SELF-ASSEMBLING METAL COATINGS FROM PHOSPHATED AND SILICONE-MODIFIED POLYURETHANE DISPERSIONS

by

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Dissertation presented for the Degree of
Doctor of Philosophy in Polymer Science

at the

University of Stellenbosch

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Stellenbosch
February 2001

Declaration

I, the undersigned, hereby declare that the work contained in this dissertation is my own original work and that I have not previously in its entirety or in part submitted it at any university for a degree.

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ABSTRACT

Self-emulsifiable and self-assembling nano-particle phosphated and siloxane-modified polyurethane dispersions, for use in metal coatings, were synthesised from a new phosphate monomer, a carboxylate monomer, a polysiloxane macroglycol and a cycloaliphatic diisocyanate, and characterised.

Crosslinked nano-particles of acrylic-modified, self-assembling, phosphated polyurethane dispersions with better water swell resistance were obtained using the phosphated nano-particles as the 'seed' to polymerise monofunctional and multifunctional acrylic monomers in the dispersed phase. This was done by reacting 2-hydroxyethyl methacrylate end-capped polyurethane with monofunctional and multifunctional acrylate monomers in the dispersed phase.

Phase inversion of the polyurethane resin from an organic solvent into dispersion was accompanied by three stages, as studied by viscosity and conductivity measurements.

In an attempt to modify existing synthesis procedures of the traditional polyurethane acrylic dispersions for which organic solvents are used, polymerisable acrylic monomers were used as diluents during the urethane-forming reaction. This resulted in overcoming the limitations of the existing process.

Particle-size analysis indicated that the above dispersions had smaller particle sizes, narrower distributions and better hydrophobicity than any reported to date. Aqueous vinyl-terminated phosphated polyurethane dispersions were studied for their viscosity behaviour under shear and showed Newtonian behaviour.

The polyurethane dispersions were evaluated for their hydrolytic stability with respect to the location of the ionic groups on the segments. Greater hydrolytic stability was obtained when the ionic groups were on the urethane hard segment. The polyurethane dispersions responded well to UV curing, a curing technique that has not received much attention to date.

The surface and interface analyses of the self-assembling coatings obtained from the phosphated and siloxane-modified polyurethane dispersions showed increased silicon enrichment at the coating/air interface and phosphorus enrichment at the metal/coating interface. Results of dynamic contact angle studies proved the poor wettability of the coatings, as shown by the increase in contact angle by probe liquids.

Dynamic thermogravimetry studies of the phosphate-containing polyurethanes showed a decrease in activation energy with increasing phosphate content. This is a good indication that phosphate-containing polyurethanes could be used as fire retarding coatings that comply with fire limit regulations.

OPSOMMING

Self-emulgeerbare en selfsamestellende, nanopartikel, fosfaat- en siloksaanbevattende poliuretaandispersies, vir gebruik as deklae vir metale, is gesintetiseer en gekarakteriseer. Die uitgangstowwe vir die bereiding was 'n splinternuwe fosfaatmonomeer, 'n karboksilaatmonomeer, 'n polisiloksaanglikol en 'n siklo-alifatiese diisosianaat.

Deur die polimerisasie van die monofunksionele en multifunksionele akriel-monomere in die dispergeerde fase in te ent met die fosfaat-bevattende nanopartikels, is kruisgebinde nanopartikels van akrielgemodifiseerde, selfsamestellende, fosfaatbevattende poli-uretaandispersies met goeie waterswelweerstand berei. Dit is bewerkstellig deur poli-uretaan, met reaktiewe hidroksietiel-endgroepe, te reageer met monofunksionele akrilaatmonomere in die gedispergeerde fase.

Fase-omkering van die poli-uretaanhars uit die organiese oplosmiddel, tot in dispersie, het in drie stappe plaasgevind. Dit is bepaal deur viskositeit en konduktiwiteit.

Bestaande metodes van sintese vir tradisionele poli-uretaanakrieldispersies, waarvoor organiese oplosmiddels gebruik is, is gewysig om die beperkinge van die bestaande metodes te oorkom. Suskes is behaal met die gebruik van polimeriseerbare akrielmonomere as verdunningsmiddels in die uretaanvormingsreaksie.

Partikelgrootte-analises het getoon dat die verkreë dispersies kleiner partikelgroottes, nouer verspreidings en beter hidrofobisiteit gehad het as enige wat tot dusver beskryf is. Die viskositeit van die wateroplosbare, vinielgetermineerde, fosfaatbevattende poli-uretanandispersies is onder afskuiwing bepaal en het Newtoniese gedrag getoon.

Die hidrolitiese stabiliteit van die poli-uretane, met betrekking tot die posisie van die ioniese groepe in die segmente, is bepaal. Die polimere met die ioniese groepe in die harde segment van die poli-uretaan het hoër hidrolitiese stabiliteit vertoon.

Kruisbinding (verharding) deur middel van UV, wat tot dusver min aandag geniet het, was baie suksesvol.

Analises van die oppervlakte en die tussenvlak van die selfsamestellende deklaag, wat van die fosfaat- en siloksaanbevattende dispersies berei is, het verhoogde siloksaanverryking by die deklaag/lug tussenvlak en verhoogde fosfaatverryking by die metaal/deklaag tussenvlak getoon. Resultate van dinamiese kontakhoekstudies het bewys dat die deklae swak benat is, dws daar was 'n toename in die kontakhoek deur peilvloeistowwe.

Termogravimetriese studies het getoon dat daar 'n afname was in die aktiveringsenergie van die fosfaatbevattende poli-uretane met 'n toenemende fosfaatinhoud. Hierdie feit dui daarop dat hierdie poli-uretane moontlik as brandvertragende deklae gebruik kan word.

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To Selam with love

"…. achievement is the knowledge that you have studied and worked hard and done the best that is in you. Success is being praised by others, and that's nice, too, but not as important or satisfying. Always aim for achievement and forget about success."

Helen Heyes, born 1900

Acknowledgements

I would like to express my sincere thanks and appreciation to:

Prof. Ron Sanderson, my promoter, for his fruitful advice, guidance and encouragement throughout this study.

Prof. Bert Klumperman and **Dr. Chris Lowe**, my external examiners, for offering their time to evaluate this work.

Prof. Harald Pasch, for the opportunity he gave me to spend three months at his analytical laboratory in Darmstadt, Germany, and to his research group for their friendship.

Dr. D. de wet Roos, for his suggestions and assistance.

Dr. M. Hurndall, for editing and proofreading this dissertation.

Mr. D. Steenkamp, for assisting me with EDX analyses.

Ms. Valesca Cloete, for assisting me with contact angle determinations.

Mr. M. van Staden from CSIR, for X-ray Photoelectron Spectroscopy (XPS) analyses.

Mr. D. Reyskens from the Plascon Research Centre, for particle size measurements.

Ms. S. Marais, for recording AFM images.

Finally, but most importantly, I want to thank **God**, through whom all things are made possible.

Publications and presentations which have emanated from this research

I. K. Mequanint and R. Sanderson, USA Patent 09207986, Nov 2000

II. K. Mequanint and R. Sanderson, Hong Kong Patent Appl. 99105771.6, March 2000

III. K. Mequanint and R. Sanderson, Proceedings to the 3rd Kenya Chemical Society International Conference, 16-20 Aug. 1999, Nairobi, Kenya

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List of abbreviations

AFM	Atomic Force Microscopy
DCA	Dynamic Contact Angle Analyser
DMF	N,N-Dimethylformamide
DMPA	Dihydroxymethyl propionic acid
DN	Degree of neutralisation
EDX	Energy Dispersive X-ray Spectroscopy
EGDMA	Ethyleneglycol dimethacrylate
EMA	Ethyl methacrylate
FTIR	Fourier Transform Infrared Spectroscopy
GPC	Gel Permeation Chromatography
HCN	Hydrogen cyanide
HDI	Hexane diisocyanate
MDI	Methylene diphenyl diisocyanate
MMA	Methyl methacrylate
DMDCA	N,N-dimethyldodecylamine
n-BMA	n-Butyl methacrylate
NDI	Naphthalene diisocyanate
NMP	N-methyl pyrollidone
TBA	Tributylamine
TDI	Toluene diisocyanate
TEA	Triethylamine
TGA	Thermogravimetry
THF	Tetrahydrofuran
TIBA	Triisobutylamine
TPA	Tripropylamine
UV	Ultraviolet
VOCs	Volatile organic compounds
XPS	X-ray Photoelectron Spectroscopy

Chapter 1

Introduction and objectives

1.1 Polyurethane dispersions

The term polyurethanes, coined by Otto Bayer in 1937, is more of a convenience than an accuracy since these polymers are neither synthesised by reacting monomeric urethane molecules nor always contain primary urethane groups. The term polyurethane includes those polymers which contain a significant number of urethane groups, regardless of what the rest of the molecule is. Polyurethanes are usually obtained by the combination of at least a difunctional isocyanate with reactants which have at least two hydroxyl groups per molecule, such as a polyether, polyester and monomeric glycols, amino groups and carboxylic groups. Therefore a polyurethane may contain, in addition to urethane groups, aliphatic and aromatic hydrocarbons, esters, ethers, amide and urea groups.

