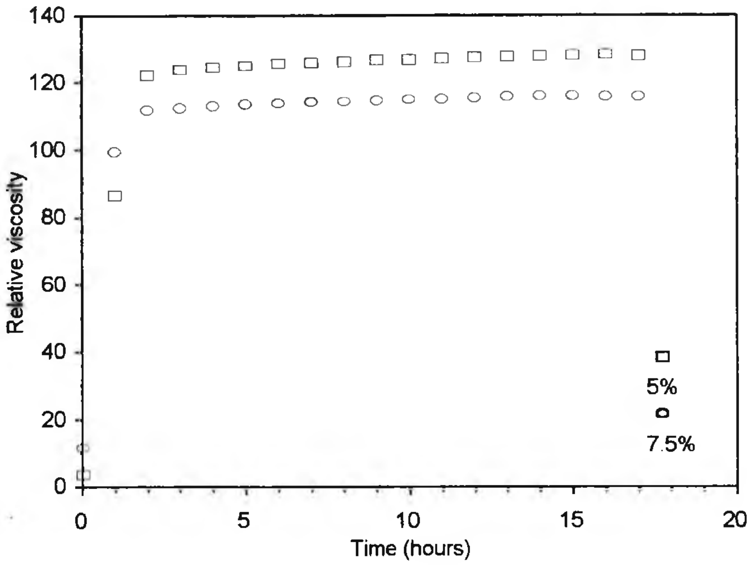

Figure (6.7) The change in viscosity over time of plastisols prepared from 1 part (wt) of methyl methacrylate - methacrylonitrile copolymers, previously prepared by aqueous emulsion polymerisation, and 9 parts (wt) butylbenzyl phthalate at 25°C. The methacrylonitrile comprised 5-7.5% (wt) of the copolymer.

6.3.7 The effect of varying the particle diameter of the polymers

The viscosities of a range of plastisols based on butylbenzyl phthalate and 98:2 (wt) methyl methacrylate - methacrylic acid copolymers of varying particle diameter, prepared by aqueous emulsion and non-aqueous dispersion polymerisation, were measured. Those based on polymer obtained by non-aqueous dispersion polymerisation, the preparation of which has been described in Section 6.1.2.1, had a polymer - plasticiser ratio of 20:80 by weight. Those based on polymer obtained by aqueous emulsion polymerisation, previously described in Section 6.2, had a ratio of 10:90 by weight. The results from the plastisols based on the polymers obtained by non-aqueous dispersion polymerisation are shown in Figure (6.8). The viscometer was programmed to carry out two shear stress cycles every hour for 17 hours. The procedure involved increasing the stress to a limiting value over two minutes, holding this value for ten seconds and then decreasing the stress to zero at twice the initial rate. The limiting stresses for the first and second cycles were 1 000 and 3 000 dyne.cm^{-2} respectively.

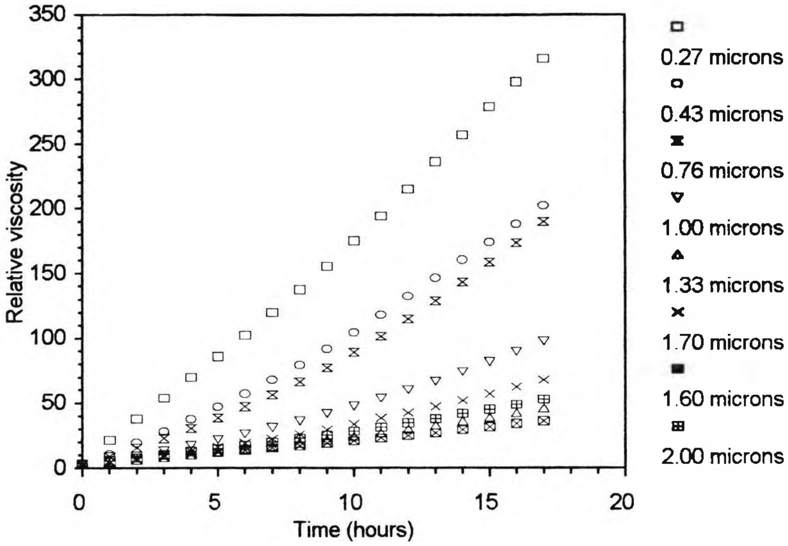

Figure (6.8) The change in viscosity over time of plastisols prepared from 2 parts (wt) of 98:2 methyl methacrylate - methacrylic acid copolymers, previously prepared by non-aqueous dispersion polymerisation, and 8 parts (wt) butylbenzyl phthalate at 25°C. The particle diameters were in the range 0.27-2.00 microns.

Plastisol stability improved as the particle diameter increased. The result for the 0.43 micron diameter particles are an average of nine experiments (n = 9) with a mean standard deviation ($\sigma_{(n-1)}$) of 20.13%. The mean standard deviation was obtained by calculating the standard deviations for each set of viscosity values for the same plastisol composition at a given hour and converting the calculated value into a percentage. The percentage standard deviations for each hour were then averaged to give the mean standard deviation (in terms of a percentage). The values of $\sigma_{(n-1)}$ and n for the experiments with polymer comprising 0.76, 1.00, 1.33, and 1.70 micron diameter particles are 20.56% and 6; 20.04% and 5; 0.97% and 2; and 28.47% and 4 respectively.

A similar trend between viscosity stability and particle diameter was observed with plastisols based on butylbenzyl phthalate and polymers obtained by aqueous emulsion polymerisation. The results are presented in Figure (6.9). The viscometer was programmed to carry out two shear stress cycles each hour for 17 hours. The procedure for the two plastisols based on the polymers with particle diameters of 0.35 and 0.46 microns comprised increasing the stress to 1500 dyne.cm^{-2} over one minute, holding this stress for twenty seconds and then decreasing the stress to zero at the same rate. The procedure for the remaining plastisol, based on batch 13.3, has already been described in Section 6.3.3.

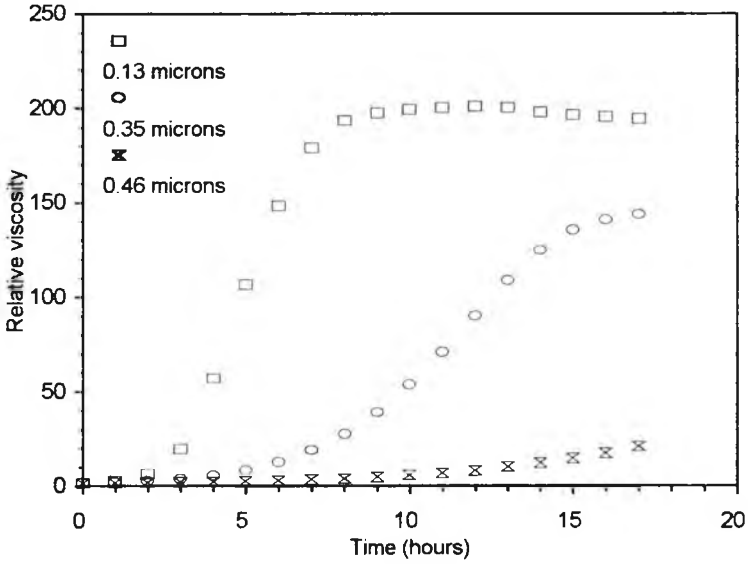

Figure (6.9) The change in viscosity over time of plastisols prepared from 1 part (wt) of 98:2 methyl methacrylate - methacrylic acid copolymers, previously prepared by non-aqueous dispersion polymerisation, and 9 parts (wt) butylbenzyl phthalate at 25°C. The particle diameters were in the range 0.13-0.46 microns.

A plot of the initial viscosities against the volume concentration of plastisols based on butylbenzyl phthalate and 98:2 (wt) methyl methacrylate prepared by non-aqueous dispersion polymerisation is shown in Figure (6.10). The experimental procedure comprised increasing the shear stress to a limiting value over one minute, holding for twenty seconds and then reducing the stress to zero at the same rate.

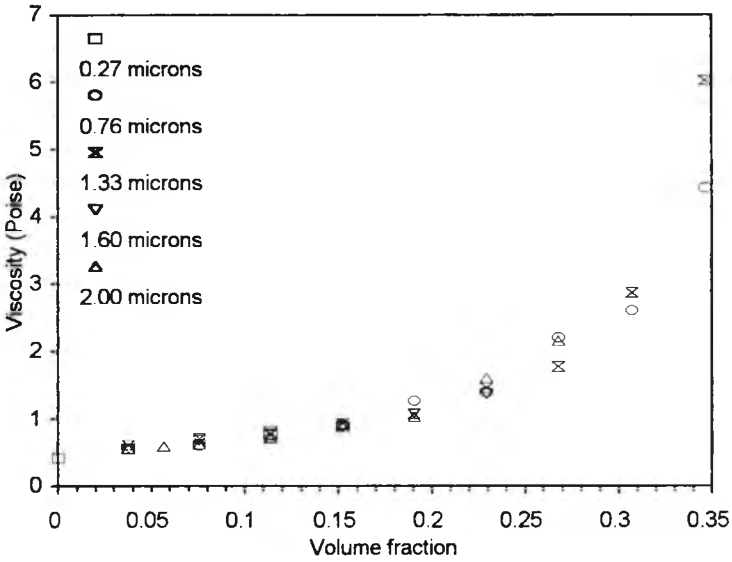

Figure (6.10) Initial viscosity versus volume fraction for plastisols based on butylbenzyl phthalate and 98:2 (wt) of methyl methacrylate - methacrylic acid copolymers prepared by non-aqueous dispersion polymerisation at 25°C. The polymer particle diameters were in the range 0.27-2.00 microns.

The limiting stresses for the plastisols containing polymer particles of diameter 0.27, 0.76, 1.60 and 2.00 microns were 1 000, 1 000, 4 000 and 1 000 dyne.cm^{-2} respectively. The limiting stresses for the plastisol containing polymer particles of 1.33 microns varied with the volume concentration ϕ. For $\phi = 0.038$, 0.307 and 0.346, the limiting stress was 3 000 dyne.cm^{-2}; for $\phi = 0.076$-0.152, the value was 1 000 dyne.cm^{-2}; and for $\phi = 0.191$-0.268, the value was 1 500 dyne.cm^{-2}. Calculations of the volume fractions from the weight fractions were carried out assuming the density of the copolymer was no different to that of poly(methyl methacrylate). The densities of the polymer and the plasticiser were taken as 1.188 and 0.9845 g.cm^{-3} respectively [16] [17].

Figure (6.10) shows that the viscosity, for these plastisols, was a function of the polymer volume fraction but independent of the particle size. The hard sphere model describing the flow behaviour of solid-liquid suspensions, introduced in Section 3.2.2, did not predict a relationship between the suspension viscosity and particle diameter. This result, therefore, supports the view that the test plastisols prepared on the automatic muller were monodisperse dispersions.

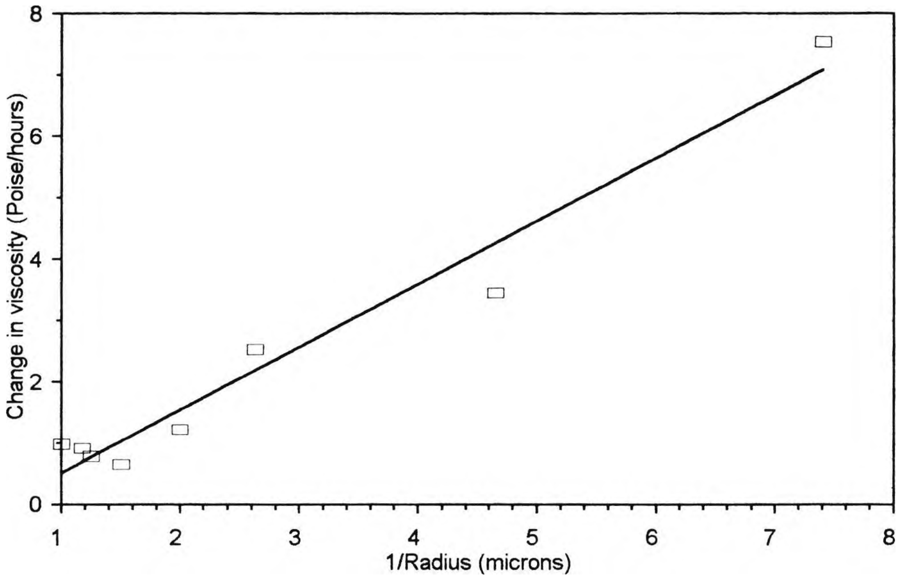

Figure 6.11 Initial increase in viscosity against reciprocal particle radius of plastisols comprising 2 parts (wt) of 98:2 (wt) methyl methacrylate - methacrylic acid copolymers, obtained by non-aqueous dispersion, and 8 parts (wt) butylbenzyl phthalate at 25°C.

A plausible hypothesis to explain the relationship between the polymer particle diameter and plastisol viscosity stability is if the initial rate of swelling were proportional to the surface to volume ratio. Thus a plot of initial rate of viscosity increase against the reciprocal of the radius, shown in Figure (6.11), should yield a linear response relationship. The result broadly supports this hypothesis.

Overall, the results suggest that acrylic plastisols ought to be formulated with as large a particle size as is practicably possible. The upper limit is defined for clear coats by the increased rate of sedimentation exhibited by larger particles [18]. For pigmented coatings, the particle size cannot greatly exceed that of the pigment particles which, for a typical pigment such as titanium dioxide, is about 0.2 - 0.3 microns [19]. The reason for this is the increased tendancy for pigment particles to cluster in the intersticial free volume of the polymer particles leading to poor hiding power and poor pigment optimisation. Pigment optimisation is important in the coatings industry as the bulk prices of pigments are generally high and can, in typical pigmented coatings, constitute a high proportion of the final costs [20].

6.3.8 The effect of varying the molecular weight of the polymers

Three plastisols were prepared based on butylbenzyl phthalate and three 92.5:7.5 methyl methacrylate - methacrylic acid copolymers of poly(styrene) equivalent peak molecular weight range 100 000 - 270 000, obtained by non-aqueous dispersion polymerisation. The polymer - plasticiser ratio was 10:90 by weight. Their viscosities were measured over 17 hours.

The viscometer was programmed to carry out two shear stress cycles every hour. The procedure comprised increasing the stress to 900 dyne.cm^{-2} over one minute, holding this stress for twenty seconds and then lowering the stress to zero at the same rate. Each of the results, shown in Figure (6.12) are an average of two experiments.

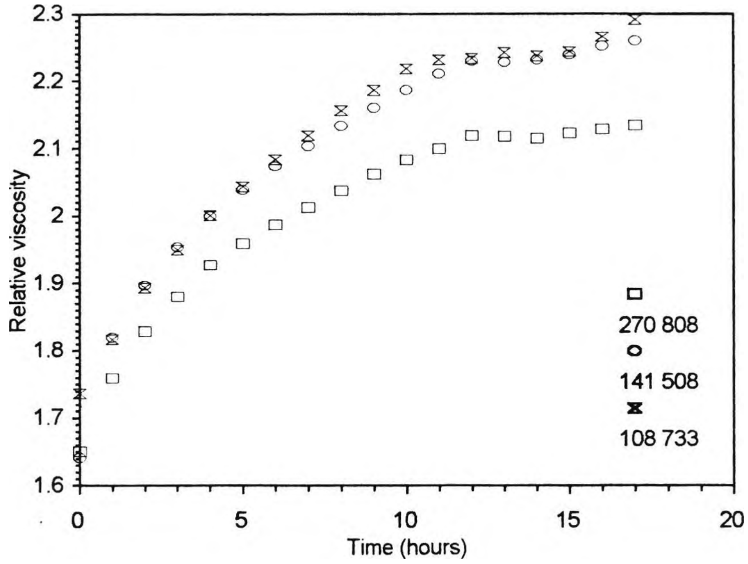

Figure (6.12) The change in viscosity over time of plastisols prepared from 1 part (wt) of 92.5:7.5 methyl methacrylate - methacrylic acid copolymers, previously prepared by non-aqueous dispersion polymerisation, and 9 parts (wt) butylbenzyl phthalate at 25°C. The poly(styrene) equivalent peak molecular weights were in the range 100 000-270 000.

It was predicted in Section 6.1.2.2 that higher molecular weight polymers ought to have a reduced rate of velocity of dissolution in plasticiser due to the increase in chain entanglement [5]. The glass transition temperature could be used as a measure of the degree of chain entanglement. It has been found that the glass transition temperature of linear polymers is proportional to the reciprocal of the number average molecular weight [21 22]. The relationship can be represented by the following empirical equation,

$$T_g = T_{g,\infty} - \frac{K}{(\alpha_R - \alpha_G)M_n} \qquad \text{Equation (6.2)}$$

where Tg is the glass transition temperature in degrees Kelvin, Tg,∞ is the glass transition temperature in Kelvin for a linear polymer of infinite molecular weight, K is a constant, α_R and α_G are the specific volume - temperature coefficients in millilitres per gram degree and Mn is the number average molecular weight in grams. Equation (6.2) follows from the decrease in the free volume with increasing molecular weight. The greater number of connected monomers leads to a decrease in the number of chain ends. However data for poly(methyl methacrylate) presented in Figure (6.13) suggests that the increase in the glass transition temperature begins to plateau at a number average molecular weight of about 40 000 [23].

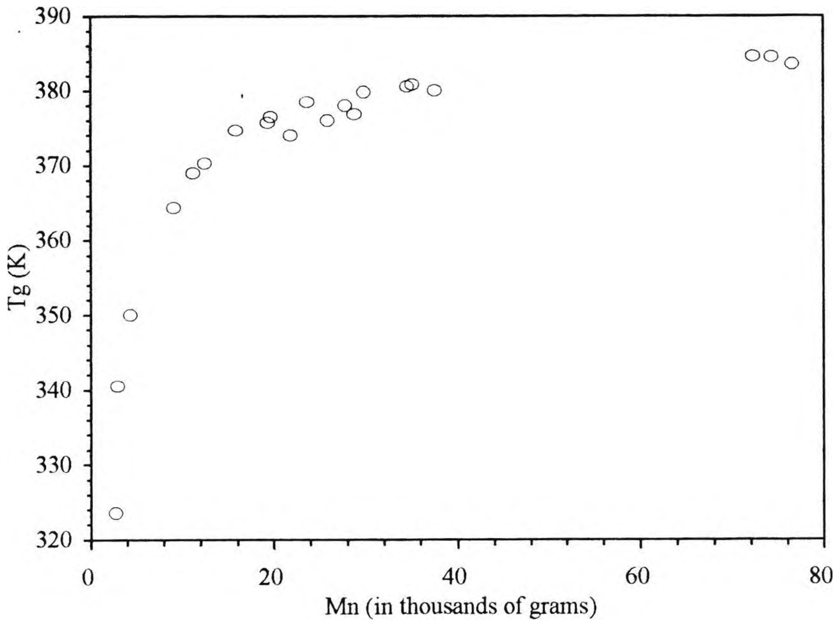

Figure (6.13) Tg (degrees Kelvin) vs. Mn (grams) for poly(methyl methacrylate) [21]

The results in Figure (6.12) indicate that changes in the molecular weight over the range investigated has little impact on plastisol stability. This suggests that the plateau region of the glass transition temperature with the number average molecular weight has already been reached.

6.3.9 The effect of polymers with a core-shell morphology

Three plastisols were prepared comprising 1 part (wt) butylbenzyl phthalate and 9 parts (wt) methyl methacrylate - methacrylic acid copolymers, obtained by non-aqueous dispersion polymerisation, with core-shell morphologies. Their viscosities were measured over a period of 17 hours. The results are shown in Figure (6.13).

The viscometer was programmed to carry out two shear stress cycles every hour. The procedure comprised, for the first cycle, increasing the stress over one minute to a limiting value of 1 000 dyne.cm^{-2}, holding for ten seconds and then lowering the stress to zero at the same rate. For the second cycle, the stress was ramped to 3 000 dyne.cm^{-2} over two minutes, held for ten seconds and then lowered to zero over two minutes. Also included in Figure (6.13), for purposes of comparison, is the result for an equivalent plastisol containing a 92.5:7.5 (wt) methyl methacrylate - methacrylic acid random copolymer (batch 6.10) prepared by non-aqueous dispersion polymerisation.

The ratio of core to shell material, comprising the polymer particles, was 3:1 by weight. All the methacrylic acid was polymerised exclusively in the shell. The three polymers comprised 1.875, 5 and 7.5% by weight methacrylic acid respectively. However, the percentage of methacrylic acid in the shell rose to 7.49, 20.00 and 35.94% by weight respectively. Further details regarding these polymers were detailed in Section 6.1.2.2.