Polyurethanes were first developed as fibre-forming polymers, as alternatives to polyamides, and surface-coating polyurethanes were introduced about 10 years later. Research into more user-friendly coatings lead to the development of water-dispersible ionic urethanes in the 1970s.

The challenges which prompted the above research were: increasingly strict environmental legislation to limit the emission of volatile organic solvents into the atmosphere (which poses a global threat) and the increasing demand for solventless coatings.

To understand the complexities of these new aqueous polymer systems, to improve and tailor-make them for various innovative end-uses and to solve technical problems related to volatile organic compounds (VOCs) is a scientific and technological challenge, as well as a common responsibility towards the safekeeping of the environment.

Polyurethane ionomers combine organic macromolecular chemistry with the inorganic chemistry of salts. Such a seemingly incompatible combination in one molecule prompts expectations of novel and interesting properties. As in the case of conventional segmented polyurethanes, polyurethane ionomers contain low-polarity flexible segments and urethane groups which are polar and capable of interchain interaction via hydrogen bonds. Ionic groups in a polyurethane tend to interact with each other and aggregate but are attached to the 'alien' hydrophobic neighbourhood.

Aqueous dispersions of polyurethanes have not only begun to replace solvent-based coatings but have also new applications in which water, for technological reasons, is required as a solvent, such as for glass fibre sizing and gelatine plasticisers for photographic layers[1]. The outstanding properties of polyurethane dispersions and ease with which the chemical compositions of the polyurethane dispersions can be varied have lead to an increase in the number of manufacturing plants and patent applications. Bayer recently announced that it will spend $5 billion on polyurethane dispersion research and development and is expanding its production plant in the USA[2]. Due to the technical and commercial importance of polyurethane dispersions, the number of patents granted has exceeded the number of scientific papers.

The modification of polyurethane ionomers with different functional groups is a growing area, for applications that require high production output and cost saving. The possibilities of incorporating many different segments with different surface properties in a single molecule open a new door for new generation coatings. In the past 10 years there has been an increase in applied polyurethane research and applications of polyurethane dispersions; different molecular species that can impart specific properties to coatings have been incorporated into the polyurethane ionomer.

For applications that require good adhesion and longer service time, polyurethanes can be modified to suit special needs. One of the potential applications of polyurethane dispersions is in a high-speed coil-coating line to fabricate pre-painted metal sheets. In an attempt to improve the adhesion of polyurethane dispersions to steel, nano-particle dispersions and further surface modifiers are required[3,4].

1.2 Objectives

The overall aim of this study was to develop self-assembling coatings for the protection of metals from environmental degradation. The following were the objectives of this study.

- To synthesise reactive phosphated nano-particle polyurethane dispersions and study their dispersion mechanisms,
- To modify the reactive, phosphated nano-particle polyurethane dispersions by methacrylate and diacrylate monomers in the dispersed phase by means of radical polymerisation and study the physical properties of the emulsion with regards to particle size and swelling properties, rheological properties and the possible use of ultraviolet curing of the dispersions,
- To synthesise phosphorous- and silicon-containing polyurethane acrylic dispersions for self-assembling coatings and study the surface properties of the coatings, and
- To study the thermal degradation of phosphorous-containing polyurethane dispersions by dynamic thermogravimetry

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3. K. Mequanint and R. Sanderson, USA Patent 09207986 (2000)
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Chapter 2

Chemistry, properties and applications of isocyanate-derived polymers

2.1 Introduction to isocyanates

Isocyanates, the esters of isocyanic acid, first synthesised by Wurtz in 1848[1], are those compounds that bear one or several –NCO groups and the entire spectrum of polymerisation processes involving them arises from the peculiar features of these moieties. Isocyantes are generally characterised by high and versatile reactivity. Aliphatic and aromatic monoisocyanates are widely used as building blocks for pharmaceutical and agricultural chemicals. Their use is mainly prompted by both the unique capability of the isocyanates to undergo nucleophilic addition reactions with many compounds and the reversibility of many isocyanate reactions that makes it possible to use them as protection groups, which can be removed when needed. Many [2+2], [2+3] and [2+4] cycloaddition reactions of isocyanates are used to synthesise heterocyclic molecules.

2.2 Reactivity of isocyanates

The high energy content and polarizability of the double bonds in an isocyanate molecule permit multiple reactions. The reactivity of isocyanates (-N=C=O) toward nucleophilic reactions is mainly determined by the positive characteristic of the carbon atom in the cumulated double bond sequence consisting of nitrogen, carbon and oxygen. The charge density is greater on oxygen and less on carbon. The resonance structure shown in Figure 2.1 indicates the partial positive charge on the central carbon atom and how substituents on the carbon group R, can influence the reactivity[2].

$$R{-}\bar{N}{=}C{=}\overline{\underline{O}} \longleftrightarrow R{-}\bar{N}{=}\overset{\oplus}{C}{-}\overset{\ominus}{\underline{\overline{O}}}| \longleftrightarrow R{-}\overset{\ominus}{\underline{\overline{N}}}{-}\overset{\oplus}{C}{=}\overline{\underline{O}} \longleftrightarrow \overset{\ominus}{R}{=}\bar{N}{-}\overset{\oplus}{C}{=}\overline{\underline{O}}$$

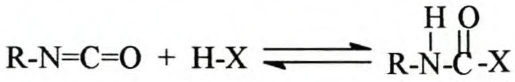
Figure 2.1 Resonance structure of the isocyanate molecule

If R represents an aromatic group, the negative charge can be delocalised to it. This explains why aromatic isocyanates are more reactive than aliphatic or cycloaliphatic isocyanates.

The reactions of isocyanates with active hydrogen compounds involve attack by a nucleophile at the electrophilic carbon of the isocyanate. Therefore, any substituent that is electron withdrawing will increase the positive charge on the carbon and increase the reactivity of the isocyanate groups toward nucleophilic attack. Conversely, electron-donating groups will reduce the reactivity of the isocyanate group. On the other hand, the reactivity of nucleophiles attacking the electrophilic carbon increases as their nucleophilicity increases.

2.2.1 Nucleophilic addition

The most important reaction of isocyanates is the formation of carbamic acid derivatives by the addition of nucleophilic reactants across the C=N double bond.



$$\text{R-N=C=O} + \text{H-X} \rightleftharpoons \text{R-}\overset{\text{H}}{\overset{|}{\text{N}}}\text{-}\overset{\text{O}}{\overset{\|}{\text{C}}}\text{-X}$$

With increasing nucleophilic character of HX, the reaction proceeds at lower temperatures. However, the above reaction product decomposes at higher temperatures to regenerate the starting materials, *i.e.* free –NCO, since the reaction is a genuine equilibrium[3].

2.2.1.1 Primary reactions

The primary reactions of isocyanates with various nucleophiles are shown in Table 2.1. The reactions have been described as primary reactions based on the relative reaction velocity. The reactions are fast and proceed at low temperatures and are useful in practical terms.