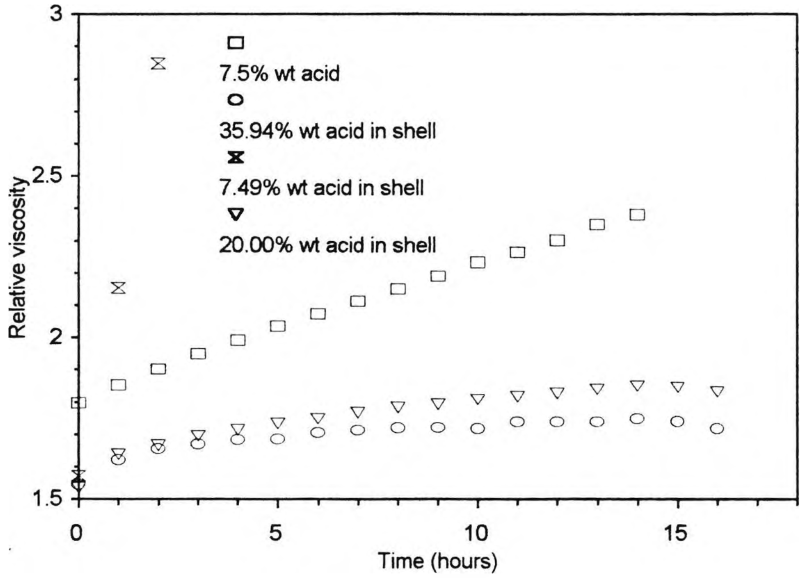

Figure (6.13) The change in viscosities with time of plastisols comprising 1 part (wt) of methyl methacrylate - methacrylic acid core-shell copolymers, prepared by non-aqueous dispersion polymerisation, and 9 parts (wt) butylbenzyl phthalate at 25°C. The core to shell ratio was 3:1 by weight with a core comprised entirely of poly(methyl methacrylate).

The ratio of core to shell material, comprising the polymer particles, was 3:1 by weight. All the methacrylic acid was polymerised exclusively in the shell. The three polymers comprised 1.875, 5 and 7.5% by weight methacrylic acid respectively. However, the percentage of methacrylic acid in the shell rose to 7.49, 20.00 and 35.94% by weight respectively. Further details regarding these polymers were detailed in Section 6.1.2.2.

The core-shell type polymers containing 5% and 7.5% by weight methacrylic acid concentrated in the shell were significantly more stable, in butylbenzyl phthalate, than the random copolymer. The polymer with only 1.875% by weight methacrylic acid was much less stable and the plastisol rose in viscosity from less than 1 Poise to 22 Poise after 13 hours. The percentage weight of methacrylic acid in the shell should, however, have been similar to that of the random copolymer. Therefore it would have been expected that the plastisol have, at least initially, comparable stability to that containing the random copolymer. The result implies that the poly(methyl methacrylate) core may not have been fully protected by the shell. It has been postulated that the shell is formed from the fusing together of independent islands of shell material[24 25]. If there is insufficient shell material for polymerisation, then it will not be completely formed leaving the core partially exposed.

6.4 Plastisol glass transition temperatures

It was suggested that copolymerisation of methacrylic acid into the polymeric phase of the methyl methacrylate based plastisols was acting to reduce the plasticising action of butylbenzyl phthalate. In order to determine if the plasticising power of butylbenzyl phthalate varied with the composition of the polymeric phase, the glass transition temperatures of two series of gelled plastisols were measured using differential scanning calorimetry.

The plastisols contained either poly(methyl methacrylate) (batch 20.2) or 92.5:7.5 (wt) methyl methacrylate - methacrylic acid copolymer (batch 16.15), both prepared by non-aqueous dispersion polymerisation. The polymer comprised 52-95% by weight of the plastisol. The plastisols were prepared by combining the appropriate amounts of plasticiser and undried polymer. All the plastisols were heated at 120°C for one hour. The experimental conditions for the glass transition measurements comprised heating the gelled plastisols from 240K to 400K at a rate of 20K/min. A typical DSC trace is shown in Section 5.2.7. where further details are given. The results are summarised in Table (6.9).

Table (6.9) Glass transition temperatures of gelled plastisols based on poly(methyl methacrylate) (batch 20.2) or a 92.5:7.5 (wt) methyl methacrylate - methacrylic acid copolymer (batch 16.15), prepared by non-aqeous dispersion polymerisation, and butylbenzyl phthalate. Measurements were obtained using differential scanning calorimetry with a heating schedule of 240-400K at 20K/min.

Undried polymer (g)		BBP (g)	% polymer in gelled plastisol (wt)		Glass transition (K)	
20.2	16.15		20.2	16.15	with 20.2	with 16.15
6.25	5.0	2.50	51.7	52.0	-	-
6.90	5.5	2.25	56.8	57.0	-	-
7.50	6.0	2.00	61.6	61.9	-	-
8.10	6.5	1.75	66.4	66.8	-	-
8.75	7.0	1.50	71.4	71.7	-	-
9.40	7.5	1.25	76.3	76.5	299	332
10.00	8.0	1.00	81.1	81.2	299	342
10.60	8.5	0.75	85.8	86.0	306	350
11.25	9.0	0.50	90.6	90.7	316	351
11.90	9.5	0.25	95.3	95.4	321	358
-	-	-	100.0	100.0	332	357

The glass transition temperatures for the gelled plastisols comprising less than approximately 75% by weight polymer could not be measured as the transitions were smeared out over too wide a temperature range. The measured glass transition of poly(methyl methacrylate) of 332K is considerably lower than the value of 378K quoted in the literature[10]. Likewise, the corresponding values for the 92.5:7.5 methyl methacrylate - methacrylic acid copolymer are 357K and 385K (calculated). The differences may be due to plasticisation of the polymers by residual unreacted monomers.

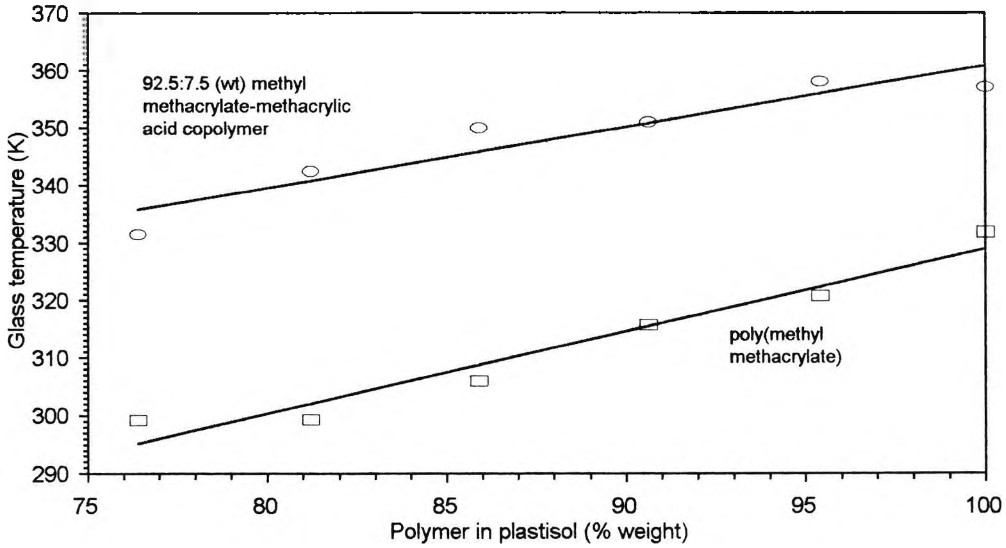

Figure (6.14) The glass transition temperature of a range of gelled plastisols based on butylbenzyl phthalate and poly(methyl methacrylate) or a 92.5:7.5 (wt) methyl methacrylate copolymer prepared by non-aqueous dispersion polymerisation. The polymer weight fraction was in the range 0.75-1.00. The measurements were obtained using differential scanning calorimetry with a heating schedule of 240-400K at 20K/min.

A plot of percentage polymer by weight against the glass transition temperature, shown in Figure (6.14), gives a linear relationship for each polymer indicative of compatability between the polymers and plasticiser. A simple ideal mixing rule can be applied to these systems and the glass transition of the plasticised polymers predicted using the linear relationship [11 26],

$$Tg = w_1Tg(1) + w_2Tg(2) \qquad \text{Equation (6.3)}$$

As the slopes are approximately the same, it can be concluded that butylbenzyl phthalate has a similar plasticising power for both polymers. Hence the presence of methacrylic acid in the polymeric phase of these plastisols does not reduce the plasticising power of butylbenzyl phthalate for the polymer.

6.5 Plastisol coatings

In order to determine whether suitable coatings could be prepared from the polymers described in Section 6.1 and Section 6.2, selected polymers which had shown resistance to plasticiser swelling, when formulated as dilute plastisols, were reformulated at a more realistic polymer - plasticiser ratio of 50:50 by weight. The plastisols were then coated onto glass panels and heated at 130°C for 30 minutes. The appearance of the plastisols was noted before and after gelling. Further details of the preparation of the coatings is included in Section 5.2.9.

Plastisol coatings were prepared from poly(methyl methacrylate) (batch 20.2), a 92.5:7.5 (wt) methyl methacrylate - methacrylic acid copolymer (batch 16.15) and a range of plasticisers. Both polymers were prepared by non-aqueous dispersion polymerisation. A record of the observations is summarised in Table (6.10). Attempts to disperse poly(methyl methacrylate) in butylbenzyl phthalate (BBP) or trixylenyl phosphate (TXP) resulted in immediate gelation indicating strong polymer - plasticiser affinity. On dispersion in Palamoll 652 (a polyester derived from adipic acid and polyfunctional alcohols), a viscous opaque paste was produced which on gelation gave a moderately flexible but opaque coating. The coating subsequently exuded the plasticiser.

Plastisols prepared from Palamoll 652 will, due to its high viscosity of 20-35 Poise at 20°C, tend to be pastes[27]. The bulkier high molecular weight plasticiser, due to a lower rate of diffusion through the polymer, requires a higher gelling temperature or a longer gelling time[12]. Gelling at too low a temperature will lead to incomplete fusion of the polymer and plasticiser and opaque coatings. Di(2-ethylhexyl) phthalate and dilinear 7,9 phthalate both produced liquid plastisols with poly(methyl methacrylate). However, it was observed that neither plasticiser was sufficiently compatible with the polymer as both coatings exhibited plasticiser exudation.

Table (6.10) Appearance of plastisols comprising 50% by weight plasticiser and 50% by weight polymer, prepared by non-aqueous dispersion polymerisation, before and after heating at 130°C for 30 minutes.

Polymer	Plasticiser	Plastisol appearance	Appearance of coating
Poly(methyl methacrylate) (batch 20.2)	BBP	Gel	
	DOP	Liquid	Flexible; plasticiser exudation
	Dilinear 7,9 phthalate	Colourless liquid	Flexible; plasticiser exudation
	TXP	Gel	
	Palamoll 652	Viscous opaque paste	Slightly flexible; opaque; plasticiser exudation
92.5:7.5 (wt) methyl methacrylate - methacrylic acid copolymer (batch 16.15)	BBP	White paste	Flexible; rough; plasticiser exudation
	TXP	White paste	Flexible; rough; plasticiser exudation

Dispersion of the 92.5:7.5 (wt) methyl methacrylate - methacrylic acid copolymer in butylbenzyl phthalate and trixylenyl phosphate produced stable plastisol pastes. However, the low degree of flow out of the coatings suggested incomplete fusion of polymer and plasticiser.

Similar plastisol coatings were also prepared based on butylbenzyl phthalate and trixylenyl phosphate and a range of 98:2 (wt) methyl methacrylate - methacrylic acid copolymers of varying particle diameter. The polymers were obtained by non-aqueous dispersion polymerisation and have been described in Section 6.1.2.1. All the coatings were clear and rubbery. The only plastisol with a liquid consistency was that comprising the polymer with a particle diameter of 0.43 microns (batch 17.30) and butylbenzyl phthalate. The remaining plastisols, principally based on polymers with larger particle diameters, were pastes. The results are summarised in Table (6.11).

They do not lend support to the hypothesis, introduced in Section 6.3.7, that plastisol viscosity stability could be improved by increasing the particle diameter of the dispersed polymeric phase.

Table (6.11) Appearance of plastisols comprising 50% by weight plasticiser and 50% by weight 98:2 (wt) methyl methacrylate - methacrylic acid copolymer, prepared by non-aqueous dispersion polymerisation, before and after heating at 130°C for 30 minutes. The particle diameters are in the range 0.43-1.70 microns

Particle diameter (μm)	Plasticiser	Plastisol appearance	Film appearance
0.43	BBP	Liquid	Slightly sticky; flexible; clear
	TXP	Thick, sticky paste	Flexible; clear
1.00	BBP	Thick, white paste	Slightly sticky; flexible; clear
1.70	BBP	Runny white paste	Flexible; clear
	TXP	Thick, white paste	Flexible; clear

These results for plastisols with a polymer-plasticiser ratio of 50:50 by weight, required for producing a coherent coating, reinforce the view, discussed in Section 3.4, that very little polymer swelling by plasticiser is required before plastisols become intractable.

6.6 Summary

The ability of poly(methyl methacrylate) to resist attack by the powerful plasticiser butylbenzyl phthalate was improved on copolymerisation of methyl methacrylate with methacrylic acid or 2-hydroxyethyl methacrylate. There was no discernable improvement on copolymerisation of methyl methacrylate with methacrylonitrile. The results may be partly explained by arguing that the comonomer has simply increased the polymer glass transition temperature and hence reduced the velocity of dissolution of the polymer by the plasticiser. Indeed, this would be expected if the comonomers did provide thermally reversible crosslinks within the polymer particles. However, methyl methacrylate - 2-hydroxyethyl methacrylate copolymers possess glass transition temperatures lower than poly(methyl methacrylate). In this case, there must be an alternative stabilising mechanism.

Difficulties encountered polymerising monomers with an appreciable solubility in water may have been responsible for the poorer stability in plasticiser exhibited by some polymers prepared using the aqueous emulsion polymerisation process. The composition of the final copolymer may have been at variance to that predicted theoretically with considerably less of the soluble monomers, such as 2-hydroxyethyl methacrylate, polymerising into the polymer particles. Increasing the molecular weight did not provide increased stability over the relatively narrow range investigated. However, increasing the particle size significantly improved plastisol stability. It is thought that this may be due to lowering of the surface to volume ratio. Polymerising methacrylic acid into a shell surrounding a poly(methyl methacrylate) core also improved the plastisol stability substantially compared to an equivalent random copolymer.

Plastisols were prepared at the commercially realistic polymer - plasticiser ratio of 50:50 by weight with polymers that exhibited good stability as dilute plastisols. However plastisol viscosity stability was insufficient, even with a weaker plasticiser such as trixylenyl phosphate. This suggested, as predicted in Section 3.4, that very little polymer swelling by plasticiser is required before the plastisols become intractable.

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CHAPTER 7-

TRANSIENTLY CROSSLINKED POLYMERS II: ACID-BASE INTERACTIONS AND METAL CROSSLINKS

This chapter, following on from Chapter 6, investigates the effects on plastisol viscosity stability of polymers containing acid-base interactions or metal ion crosslinks. The acid-base crosslinks were formed, as described in Section 4.1.1, between methacrylic acid and 2-(dimethylamino)ethyl methacrylate copolymerised with methyl methacrylate. The metal ion crosslinks were formed by neutralisation of methyl methacrylate - methacrylic acid copolymers by butyl lithium, diethyl zinc and diisobutyl aluminium hydride. The polymers were prepared using both non-aqueous dispersion and aqueous emulsion polymerisation techniques.

The prepared polymers were dried and redispersed into the plasticiser butylbenzyl phthalate. The stability of these simple plastisols was assessed in the liquid form and as an applied coating. Liquid stability was determined, as described in Section 5.2.6, by measuring the change in viscosity over time. Coating stability was assessed on the basis of visual examination for plasticiser exudation and mechanical integrity.

The chapter starts with an account of the preparation of polymers containing acid-base interactions, by aqueous emulsion polymerisation, and their assessment for formulation in plastisols. This is followed by a description of the preparation of polymers containing metal ion crosslinks using both non-aqueous dispersion and aqueous emulsion polymerisation. The viscosity stability of plastisols formulated from these polymers and butylbenzyl phthalate is then described. Finally, details are given on the nature of the coatings obtained from the plastisols.

7.1 Polymers containing acid-base interactions

Polymers based on methyl methacrylate, methacrylic acid and 2-(dimethylamino)ethyl methacrylate were prepared using an emulsion polymerisation technique. The technique has already been described in detail in Sections 3.1.2 and 6.2 and requires no detailed explanation.

7.1.1 The preparation of polymers by aqueous emulsion polymerisation

The polymers were prepared using a seed and feed method. At a pH of less than 7, which is the case for unbuffered persulphate initiated polymerisations, the formation of cationic polymeric species can cause coagulation or flocculation of any anionic polymeric species[1]. Thus, not only was methacrylic acid and 2-(dimethylamino)ethyl methacrylate added in separate sequential feeds, but addition of approximately 1% by weight of a 10% w/v sodium bicarbonate solution, after completion of the first half of the feed containing methacrylic acid, was necessary to raise the pH from 2.5 to 5.0. The pH was further adjusted upwards to 7.0 by the addition of small amounts of n-butylamine before polymerisation was continued with addition of the second half of the feed containing 2-(dimethylamino)ethyl methacrylate. The final pH of the polymers was 7.0. Two polymers were prepared with compositions of 95:2.5:2.5 and 90:5:5 by weight methyl methacrylate - methacrylic acid - 2-(dimethylamino)ethyl methacrylate respectively. The particle diameters were 0.15 microns. Although amines do act as free radical scavengers, this was not reflected as low monomer conversions[1].

7.1.2 Plastisol stability

Plastisols were prepared with the polymers described in Section 7.1.1 and butylbenzyl phthalate at a polymer - plasticiser ratio of 10:90 by weight according to the procedure described in Section 5.2.6. The viscometer was programmed to carry out two shear stress cycles every hour for 17 hours. The procedure for both plastisols comprised increasing the stress to 1 000 dynes.cm^{-2} over one minute, holding for twenty seconds and then allowing the stress to fall to zero over one minute.

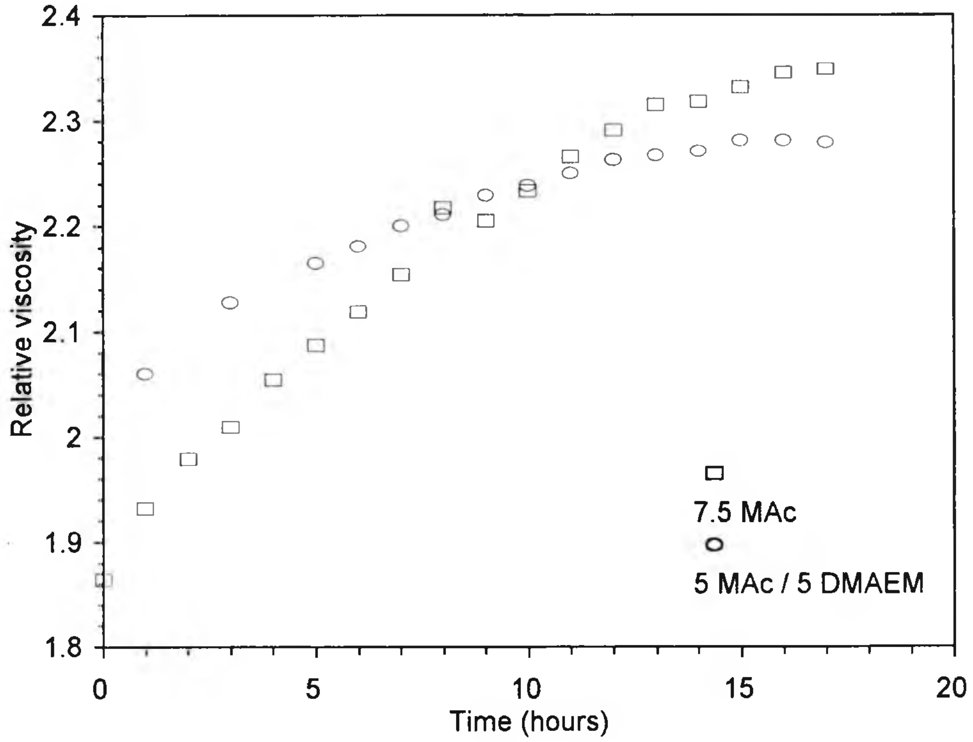

Figure 7.1 The effect of acid - base interactions on plastisol stability at 25°C. Comparison between a 5% by weight methacrylic acid and 5% by weight 2-(dimethylamino)ethyl methacrylate terpolymer (dispersion 13.17), and a 7.5% by weight methacrylic acid copolymer (dispersion 13.5). Polymer - butylbenzyl phthalate ratio 10:90 by weight.

The plastisol containing the polymer with the lower levels of methacrylic acid and 2-(dimethylamino)ethyl methacrylate exhibited a pronounced yield stress (the minimum stress required for cone movement). Therefore, it was not possible to fit a Newtonian model to the experimental curves to obtain viscosity values. The result obtained using the other polymer, with higher levels of methacrylic acid and 2-(dimethylamino)ethyl methacrylate, is shown in Figure (7.1). The earlier result for a plastisol based on butylbenzyl phthalate and a 92.5:7.5 (wt) methyl methacrylate - methacrylic acid copolymer (batch 13.5), described in Chapter 6, is shown for comparison.

The plastisol based on the methyl methacrylate - methacrylic acid copolymer rose in relative viscosity from 1.86 to 2.35 after 17 hours. That containing the polymer with acid-base interactions rose from 2.06 after one hour to 2.28 after 17 hours. The viscosity stability of the plastisol containing the polymer with acid-base interactions is thus found to be only slightly superior to that prepared from the 92.5:7.5 (wt) methyl methacrylate - methacrylic acid copolymer.

7.2 Polymers containing metal ion crosslinks

Polymers containing metal ion crosslinks were prepared using both non-aqueous dispersion and aqueous emulsion polymerisation techniques. The strategy was to neutralise the carboxylic acid groups of a methyl methacrylate - methacrylic acid copolymer with an organometallic compound or a metal hydride. This would leave metal carboxylate groups and an innocuous byproduct such as hydrogen. The metal carboxylate groups could then, as described in Section 2.1.4.2, form ion pairs and cluster together. The result is a polymer particle containing metal ion clusters, playing the role of thermally reversible crosslinks, linked together by polymer chains. The preparative techniques and the effect on plastisol viscosity stability of using polymers containing metal ion crosslinks are examined below.

7.2.1 The preparation of polymers by non-aqueous dispersion polymerisation

The theory of non-aqueous dispersion polymerisation and details on the preparation of polymers using this technique are given in Sections 3.1.2 and 6.1. The first attempt at preparing a polymer containing metal ion crosslinks using this technique involved the direct addition of calcium hydride during the polymerisation step of a one-shot preparation of 95:5 (wt) methyl methacrylate - methacrylic acid copolymer. The byproduct of the reaction of methacrylic acid and calcium hydride was hydrogen. However, there was a tendency to generate large quantities of unwanted metal residues. Addition of a 21% by weight solution of sodium ethoxide in ethanol to a previously prepared methyl methacrylate - methacrylic acid copolymer at room temperature led to flocculation. The addition of ethanol may have led to desorption of the steric stabiliser or flocculation by exceeding what is termed the critical flocculation point (see Section 3.1.1) [2].

It was felt that neutralisation of the carboxylic acid groups of the steric stabiliser might be leading to flocculation of the polymer particles. Therefore polymers stabilised wiith a 50:45:5 (wt) precursor - methyl methacrylate - glycidyl methacrylate comb stabiliser were prepared. The polymer flocculated on addition of aluminium tri-(sec-butoxide) and aluminium isopropoxide. The by-products of neutralisation were 2-butanol and 2-propanol. In order to eliminate any possibility of interactions, that may be responsible for flocculation of the polymer, between the organometallic compounds and reactive groups on the stabiliser, the hydroxy groups on the stabiliser were acetylated. The resulting stabiliser was found, however, to be insoluble in the polymerisation solvent mixture.

7.2.1.1 The preparation of polymers stabilised by a lauryl methacrylate stabiliser precursor

A stabiliser precursor free of hydroxyl or carboxylic acid groups, that could react with organometallic compounds or metal hydrides resulting in polymer flocculation, was prepared. The stabiliser precursor comprised 97% by weight lauryl methacrylate and 3% by weight allyl methacrylate. It was a single step preparation. Details are given in Box (7.1).

Two polymers based on this stabiliser precursor were prepared. Details of the preparation of a 95:5 (wt) methyl methacrylate - methacrylic acid copolymer (batch 22.42) are given in Box (7.2). A 92.5:7.5 (wt) methyl methacrylate - methacrylic acid copolymer was also prepared with a particle diameter range of 0.22-0.52 microns (batch 22.44). Benzoyl peroxide was used to initiate reaction between the allyl group on the stabiliser precursor and the monomers. This initiator strongly abstracts hydrogens and may have initiated graft polymerisation onto the stabiliser precursor[3]. The half life is longer than that of 2,2'-azobis-2-methylbutyronitrile and consequently required a one hour induction period and long feed time[4]. A small quantity of toluene was added to the reaction mixture to help solubilise this initiator. The particle size distribution was broader than with previous polymer preparations. This may be attributed to use of a stabiliser precursor in place of a preformed comb stabiliser.

Box (7.1) Preparation of a 97:3 (wt) lauryl methcarylate - allyl methacrylate stabiliser precursor (batch 2366/147b).

Shellsol D40	8.93	g
n-Hexane	50.61	g
Feed Stage:		
Lauryl methacrylate	33.95	g
Allyl methacrylate	1.05	g
2,2' - azobis - 2 - methylbutyronitrile	0.46	g
Ethyl acetate	5.00	g

The solvent mixture was heated to 80°C under nitrogen with a water bath at which point the feed was added over a period of 4.5 hours. The final non-volatile content was 33.8 % by weight.

The polymers were neutralised by addition of solutions of butyl lithium, diethyl zinc and diisobutyl aluminium hydride (DIBAL-H). The organometallic compounds were supplied as 1.6 M, 1.0 M and 1.0 M solutions respectively in mixed hexanes but were diluted further to 0.2 M with mixed hexanes. The solutions were then added dropwise to the dispersions over a period of 1-2 hours. The amount added was dictated by the degree of neutralisation required and on the basis that butyl lithium, diethyl zinc and diisobutyl aluminium hydride were respectively mono- di- and tri-valent. Values in excess of 100% neutralisation were obtained using diethyl zinc and diisobutyl aluminium hydride on the basis that 100% neutralisation by diethyl zinc meant that each zinc ion was associated with one carboxylic acid group, and 100% neutralisation by diisobutyl aluminium hydride meant that each aluminium ion was associated with one carboxylic acid group.

Box 7.2 Preparation of a 95:5 by weight methyl methacrylate - methacrylic acid copolymer (batch 22.42) by a non-aqueous dispersion polymerisation technique using a lauryl methacrylate - allyl methacrylate stabiliser precursor.

First charge:

Shellsol D40	32.69 g
n-Hexane	185.26g
Toluene	10.50 g
Stabiliser precursor	15.53 g
Benzoyl peroxide	1.02 g

The first charge was heated under nitrogen at 85°C for one hour after which an initial charge of 8.75 g of methyl methacrylate was made. The reactants were heated for a further hour. The feed was then added over a period of approximately 7 hours.

Feed:

Methyl methacrylate	91.00 g
Methacrylic acid	5.25 g

The final particle diameter, determined by electron microscopy, was 0.38 μm.

7.2.1.2 The preparation of polymers stabilised by a 12-hydroxystearic acid comb stabiliser

Polymers containing metal ion crosslinks were also successfully prepared stabilised with a poly(12-hydroxystearic acid) based comb stabiliser. A 95:5 (wt) methyl methacrylate - methacrylic acid copolymer (batch 21.16) was prepared using the one-shot method described in Section 6.1.2.1. Modifications to the original method included using a 68:32 mixture of n-hexane and Isopar M as solvent and addition of 3% of the total weight n-propanol to improve the solvency of the mixture for methacrylic acid. The total level of monomer was 30% of the total weight. The final particle diameter was 0.31 microns. The polymer was neutralised with butyl lithium, diethyl zinc and diisobutyl aluminium hydride. A metal ion containing version of the 92.5:7.5 (wt) methyl methacrylate - methacrylic acid copolymer with a core-shell morphology (batch 22.51), described in Section 6.1.2.2, was also prepared by neutralisation with butyl lithium and diethyl zinc.

It is conceivable that the organometallic compounds are simply reacting with the n-propanol, however the stability of plastisols prepared from these polymers, the results of which are presented in Section 7.2.3.2, suggest that the polymer has, to some extent, been neutralised. Thus it appears that these polymers can be prepared with steric stabilisers containing low levels of hydroxyl and carboxylic acid groups.

7.2.2 The preparation of polymers by aqueous emulsion polymerisation

Two polymers containing metal ion crosslinks were prepared using aqueous emulsion polymerisation. The first was a 95:5 (wt) methyl methacrylate - potassium salt of 3-sulphopropyl methacrylate (3-SPM) copolymer (batch 22.28) prepared using a one-shot method. The details of the preparation are given in Box (7.3).

Sodium bicarbonate was added to the emulsion as a buffer against the fall in pH, associated with the use of potassium persulphate initiator, and thus maintain the dissociated state of 3-sulphopropyl methacrylate. Electrolytes can, as described in Section 3.1.1, flocculate electrostatically stabilised polymer dispersions. Consequently, the anionic surfactant sodium dioctylsulphosuccinate (Aerosol OT) and the non-ionic surfactant Brij 35 (polyoxyethylene (23)-lauryl ether) were used in combination to enhance polymer stabilisation in the presence of this additional electrolyte.

Box (7.3) One-shot preparation of a 95:5 (wt) methyl methacrylate - 3-SPM, K copolymer by aqueous emulsion polymerisation (batch 22.28)

Distilled water	69.41	g
Methyl methacrylate	28.50	g
3-SPM, K	1.50	g
Aerosol OT	0.15	g
Brij 35	0.15	g
Sodium bicarbonate	0.22	g
Potassium persulphate	0.07	g

Polymerisation was undertaken at approximately 80°C to produce 0.10 μm diameter particles. The final pH was 6.70.

The second polymer (batch 22.30) comprised 95% (wt) methyl methacrylate and 5% (wt) sodium methacrylate (MAc, Na). Details of this preparation are given in Box (7.4).

Unsuccessful attempts were also made to incorporate zinc, in the form of zinc oxide, and barium, in the form of barium hydroxide, into a 95:5 (wt) methyl methacrylate - methacrylic acid copolymer in the same manner as for sodium. In both cases, the methacrylic acid was neutralised with the salt in the manner described in Box (7.4). On polymerisation, the polymer formed a separate and distinct layer from the aqueous phase.

Box (7.4) Preparation of a 95:5 (wt) methyl methacrylate - sodium methacrylate emulsion copolymer by aqueous emulsion polymerisation (batch 22.30)

Initial charge:

Distilled water	40.00	g
Methacrylic acid	1.50	g
1 M NaOH	17.5	g

After the addition of 1 M sodium hydroxide solution which brought the pH up from 3.2 to 9.7, the remaining ingredients were added.

Remaining charge:

Distilled water	11.91	g
Methyl methacrylate	28.50	g
Aerosol OT	0.15	g
Brij 35	0.15	g
Potassium persulphate	0.07	g

The polymerisation was carried out at approximately 80°C to produce particles 0.20 μm in diameter. The final pH was 7.15.

The Schultz-Hardy rule states that the critical coagulation concentration, which is the minimum concentration of a particular electrolyte required to produce rapid coagulation of the polymer particles for a given concentration of particles, is a function of the valency of the ions of opposite charge to that residing on the particle surface (counter-ions). The critical coagulation concentrations for counter-ions of valency 1, 2 and 3 are 1 : 0.013 : 0.0016. As divalent ions are sixty times more effective at coagulating a given latex than monovalent ions, the presence of the divalent zinc and barium ions may have prevented formation of electrostatically stabilised polymer particles by reducing the electrostatic energy barrier, described in Section 3.1.1.1, to coagulation [5]. It has been reported that neutralisation of carboxylic polyacrylates with oxides of zinc and barium requires heating of the mixture to 65-175°C [6].

7.2.3 Plastisol stability

The polymers described in Sections 7.2.1 and 7.2.2 were formulated as plastisols with butylbenzyl phthalate. Their viscosites were then measured over 17 hours to assess the effect of metal ion crosslinks on the ability of the polymer to resist swelling by the plasticiser. Further details on the method, including isolation of the polymer particles, are described in Section 5.2.6.

7.2.3.1The viscosity stability of plastisols containing polymers stabilised by a lauryl methacrylate stabiliser precursor

Plastisols were prepared with the neutralised lauryl methacrylate stabilised polymers (batches 22.42 and 22.44) and butylbenzyl phthalate. The polymer - plasticiser ratio was 10:90 by weight. The plastisol viscosities were measured over 17 hours. The viscometer was programmed to carry out two shear stress cycles an hour. The procedure involved, for the first cycle, increasing the stress up to 1 000 dyne.cm^{-2} over one minute, holding for ten seconds and then lowering the stress to zero over one minute. The second cycle was similar except that the limiting stress of 3 000 dyne.cm^{-2} was reached after two minutes. The results are shown in Figures (7.2) and (7.3).

Figure (7.2) shows the results using the polymers with 5% weight polymer methacrylic acid. The result for a plastisol based on an unneutralised poly(12-hydroxystearic acid) stabilised 95:5 (wt) methyl methacrylate - methacrylic acid copolymer (batch 6.2) and butylbenzyl phthalate appears for comparison. The effect of formulating plastisols with the neutralised polymers dramatically improved their viscosity stability relative to that containing the unneutralised polymer. The plastisol containing the polymer 50% neutralised with butyl lithium was the most stable. The relative viscosity only rose from 1.83 to 2.29 over 16 hours. In comparison, the plastisol containing the unneutralised lauryl methacrylate stabilised polymer rose from 2.00 to 4.26 over the same period. Although neutralisation of the polymer with diethyl zinc also produced more stable plastisols, increasing the degree of neutralisation from 50% to 142% appeared to offer no significant advantage.

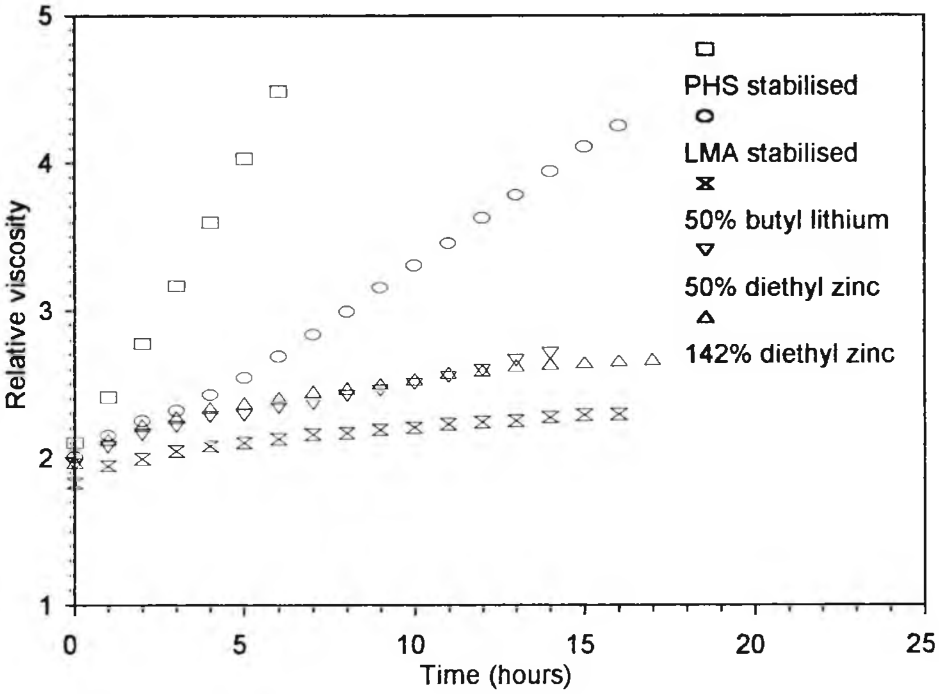

Figure (7.2) The stability of plastisols based on a lauryl methacrylate stabilised 95:5 (wt) methyl methacrylate - methacrylic acid copolymer neutralised with a range of organometallic compounds at 25°C. The polymer - butylbenzyl phthalate ratio was 10:90 by weight. An equivalent poly(12-hydroxystearic acid) (PHS) stabilised copolymer (batch 6.2) is included for purposes of comparison.

The poly(12-hydroxystearic acid) stabilised copolymer (batch 6.2) was considerably less stable than the unneutralised lauryl methacrylate stabilised version. A plausible reason may be the difference in particle size and distribution. The lauryl methacrylate stabilised copolymer particles are larger and thus less likely to swell as quickly as the smaller poly(12-hydroxystearic acid) stabilised copolymer particles. The importance of particle size to the ability of a polymer to resist plasticiser swelling has been discussed in Section 6.3.7.

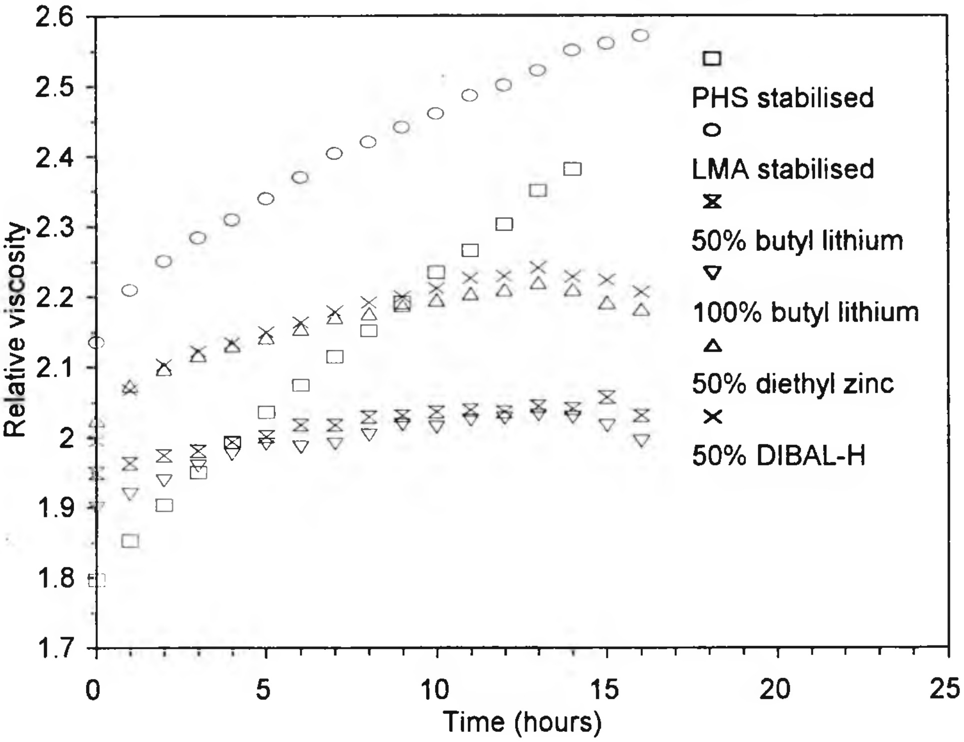

Figure (7.3) The viscosity stability of plastisols based on a lauryl methacrylate stabilised 92.5:7.5 (wt) methyl methacrylate - methacrylic acid copolymer neutralised with a range of organometallic compounds at 25°C. The polymer - butylbenzyl phthalate ratio was 10:90 by weight. An equivalent poly(12-hydroxystearic acid) (PHS) stabilised copolymer (batch 6.10) is included for purposes of comparison.

The viscosity stability of the plastisols formulated with the polymers containing 7.5% weight polymer methacrylic acid showed the same trends as for those containing the polymer with 5% weight polymer methacrylic acid. The plastisols formulated with polymers neutralised with butyl lithium were the most stable. Increasing the degree of neutralisation from 50% to 100% brought no benefit in terms of plastisol stability. The implication is that only carboxylic groups near the particle surface were neutralised and that they constituted less than 50% of the total. This may be because once the surface groups were neutralised, the charged ions might well have repelled the remaining metal ions from diffusing into the centre of the polymer particle. The plastisols containing the polymers 50% neutralised with di-isobutyl aluminium hydride and diethyl zinc had equivalent stabilities.

The ionic radii of Li^+, Zn^{2+} and Al^{3+} are 0.068 nm, 0.074 nm and 0.045 nm respectively[7]. The strength of chain association to the metal ions should therefore be $Li^+ < Zn^{2+} < Al^{3+}$. This order is not reflected in the stabilities of the plastisols containing the neutralised polymers. Diisobutyl aluminium hydride, a powerful reducing agent, does confer some degree of stability[8]. Given that the improvement is not as great as that seen with lithium, it is possible that the aluminium has reacted with only one acid group. The remaining isobutyl groups, still attached to the metal ion, might make clustering of the ions, and formation of effective reversible crosslinks, difficult on steric grounds. A similar argument may explain the poor performance of zinc relative to lithium.

7.2.3.2The viscosity stability of plastisols containing polymers stabilised by a 12-hydroxystearic acid comb stabiliser

The viscosity of plastisols comprising the neutralised versions of the poly(12-hydroxystearic acid) stabilised 95:5 (wt) methyl methacrylate - methacrylic acid copolymer (batch 21.16), prepared in Section 7.2.1.2, and butylbenzyl phthalate were measured over 16 hours. The plastisols were prepared in the same manner as described in Section 7.2.3.1. The experimental conditions also remained unchanged. The results are shown in Figure (7.4).

The plastisols formulated with the butyl lithium and diethyl zinc neutralised polymers increased in viscosity less than the plastisol based on the unneutralised polymer over the experimental time period. In contrast, the viscosity of the plastisol containing the diisobutyl aluminium hydride neutralised polymer increased at a greater rate. Neutralisation of the polymer with diethyl zinc appeared to be the most effective treatment rendering the polymer least susceptible to plasticiser swelling. The plastisols based on the polymers 50% neutralised with respectively diethyl zinc and butyl lithium increased in relative viscosity from 1.67 after one hour to 2.15 after 16 hours and 1.69 to 2.67 after 16 hours. The plastisol based on the unneutralised polymer increased in relative viscosity from 1.40 to 3.20 over 16 hours. Increasing the degree of neutralisation from 50% to 100% appeared to render the resulting plastisols less stable in terms of viscosity.