Table 2.1 Primary reactions of isocyanates with nucleophiles

Co-reactant	**Reaction product and comments**
Hydroxyl-containing compounds	$R\text{-}N{=}C{=}O + R'OH \longrightarrow -NH\text{-}C{=}O\text{-}OR'$ (polyurethanes) The reaction proceeds under mild conditions to form carbamic acid esters. The nucleophilic attack of the alcohol on the carbon atom of the isocyanate group is followed by a 1,3 shift of the hydrogen atom.
Primary and secondary amines	$R\text{-}N{=}C{=}O + H_2N\text{-}R' \longrightarrow R\text{-}NH\text{-}C{=}O\text{-}NHR'$ (urea) The amines are strongly nucleophilic and the reaction is vigorous, even at room temperature.
Water	$R\text{-}N{=}C{=}O + H_2O \longrightarrow RNHCOOH \longrightarrow CO_2 + RNH_2$ Carbamic acid is unstable under normal circumstances; it splits to form CO_2 and the corresponding amine. Further addition of R-N=C=O leads to urea formation.
Carboxylic acids	Amides are formed *via* the thermally-unstable mixed anhydrides (a), or by dehydration to the carboxylic anhydride and urea (b). (a) $R\text{-}N{=}C{=}O + R'COOH \longrightarrow (RNHCOOCOR') \longrightarrow RNHCOR' + CO_2$ (b) $2\ R\text{-}N{=}C{=}O + 2\ R'COOH \longrightarrow RNHCONHR' + (RCO)_2O + CO_2$

2.2.1.2 Secondary reactions

In the urethane group, a slightly acidic hydrogen atom is attached to the nitrogen. The polyaddition reaction of isocyanates to urethanes can therefore lead to the formation of allophanates under more energetic conditions. Since, in the absence of catalysts, the reaction needs moderately high temperatures (120-140^{0}C), side reactions lead to high molecular weight polymers. In most cases catalysts are used to obtain maximum reaction velocities with minimum side reactions. Allophanate-modified polyisocyanates can also be formulated with excess –NCO, as shown below.

$$R\text{-}NCO + R_1\text{-}NHCOOR_2 \longrightarrow R\text{-}NHCONR_1COOR_2$$

The hydrogen atoms in the urea group are more acidic than those in the urethane. This is the reason why an isocyanate tends to attach itself more easily to the urea than to the urethane. Analogous to allophanate formation, branched biuret groups are formed in this reaction, as is shown below.

$$R\text{-}NCO + R_1NHCONHR_2 \longrightarrow RNHCONR_1CONHR_2$$

2.2.2 Self-addition reactions

In a technical sense, the addition of nucleophiles to isocyanates does not cover all-important reactions. The highly unsaturated character of the R-N=C=O group allows, under specific conditions, dimerisation, trimerisation and condensation reactions.

2.2.2.1 Dimerisation

Similar to ketenes, aromatic isocyanates dimerise to four-membered ring uretidiones (see Figure 2.2). The poor thermal stability of the uretidione ring renders it susceptible to a reverse reaction. While MDI dimerises reasonably at room temperature, even without a catalyst, the dimerisation of TDI was found to be slower due to the hindering effect of the methyl group attached to the aromatic radical[4].

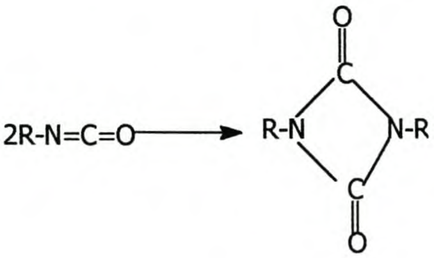


Figure 2.2 Dimerisation of isocyanates to uretidiones

The dimerisation reaction proceeds at ambient temperature in a highly polar solvent, such as DMF, with alkaline catalyst. The product depolymerises readily and hence the reaction is of no technical use. Due to this splitting, dimerisation of aromatic isocyanates is restricted to only thermal crosslinking applications. Dimer formation can be catalysed by trialkylphosphines and dialkylarylphosphines. Once the desired dimerisation is achieved, deactivation of the catalyst can be done with benzoylchloride. Some commercial producers of dimers also use pyridine as a weak catalyst and a solvent. Unlike aromatic isocyanates, dimerisation of aliphatic and cycloaliphatic isocyanates was not possible in the early stages of isocyanate technology[5].

2.2.2.2 Trimerisation

Trimerisation of isocyanates to form stable isocyanurate rings as shown in Figure 2.3, is more valuable than dimerisation. Trimerisation is usually catalysed by strong bases. After a given degree of trimerisation, the reaction has to be terminated with *o/p*-toluene-sulphonic acid-methylester to avoid brittle polycyclic and crossliked structures. While aliphatic and cycloaliphatic isocyanates convert directly to trisubstituted isocyanurates without the formation of the dimer intermediates, aromatic isocyanates form trimers *via* the dimer intermediate. Aliphatic and cycloaliphatic isocyanates can either be trimerised alone or mixed with aromatic polyisocyanates. The isocyanurates are mainly used for light-stable and weather-resistant coatings.

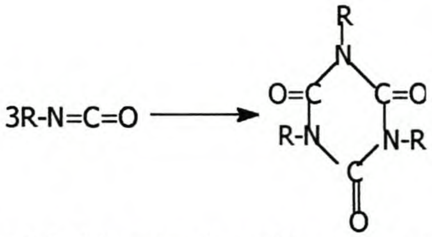


Figure 2.3 Trimerisation of isocyanates to isocyanurates

2.2.3 Condensation reactions

In addition to nucleophilic and self-addition reactions, isocyanates also undergo condensation reactions to form some commercially important polymers.

2.2.3.1 Polycarbodiimides

At high temperature and in the presence of special phosphorus compounds eg. 1-ethyl-3-methyl-3-phospholine-1-oxide as catalyst, polyisocyanate-dimers and isocyanurates can be converted to substituted carbodiimides with the cumulative double bond –N=C=N-. In the absence of catalyst the reaction will take place at higher temperatures. Diisocyanates form linear carbodiimides, while polyfunctional polyisocyanates convert to branched polycarbodiimides. Polycondensates of this type have extremely high melting ranges. It has been reported[6] that the polycarbodiimide films of MDI melt at 280^0C and the polycarbodiimide films of NDI have a melting point in excess of 350^0C. As typical heterocumulenes, carbodiimides can add isocyanates to form uretone-imines as shown in Figure 2.4 and they also add water to form ureas.

The formation of polycarbodiimides from aromatic diisocyanates is best conducted in a hydrocarbon solvent using a phospholene oxide catalyst[7]. The reaction proceeds at room temperature with the elimination of carbon dioxide. The resulting polymers are thermosets, where crosslinking occurs *via* a cyclo-addition mechanism. In order to obtain processable linear polymers the diisocyanates have to be copolymerised with monoisocyanates as a chain stopper[8]. Oligomeric carbodiimides are efficient stabilisers for polyesters, polyether-based polyurethanes and polyurethane-ureas. If the diisocyanate is TDI, then the corresponding carbodiimide is a linear polymer that can be further reacted with nucleophiles across the N=C=N bond[9]. When the polymers are used for low-density foams the carbon dioxide gas generated in the reaction is used as a blowing agent.

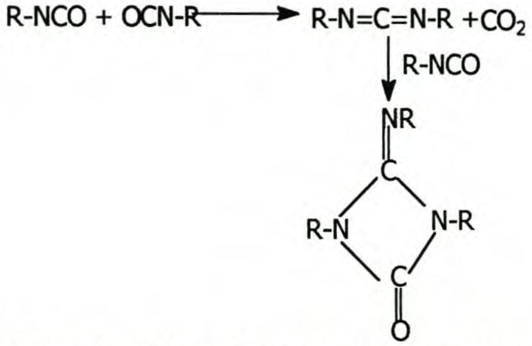


Figure 2.4 Condensation of isocyanates to form carbodiimides and subsequent urethone-imines

2.2.3.2 Polyamides

The reaction of isocyanates and carboxylic acids as an alternate route for the synthesis of aromatic diamine-based polyamides is receiving great attention[10]. As in the preparation of polycarbodiimides, the preparation of polyamides from isocyanates liberates CO_2.

$$OCN\text{-}R\text{-}NCO + HOOC\text{-}R_1\text{-}COOH \rightarrow \text{-}[R\text{-}NHCO\text{-}R_1\text{-}CONH\text{-}]_n + 2CO_2$$

Polyamide segmented elastomers are produced by the condensation of MDI with dicarboxylic acids as extenders and a carboxylic acid-terminated aliphatic polyester, polycarbonate or polyether prepolymer as a soft segment[10] by reactive extrusion. The preparation of some engineering thermoplastics have been reported by reacting MDI with azelaic acid or mixtures of azelaic acid and adipic acid[11]. Multiblock copolymers are obtained by reacting a mixture of isophthalic and azelaic acids with MDI. A prepolymer is formed, which is subsequently reacted with α,ω-bis(10-carboxydecyl) polydimethylsiloxane[12].