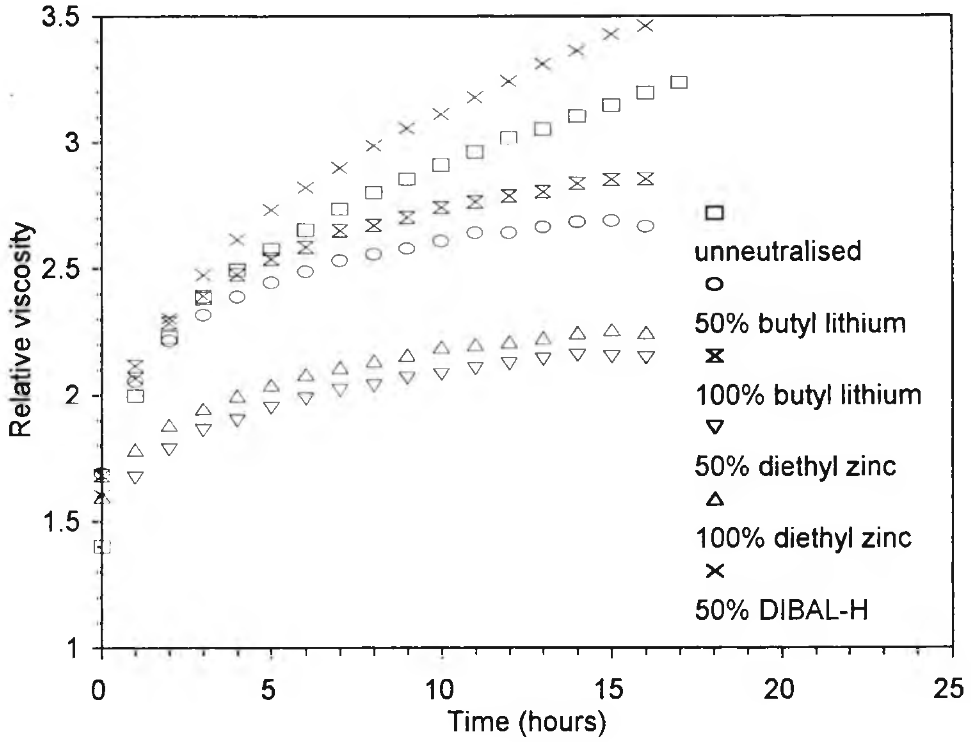

Figure (7.4) The viscosity stability of plastisols based on a 95:5 (wt) methyl methacrylate - methacrylic acid copolymer (batch 21.16) neutralised with a range of organometallic compounds at 25°C. Polymer - butylbenzyl phthalate ratio 10:90 by weight.

In contrast to the results obtained with the lauryl methacrylate stabilised polymers, greater improvements in plastisol viscosity stability were seen with polymers neutralised with diethyl zinc over those neutralised with butyl lithium. This may be due to the higher charge density of Zn^{2+} than Li^{+} binding the polymer chains more strongly and reducing the rate of plasticiser diffusion. An alternative explanation may be a greater tendency for butyl lithium to react with the hydroxy groups on the steric stabiliser. This would leave fewer butyl lithium molecules to neutralise the carboxylic groups residing within the polymer particles. As yet, the destabilising effect on the viscosity of the plastisol containing the polymer neutralised with diisobutyl aluminium hydride cannot be explained.

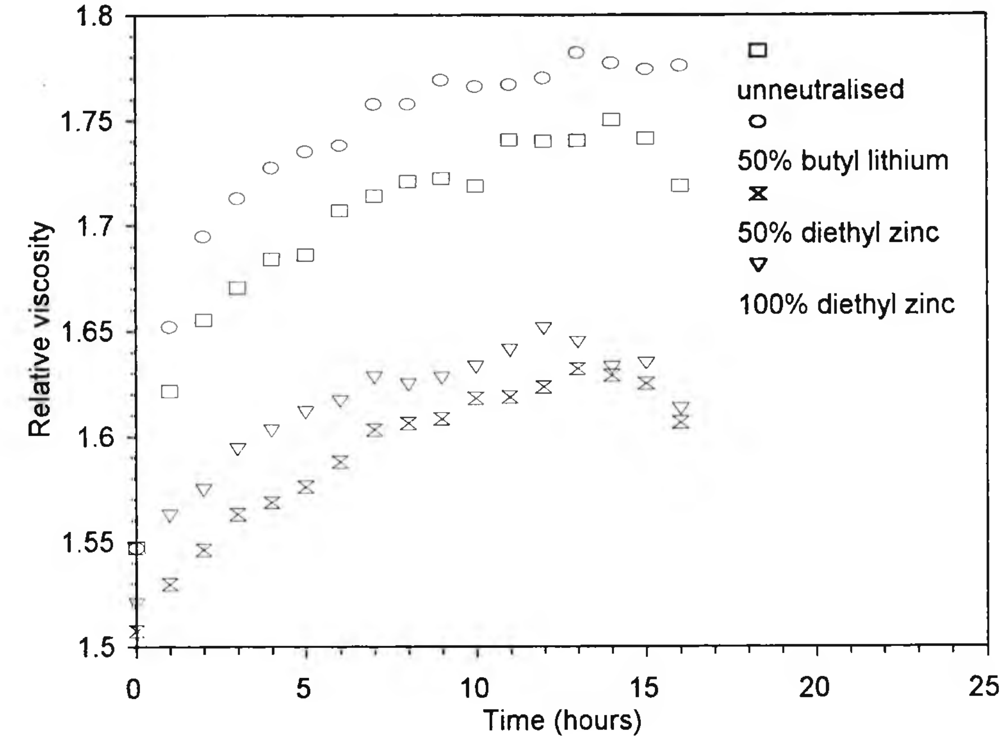

Figure (7.5) The viscosity stability of plastisols based on a 92.5:7.5 methyl methacrylate - methacrylic acid core-shell copolymer (batch 22.51) neutralised with a range of organometallic compounds at 25°C. Polymer - butylbenzyl phthalate ratio 10:90 by weight.

Plastisols were prepared based on neutralised 92.5:7.5 (wt) methyl methacrylate - methacrylic acid copolymers incorporating a core-shell type morphology (batch 22.51), prepared in Section 7.2.1.2, and butylbenzyl phthalate. The viscosity stability of the plastisols was tested under the same experimental conditions as described for the lauryl methacrylate stabilised polymers in Section 7.2.3.1. The results are shown in Figure (7.5).

The diethyl zinc neutralised polymers were the most stable in butylbenzyl phthalate. At 50% neutralisation, the plastisol increased in relative viscosity from 1.51 to 1.61 over 16 hours. In contrast, over the same period, the relative viscosity of the plastisol containing the unneutralised polymer rose from 1.55 to 1.72. Increasing the degree of neutralisation to 100% led to a plastisol that was slightly less stable than that containing the 50% neutralised polymer. Neutralisation with butyl lithium appeared to render the polymer more susceptible to plasticiser swelling.

Polymers neutralised to 50%, 100% and 200% by diethyl zinc and the unneutralised polymer were reformulated as more concentrated plastisols with 40% by weight polymer in butylbenzyl phthalate. The viscosities of these plastisols were measured over 16 hours. The experimental procedure for the plastisol containing the 200% neutralised polymer was as described for the lauryl methacrylate stabilised polymers in Section 7.2.3.1. That for the remaining plastisols comprised increasing the shear stress to 1 000 dynes.cm^{-2} over one minute, holding for ten seconds and then allowing the stress to fall to zero over one minute. The plastisol containing the unneutralised polymer exhibited quite severe shear thickening behaviour and consequently the Newtonian viscosity could not be calculated. The results for the other plastisols are shown in Figure (7.6).

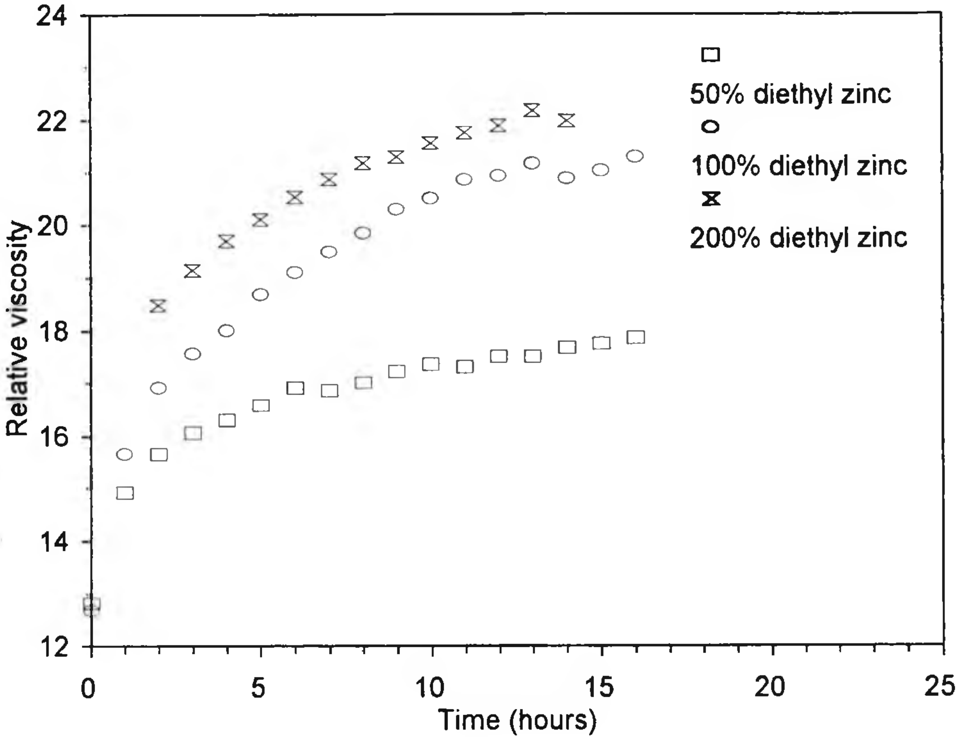

Figure (7.6) The viscosity stability of plastisols based on a 92.5:7.5 methyl methacrylate - methacrylic acid core-shell copolymer (batch 22.51) neutralised with diethyl zinc at 25°C. Polymer - butylbenzyl phthalate ratio 40:60 by weight.

In agreement with earlier observations, the plastisol viscosity stability worsened on increasing the degree of neutralisation. The plastisol that increased in viscosity the least contained the polymer neutralised to 50% with diethyl zinc. The relative viscosity rose from 12.8 to 17.7 after 14 hours. Over the same time period, the plastisols containing the polymers neutralised to 100% and 200% rose in relative viscosity to 20.9 and 22.0 respectively.

7.2.3.3 The viscosity stability of plastisols containing polymers prepared by aqueous emulsion polymerisation

The metal ion containing polymers prepared by aqueous emulsion polymerisation, described in Section 7.2.2, were formulated with butylbenzyl phthalate as dilute plastisols. The polymer - plasticiser ratio was 10:90 by weight. Their viscosities were measured over 16 hours using the same experimental procedure described for the lauryl methacrylate stabilised polymers in Section 7.2.3.1. The polymers comprised a 95:5 (wt) methyl methacrylate - 3-SPM, K (batch 22.28) and a 95:5 (wt) methyl methacrylate - sodium methacrylate (batch 22.30) copolymer. Both plastisols initially exhibited Newtonian behaviour. Over time, they started to show increasing signs of shear thinning behaviour and it became difficult to adequately fit a Newtonian model to the data to obtain values for the viscosity. Difficulties in polymerising potassium 3-sulphopropyl methacrylate and sodium methacrylate, both of which have high degrees of water solubility in aqueous media, cast some doubt on the true compositions and morphologies of the two polymers. Therefore, the behaviour of the polymers in butylbenzyl phthalate may not be a true reflection of their nominal compositions.

7.3 Plastisol coatings

In order to assess the coating properties of the metal ion containing polymers prepared in Section 7.2, plastisols were prepared, based on 95:5 (wt) methyl methacrylate - methacrylic acid copolymers and butylbenzyl phthalate, at a polymer - plasticiser ratio of 50:50 by weight. The plastisols were then applied to a glass panel with a number 7 K-bar and heated at 130°C for 30 minutes. The appearance of the plastisols both before and after gelling was noted. The observations are summarised in Table (7.1).

The plastisol based on the poly(12-hydroxystearic acid) stabilised polymer (batch 21.16) was easier to manipulate than the equivalent plastisol based on the lauryl methacrylate stabilised polymer (batch 22.42). Neutralisation of the polymers with diethyl zinc and diisobutyl aluminium hydride did not appear to improve the initial viscosities of the resulting plastisols. The clarity of the coatings suggested that the plastisols were fully gelled at 130°C. The lack of any sign of plasticiser exudation from the coatings indicated that neutralisation of the polymers had not had an adverse effect on their compatibility with butylbenzyl phthalate.

Table (7.1) Appearance of plastisols comprising 50% by weight butylbenzyl phthalate and 50% by weight polymer before and after gelling at 130 °C for 30 minutes.

Polymer	Un-/neutralised	Plastisol appearance	Film appearance
5% methacrylic acid	Unneutralised	White runny paste	Clear, smooth and dry
	50% DIBAL-H	Runny paste	Clear and dry
5% methacrylic acid	Unneutralised	White paste	Clear, smooth and dry
(lauryl methacryalate	50% diethyl zinc	White paste	Clear, smooth and dry
stabilised)	100% diethyl zinc	White paste	Clear, smooth and dry
	142% diethyl zinc	White paste	Clear, smooth and dry

The initial viscosities of plastisols containing polymers stabilised with poly(lauryl methacrylate) appear consistently higher than those containing equivalent polymers stabilised with poly(12-hydroxystearic acid). The experimental evidence supports this claim for both dilute and concentrated plastisols. The reason for this may lie with the molecular weights of the stabilisers. The stabiliser precursor based on lauryl methacrylate was prepared using a free radical initiator. Free radical polymerisations generally lead to high molecular weight polymers. Poly(12-hydroxystearic acid) was prepared by a condensation reaction which led to a number average molecular weight of about 2 500. Both stabilisers would probably be swollen in butylbenzyl phthalate. The higher molecular weight stabiliser would give the polymer particles a greater apparent volume in butylbenzyl phthalate. This would be reflected as a greater apparent polymer volume fraction and a higher viscosity.

7.4 Summary

The viscosity stability of plastisols based on methyl methacrylate - methacrylic acid copolymers, obtained by non-aqueous dispersion polymerisation, and butylbenzyl phthalate was improved by neutralising the polymer with certain organometallic compounds. The greatest improvement in plastisol stability when using polymers stabilised by poly(lauryl methacrylate) was obtained with butyl lithium as the neutralising agent. For the plastisols containing polymers stabilised by poly(12-hydroxystearic acid), diethyl zinc was found to be most effective as the neutralising agent.

The plastisols formulated with the poly(12-hydroxystearic acid) stabilised polymers were more fluid than those based on the poly(lauryl methacrylate) stabilised polymers. This was attributed to the differences in stabiliser molecular weight and their effect on the apparent particle volume in butylbenzyl phthalate.

No further improvements in plastisol stability were observed on increasing the degree of neutralisation of the polymers beyond 50%. This was attributed to the fact that only those carboxylic groups nearest the particle surface reacted. If the polymers could have been heated to above their glass transition temperatures without the risk of destabilising the dispersion, it may have been possible to react more of the groups and produce polymers even more resistant to plasticiser swelling.

Polymers containing metal ions were also prepared by aqueous emulsion polymerisation. The plastisols formulated with these polymers showed poor viscosity stability. Potassium 3-sulphopropyl methacrylate and sodium methacrylate were particularly difficult to polymerise, as they are highly water soluble, and hence there was uncertainty over the true compositions of the polymers. Therefore, it may be unwise to attempt to relate the performance of these polymers, in plasticiser, to their compositions. A more indepth characterisation of all the polymers, in particular in regard to their morphologies, would have assisted analysis of the results from the viscometry.

Despite the undoubted improved resistance, compared to poly(methyl methacrylate), of polymers with metal ion crosslinks to swelling by butylbenzyl phthalate, plastisols formulated at polymer-plasticiser ratios approaching 50:50 by weight still do not show acceptable viscosity stability.

References

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CHAPTER 8-

COVALENTLY CROSSLINKED POLYMERS

Polymers were prepared with covalent crosslinks. The effect of the crosslinks on the rate of swelling of the polymers, when formulated as plastisols, was measured viscometrically. A treatment of the theory of swellable networks is presented in Section 3.3.2. The polymers were prepared using non-aqueous dispersion and aqueous emulsion polymerisation techniques. Three types of polymer were prepared using the former technique. They comprised:

(a) a terpolymer of methyl methacrylate, methacrylic acid and glycidyl methacrylate, the crosslinks being formed by a ring opening reaction between the glycidyl and carboxylic groups;

(b) a copolymer of methyl methacrylate and a preformed urethane diacrylate; and

(c) polymers prepared with comb stabilisers which, through pendant methacrylate groups, formed covalent bonds with the surface of the polymer particles.

Covalently crosslinked polymers prepared using the aqueous emulsion polymerisation technique were based on methyl methacrylate and ethylene glycol dimethacrylate.

The polymers were then dried and redispersed in plasticiser. The stability of the resulting plastisols was determined viscometrically, typically over a period of 17 hours. The coating properties of the plastisols, applied to glass panels, was visually assessed. Each step is now considered in detail in the order described above.

8.1 The preparation of the polymers

Polymers were prepared containing covalent crosslinks both within the polymer particle interior and on the particle surface by non-aqueous dispersion polymerisation. The seed and feed method, described in Section 6.1.2.2, was used. The polymers prepared by aqueous emulsion polymerisation possessed exclusively internal crosslinks. Again, the general technique has been given in Section 6.2. The theories of both non-aqueous dispersion and aqueous emulsion polymerisation were presented in Section 3.1.2. An account of the preparation of the polymers, by non-aqueous dispersion polymerisation, with internal and then surface crosslinks will be given. This will be followed by a description of the preparation of the polymers by aqueous emulsion polymerisation.

8.1.1 The preparation of polymers with internal crosslinks by non-aqueous dispersion polymerisation

Polymers with internal crosslinks, obtained by non-aqueous dispersion polymerisation, were prepared based on epoxide ring opening and urethane chemistry. The polymer incorporating epoxide ring opening chemistry (batch 16.9) was prepared as a conventional 95:2.5:2.5 methyl methacrylate - methacrylic acid - glycidyl methacrylate terpolymer. The solvent comprised an 85:15 mixture of n-hexane and Shellsol D40. Separation of glycidyl methacrylate and methacrylic acid was necessary in order to prevent subsequent flocculation of the polymer. Thus, glycidyl methacrylate was added during the first half of the feed and methacrylic acid during the second half. The total feed time was extended from the usual two hours to five hours to ensure that the reaction was carried out under monomer starved conditions. This reduced the risk of glycidyl methacrylate and methacrylic acid mixing and consequent polymer flocculation. On completion of the polymerisation, covalent crosslinks were formed by the catalysed reaction between the glycidyl and the carboxylic groups. This involved replacement of n-hexane with Shellsol D40, addition of 0.45% by weight Cordova AMC II (a chromium III octoate solution) and heating for 10.5 hours at 120°C. It was later found possible to carry out the reaction at the same temperature uncatalysed. The particle diameter, measured with an electron microscope, was 1.33-1.83 microns.

Box (8.1) Preparation of urethane diacrylate (HEMA-IPDI)

Initial charge:

IPDI	24.10 g	(0.11 moles)
Dimethyl sulphoxide	18.16 g	
DBTDL	0.06 g	

The initial charge was heated to 60°C, under an air purge, at which point the following mixture was added rapidly.

Feed:

HEMA	32.42 g	(0.25 moles)
Dimethyl sulphoxide	36.32 g	
t-Butyl catechol	0.056 g	

Heating was continued and the progress of the reaction monitored by observing the reduction in the isocyanate stretching peak at 2260 cm^{-1} in the infra-red spectrum[1]. After 9.5 hours, the following further addition was made.

Post-addition:

HEMA	12.91 g	(0.10 moles)
Dimethyl sulphoxide	9.08 g	
DBTDL	0.035 g	

Heating was continued for a further 3.5 hours. On cooling, the dimethyl sulphoxide and excess 2-hydroxyethyl methacrylate was extracted with water. To aid this extraction, ethyl acetate was used as a solvent for the diacrylate. The ethyl acetate was later evaporated off to leave the pure diacrylate. The infra-red spectrum of the final product showed that all the isocyanate had reacted and that there was no residual unreacted 2-hydroxyethyl methacrylate.

A polymer with urethane crosslinks was prepared in two steps. The synthesis involved the preparation of a urethane diacrylate precursor which was subsequently polymerised with methyl methacrylate following the seed and feed method described in Section 6.1.2.2. The diacrylate was the reaction product of two moles of 2-hydroxyethyl methacrylate and one mole of isophorone diisocyanate. The preparation was adapted from the literature and details are provided in Box (8.1) [2]. During polymerisation, the diacrylate was added during the second half of the feed. The composition of the polymer was 95:5 (wt) methyl methacrylate - urethane diacrylate (batch 20.8/1). The particle diameter, using microscopy, was 0.16-0.21 microns.

8.1.2 The preparation of polymers with surface crosslinks by non-aqueous dispersion polymerisation

Polymers particles with surface crosslinking, obtained by non-aqueous dispersion polymerisation, were prepared by covalently bonding the stabiliser chains to the surface of the polymer particles. This was accomplished by two routes. The first route involved the preparation of a 90:10 (wt) methyl methacrylate - glycidyl methacrylate comb stabiliser (batch 2366/1) according to the method described in Section 6.1.1. The comb stabiliser was used to prepare a 95:5 (wt) methyl methacrylate - methacrylic acid copolymer (batch 17.1) according to the seed and feed method described in Section 6.1.2.2. At the end of the feed stage, a final addition of 0.05% by weight of the initiator, 2,2'-azobis-2-methylbutyronitrile, was made. After the polymerisation, the stabiliser was locked on to the particle surface by reacting the glycidyl groups in the stabiliser with the carboxylic groups in the polymer[3]. This was accomplished by heating the polymer to 120°C and holding for four hours. The particle diameter, using microscopy, was 0.20-0.37 microns.