2.2.3.3 Poly(amide-imides) and polyimides

Poly(amide-imides) are obtained from the reaction of MDI with trimellitic anhydride in NMP, in the presence of small amount of water[13]. The solution is directly converted into films or fibres since, after isolation, the polymer is no longer soluble in the polar solvent. The crosslinking of the polymer is due to side reactions of MDI with the NMP[14]. Storage-stable poly(amide-imides) intended for coating applications are obtained by adding cresol-blocked MDI and trimellitic anhydride[15].

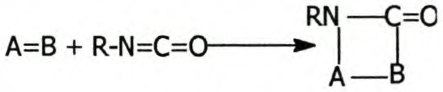
2.2.3.4 Other heterocyclic polymers

Wide ranges of heterocyclic polymers can be obtained from reactions of aromatic diisocyanates and suitable comonomers. The reaction paths involve addition/condensation sequences. In the 1970s Exxon developed poly(parabanic acids) from MDI and HCN in DMF or NMP, using sodium cyanide as a catalyst[16]. During the first step of the reaction, linear cyanoformamidines are formed by a polyaddition reaction. This is followed by cyclization to form poly (iminoimidazolidinones) and subsequent hydrolysis to yield the final product. This process has subsequently been discontinued, presumably because of the toxicity of HCN.

2.2.4 Other reactions

2.2.4.1 Cycloaddition reactions

The [2+2] cycloaddition of isocyanates to numerous co-reactants containing an A=B double bond is a convenient method for the synthesis of four-membered-ring heterocyclic compounds.



The [2+3] cycloaddition reactions of isocyanates afford five-membered-ring hetrocyclic compounds. The typical co-reactants in the [2+3] system are 1,3 dipolar compounds or three-membered compounds that can undergo ring opening to generate the dipolar species. The [2+3] cycloaddition reaction usually proceeds across the C=N double bond of the isocyanate, although it has been observed to proceed across the C=O double bond. The three-membered ring compounds that generate 1,3-dipolar intermediates with or without added catalyst include the cyclopropanes, oxiranes, aziridines, oxaziridines and diaziridines[17].

Finally, isocyanates undergo [2+4] cycloaddition reactions with 1,3-dienes, heterodienes, conjugated Schiff bases and other cumulenes. Examples of the [2+4] cycloadditon reactions of isocyanates are with dienes (Diels-Alder reaction) or with dipolar co-reactants[17]

2.2.4.2 Insertion reactions

Another interesting reaction that isocyanates undergo is insertion into many single bonds. Metal alkoxides and metal amides undergo such a reaction. The insertion reaction of an isocyanate into a co-reactant **A-B** involves a stepwise process. The insertion product forms either a single bond between the **N** atom of the isocyanate and **A** or it can be formulated as a coordinated adduct forming bonds involving both the **N** and **O** atoms of the isocyanate.

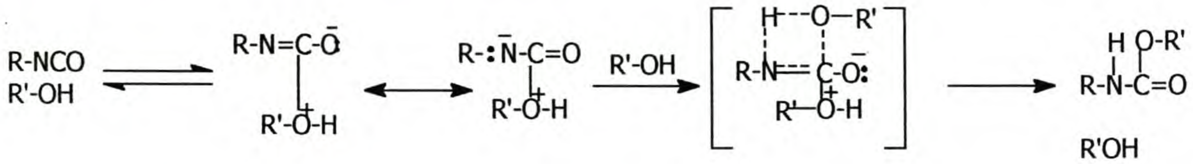
The insertion reactions that have been investigated in detail are: insertion into C-H bond, insertion into O-C-O, insertion into N-C-N, insertion into C-halogen bonds, and insertion into organometallic compounds.

2.3 Introduction to the synthesis of polyurethanes

Notwithstanding the multitude of different products based on macromolecular polyurethanes and their very wide range of properties, which can be tailor-made for a very wide range of applications, all these products are chemically very similar. Polyurethane is the collective name for an extensive group of polymers with very different compositions and varied property profiles that have the urethane group in common. A urethane group is essentially a carbamic acid ester, *i.e.* ester-amide derivatives of carbonic acids. The instability of the carbamic acid intermediate does not permit direct esterification of the acid with an alcohol and, subsequently, almost all commercial polyurethanes are made by a diisocyanate polyaddition process.

2.3.1 Preparation of polyurethanes by the isocyanate route

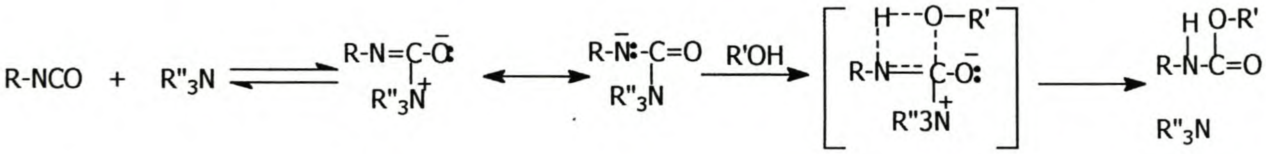
Among the various types of reactions that isocyanates undergo, the reaction between R-N=C=O and R'OH is commercially valuable and well studied. In the absence of added catalyst the reaction proceeds as follows[18].



Electron-withdrawing groups on the isocyanate molecule and electron-donating group on the active hydrogen molecule increase the rate of reaction. The complex formed between the isocyanate and the alcohol involves electron-pair donation rather than hydrogen bonding.

2.3.1.1 Effects of catalysts

Nucleophilic reactions between isocyanates and active hydrogen compounds are extremely susceptible to catalysis and, as a result, many commercial applications of isocyanates utilise catalysed reactions. Acids and acid halides prolong the reaction whereas basic compounds, such as tertiary amines and metal compounds, accelerate it. The most widely used catalysts are tertiary amines and certain metal compounds, particularly those derived from tin. The proposed mechanism of tertiary amine (R''_3N) catalysis is believed to proceed as follows [19]

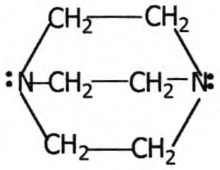


For a series of amine catalysts, the catalytic activity parallels the base strength of the amine except when steric effects become pronounced. The activities of tertiary amines, due to the steric effect caused by increases in the sizes of the substituents, in a phenyl isocyanate-butanol reaction are shown in Table 2.2.

Table 2.2 Catalytic activities of various tertiary amines in a phenyl isocyanate-butanol reaction[19].

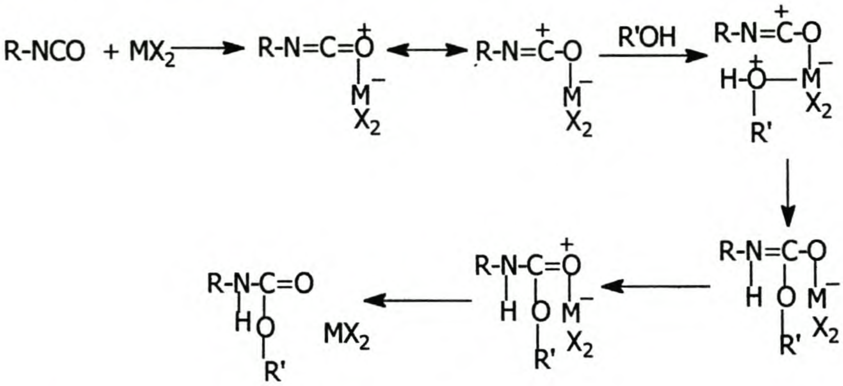
Amine	**Base strength ($_p$ka)**	**Relative activity**
Trimethylamine	9.9	2.2
Ethyldimethylamine	10.2	1.6
Diethylmethylamine	10.4	1
Triethylamine	10.8	0.9
Triethylenediamine	8.2	3.3

In the case of triethylenediamine (structure 2-I), the steric hindrance for complex formation is low and, although this amine is weak base, it is a powerful catalyst.



Structure 2-I

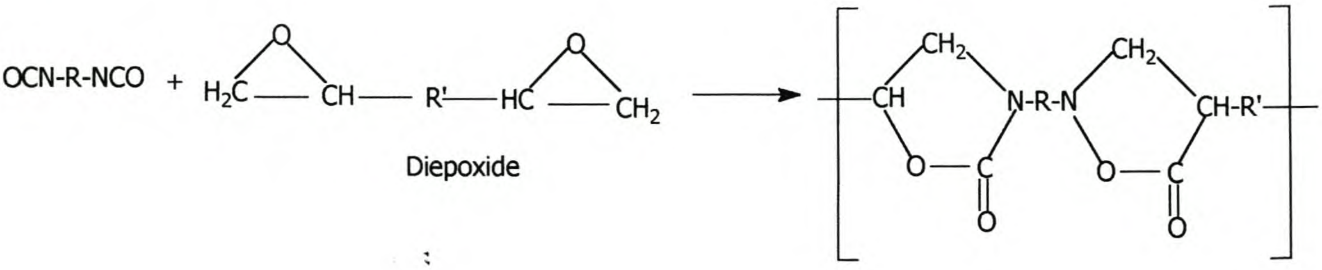
Metal salt catalysts of the type MX_2 operate *via* the following mechanism [20].



Basic and metal compounds are not the only catalysts used in urethane formation. The urethane group itself has a catalytic effect on the reaction. Hydrogen bonding and the nature of the solvent used also play roles in the catalytic process. Metal catalysts activate the isocyanate groups by making them more electrophilic whereas basic catalysts make the hydroxyl groups more nucleophilic.

In the absence of catalyst, the reactivities of acidic hydrogen compounds towards isocyanates are, in decreasing order of reactivity: aliphatic amines, aromatic amines, primary alcohols, water, secondary alcohols, tertiary alcohols, phenols, carboxylic acids, ureas, amides and urethanes.

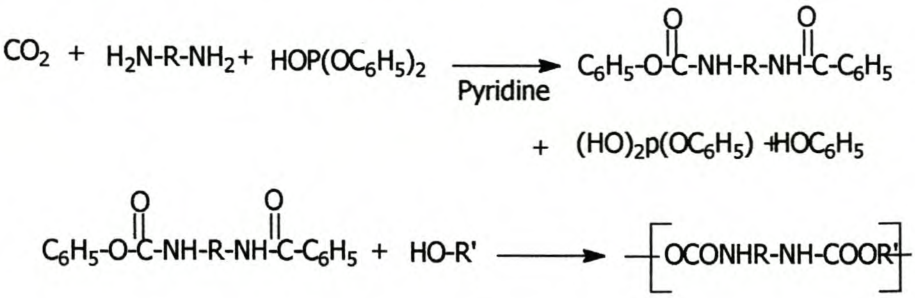
Cyclic urethanes can be commercially prepared by the reaction of isocyanates with 2-epoxides[21,22]. Poly (2-oxazolidones) that contain cyclic urethane groups are synthesised by this method, as shown below.



2.3.2 Preparation of polyurethanes by the non-isocyanate route

In applications where the low reaction temperature of the reaction of an isocyanate with a polyol is not required or when the corresponding isocyanate is not available, non-isocyanate routes can be used to prepare isocyanates. For example:

1. Low-temperature coupling reactions of amines with CO_2 under mild conditions and in the presence diphenyl phosphite and pyridine have been used successfully to prepare aromatic polyurethanes and polyureas[23].



$$CO_2 + H_2N\text{-}R\text{-}NH_2 + HOP(OC_6H_5)_2 \xrightarrow[\text{Pyridine}]{} C_6H_5\text{-}O\text{-}\overset{\overset{O}{\|}}{C}\text{-}NH\text{-}R\text{-}NH\text{-}\overset{\overset{O}{\|}}{C}\text{-}C_6H_5 + (HO)_2p(OC_6H_5) + HOC_6H_5$$

$$C_6H_5\text{-}O\text{-}\overset{\overset{O}{\|}}{C}\text{-}NH\text{-}R\text{-}NH\text{-}\overset{\overset{O}{\|}}{C}\text{-}C_6H_5 + HO\text{-}R' \longrightarrow \left[OCONHR\text{-}NH\text{-}COOR' \right]$$

2. Oxidative alkoxycarbonylation of primary amines with CO and an alcohol was also found to yield carbamates[24]. In this process high yields of urethane from low-cost intermediates can be produced.

$$R\text{-}NH_2 + CO + R'OH + \tfrac{1}{2}\,O_2 \xrightarrow{Pd,\,I_2} R\text{-}NHOCOR' + H_2O$$

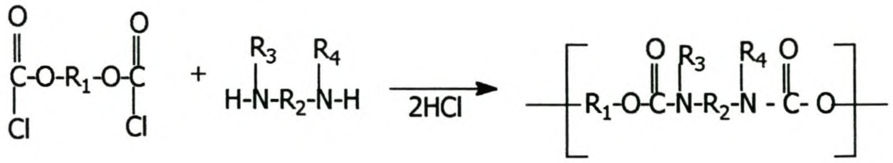
A modification of the above reaction is to substitute both the amine and the oxygen with nitro compounds[25] and utilise selenium compounds as the catalyst. A limitation here is that it is necessary to use three mole of CO for every urethane bond formed.

$$R\text{-}NO_2 + 3CO + R_1OH \xrightarrow{Se} RNH\text{-}OCOR_1 + 2CO_2$$

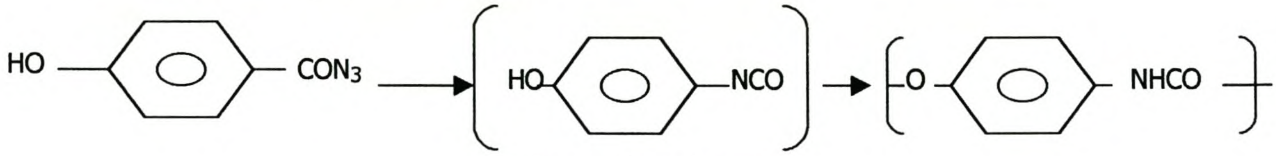
3. Polyurethanes can also be prepared by the transamination of a carbonate with a diamine[25].

$$R_1OOC\text{-}OR_2 + RNH_2 \longrightarrow RNH\text{-}OCOR_1 + R_2OH$$

4. Thermally-stable poly (N-alkyl urethanes) that can not be produced by the usual polyaddition process can also be prepared from bischloroformate esters and diamines such as piperazine.

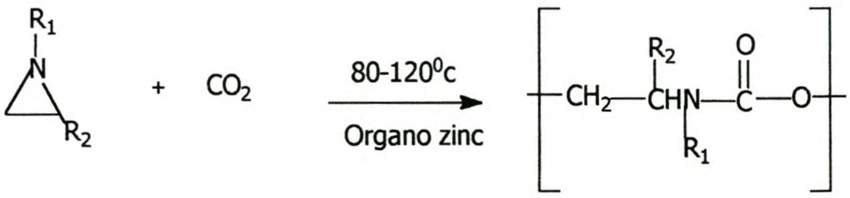


5. Thermolysis of *p*-hydroxybenzoylazide *via* the hydroxy phenyl isocyanate intermediate has been reported to yield urethane[26].



hydroxy phenylisocyanate
intermediate

6. The copolymerisation of aziridenes with carbon dioxide has also been reported[27].



2.4 Structural properties of segmented polyurethanes

The properties of "pure" polyurethanes such as those formed from hexane diol and 1,6-hexane diisocyanate are similar to crystalline polyamides with a multitude of inter-urethane hydrogen bonds between the chains, which have high strength and dimensional stability. On the other hand, those polyurethanes formed from flexible, long chain polyether or polyester diols and, say, TDI are flexible, with low dimensional stability. In both the above cases, the products have only one phase and do not possess hard segment features.

Segmented polyurethanes are composed of long chain polyethers or polyester polyols, a diisocyanate and chain extender (glycol, water or diamine). From a polymer physics standpoint, these polymers are a new class of elastomeric products. They are characterised by a segmented structure (block copolymer structure) of the primary chain. The secondary and tertiary structures and, consequently, the morphology of these polyurethanes, are dependent on the chemical composition and the length of the segments (blocks). The reason for the high property level is due to the two or poly-phase structure. Typical segmented polyurethanes, for example thermoplastic polyurethane elastomers as well as fibres and coatings, are predominantly linear.

2.4.1 Hard and soft segments of polyurethanes

A polyurethane prepared from one mole of a long chain diol, one mole of a short chain diol and two moles of a diisocyanate has alternate soft segments in coiled form, which are quite mobile, and stiff oligo-urethane hard segments, as shown in Figure 2.5.