The second route to a polymer particle with surface crosslinks involved reacting pendant methacrylate groups on a reactive comb stabiliser with the growing polymer particle during polymerisation[4]. A reactive stabiliser (batch 2366/51) was prepared from an existing 98:2 methyl methacrylate - methacrylic acid comb stabiliser (batch 2335/165) by reacting a portion of the free carboxylic groups with glycidyl methacrylate.

Box (8.2) Preparation of reactive stabiliser with pendant methacrylate groups (batch 2366/51)

The light solvent fraction was removed from 100 g of the comb stabiliser (batch 2335/165) and replaced with butyl acetate. The following mixture was then added.

Charge:

Ethyl acetate	1.000	g
Glydidyl methacrylate	0.047	g
Dimethyl laurylamine	0.104	g

This implied a 1.3 molar excess of glycidyl over carboxylic groups. After heating the reactants at 120°C for 5.5 hours, the acid value had dropped from the theoretical value of 6.52 mg(KOH)/g to 2.24 mg(KOH)/g. The composition of the reactive stabiliser was 49:51 (wt) poly(12-hydroxystearic acid) precursor - methacrylate copolymer. The methacrylate copolymer comprised 94.0:1.9:4.1 (wt) methyl methacrylate - methacrylic acid - glycidyl methacrylate. The final non-volatile content was 34.2% by weight.

A 92.5:7.5 (wt) methyl methacrylate - methacrylic acid copolymer (batch 20.1) was prepared with the reactive stabiliser (batch 2366/51) using the seed and feed technique. The seed stage was stabilised with a conventional 98:2 (wt) methyl methcrylate - methacrylic acid comb stabiliser. The reactive stabiliser was used exclusively during the feed stage. After the feed stage had finished, two additions of initiator, 2,2'-azobis-2-methylbutyronitrile, totalling 0.1% by weight, were added at fifteen minute intervals. The particle diameter was 0.14 microns.

A stabiliser was also synthesised using a methyl methacrylate - glycidyl methacrylate comb stabiliser as the starting material and adding methacrylic acid. This method appeared to be less prone to gelation than that described in Box (8.2). A 90:10 (wt) methyl methacrylate - glycidyl methacrylate comb stabiliser (2366/126) was prepared, as decribed in Section 6.1.1, from a poly(12-hydroxystearic acid) precursor (2366/125). Approximately half the glycidyl groups were reacted with methacrylic acid. The stabiliser had a final acid value of 1.23 mg(KOH)/g and a non-volatile content of 32.3%. The molecular weights (Courtaulds) are given in Table (8.2). A 98:2 methyl methacrylate - methacrylic acid copolymer (batch 21.21) was prepared with 7.3% by weight stabiliser on monomer. The final particle diameter was 0.10-0.30 microns. A summary of the reactive stabilisers is given in Table (8.1).

Table (8.1) Reactive steric stabilisers

Batch number	2366/51	2366/110/9
Prepared from	2335/165	2366//126
Modification	1.3 molar excess of GMA	0.5 molar excess of MAc
Acid value (mg(KOH)/g)	2.24	1.23
Non-volatile content (% wt)	34.2	32.3
Molecular weight†		
Mw	-	16976 17069
Mn	-	6167 6131
Mp	-	10450 10450
Polydispersity (Mw/Mn)	-	2.75 2.78

† Courtaulds

Details of the stabiliser precursor (batch 2366/125) and comb stabilisers (batches 2366/1 and 2366/126) referred to in this section and not already mentioned in Chapter 6 are summarised in Table (8.2).

Table (8.2) Stabiliser precursors and comb stabilisers

Batch number	2366/125	2366/1	2366/126
Type and composition (wt)	Precursor	50:45:5 PHS/MMA/GMA	50:45:5 PHS/MMA/GMA
Prepared from	-	2335/163	2366/125
Acid value (mg(KOH)/g	0.12	-	-
Non-volatile content (% wt)	68.2	32.9	33.4
Molecular weight†			
Mw	5044, 4984	-	24839, 24591
Mn	2762, 2700	-	6238, 6107
Mp	3813, 3731	-	16910, 16302
Polydispersity (Mw/Mn)	1.83 1.84	-	3.98 4.03

† Courtaulds

The polydispersity of the precursor was about two, the value predicted from the theory of stepwise polymerisations[5]. Likewise, the molecular weights of the comb stabilisers and reactive stabilisers, obtained by gel permeation chromatography, are typical being in the range Mw = 20 000-35 000 and Mn = 6 000-15 000 [6].

8.1.3 The preparation of polymers with internal crosslinks by aqueous emulsion polymerisation

A series of polymers were prepared with internal crosslinks by aqueous emulsion polymerisation. The series comprised methyl methacrylate - ethylene glycol dimethacrylate copolymers with 1.5%, 5% and 7.5% by weight ethylene glycol dimethacrylate. The particle diameters were in the range 0.10-0.17 microns. Two 87.5:7.5:5 methyl methacrylate - methacrylic acid - ethylene glycol dimethacrylate terpolymers were also prepared with particle diameters of 0.13 microns and 0.38 microns. The polymerisations were carried out according to the method described in Section 6.2 except for the large particle size terpolymer (batch 20.19) where the anionic surfactant, sodium dioctylsulphosuccinate, was omitted from the seed stage.

The particle diameters were measured by scanning electron microscopy according to the method decribed in Section 5.2.4. The results are summarised in Table (8.3).

Table (8.3) Crosslinked polymers prepared by aqueous emulsion polymerisation

Batch number	Composition (wt)	pH	Particle diameter[a] (μm)
19.7	98.5:1.5 MMA - EGDM	-	0.10
13.11	95:5 MMA - EGDM	2.5 - 3.0	0.17
20.12	92.5:7.5 MMA - EGDM	-	0.10
16.10	90:5:5 MMA - MAc - EGDM	2.0	0.13
16.11	87.5:7.5:5 MMA - MAc - EGDM	2.0	0.13
20.19	87.5:7.5:5 MMA - MAc - EGDM	-	0.38

[a] Scanning electron microscope

8.2 Determination of degree of crosslinking: gel content measurements

In order to determine the extent of crosslinking within the polymers, three methods were used to determine the fraction of crosslinked material. The crosslinked, or gel, fraction of the polymer was that fraction which was insoluble in methylethyl ketone. The three methods, described in Section 5.2.8, were based on using a centrifuge, a centifuge and ballmill in combination and Soxhlet extraction apparatus. A summary of the results is given in Table (8.4).

As expected, none of the test methods indicated the presence of crosslinked material in a 95:5 (wt) methyl methacrylate - methacrylic acid copolymer (batch 13.4) prepared by non-aqueous dispersion polymerisation. The remaining polymers, all crosslinked, possessed a gel fraction. The values obtained for a 95:5 (wt) methyl methacrylate - ethylene glycol dimethacrylate copolymer, prepared by aqueous emulsion polymerisation (batch 13.11), varied not only with the test method but for a given method. In contrast, the values obtained for the two methyl methacrylate - methacrylic acid - glycidyl methacrylate terpolymers were similar using the ballmill method. Using the Soxhlet extraction method, consistent values were obtained for the catalytically crosslinked terpolymer although significantly higher than when using the ballmill method. The lower values obtained from the ballmill method may be due to lightly crosslinked polymer being inadequately centrifuged out and being subsequently discarded when the soluble polymer fraction is decanted. The Soxhlet method, which relies on a filter paper to separate the soluble and insoluble fractions, would retain lightly crosslinked material.

Table (8.4) Percentage gel content of crosslinked polymers

Batch number	Composition (wt)	Centrifuge (% wt gel)	Ballmill (% wt gel)	Soxhlet (% wt gel)	Comments
13.4	95:5 MMA - MAc	0	0	0	-
13.11	95:5 MMA - EGDM	42.0	56.3/89.1	61.6/84.1	-
16.9	95:2.5:2.5 MMA - MAc - GMA	33.0	35.7	-	uncatalysed
16.9	95:2.5:2.5 MMA - MAc - GMA	-	32.4	86.8/87.5/84.6/ 78.7/84.6	catalysed
20.6	84.45:10:5.55 MMA - HEMA - IPDI	-	-	56.6	-
20.8/1	95:5 MMA - urethane diacrylate	-	-	60.0	-
17.1	95:5 MMA - MAc	-	72.5	-	with 2366/1
20.1	92.5:7.5 MMA - MAc	-	-	65.4	with 2366/51 in feed only

8.3 Plastisol stability

The effectiveness of introducing covalent crosslinks on reducing the rate of swelling of polymers, formulated as plastisols, was measured viscometrically. The plastisols were prepared by drying the polymers and redispersing them in butylbenzyl phthalate. The viscosities of the plastisols were then measured every hour for up to 17 hours. The method, including isolation of the polymer particles, was described in detail in Section 5.2.6. An account of the results obtained with the polymers prepared by non-aqueous dispersion and then aqueous emulsion polymerisation is given. This is followed by a description of an attempt to estimate the degree of polymer swelling.

8.3.1 The viscosity stability of plastisols containing polymers prepared by non-aqueous dispersion polymerisation

Figure (8.1) depicts the viscosity stabilities of five plastisols based on the crosslinked polymers, obtained by non-aqueous dispersion polymerisation, described in Section 8.1.1 and Section 8.1.2 and butylbenzyl phthalate. Also shown, for purposes of comparison, is a plastisol comprising a 92.5:7.5 (wt) methyl methacrylate - methacrylic acid copolymer (batch 6.10), obtained by non-aqueous dispersion polymerisation, and butylbenzyl phthalate (curve (a)). The polymer - plasticiser ratio was in the range 10-20:90-80 by weight. The viscometer was programmed to carry out two shear stress cycles an hour. The experimental procedure for the plastisols containing the 95:2.5:2.5 (wt) methyl methacrylate - methacrylic acid - glycidyl methacrylate terpolymer (batch 16.9), the methyl methacrylate - urethane diacrylate copolymer (batch 20.8/1) and the 92.5:7.5 (wt) methyl methacrylate - methacrylic acid copolymer with a reactive stabiliser (batch 20.1) (curves (b), (c) and (e)) was as follows. The stress was increased steadily to a limiting value over two minutes, held for ten seconds and then allowed to fall to zero over one minute. The limiting stresses for the first and second cycles were 1 000 and 3 000 dyne.cm^{-2} respectively. The procedure for the two plastisols containing the 95:5 (wt) methyl methacrylate - methacrylic acid copolymer with the locked on stabiliser (batch 17.1) and the 98:2 (wt) methyl methacrylate - methacrylic acid copolymer with a reactive stabiliser (batch 21.21) (curves (d) and (f)) were similar. For the former, the limiting stress for both cycles was 1 500 dyne.cm^{-2} whilst for the latter, they were 1 000 and 3 000 dyne.cm^{-2} for the first and second cycles respectively. In addition, for the latter plastisol, the limiting stress, during the first cycle only, was reached in one minute.

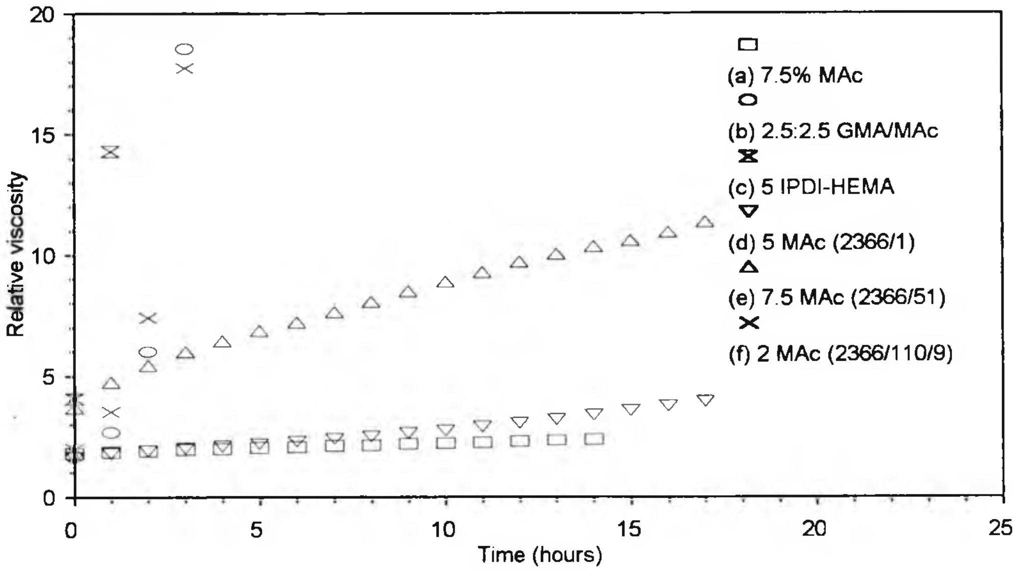

Figure (8.1) The viscosity stability of plastisols comprising crosslinked polymers, prepared by non-aqueous dispersion polymerisation, and butylbenzyl phthalate at 25°C. The polymer - plasticiser ratio was 10:90 by weight except for plastisols (c) and (e) when the ratio was increased to 20:80.

The results in Figure (8.1) show that all the plastisols formulated with the covalently crosslinked polymers had poorer viscosity stability than that containing an uncrosslinked 92.5:7.5 (wt) methyl methacrylate - methacrylic acid copolymer (curve (a)). The plastisol containing the 95:5 (wt) methyl methacrylate - urethane diacrylate copolymer (batch 20.8/1) increased in relative viscosity up to 1200 after only eight hours (curve (c)). The urethane linkage may have rendered the polymer more compatible with the plasticiser. The plastisol prepared with the 98:2 (wt) methyl methacrylate - methacrylic acid copolymer stabilised with a reactive stabiliser (batch 21.21) increased in relative viscosity to 135 after 17 hours (curve(f)). This was higher than an equivalent plastisol containing a polymer stabilised with an unreactive comb stabiliser (batch 8.6). The plastisol prepared with a 95:2.5:2.5 (wt) methyl methacrylate - methacrylic acid - glycidyl methacrylate terpolymer (batch 16.9) which had been crosslinked by heating at 120°C rapidly increased in relative viscosity reaching 133 after 17 hours (curve (b)). The viscosities of these two plastisols were very high after 17 hours as the crosslinked polymers were unable to fully dissolve and remained as swollen particles.

The plastisol with the 92.5:7.5 (wt) methyl methacrylate - methacrylic acid copolymer stabilised with a reactive stabiliser (batch 20.1) showed relatively moderate viscosity stability given that the plastisol was formulated with 20% by weight polymer (curve (e)). However, even this degree of swelling of the polymer by the plasticiser still meant that stability would be insufficient at commercial polymer - plasticiser ratios. The plastisol containing the 95:5 (wt) methyl methacrylate - methacrylic acid copolymer with the locked on stabiliser (batch 17.1) (curve (d)) showed comparable viscosity stability to the plastisol with the uncrosslinked polymer.

8.3.2 The viscosity stability of plastisols containing polymers prepared by aqueous emulsion polymerisation

The results of measurement of the viscosity stability of plastisols based on butylbenzyl phthalate and polymers containing ethylene glycol dimethacrylate are shown in Figure (8.2). The polymer - plasticiser ratio was 10:90 by weight. The viscometer was programmed to carry out two shear stress cycles an hour for up to 17 hours. The same experimental procedure was used for the plastisols containing the polymers with 1.5% (wt) and 7.5% (wt) ethylene glycol dimethacrylate (batches 19.7 and 20.12 respectively) and a 87.5:7.5:5.5 (wt) methyl methacrylate - methacrylic acid - ethylene glycol dimethacrylate (batch 20.19). It comprised increasing the stress uniformly up to a limiting value over two minutes, holding for ten seconds and then allowing the stress to fall to zero over one minute. The limiting stresses for the first and second cycles were 1 000 and 3 000 dyne.cm^{-2} respectively. For the plastisols containing a 90:5:5 (wt) and another 87.5:7.5:5.5 (wt) methyl methacrylate - methacrylic acid - ethylene glycol dimethacrylate terpolymer (batches 16.10 and 16.11 respectively), the procedure was similar except that the limiting stresses for the first and second shear cycles were 200 and 1 000 dyne.cm^{-2} respectively. The experimental procedure for the plastisol prepared with the 95:5 (wt) methyl methacrylate - ethylene glycol dimethacrylate copolymer (batch 13.11) comprised increasing the stress up to 1 000 dyne.cm^{-2} over one minute, holding at this stress for twenty seconds and then reducing it to zero over one minute. Also included in Figure (8.2), for purposes of comparison, is the viscosity stability result for a plastisol containing a 92.5:7.5 (wt) methyl methacrylate - methacrylic acid copolymer (batch 13.5).

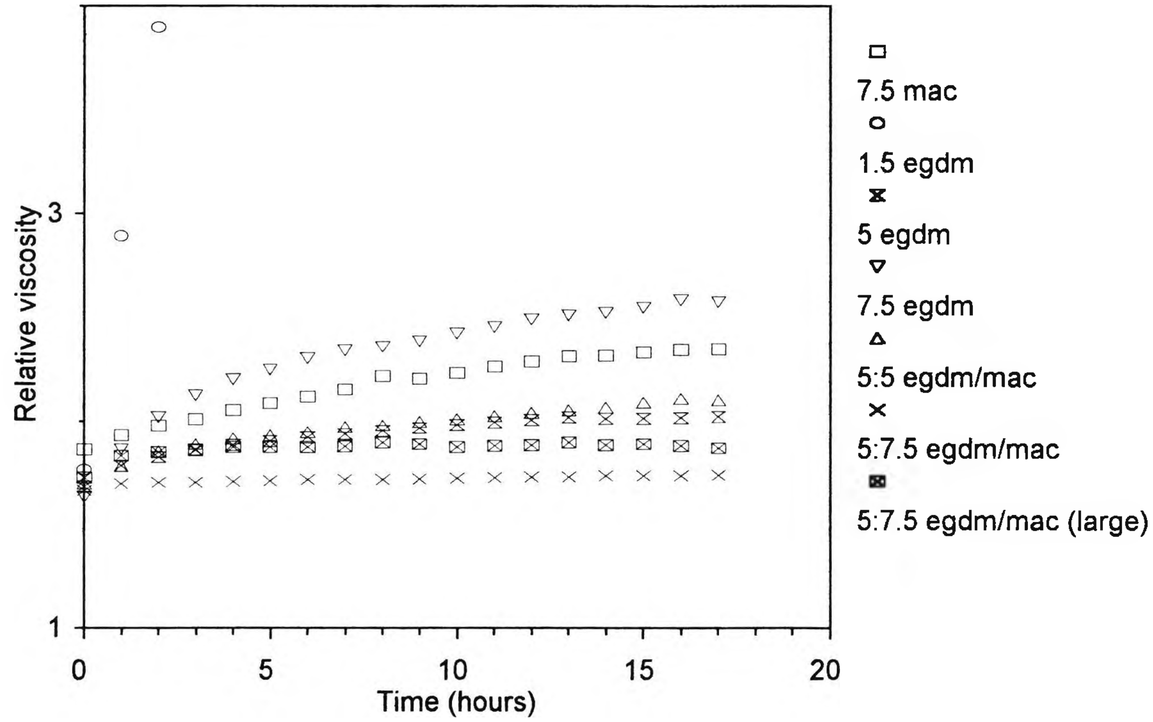

Figure (8.2) The viscosity stability of plastisols comprising crosslinked polymers, prepared by non-aqueous dispersion polymerisation, and butylbenzyl phthalate at 25°C. The polymer - plasticiser ratio was 10:90 by weight.

The polymer containing 5% by weight ethylene glycol dimethacrylate appeared to be less susceptible to swelling by butylbenzyl phthalate than the methyl methacrylate - methacrylic acid copolymer. However, no benefit was derived on increasing the level of comonomer any further. Ethylene glycol dimethacrylate has, relative to methyl methacrylate, a high degree of solubility in water. Polymerisation of this monomer at high levels may result in polymers with large amounts of residual monomer. On drying, the monomer may act as a plasticiser for the polymer and accelerate swelling of the polymer by butylbenzyl phthalate. Alternatively, the tendency for ethylene glycol dimethacrylate to form cyclic structures from intramolecular reactions may increase as the concentration increases[7]. These structures will not contribute to the network and the polymer will have a lower effective degree of crosslinking.

A further decrease in the susceptibility of the polymer to swelling by butylbenzyl phthalate was shown by a 97.5:7.5:5 (wt) methyl methacrylate - methacylic acid - ethylene glycol dimethacrylate terpolymer (batch 16.11). A version of this terpolymer with a larger particle diameter of 0.38 microns (batch 20.19) brought no additional benefit at this polymer - plasticiser ratio.

8.3.3 Determination of the degree of polymer swelling

An attempt was made to estimate the degree of polymer swelling, in di(2-ethylhexyl) phthalate and butylbenzyl phthalate, of a polymer that had a low rate of swelling in butylbenzyl phthalate. Two series of plastisols were prepared based on butylbenzyl phthalate and di(2-ethylhexyl) phthalate at different volume fractions. The viscosities of the plastisols were measured at five minute intervals over half an hour. The polymer was a 95:5 (wt) methyl methacrylate - methacrylic acid copolymer with a locked on stabiliser (batch 17.1).