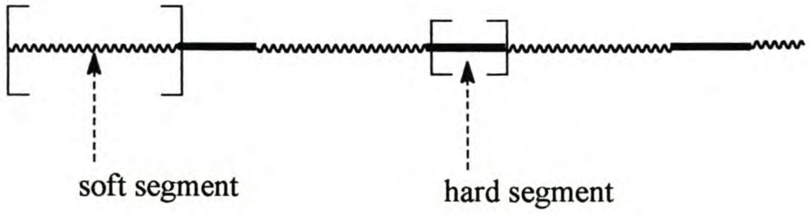


Figure 2.5 Schematic representation of soft and hard segments in segmented polyurethanes

Under practical conditions the structure of the soft segment as well as the urethane reaction follow a statistical Flory distribution[28] and a higher amount of hard segments is formed than one could theoretically predict. This is especially true for polyester-based urethanes. The polyester diols used in the preparation of segmented polyurethanes always contain considerable amounts of low molecular weight glycols, which contribute to the formation of more hard segments.

2.4.2 Segregation and domain morphology

The two-phase feature of segmented polyurethanes is related to the limited compatibility of the block of the urethane groups formed (from the diisocyanate and the low molecular weight chain extender) with the soft segment macroglycol. In the early stage of the reaction the chain extender reacts with the diisocyanate, forming oligourethane groups, which improve compatibility with the soft segment glycol. As the reaction proceeds, macromolecules, which exhibit segmented structure, are formed[29]. The mainly non-polar, low-melting, soft segments are incompatible with the polar, high-melting, hard segments. Hard segments, which are prepared separately, are usually insoluble in oligomeric macroglycols at temperatures below 120^0 C. As a result, phase separation (segregation) occurs and, simultaneously, covalently linked microphases are formed. This process of phase segregation continues with decreasing temperature.

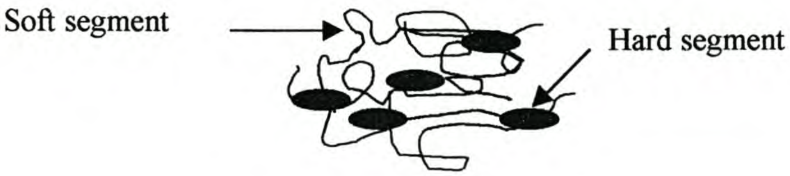


Figure 2.6 Schematic representation of the domain structure in segmented polyurethanes

Segmented polyurethanes are made by covalently joining two dissimilar segments along the polymer backbone. At the service temperature, the soft segment component is viscous or rubbery, while the hard segment is glassy or semicrystalline. The unique properties of these copolymers are directly related to their two-phase microstructure with hard domains acting as reinforcing fillers and as a thermally labile crosslinks.

2.4.3 Factors affecting the degree of microphase separation

The degree of microphase separation between hard and soft segments depends on the hard/hard-segment and hard/soft-segment interactions. These are controlled by segmental polarity differences, intra- and inter-segmental interaction, crystallizability of either of the segments, the block lengths, and overall composition of the polyurethane[30].

The urethane groups are more polar than the long chain non-polar soft segment and the polymer made from the highly non-polar soft segment causes hard segment cohesion and phase separation[31-35]. Furthermore, urea-containing hard segments, which are formed from low molecular weight diamines or water, are more polar than urethane-containing hard segments (due to a higher concentration of NH-dipoles) and a high degree of segregation is observed. Typical hard segments have a molecular length of about 25-150Å.

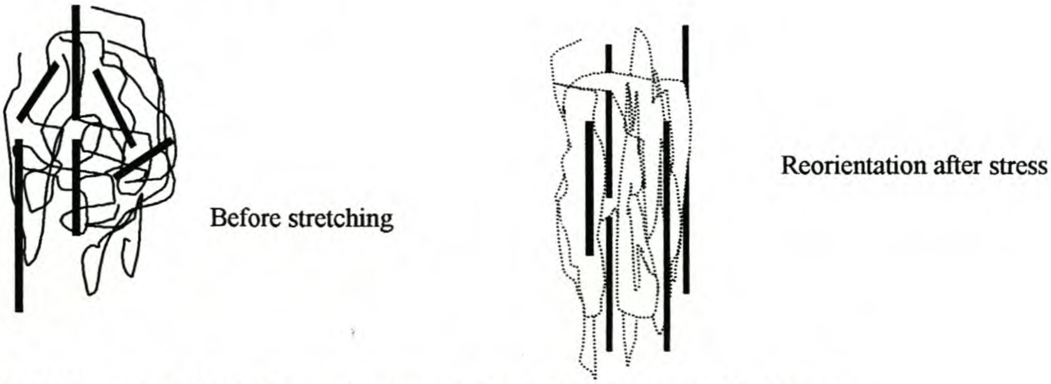
However, if the soft segment is relatively polar, phase mixing will be favoured[36] and, due to incomplete phase separation, interconnected or isolated hard segment domains are found to be present in the soft segment. An increase in the soft segment glass transition temperature (T_{gs}) of the polyurethane is observed as a result of dissolved hard segments present in the soft segment moiety[37].

The main driving force in segmental segregation is hydrogen bonding. The tendency to undergo microphase separation is to a large extent governed by interactions tending to promote cohesion between the hard segments. Inter-urethane hydrogen bonding with the –NH group acting as the proton donor and the urethane carbonyl as the proton acceptor, is generally considered to contribute significantly to hard-domain cohesion and phase segregation. Hydrogen bonding can also occur between soft segments and hard segments where the –NH group acts as a donor and either the ester carbonyl or the ether oxygen acts as an acceptor.

The crystalizability of each or one of the segments also plays a role in phase separation. Xiu et al[38] found that in polyether urethane-ureas, hard segment crystallisation was higher than in the corresponding polyester urethane-ureas with the same hard segment content due to inter-urethane hydrogen bonding. In polyether urethane-ureas hydrogen bonds form between the –NH and C=O of the urethane (inter-urethane), favouring crystalisation (cohesion), whereas in polyester urethane-ureas hydrogen bonding also occurs between the –NH of the urethane and C=O of the ester, hindering crystallisation. It has also been shown[39] for both polyester and polyether type soft segments that the extent of phase separation increases with an increase in the molecular weight of the soft segment. The symmetry of the diisocyanate and of the specific chain extender used also play a role. Chain extenders that have an even number of CH_2 groups in their backbone yield hard segments and have higher melting ranges than those chain extenders that have an odd number of methylene groups[40].

2.4.4 Effects of hard segment domains on mechanical and thermal properties

The thermo-mechanical properties of linear segmented polyurethanes are very different to those of chemically-crosslinked polyurethanes. When mechanical forces are applied within the hard segment domain, changes in the orientation and mobility of structures such as plastic deformation, strain-induced softening and the Mullins effect take place. During such applied forces, the initial hydrogen bonding is lost and new, energetically more favourable hydrogen bonding takes place. Tension is more evenly distributed, the single bonds are less stressed and, as a result, the resistance of the material to further stress is increased (Figure 2.7). This effect contributes to high tensile strength, elongation and tear strength. The melting range of the hard segment domains determines the dimensional thermal stability of linear segmented polyurethanes. Above the melting temperature, the material shows thermoplastic flow.



Before stretching

Reorientation after stress

Figure 2.7 Schematic illustration of segmental orientation on applied stress

2.4.5 The effect of the soft segment matrix on thermal and mechanical properties

The mobility of the molecular chains of the soft segment in segmented polyurethanes causes reversible elastomeric properties, specifically cold flexibility and differences in ultimate stress values. The mobility depends, to a large extent, on the chemical nature and chain length of the soft segment. In order to obtain good elastomeric properties, especially impact resistance, the soft segment should be amorphous and possess a low enough glass-transition temperature[41].

In products containing large amounts of hard segments (above 50%), the mobility of the soft segments is considerably reduced. Generally, polyurethane films with polyester diols as a soft segment have better tensile strength than the corresponding polyether polyurethanes, but the latter have improved water vapour permeability and hydrolytic resistance[42].

2.4.6 Crosslinked polyurethanes

Although crosslinked polyurethanes are no longer thermoplastic, melting of the hard segment domains is observed in the form of softening[43]. With increasing crosslink density, the values of elongation, set, and compression set decrease, while the tensile strength initially increases but later decreases. When linear segmented polyurethanes are crosslinked, physical and chemical crosslinking effects overlap. However, if the polyaddition reaction is carried out directly in the presence of tri-, or higher, functional polyisocyanates or polyols, which lead to an early network formation, the formation of physically crosslinked domains can be prevented. At low chemical crosslinking the elasticity modulus decreases and, under extreme conditions, segregation will not occur at all.