The di(2-ethylhexyl) phthalate plastisols did not increase in viscosity over the duration of the experiments. For the di-(2-ethylhexyl) phthalate plastisols, the viscometer was programmed to carry out a single shear stress cycle comprising increasing the stress up to 1 000 dyne.cm^{-2} over one minute, holding for ten seconds and then lowering the stress to zero over one minute. The results are shown in Figure (8.3). The density of di(2-ethylhexyl) phthalate was taken as 0.9845 [8].

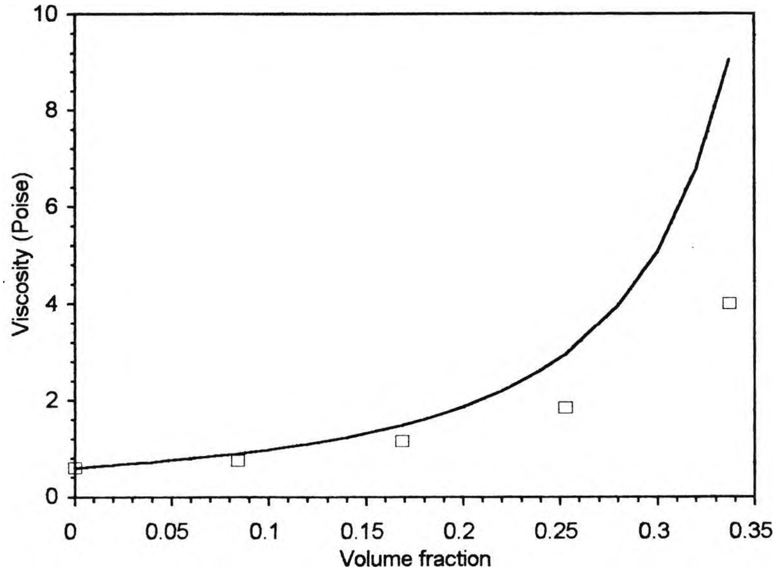

Figure (8.3) Initial viscosity against volume fraction of dilute plastisols comprising a 95:5 (wt) methyl methacrylate - methacrylic acid copolymer with a locked on stabiliser (batch 17.1) and di(2-ethylhexyl) phthalate at 25°C. The squares denote the best fit for the Krieger-Dougherty equation. The solid line is the same equation given $[\eta] = 2.5$ and $\phi_c = 0.74$.

By fitting the Krieger-Dougherty equation (Equation (3.10)) to the viscosity data, the coefficients $[\eta]$, the intrinsic viscosity, and ϕ_c, the critical packing fraction, were obtained. The values were 2.95 and 0.439 respectively. The value for the intrinsic viscosity was higher than that predicted by the Einstein equation (Equation (3.9)) which assumes the value of 2.5. The value for the critical packing fraction did not correspond to any of the more common packing arrangements for monodisperse spheres which are given in Table (8.5) [9]. The results imply that either the particles are asymmetric or there are particle aggregates in the plasticiser[9].

It is possible to calculate the increase in particle volume over time by substitution of Equation (3.11), which relates the effective volume of a spherical particle to the thickness of an adsorbed layer, into the Krieger-Dougherty equation. The thickness of the adsorbed layer, δ, is then redefined as the increase in radius due to particle swelling. However, for the butylbenzyl phthalate plastisols, calculation of the intrinsic viscosity and the critical packing fraction was not possible due to instantaneous swelling of the polymer particles on dispersion into the plasticiser. The values obtained from the di-(2-ethylhexyl) phthalate plastisols were not used as substitutes as the applicability of these values to the butylbenzyl phthalate plastisols was questionable.

Table (8.5) The maximum packing fraction of various arrangements of monodisperse spheres[9]

Arrangement	Maximum packing fraction
Simple cubic	0.52
Minimum thermodynamically stable configuration	0.648
Hexagonally packed sheets just touching	0.605
Random close packing	0.637
Body-centred cubic packing	0.68
Face-centred cubic/hexagonal close packed	0.74

8.4 Plastisol coatings

The coating properties of plastisols containing the polymers with covalent crosslinks described in Section 8.1 and a variety of plasticisers were assessed. The plasticisers included butylbenzyl phthalate (BBP), trixylenyl phosphate (TXP) and dilinear 7,9 phthalate (DL79P). The polymer - plasticiser ratio was 50:50 by weight. The appearance of the plastisols before and after heating at 130°C for 30 minutes was noted. The films were prepared in the manner described in Section 5.2.9. The results are summarised in Table (8.6).

All the plastisols had the consistency of thick pastes. The coatings comprising the 92.5:7.5 (wt) methyl methcrylate - ethylene glycol dimethacrylate copolymer (batch 20.12) in butylbenzyl phthalate or trixylenyl phosphate were opaque and possessed very little mechanical strength. The plastisols were not fully gelled, due possibly to too high a degree of crosslinking. On the basis of coating clarity, the plasticising ability of the three plasticisers compounded with the 87.5:5:7.5 (wt) methyl methacrylate - methacrylic acid - ethylene glycol dimethacrylate terpolymer (batch 16.11) were TXP > BBP > DL79P. The bulk of the 95:5 (wt) methyl methacrylate - methacrylic acid copolymer with the locked on stabiliser (batch 17.1) seemed to gel well with butylbenzyl phthalate, but a small fraction remained undissolved and gave the coating a bitty appearance. The coating comprising a 98:2 (wt) methyl methacrylate - methacrylic acid copolymer with a reactive stabiliser (batch 21.21) in butylbenzyl phthalate, though clear and well gelled, had poor flow out.

Table (8.6) Appearance of plastisols comprising 50% by weight plasticiser and 50% by weight polymer before and after heating at 130°C for 30 minutes.

Polymer	Polymer composition	Plasticiser	Plastisol appearance	Film appearance
21.21	98:2 MMA/MAc (with 2366/110/9)	BBP	Sticky white paste	Clear and uneven
17.1	95:5 MMA/MAc (with 2366/1)	BBP	White paste	Clear, flexible but bitty
20.12	92.5:7.5 MMA/EGDM	BBP	Thick white paste	Opaque and flexible; no mechanical strength
20.12	92.5:7.5 MMA/EGDM	TXP	Thick white paste	Opaque and flexible; no mechanical strength
16.11	87.5:7.5:5 MMA/MAc/EGDM	BBP	Thick white paste	Slightly opaque and flexible
16.11	87.5:7.5:5 MMA/MAc/EGDM	TXP	Thick white paste	Flexible
16.11	87.5:7.5:5 MMA/MAc/EGDM	DL79P	Thick white paste	Slighly opaque; no mechanical strength; exudes plasticiser

The pasty consistency of the plastisols containing the methyl methacrylate - methacrylic acid - ethylene glycol dimethacrylate terpolymer would not be immediately predicted from their performance during the viscometry. The terpolymers were prepared by aqueous emulsion polymerisation and electrostatic effects, as explained in Section 3.4, may have led to an increase in the apparent volume fraction of the dispersed phase, and hence viscosity of the plastisols.

8.5 Summary

In seeking to reduce the premature swelling of the polymer phase in plastisols, polymers were prepared with covalent crosslinks that would bind the polymer chains together reducing the degree of swelling. The level of covalent crosslinking must allow the polymer to be adequately swollen by the plasticiser at elevated temperature so producing a coherent coating. Thus, covalent crosslinking would only be able to reduce the rate of swelling of the polymer by plasticiser rather than prevent it altogether. The theory was discussed in Section 3.3.2. Polymers were prepared with both internal and surface crosslinks using both non-aqueous dispersion and emulsion polymerisation techniques.

Two polymers with crosslinks within the interior of the polymer particles were prepared by non-aqueous dispersion polymerisation. A copolymer of methyl methacrylate and a urethane diacrylate swelled greatly in butylbenzyl phthalate. The urethane linkage appeared to have increased the affinity of the polymer to the plasticiser. A crosslinked terpolymer of methyl methacrylate, methacrylic acid and glycidyl methacrylate was prepared by reaction of the glycidyl and carboxylic groups. A plastisol prepared with this polymer and butylbenzyl phthalate had particularly poor viscosity stability. Characterisation of the polymer particle morphology may have indicated the reasons for the poor stability of this polymer in butylbenzyl phthalate.

The non-aqueous dispersion polymerisation technique was also used to prepare polymers with surface crosslinks by locking the steric stabiliser onto the particle surface. Polymers prepared with reactive stabilisers containing pendant methacrylate groups showed insufficient stability in butylbenzyl phthalate and swelled rapidly. Measurements of the surface coverage of these stabilisers would have aided interpretation of the viscometry experiments. A 95:5 (wt) methyl methacrylate - methacrylic acid copolymer with a glycidyl methacrylate containing comb stabiliser locked onto the polymer particle surface (batch 17.1) showed stability in butylbenzyl phthalate equivalent to an uncrosslinked 92.5:7.5 (wt) methyl methacrylate - methacrylic acid copolymer. An attempt at estimating the degree of particle swelling of these plastisols implied that the polymer particles swelled instantaneously on dispersion into the plasticiser.

Polymers prepared by aqueous emulsion polymerisation were effectively crosslinked with ethylene glycol dimethacrylate. A further improvement in polymer stability in butylbenzyl phthalate was obtained with methyl methacrylate - ethylene glycol dimethacrylate - methacrylic acid terpolymers. However, on elevating the polymer-plasticiser ratio from 10:90 by weight, used for the viscometry, to 50:50 by weight, the minimum required for preparation of a coating, the consistency of the plastisols changed from a fluid to a thick paste. This may be due, as explained in Section 3.4, to an increase in the apparent volume fraction, and hence viscosity, from the effects of the electrostatic double layer.

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CHAPTER 9-

THE OSMOTIC LIMITATION OF SWELLING

In the theoretical treatment of the osmotic limitation of swelling described in Section 3.3.3, it is assumed that the linear polymer is not compatible with the crosslinked polymer. It was shown that the swelling of a reversibly crosslinked polymer dispersed in a good solvent could be arrested altogether by introduction into the solvent phase of a linear polymer incompatible with the crosslinked polymer. Furthermore, the volume fraction of linear polymer required for deswelling decreased with reduction in molecular weight. This seemed a potentially powerful method for restricting the premature swelling, described in Section 1.4, of the dispersed polymer phase in acrylic plastisols that takes place at ambient temperatures. Although the concept of the osmotic limitation of swelling crosslinked polymers by introduction of a linear polymer dissolved in the solvent phase is not new, the crosslinked polymers had always been studied in bulk rather than as dispersed and stabilised submicron sized particles[1] [2] [3] [4] [5] [6] [7] [8].

The investigation of the osmotic limitation of swelling, as applied to acrylic plastisols, comprised the preparation of low molecular weight linear homopolymers based on butyl acrylate and methyl methacrylate. A range of commercially available low molecular weight polyesters was also assembled. Solutions were prepared of all the low molecular weight polymers in butylbenzyl phthalate at varying concentrations. The swelling behaviour, in the polymer solutions, of a variety of dispersed crosslinked polymers prepared by aqueous emulsion and non-aqueous dispersion polymerisation was investigated viscometrically. The crosslinked polymers comprised those with covalent and metal ion crosslinks and weaker associations such as hydrogen bonding. Finally, plastisol coatings, prepared from potentially stable combinations of butylbenzyl phthalate, crosslinked and linear polymers were examined for their suitability for use in industrial environments.

9.1 Low molecular weight linear polymers

Low molecular weight linear homopolymers based on butyl acrylate and methyl methacrylate were prepared by free radical polymerisation of the monomers in the presence of large quantities of chain transfer agent. The choice of poly(butyl acrylate) was made as it had been observed that mixtures of low molecular weight poly(methyl methacrylate) and poly(butyl acrylate) in solution phase separate[9]. The degree of incompatibility would probably not be as high as for poly(styrene) and poly(methyl methacrylate), however poly(butyl acrylate) would probably be more compatible in a plastisol film. The methods of preparation are described in Section 9.1.1. A number of commercial polyesters were also obtained to complement poly(butyl acrylate) and poly(methyl methacrylate). The chemical nature and some physical properties of these materials are described in Section 9.1.2.

9.1.1 The preparation of low molecular weight poly(butyl acrylate) and poly(methyl methacrylate)

Homopolymers of butyl acrylate and methyl methacrylate were prepared both in butyl phthalate and isopropanol. Polymerisation was initiated using 1% (wt) on monomer of 2,2'-azobis-2-methylbutyronitrile. In the plasticiser medium, the chain transfer agent was octyl mercaptan. Polymerisations in isopropanol did not require mercaptan as a chain transfer agent as the solvent itself fulfilled this role. The monomer comprised about 30-40% of the total weight. Details of a typical polymerisation are given in Box (9.1).

Lower molecular weights were achieved by increasing the charge of octyl mercaptan to 0.60% by weight of the total (batch 2366/30) and by substituting butylbenzyl phthalate for isopropanol (batch 2366/61). Poly(methyl methacrylate) was also prepared using the same techniques. It was observed that poly(methyl methacrylate) possessed a much higher viscosity than poly(butyl acrylate). This was due to steric hindrance to bond rotation from the pendant methyl group. The results are summarised in Table (9.1).

Box (9.1) Preparation of poly(butyl acrylate) in butylbenzyl phthalate (batch 2366/23)

Initial charge:

Butyl acrylate	40.0	g
2,2'-azobis-2-methylbutyronitrile	0.4	g
Butylbenzyl phthalate	58.8	g
Octyl mercaptan	0.4	g

The reaction, conducted under a nitrogen purge, took place at 90°C. After 3.5 hours, an additional charge of 0.2g of initiator was made followed an hour later by a second identical charge. The total time for reaction was 5.5 hours. The average molecular weights of the polymer, in equivalent poly(styrene), were for Mw, Mn and Mp 16 797, 7 001 and 14 842 respectively (Cray Valley Products).

The polydispersities of poly(butyl acrylate) with octyl mercaptan as the chain transfer agent are significantly lower than that of the polymer prepared in isopropanol. The polydispersities of radical chain polymerisations taken to high conversion are quite broad being typically in the range 2-5 [10].

Table (9.1) Low molecular weight poly(butyl acrylate) and poly(methyl methacrylate)

Batch number	Description	Comment	Mw[a]	Mn[a]	Mp[a]	Polydispersity (Mw/Mn)
2366/23	poly(butyl acrylate)	0.40% wt total octyl mercaptan	16797	7001	14842	2.40
2366/30	poly(butyl acrylate)	0.60% wt total octyl mercaptan	13046	6138	11627	2.12
2366/61	poly(butyl acrylate)	Isopropanol	10241i 10258i	3430i 3480i	8163i 8284i	2.98 2.95
2366/137/1	poly(methyl methacrylate)	Isopropanol	-	-	-	-
2366/137/2	poly(methyl methacrylate)	0.40% wt total octyl mercaptan	-	-	-	-

[a] Cray Valley Products and Courtaulds (i)

9.1.2 Commercial polyesters

A range of commercial polyesters was assembled. Their molecular weights were measured, according to the method described in Section 5.2.3, and found to range from a few hundred to a few thousand. Given the increasing importance of end groups and the non-linear relationship of refractive index with molecular weight when performing gel permeation chromatography of low molecular weight polymers, the average molecular weights, given in Table (9.2), are only guideline values. In addition, the extinction coefficient for ultra-violet absorption is also dependent on the degree of polymerisation [11].

Table (9.2) Commercial polyesters

Commercial name	Description	Mw[a]	Mn[a]	Mp[a]	Polydispersity (Mw/Mn)
Uraplast W10[c]	-	low hundreds			-
Ultramol III	Polyadipate	4461	2646	3489	1.68
		4448	2637	3489	1.69
Paraplex WP-1	Polymeric	very low			-
Acronal LR 8820	Soft resin	11307	4402	6607	2.57
		11380	4415	6720	2.58
Reoplex 1102	Polyester	~2000	~2000	~2000	-
Uraplast RA 11	Polyadipate	5667	3215	4112	1.76
		5639	3228	4120	1.75
Reoplex GL	Polyester	low hundreds			-
Witamol 600 Stab	Polyester	-	-	570[b]	-

[a] Courtaulds

[b] Hüls literature

[c] Linear saturated polyester based on orthophthalic acid

9.2 Plastisol stability

The stability of plastisols is dependent on the swelling behaviour of the dispersed polymer phase. This behaviour was investigated by making measurements of the plastisol viscosity over time. If the dispersed polymer swelled, the effective polymer volume fraction increased and the measured viscosity rose. A more detailed account of the experimental procedure, including the isolation of the polymer particles, is given in Section 5.2.6.

The low molecular weight polymers described in Section 9.1 were dissolved in butylbenzyl phthalate in varying concentrations. Plastisols were prepared by dispersing a number of crosslinked polymers, previously prepared using aqueous emulsion and non-aqueous dispersion polymerisation techniques, into the polymer solutions. The crosslinked polymers have all been described in previous chapters. The viscosities of the low molecular weight polymer solutions were measured in order to calculate the relative changes in viscosity of the plastisols. These results are presented in Section 9.2.1. This is followed by a description of the stability of plastisols prepared with poly(butyl acrylate) and poly(methyl methacrylate), and then those prepared with the commercial polyesters.

9.2.1 Low molecular weight linear polymers in butylbenzyl phthalate

All the low molecular weight polymers were prepared as solutions in butylbenzyl phthalate. Poly(butyl acrylate) and poly(methyl methacrylate) were prepared as 5% by weight solutions except for batch 2366/30 which was also prepared at concentrations of 7.5%, 10.0%, 12.5% and 15% by weight. The viscosities of these solutions were measured on a cone and plate viscometer and are given in Table (9.3).

Table (9.3) Solution viscosities of poly(butyl acrylate) and poly(methyl methacrylate) in butylbenzyl phthalate at 25°C.

Batch number	Type of polymer	Polymer concentration (% wt)	Viscosity (Poise)[a]
2366/23	Poly(butyl acrylate)	5.0	0.6418 (0.0022)
2366/30	Poly(butyl acrylate)	5.0	0.6420 (0.0013)
2366/30	Poly(butyl acrylate)	7.5	0.7165 (0.0019)
2366/30	Poly(butyl acrylate)	10.0	0.9384 (0.0013)
2366/30	Poly(butyl acrylate)	12.5	0.9833 (0.0025)
2366/30	Poly(butyl acrylate)	15.0	1.183 (0.004)
2366/61	Poly(butyl acrylate)	5.0	0.6432 (0.0026)
2366/137/1	Poly(methyl methacrylate)	5.0	0.9787 (0.0094)
2366/137/2	Poly(methyl methacrylate)	5.0	0.9358 (0.0072)

[a] $\sigma_{(n-1)}$ in brackets for n = 9

The viscometer was programmed to apply an increasing shear stress over two minutes from zero up to a maximum of 1 500 dyne.cm^{-2} (3 000 dyne.cm^{-2} for the solution comprising 12.5% by weight poly(butyl acrylate) in plasticiser). This stress was then held for ten seconds and then reduced to zero over one minute. This was then repeated eight times without interval. The viscosity was calculated from the gradient of the upward part of the shear stress cycle.

The commercial polyesters were prepared as solutions with 20% by weight polymer. Solutions of Reoplex GL and Uraplast W10 were also prepared with only 10% by weight polymer. The viscosities of the solutions were measured and are given in Table (9.4).

Table (9.4) Solution viscosities of a range of commercial low molecular weight polyesters in butylbenzyl phthalate at 25°C.

Polyester	Polyester viscosity (Poise)	Polymer concentration (% wt)	Solution viscosity (Poise)[a]
Witamol 600 Stab	2.894	20	0.5848 (0.0001)
Ultramol III	57.86	20	1.541 (0.005)
Paraplex WP-1	0.6860	20	0.5336 (0.0016)
Acronal LR 8820	231.1	20	1.424 (0.003)
Reoplex 1102	14.58	20	0.9861 (0.0020)
Uraplast RA 11	-	20	2.031 (0.009)
Reoplex GL	6.159	10	0.5557 (0.0011)
Reoplex GL	6.159	20	0.6360 (0.0015)
Uraplast W10	0.4684	10	0.4458 (0.0014)
Uraplast W10	0.4684	20	0.4425 (0.0009)

[a] $\sigma_{(n-1)}$ in brackets for n = 9

The viscometer was programmed to apply an increasing shear stress over two minutes from zero up to a limiting value. This stress was held for ten seconds and then decreased to zero over one minute. This was repeated eight times at five minute intervals. The limiting stresses for the dilute and semi-dilute solutions were 3 000 and 1 500 dyne.cm^{-2} respectively. The viscosity was calculated from the gradient of the upward part of the shear stress cycle.

The viscosities of the polyesters, as delivered, were also measured. The values were calculated from the upward part of a single shear stress cycle. The cycle comprised applying an increasing stress over one minute from zero to 600 or 800 dyne.cm^{-2}, holding this limiting value for ten seconds and then lowering the stress back to zero over one minute.

9.2.2 The effect of low molecular weight poly(butyl acrylate) and poly(methyl methacrylate) solutions on plastisol viscosity stability

Plastisols were prepared comprising 10 parts by weight crosslinked polymer and 90 parts by weight linear polymer solution. The crosslinked polymer, previously described in Section 7.2.1.2, was a 95:5 (wt) methyl methacrylate - methacrylic acid copolymer (batch 21.16) prepared by non-aqueous dispersion polymerisation. The polymer solutions comprised 5% by weight poly(butyl acrylate) or poly(methyl methacrylate) in butylbenzyl phthalate. The plastisol viscosities were measured over a time period of seventeen hours and the results are presented in Figure (9.1). The viscometer was programmed to carry out two shear stress cycles an hour. The procedure comprised applying an increasing stress from zero to a limiting value over one minute, for the first cycle, and over two minutes for the second, holding this stress for ten seconds and then reducing it to zero at the same rate. The limiting stresses for the first and second cycles were 1 000 and 3 000 dyne.cm^{-2} respectively.

The presence of dissolved low molecular weight linear poly(butyl acrylate) and poly(methyl methacrylate) in the plasticiser phase appeared to improve the viscosity stability of the plastisols. The greatest improvement was achieved with the poly(butyl acrylate) of highest number average molecular weight. The results for the two remaining plastisols containing poly(butyl acrylate) and those containing poly(methyl methacrylate) were comparable.

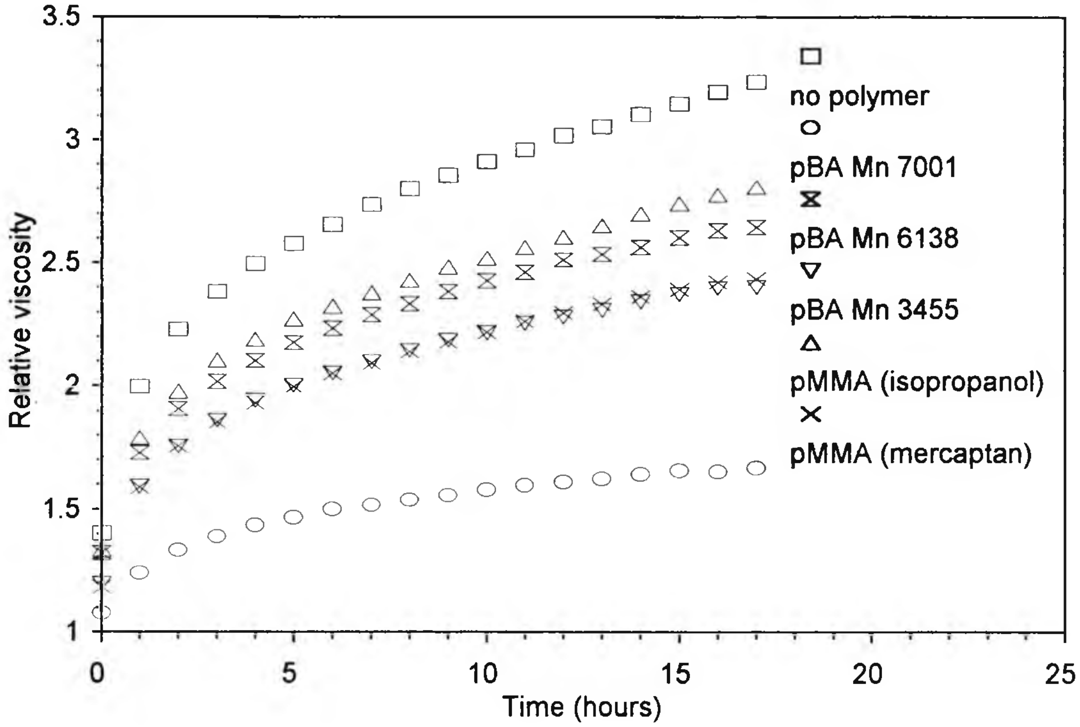

Figure (9.1) The viscosity stability of plastisols comprising 10 parts (wt) of a 95:5 (wt) methyl methacrylate - methacrylic acid copolymer (batch 21.16) and 90 parts (wt) polymer solution at 25°C. The polymer solutions comprised 5% by weight poly(butyl acrylate) or poly(methyl methacrylate) in butylbenzyl phthalate.

Plastisols were prepared comprising 10 parts (wt) a 95:5 (wt) methyl methacrylate - methacrylic acid copolymer (batch 21.16) and 90 parts (wt) polymer solutions based on poly(butyl acrylate) of number average molecular weight 6138 and butylbenzyl phthalate. The concentration of poly(butyl acrylate) in butylbenzyl phthalate was in the range 5-15% by weight. The plastisol viscosities were measured over a duration of up to seventeen hours. The experimental procedure has been described above.

Improvements in plastisol viscosity stability were seen as the level of linear polymer increased to 10% by weight of the plasticiser phase. The results are shown in Figure (9.2).

The theory of the osmotic limitation of swelling, described in Section 3.3.3, predicted that the volume fraction of linear polymer dissolved in the solvent phase required for deswelling of the cross-linked polymer phase decreases as the molecular weight of the linear polymer falls. However, Figure (9.1) shows that the most stable plastisol was produced with the highest molecular weight linear polymer (poly(butyl acrylate)). The theory assumes that the linear polymer does not penetrate the cross-linked polymer. If this is not the case, then the cross-linked polymer will swell more than predicted theoretically. Swelling of the cross-linked polymer by linear polymer or plasticiser will affect the concentration of the polymer solution. This complicates interpretation of the results.

It has been shown, for the cross-linked poly(styrene) - linear poly(styrene) system, that complete exclusion of the polymers takes place when the molecular weight of the linear polymer increases beyond a certain limit[2]. This limit is possibly related to the pore size of the cross-linked polymer. Thus, it is possible that even greater improvements in plastisol viscosity stability could be seen if the molecular weight of poly(butyl acrylate) were increased.

The theory says that the swelling of the cross-linked polymer should reduce to zero on increasing the volume fraction of a linear polymer of given molecular weight. This is reflected in the results given in Figure (9.2). However, no further improvement in viscosity stability is seen beyond 10% w/w linear polymer. Again, this result implies that there is penetration of the linear polymer into the cross-linked polymer. As the concentration of the linear polymer increases, the amount penetrating into the cross-linked polymer increases more than compensating for osmotic limitation of swelling[3].

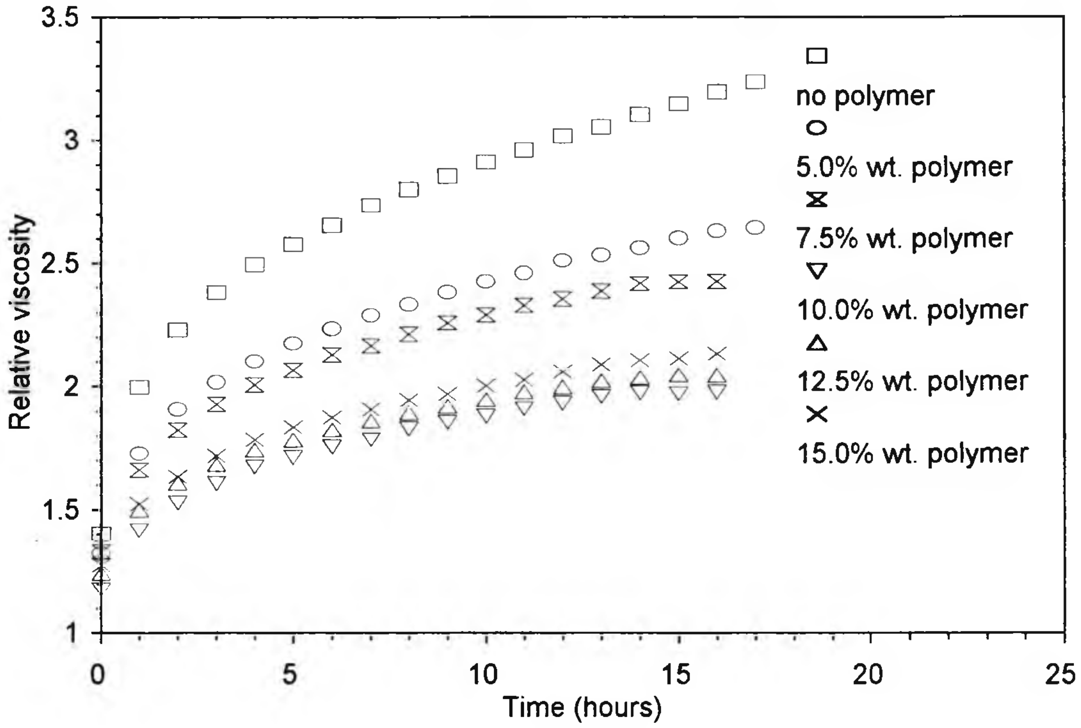

Figure (9.2) The viscosity stability of plastisols comprising 10 parts (wt) of a 95:5 (wt) methyl methacrylate - methacrylic acid copolymer (batch 21.16) and 90 parts (wt) polymer solution at 25°C. The polymer solutions comprised 5-15% by weight poly(butyl acrylate) of number average molecular weight 6138 in butylbenzyl phthalate.

9.2.3 The effect of commercial low molecular weight polyesters solutions on plastisol viscosity stability

Plastisols were prepared comprising 10 parts (wt) of a 95:5 (wt) methyl methacrylate - methacrylic acid copolymer (batch 6.2) and 90 parts (wt) polymer solutions. The copolymer, described in Section 6.1.2.2, was prepared using a non-aqueous dispersion polymerisation technique. The polymer solutions comprised 20 parts (wt) of the commercial low molecular weight polyesters, described in Section 9.1.2, dissolved in 80 parts (wt) butylbenzyl phthalate. The plastisol viscosity was measured over 17 hours using the experimental procedure described in Section 9.2.2. The results are shown in Figure (9.3).

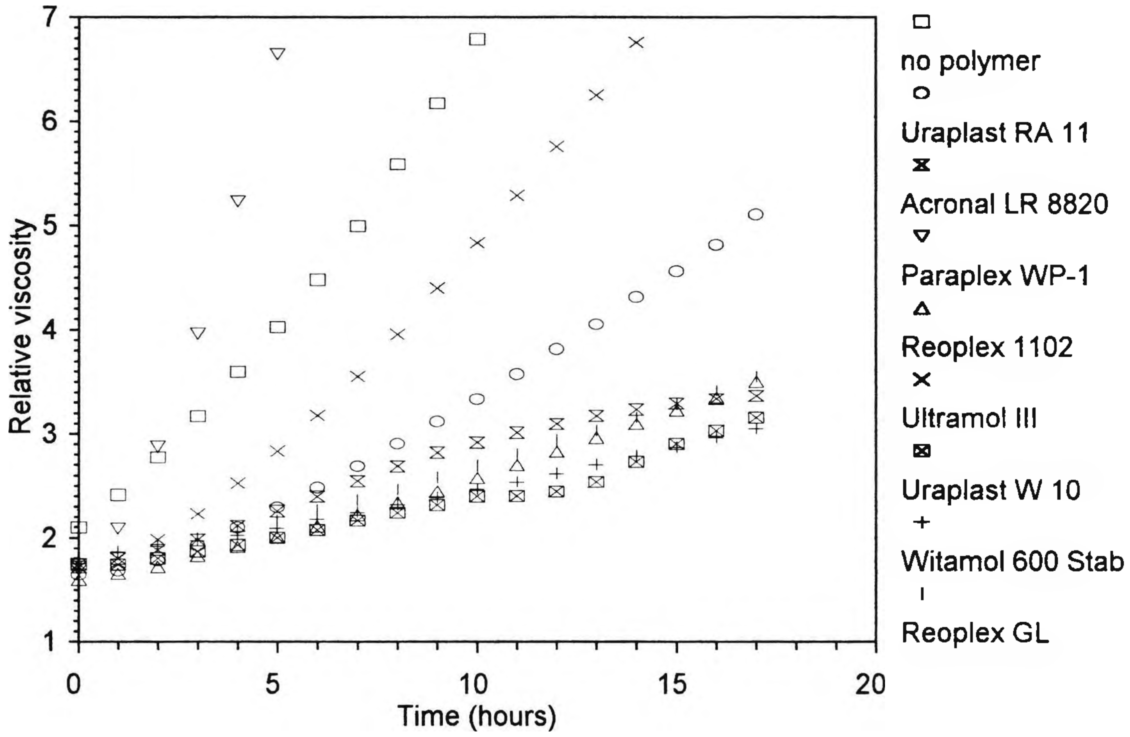

Figure (9.3) The viscosity stability of plastisols comprising 10 parts (wt) of a 95:5 (wt) methyl methacrylate - methacrylic acid copolymer (batch 6.2) and 90 parts (wt) polymer solution at 25°C. The polymer solutions comprised 20% by weight commercial low molecular weight polyesters in butylbenzyl phthalate.

The plastisol viscosity was, in general, improved on addition of the commercial polyesters to the plasticiser phase. Only Paraplex WP-1 appeared to destabilise the plastisol. The relative viscosities of this plastisol rose from about 1.7 to 21.2 over 14 hours. The relative viscosity of the plastisol without added linear polymer rose, over a comparable period, from 2.1 to 9.31. The remaining plastisols had relative viscosities, after 17 hours, ranging from 8.31, for Ultramol III, to 3.04, for Witamol 600 Stab. As the weight fraction of linear polymer in butylbenzyl phthalate remained unchanged irrespective of the molecular weight, direct comparisons between the performances of the plastisols is not possible.

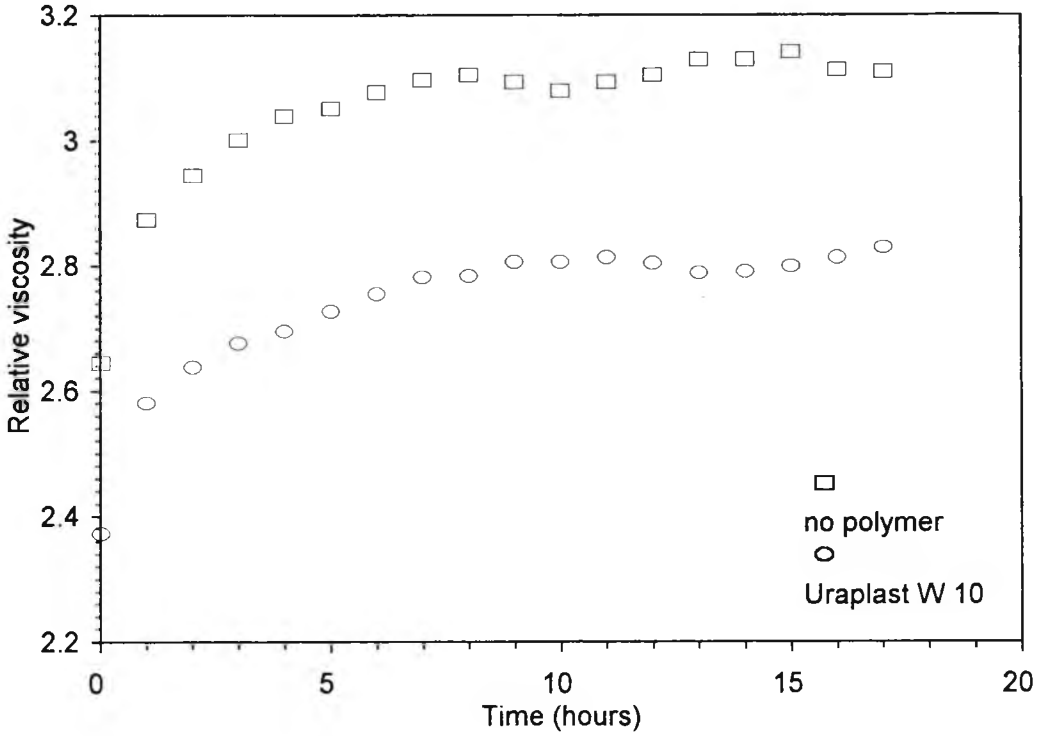

Figure (9.4) The viscosity stability of a plastisol comprising 20 parts (wt) of a 87.5:7.5:5 (wt) methyl methacrylate - methacrylic acid - ethylene glycol dimethacrylate terpolymer (batch 20.19) and 80 parts (wt) polymer solution at 25°C. The polymer solution comprised 20% by weight Uraplast W 10 in butylbenzyl phthalate.

A plastisol was prepared comprising 20 parts (wt) 87.5:7.5:5 (wt) methyl methacrylate - methacrylic acid - ethylene glycol dimethacrylate terpolymer (batch 20.19) and 80 parts (wt) a 20% (wt) solution of Uraplast W 10 in butylbenzyl phthalate. The terpolymer, prepared using an aqueous emulsion polymerisation technique, was described in Section 8.1.3. The plastisol viscosity was measured over 17 hours. The viscometer was programmed to carry out two shear stress cycles an hour. The procedure involved applying an increasing stress over two minutes from zero to a limiting value, holding this for ten seconds and then reducing the stress back to zero over two minutes. The limiting stresses for the first and second cycles were 1 000 and 3 000 dyne.cm^{-2} respectively. The results are shown in Figure (9.4).

Addition of Uraplast W 10 to the plasticiser phase of this plastisol brought no benefit in terms of viscosity stability. However, the relative viscosity was lowered by 0.27 over the period of the measurements. The viscosities of Uraplast W 10 and butylbenzyl phthalate are similar and therefore the viscosity of the solution would not be expected to change by much over the course of the experiment. Thus, the changes in viscosities are real and would not be greatly affected by changes in the polymer solution viscosities. Due to the exponential relationship between dispersed polymer phase volume and relative viscosity, discussed in Section 3.2.2, the degree of swelling of the cross-linked polymer may have decreased on addition of Uraplast W 10. Calculation of this would require values for the intrinsic viscosity and the critical packing fraction.

Plastisols were prepared comprisong 10 parts (wt) a 92.5:7.5 (wt) methyl methacrylate - methacrylic acid copolymer with a core-shell morphology (batch 22.51) and 90 parts (wt) polymer solution. The copolymer, previously described in Section 6.3.9, was prepared using a non-aqueous dispersion polymerisation process. The polymer solutions comprised 10% by weight Uraplast W 10 and Reoplex GL in butylbenzyl phthalate. The plastisol viscosities were measured over 17 hours. The experimental conditions were described in Section 9.2.2. The results are shown in Figure (9.5).

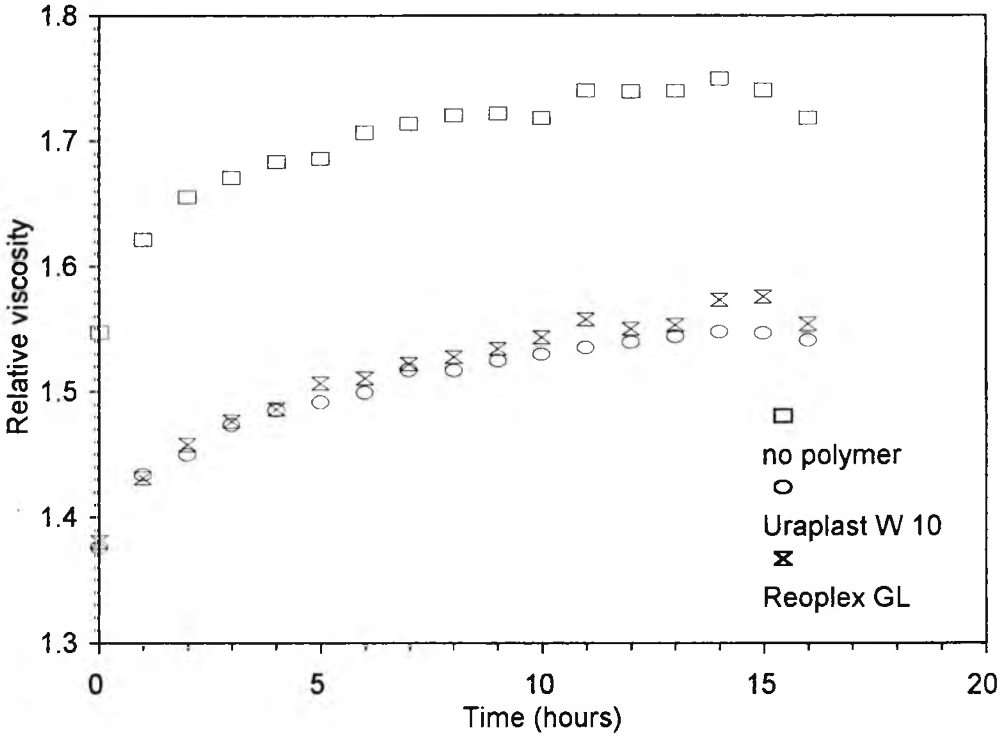

Figure (9.5) The viscosity stability of plastisols comprising 10 parts (wt) of a 92.5:7.5 (wt) methyl methacrylate - methacrylic acid copolymer with a core-shell morphology (batch 22.51) and 90 parts (wt) polymer solution at 25°C. The polymer solution comprised 10% by weight Uraplast W 10 and Reoplex GL in butylbenzyl phthalate.

Plastisol viscosity stability was not improved on addition of Uraplast W 10 or Reoplex GL to the plasticiser phase. However the relative viscosities were lowered by about 0.17. This was significant as the plastisols only increased in relative viscosity by about 0.16 over 17 hours. The viscosity of Reoplex GL is much higher than that of butylbenzyl phthalate and thus changes in the composition of the plasticiser phase would have a significant effect on the overall viscosity. The true change in relative viscosity may be quite different to that shown in Figure (9.5). The implication is that the cross-linked polymer swells instantly on dispersion in butylbenzyl phthalate, swelling even more over a period of time. In the solutions of Uraplast W10 or Reoplex GL, the cross-linked polymer deswells to some extent on contact, though it swells with time.