2.5 Polyurethane ionomers

Segmented polyurethane ionomers are a specific class of ion-containing urethane polymers, which typically possess less than 15 mole % ionic groups covalently attached to a hydrocarbon backbone. Those polymers with higher ionic groups are classified as polyelectrolytes[44]. The combination of a low ionic content and a low polarity backbone results in a class of polyurethanes which is of scientific, technological and commercial interest[45-50].

Polyelectrolytes contain numerous ionic centres more or less evenly distributed. These ionic centres are separated by only short chain, polar segments. Ionomers, on the other hand, are segmented polymers in which the ionic groups are separated by long chain, non-polar segments. The coulombic forces that exist between ionic groups of neighbouring molecules overlap the interchain interactions and, in the presence of water, the ionic centres are hydrated. This effect enables ionomers to form stable dispersions in water. The supra-molecular structure and corresponding properties of ionomers depend, to a large extent, on the location of the ionic group within a segmented polymer chain. If the ionic centre is located in the hard segment it will, due to its aligning effect, favour the formation of domain morphology.

Polyurethanes which contain basic nitrogen in the hard segment and exhibit plasticity and lack of strength can be converted into high tensile-strength elastomers upon quaternization. The increase in polarity of the hard segment, the formation of hydrogen bonding, an increase in the melting point and, therefore, the formation of hard segment domains explain this phenomenon[51]. Water can reversibly eliminate this type of crosslinking mechanism. The partial "inorganic" nature of ionomers provides specific interactions with inorganic fillers, for example, glass fibres.

An aqueous polyurethane dispersion is a binary colloidal system in which hydrophobic urethane segments are dispersed in a continuous aqueous medium. Since an appropriate combination of hydrophobic and hydrophilic segments acts as an emulsifier, no external emulsifier is needed. Apart from the advantage of environmental friendliness, aqueous polyurethane dispersions can also be prepared with high molecular weights since the viscosity of the dispersion is independent of the molecular weight of the dispersed polymer particles.

The concept of polyurethane ionomers arises from the extension of the ionomer polymer field to polyurethanes, to incorporate the advantages of both fields. The introduction of ionic functionality brings about dramatic changes in the properties of the polyurethanes; for example, waterproof polyurethanes can be made into water wetting or even water soluble polyurethanes. Patents from the companies Farbenfabriken and Bayer [52-54] revealed the invention of water-soluble polyurethanes which contained ionic functionality in the chain. A good review article on this fascinating field of polyurethane ionomers was published by Dietrich et. al[55] in 1970.

2.5.1 Synthetic approach to polyurethane ionomers

Di or polyisocyanates, the major raw materials in polyurethane synthesis, are sensitive to water, hence the use of water as solvent or diluent in polyurethane preparation is not possible. It is however possible to incorporate hydrophilic segments into hydrophobic polyurethane so that the resulting polymer is dispersed, or sometimes even dissolved, in water. As in the field of ionic polymers, the ionic groups in polyurethanes can be incorporated into the polymer chain either as the basic component or by post-polymer-modification techniques. Recently the post-polymerisation of polyurethane macroiniferters has also been used to synthesise polyurethane ionomers[56].

2.5.2 Types of polyurethane ionomers

Depending on the types of stabilising mechanisms, polyurethane ionomers are classified as cationics, anionics and zwitterionomers, and are discussed below.

2.5.2.1 Polyurethane cationomers

Most of the earlier work done in the field of polyurethane ionomers was on cationic polyurethanes. Polyurethane cationomers, often called polyammonium-polyurethanes, are prepared by the reaction of diisocyanates with N-alkyl and sulphur-containing diols, followed by the quaternisation of the nitrogen atom or 'ternisation' of the sulphur atom[57-67, see Figure 2.8]. When solubility permits, even quaternised salts of diamines are used directly as chain extenders to prepare polyurethane cationomers[68]. Similarly, cationic polyurethanes with tertiary sulphonium groups can be prepared when the *tert*-aminoglycol is substituted for thiodiglycol (bis-2-hydroxy ethyl sulphide). Figure 2.9 lists the most common ionic monomers used in the synthesis of cationic polyurethanes.

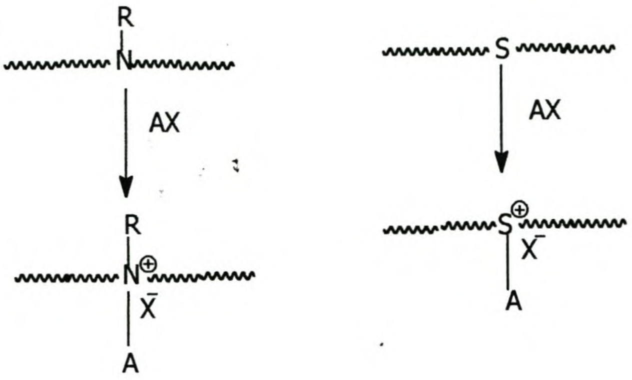


Figure 2.8 Schematic illustration of polyurethane cationomer preparation.

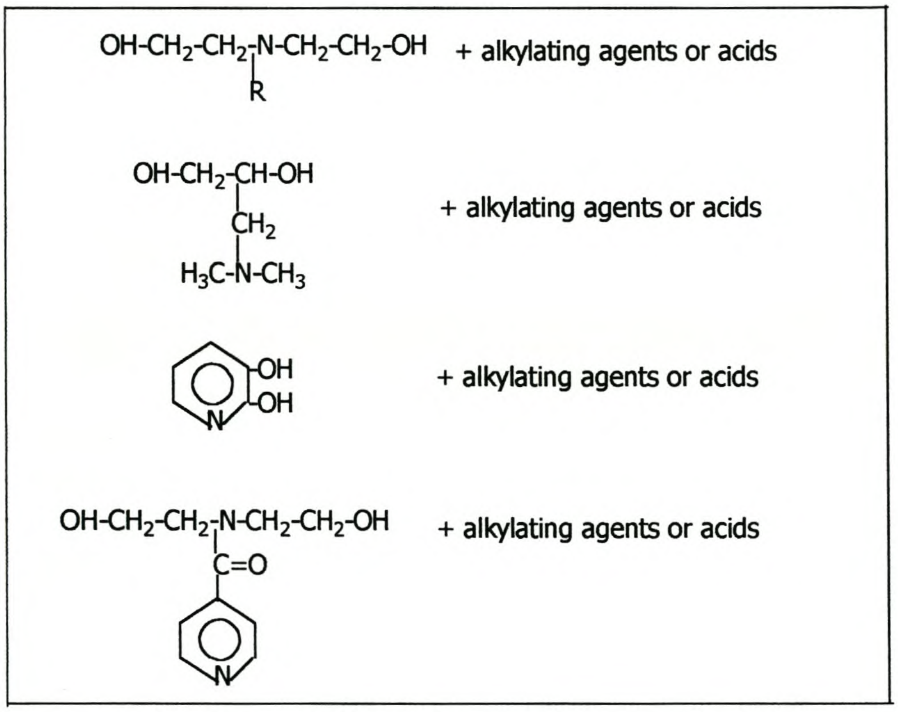


Figure 2.9 Representative monomers used as ionic centres in the synthesis of cationic polyurethanes.

2.5.2.2 Polyurethane anionomers

These classes of ionomers, the most important commercially viable ionomers, are prepared by the reaction of diisocyanates containing ionic groups with diols, or by the reaction of diisocyanates with ionic diols. Lorenz and co-workers[68-71] and George and co-workers[72-74] carried out studies on the introduction of new ionic diol components to polyurethane ionomers. They synthesised a series of sulfonic acid and phosphoric acid-containing diols and used them as chain extenders with polyurethane pre-polymers to obtain anionomers. Similarly, anionomers containing carboxylate groups were prepared and studied by various groups [75-80]. Rajan et.al.[81] prepared polyurethane anionomers by reaction across unsaturated sites on the polyurethane chain, but some amount of polymer degradation was observed. Apart from different spatial architectures of the ionic groups in polymer backbones, metal-containing polyurethanes which contain acidic groups in main chains, ionenes based on anhydrides and urethane-amide groups have also been studied[82-85].