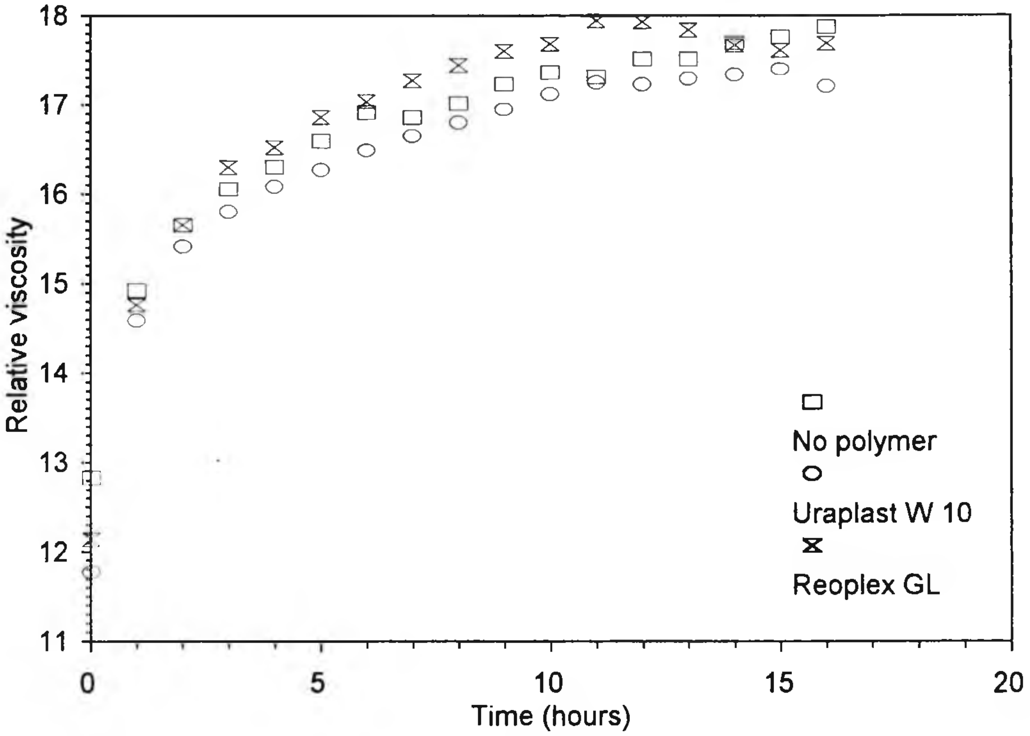

Figure (9.6) The viscosity stability of plastisols comprising 40 parts (wt) of a 92.5:7.5 (wt) methyl methacrylate - methacrylic acid copolymer with a core-shell morphology (batch 22.51) 50% neutralised with diethyl zinc and 60 parts (wt) polymer solution at 25°C. The polymer solution comprised 10% by weight Uraplast W 10 and Reoplex GL in butylbenzyl phthalate.

The core-shell polymer was then 50% neutralised with diethyl zinc in the manner described in Section 7.2.1.2. The plastisols were then remade but with 40% by weight metal ion cross-linked polymer. The plastisol viscosities were measured over 16 hours. the viscometer was programmed to carry out two shear stress cycles an hour. The experimental procedure for the two plastisols with added Uraplast W 10 and Reoplex GL has been given in Section 9.2.2. That for the remaining plastisol involved applying an increasing stress over one minute from zero to a limiting value of 1 000 dyne.cm^{-2}, holding this value for ten seconds and then lowering the stress back down to zero over one minute. The results are shown in Figure (9.6).

There was little difference in viscosity stability between the plastisols with and without dissolved linear polyester in the plasticiser phase. The relative viscosities of all three plastisols increased from approximately 12 to 17 over 16 hours. As explained above, it is difficult to relate the performance of the plastisol containing Reoplex GL to the degree of swelling of the cross-linked polymer due to the varying plasticiser phase viscosity. Although changes in viscosity are a measure of the stability of a plastisol formulation, in this case it reveals very little that can explain the viscosity behaviour.

9.3 Plastisol coatings

Cross-linked polymers that had shown significantly improved resistance to swelling by butylbenzyl phthalate, over poly(methyl methacrylate), were reformulated as plastisols at a polymer-plasticiser ratio of 50:50 by weight. This is the minimum level of polymer required in a plastisol if it is to have acceptable properties as an industrial coating. All but one of the cross-linked polymers were prepared by non-aqueous dispersion polymerisation. The plasticiser phase generally comprised a solution of a low molecular weight polymer in butylbenzyl phthalate. Coatings were prepared by applying the plastisol onto clean glass panels and gelling it at 130°C for 30 minutes. Further details have been given in Section 5.2.9. The appearance of the plastisols both before and after gelling was recorded. Not all the plastisols were prepared as coatings and the results for these are summarised in Table (9.5). The results for the remaining plastisols are presented in Table (9.6).

Table (9.5) Plastisols of polymer-plasticiser ratio 50:50 by weight

Batch number	Polymer composition	Plasticiser	Appearance
6.2	5 MAc	20% wt. Uraplast W 10 in BBP	Solid
6.6	10 MAc	20% wt. Uraplast W 10 in BBP	Solid
6.6	10 MAc	20% wt. DOP in BBP	Solid
22.51	7.5 MAc core-shell	20% wt. Uraplast W 10 in BBP	Viscous liquid
22.52	1.875 MAc core-shell	20% wt. Uraplast W 10 in BBP	Viscous liquid
22.53	5 MAc core-shell	20% wt. Uraplast W 10 in BBP	Viscous liquid
22.42	5 MAc LMA stabilised	20% wt. Uraplast W 10 in BBP	White paste
22.42	5 MAc LMA stabilised 142% Zn neutralised	20% wt. Uraplast W 10 in BBP	White paste
22.44	7.5 MAc LMA stabilised 50% Zn neutralised	DOP	Liquid
22.44	7.5 MAc LMA stabilised 50% Zn neutralised	20% wt. DOP in BBP	Runny paste
22.44	7.5 MAc LMA stabilised 50% Zn neutralised	20% wt. pBA (2366/30) in BBP	White paste
22.44	7.5 MAc LMA stabilised 50% Zn neutralised	20% wt. Reoplex GL in BBP	Runny paste
22.44	7.5 MAc LMA stabilised 50% Zn neutralised	20% wt. Witamol 600 Stab in BBP	White paste
22.44	7.5 MAc LMA stabilised 50% Li neutralised	BBP	White paste
22.44	7.5 MAc LMA stabilised 50% Li neutralised	20% DOP in BBP	Runny white paste
22.44	7.5 MAc LMA stabilised 50% Li neutralised	10% wt. TXP in BBP	White paste
22.44	7.5 MAc LMA stabilised 50% Li neutralised	10% wt. DL79P in BBP	Runny white paste
22.44	7.5 MAc LMA stabilised 50% Li neutralised	20% wt. Uraplast W 10 in BBP	Runny paste
22.44	7.5 MAc LMA stabilised 50% Li neutralised	20% wt. Reoplex 1102 in BBP	White paste

Plastisols comprising either 95:5 (wt) methyl methacrylate - methacrylic acid (batch 6.2) or 90:10 (wt) methyl methacrylate - methacrylic acid (batch 6.6) copolymers and a solution of 20% by weight Uraplast W 10 in butylbenzyl phthalate gelled immediately. Substitution of the homogeneous methyl methacrylate - methacrylic acid copolymers by polymers of similar overall composition but with a core-shell morphology did yield more tractable plastisols.

Plastisols comprising poly(lauryl methacrylate) stabilised methyl methacrylate - methacrylic acid copolymers containing metal ion crosslinks, described in Section 7.2.1.1, and a variety of low molecular weight esters or polyesters in butylbenzyl phthalate had the consistency of pastes. The rheology of dispersions of these copolymers in plasticiser has been discussed in Section 7.3. Only the plastisol based on di(2-ethylhexyl) phthalate (DOP), rather than butylbenzyl phthalate, was fluid. Given that di(2-ethylhexyl) phthalate is a weak solvent for poly(methyl methacrylate), this result would be expected.

Given the appearance of plasticiser exudation from the gelled film, butylbenzyl phthalate did not appear to be fully compatible with the 87.5:7.5:5 (wt) methyl methacrylate - methacrylic acid - ethylene glycol dimethacrylate terpolymer (batch 20.19 prepared by aqueous emulsion polymerisation). The cross-link density was probably too high. Addition of poly(butyl acrylate) made the plasticiser even less compatible.

Plastisols were prepared comprising a 95:5 (wt) methyl methacrylate - methacrylic acid copolymer (batch 21.16) and solutions of all the commercial low molecular weight linear polyesters, except Paraplex WP-1, in butylbenzyl phthalate. At a level of 20% (wt) linear polymer in butylbenzyl phthalate, all the plastisols formed pastes except for those containing Uraplast W 10 and Reoplex GL which were liquid. All the plastisols gelled well except for that containing Acronal LR 8820 which showed some plasticiser exudation. However, there was some incompatibility between the cross-linked polymer and polymer solution when the level of linear polymer was increased to 50% (wt) in butylbenzyl phthalate.

Table (9.6) Plastisols of polymer-plasticiser ratio 50:50 by weight before and after gelling at 130°C for 30 minutes.

Polymer batch number	Plasticizer	Plastisol appearance	Film appearance
21.16[a]	BBP	Runny white paste	Clear, dry and smooth
21.16	20% wt. Uraplast W10 in BBP	White liquid	Slightly soft, clear and dry
21.16	20% wt. Uraplast RA11 in BBP	Thick white paste	Clear, dry and rough
21.16	20% Reoplex 1102 in BBP	Runny white paste	Soft, clear, dry and smooth
21.16	20% Witamol 600 Stab in BBP	White paste	Clear, dry and smooth
21.16	20% wt. Reoplex GL in BBP	Liquid	Soft, clear and dry
21.16	20% wt. Ultramol III in BBP	Paste	Slightly sticky, clear and rough
21.16	20% wt. Acronal LR8820 in BBP	Paste	Clear, rough, plasticizer exudation
21.16	40% wt. 2366/30 in BBP	Runny paste	Clear, plasticizer exudation
21.16	50% wt. Uraplast W10 in BBP	Liquid	Clear, smooth, plasticizer exudation
21.16	50% wt. Acronal LR8820 in BBP	Runny paste	Slightly opaque, extensive plasticizer exudation
20.19[b]	BBP	White and viscous	Clear, slight plasticizer exudation
20.19	10% 2366/61 in BBP	White paste	Opaque, slight plasticizer exudation

[a] 95:5 (wt) methyl methacrylate - methacrylic acid copolymer (described in Section 7.2.1.2) prepared by non-aqueous dispersion polymerisation

[b] 87.5:7.5:5 (wt) methyl methacrylate - methacrylic acid - ethylene glycol dimethacrylate terpolymer (described in Section 8.1.3) prepared by aqueous emulsion polymerisation

The appearances of the two plastisols based on 95:5 (wt) methyl methacrylate - methacrylic acid copolymers and a solution of 20% by weight Uraplast W 10 in butylbenzyl phthalate were quite different. The fluid nature of the plastisol based on batch 21.16 as opposed to the gelled appearance of the plastisol based on batch 6.2 could be ascribed, as discussed in Section 6.3.7, to the differences in particle size.

Batch 21.16 had a particle diameter of 0.31 microns whilst batch 6.2 had a particle diameter of only 0.20 microns.

Generally, the appearance of the plastisols summarised in Table (9.5) and Table (9.6) mirrors the results from the viscometry. Although some of the plastisols appear quite fluid initially, the viscosities rise quickly on standing. None show lasting viscosity stability.

9.4 Summary

The theory of osmotic limitation of swelling, introduced in Section 3.3.3, suggests that the degree of swelling of a cross-linked polymer in a good solvent can be controlled by addition of a dissolved linear polymer to the solvent phase that does not penetrate the cross-linked polymer. The validity and application of this theory to the problem of stabilising acrylic plastisols was investigated.

Low molecular weight linear poly(butyl acrylate) and poly(methyl methacrylate) were prepared by free radical polymerisation. Commercial low molecular weight polyesters were assembled. The polymers were then dissolved in butylbenzyl phthalate. Cross-linked polymers, prepared by non-aqueous dispersion and aqueous emulsion polymerisation techniques, that had shown good resistance to swelling by butylbenzyl phthalate were dispersed in the solutions of linear polymer. Significant improvements in the viscosity stability of plastisols based on a 95:5 (wt) methyl methacrylate - methacrylic acid copolymer were observed. With more highly cross-linked polymers, the improvement in plastisol viscosity stability was less marked.

The results were difficult to interprete as the composition, and hence viscosity, of the plasticiser phase changed during the course of the viscosity measurements as the cross-linked polymer swelled. Intepretation was further complicated as there was evidence that poly(butyl acrylate) did penetrate the cross-linked polymer. This would reduce the deswelling effect of the osmotic pressure.

If there was some compatibility between the cross-linked and linear polymer, exclusion of the linear polymer from the cross-linked polymer could be accomplished by increasing the molecular weight of the linear polymer. The linear polymer would then be too large to enter the pores of the cross-linked polymer network. This effect was seen with the short series of poly(butyl acrylate) of ascending molecular weight where the most stable plastisol contained the polymer of highest molecular weight.

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CHAPTER 10-
CONCLUSION

Plastisols constitute a large proportion of the coated steel strip market. A plastisol comprises a dispersion of polymer, generally poly(vinyl chloride) produced by aqueous emulsion or suspension polymerisation processes, that is subsequently dried and redispersed in an essentially non-volatile diluent plasticiser such as di(2-ethylhexyl) phthalate. On the application of heat, the plastisol will rise in viscosity until it gels ultimately forming a coherent plasticised mass.

The objective of the work was the preparation of a prototype acrylic plastisol, for reasons outlined in Section 1.4, with improved stability that would be suitable for commercial development by industry. Although this objective was not achieved during the course of the study, progress was made. Several potentially successive routes towards a stable acrylic plastisol were identified.

Loss in plastisol stability manifests itself as an increase in viscosity to the point where the plastisol completely gels. On a microscopic level, the increase in viscosity is attributable to uncontrolled swelling of the dispersed polymer phase by the plasticiser. The strategy employed was to introduce into acrylic particles a mechanism for restricting particle swelling which was analogous to the microcrystallinity found in poly(vinyl chloride). It is the thermally responsive microcrystalline nature of poly(vinyl chloride) that is credited with being responsible for the stability of vinyl plastisols.

From consideration of the theory, thermally reversible cross-links, such as hydrogen bonding or metal ion cross-linking, could restrict the swelling of the polymer particles by a plasticiser. Limited covalent cross-linking could also be useful. A mechanism relying on the osmotic limitation of particle swelling, by dissolution of a low molecular weight species into the plasticiser, offered a route to a stable plastisol which could show zero swelling at room temperature.

By treating plastisols as suspensions of monodisperse spheres in a liquid medium, it was predicted that dispersing polymers prepared by aqueous emulsion polymerisation into a plasticiser of high dielectric constant could lead to plastisols with elevated viscosities. This was attributed to the effective increase in particle size, and hence volume fraction of the suspended phase, due to the contribution of the electrostatic double layer. The exponential form of equations relating the viscosity of monodisperse suspensions to the volume fraction of the suspended phase implied that little in the way of swelling would be required before the maximum packing fraction was exceeded. Beyond the maximum packing fraction, the suspension would cease to flow.

A programme of work was devised to systematically explore different ways of incorporating crosslinks into acrylic particles and investigate their effect on the ability of the polymer to resist swelling by plasticiser. The polymers were prepared by non-aqueous dispersion and aqueous emulsion polymerisation. The principle plasticiser was butylbenzyl phthalate. Plastisol stability was monitored viscometrically using a cone and plate viscometer. The applicability to acrylic plastisols of the theory of osmotic limitation of swelling was also tested. A summary of the results of the experimental work is given.

10.1 Summary of experimental work

Copolymerisation of methyl methacrylate with up to 10% (wt) methacrylic acid or 15% (wt) 2-hydroxyethyl methacrylate led to polymers with improved stability, with respect to poly(methyl methacrylate). This was attributed to hydrogen bonding between neighbouring carboxyl or hydroxyl groups. This view was partially supported by experimental evidence that showed that, for methyl methacrylate - methacrylic acid copolymers only, the polymer glass transition temperature increased with the level of methacrylic acid. Calculated polymer glass transition temperatures for methyl methacrylate - methacrylic acid copolymers were also in agreement.

Polymers containing metal ions showed enhanced resistance to plasticiser swelling. They were prepared by neutralisation of carboxylic group containing polymers with organometallic compounds such as diethyl zinc. No further improvements were observed beyond neutralisation of 50% of the carboxylic acid functionality. Although the polymer glass transition temperatures were neither measured or calculated, they might be expected to rise on incorporation of the metal ions. Metal ions are known to cluster together forming thermally reversible cross-links[1].

Covalent cross-links were successfully introduced into poly(methyl methacrylate) by copolymerisation of methyl methacrylate with the tetrafunctional monomer ethylene glycol dimethacrylate. These polymers proved very resistant to swelling by plasticiser. However, if the level of tetrafunctional monomer was too high, the polymer became insoluble in the plasticiser. The plastisol was unable to gel fully and the plastisol coatings lacked mechanical strength. Any correlation between the cross-link density and the glass transition temperature is, for highly cross-linked polymers, broad and ill-defined, but for lightly cross-linked polymers there is a strong linear relationship[2].

Copolymerisation of methyl methacrylate with up to 7.5% by weight ethylene glycol dimethacrylate, forming covalent cross-links, resulted in polymers with improved resistance to swelling by butylbenzyl phthalate. However, at high levels of cross-linker, the plasticiser could not fully gel the polymer and the coatings were brittle lacking mechanical strength. At lower levels of cross-linker, the polymer swelled too much and the plastisol was unstable.

In order to test the theory of osmotic limitation of swelling to acrylic plastisols, low molecular weight linear poly(butyl acrylate) and poly(methyl methacrylate) were prepared by free radical polymerisation. The polymers were dissolved in butylbenzyl phthalate. Plastisols were prepared by dispersing cross-linked polymers into the polymer solutions. The presence of the linear polymers improved the stability of the plastisols. The theory assumes that there is no mixing of the linear and cross-linked polymer. The results from viscometry suggested that poly(butyl acrylate) partially penetrated a 95:5 (wt) methyl methacrylate - methacrylic acid copolymer. However, the degree of exclusion of poly(butyl acrylate) from the cross-linked polymer could be enhanced by increasing the molecular weight of the linear polymer.

It was predicted in Section 6.1.2.2 that higher molecular weight polymers ought to have a reduced rate of velocity of dissolution in plasticiser due to the increase in chain entanglement[3]. Attempts at improving plastisol stability by increasing the molecular weight of the cross-linked polymer met with failure. It was thought that the range of molecular weight, peak molecular weight range 100 000 to 270 000 poly(styrene) equivalent, was too narrow. Increasing the particle size of the disperse phase polymer did, however, reduced the rate of particle swelling. This was attributed to the decrease in the surface to volume ratio.

Concentrating functional groups, such as carboxylate groups, in the outer regions of the polymer particles by varying the composition of the feed monomer mix during polymerisation also lead to improved plastisol stability. Combining this core-shell morphology with metal ion cross-linking further reduced the rate of swelling of the cross-linked polymer in plasticiser.

10.2 Strategies for future work

Although the original objective of this work, to prepare a stable prototype acrylic plastisol, was not achieved, several potentially successful routes to this goal were identified.

The principal plasticiser used throughout the work was butylbenzyl phthalate. It was chosen in the full knowledge that it had a strong solvent action as this would provide the greatest test to plastisol stability. However, it is too strong a solvent for practical use. It was observed that plastisols based on polymers prepared by aqueous emulsion polymerisation generally had higher viscosities than those based on polymers prepared by non-aqueous dispersion polymerisation. This was attributed to electrostatic effects exacerbated by the high dielectric constant of butylbenzyl phthalate. Future work should involve using a more weakly solvating plasticiser possessing a lower dielectric constant.

Stronger metal ion cross-links are formed from polymers based on sulphonate rather than carboxylate groups reacted with organometallic compounds. It has been shown that the metal ion clusters, responsible for thermally reversible cross-linking, in sulphonated poly(styrene) persist at some 70K higher than those in carboxylated poly(styrene)[4]. Plastisols prepared from these polymers may show greater stability. Furthermore, heating of carboxylate or sulphonate containing polymers above their glass transition temperatures during neutralisation may increase the degree of neutralisation and assist in the formation of metal ion clusters[1, 4]. Copolymers with crystalline phases, similar to that in poly(ethylene), can be prepared by block copolymerisation. Plastisols based on these polymers may ought to be more stable than those based on randomly copolymerised polymers.

Application of osmotic limitation of swelling to acrylic plastisols could lead to plastisols with enhanced stability. A more detailed study of the osmotic limitation of swelling using lower molecular weight linear polymers that are incompatible with methyl methacrylate, such as poly(styrene), might lead to behaviour that more closely follows the theoretical predictions. An alternative is to use higher molecular weight linear polymers which would also be excluded from the cross-linked polymer network by virtue of their large radius of gyration. A collaborative study between the Paint Research Association and Bristol University is currently in progress on the effect of dissolved low molecular weight polymers on the rheology of microgels[5]. The study will focus on the stability of the polymer dispersions with particular emphasis on whether the microgel particles flocculate or swell.

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