2.5.2.3 Polyurethane zwitterionomers

Polyurethanes that do not contain tertiary amino groups can also be converted into zwitterionomers by the initial exchange of urethane protons using NaH or NaOH, followed by the reaction of sultones or lactones to form ionomers[86]. Cooper and co-workers[87] synthesised polyurethane zwitterionomers by quaternising the tertiary nitrogen in the polyurethane chain using trimethylene sulphone, as illustrated in Figure 2.10

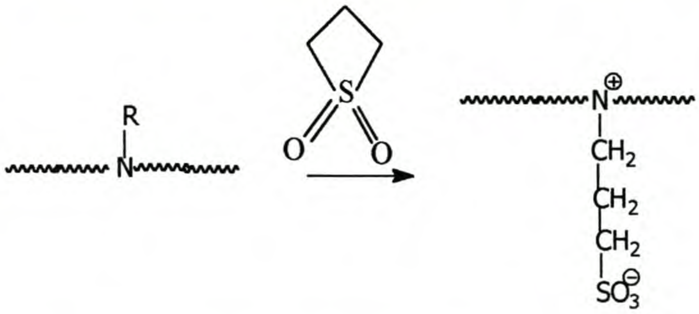


Figure 2.10 Schematic representation of the synthesis of polyurethane zwitterionomers

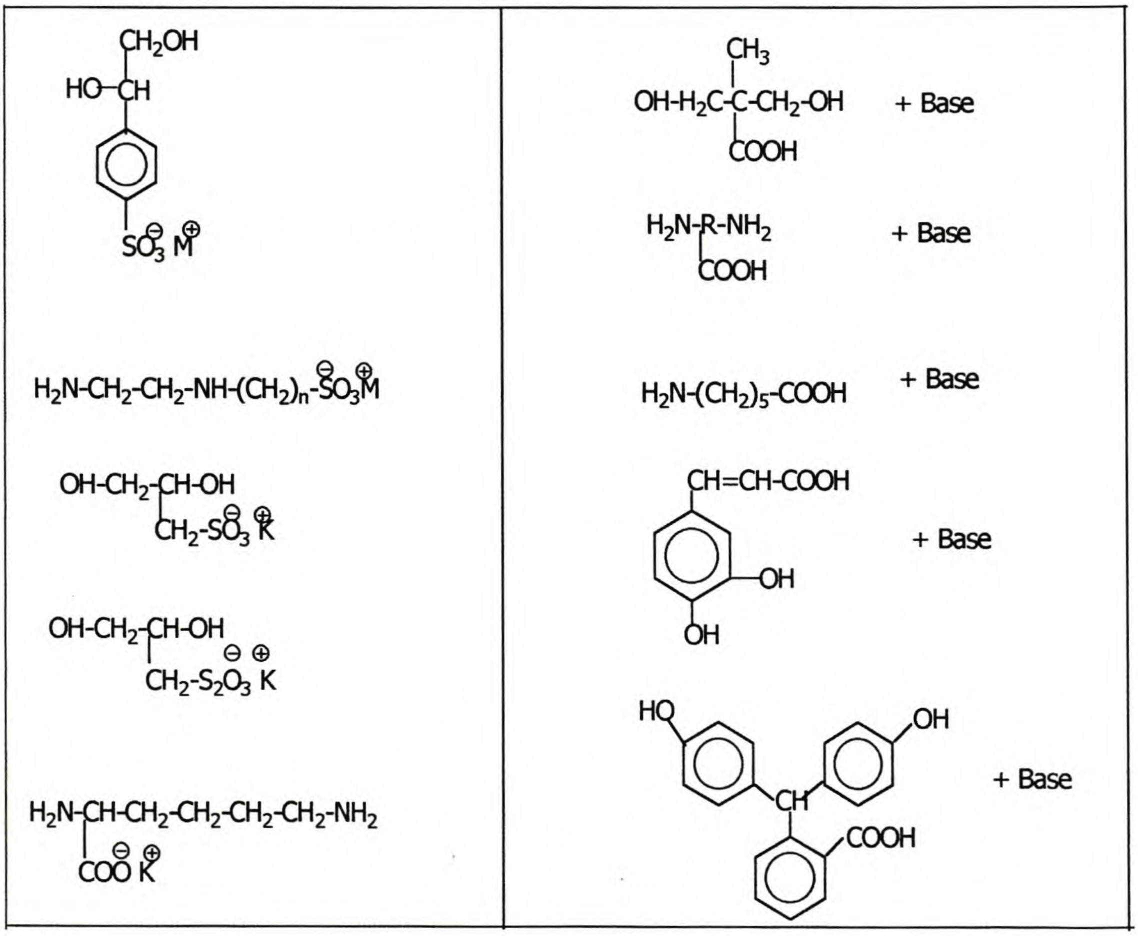
2.6 Incorporation of ionic groups into polyurethanes

Ionic groups in polyurethane ionomers, as in any other ionic polymers, can be incorporated into the polymer chain as a basic component or by post-polymer-modification techniques. In order to obtain anionic polyurethanes dispersible in water, diols bearing a carboxylic acid or a sulphonate group are usually introduced. The acid group is then subsequently neutralised by a base such as a tertiary amine. In polyurethanes, the ionic groups are incorporated: by the use of polyols containing ionic groups, by means of ionic diisocyanates and by the use of ionic diols as chain extenders.

2.7 Carboxylic acid co-monomers for polyurethane anionomers

A wide range of carboxylic acid monomers has been used in the synthesis of polyurethane anionomers. Upon neutralising the acid groups with bases, ionic centres are generated. The acids typically employed were either amino functional or hydroxy acids. Milligan et.al.[88] used 2,2-dihydroxymethyl carboxylic acid as the inorganic component for preparing polyurethane anionomers. This monomer, commonly known as dimethylol propionic acid (DMPA), is commercially available and the most widely used to date.

Table 2.3 Functional monomers used in the synthesis of anionic polyurethane dispersions



Ramesh and Radhakrishnan[89] used phenolphthaleins; for example, (2-[Bis(4-hydroxyphenyl)methylbenzoic) acid. Mahesh et.al[90] used 3,4-dihydroxycinnamic acid to prepare carboxylic acid-terminated urethane anionomers. More recently, Huang et.al[91] attempted to use L-2,5-diaminovaleric acid and *p*-amino benzoic acid as potential ionic centres. Table 2.3 lists the major ionic functional groups used in the preparation of anionic polyurethane dispersions.

2.8 Ionic versus non-ionic polyurethanes

Ionomer dispersions are produced without emulsifiers and are stabilised solely by the built-in ionic centres that are arranged mainly on the particle surface[92]. The same structural principle can be applied to produce pure non-ionic dispersions if lateral or terminal hydrophilic polyether residues, like polyethylene glycol, replace the ionic centres. In this class of dispersions, the dispersion process should be kept below 60^0C. This is because polyethylene glycol ether units loose their hydrophilicity with increasing temperature, resulting in unstable dispersions. Table 2.4 compares the advantages and limitations of ionic and non-ionic dispersions.

Table 2.4 Advantages and limitations of ionic and non-ionic dispersions

Dispersion type	**Advantages**	**Disadvantages**
Ionic dispersions	➢ Self-dispersibility ➢ High dispersion stability ➢ Good film-forming properties ➢ Resistance to solvents, especially after curing ➢ Good gloss and adhesion	➢ Increased sensitivity to water: swelling ➢ Turbidity (becomes white on storage) ➢ Softening ➢ Hydrolytic decomposition
Non-ionic dispersions	➢ Low viscosity at high solids content ➢ Resistant to frost, change in pH, electrolytes, mechanical force and solvents ➢ Good hydrolytic stability	➢ Thermocoagulation due to the negative temperature gradient of the solubility of the polyether segment

To overcome the limitations of each type of dispersion, ionic and non-ionic hydrophilic groups were found to have synergistic effects. By combining the two types, the overall hydrophilicity can be minimised and satisfactory resistance to frost and electrolytes can be obtained[93].

2.9 Chemical modifications of ionomers

The mechanical properties of polyurethane ionomer films and their resistance to water, solvents and other chemicals can be improved by means of chemical modifications. For this, the dispersions may be crosslinked either internally or externally, as described below.

2.9.1 Graft and block copolymerisation

The grafting of vinyl monomers into polyurethane is usually accomplished in the aqueous phase, using conventional emulsion polymerisation techniques. Monomer and free radical initiators are added to the aqueous phase and grafting is carried out at moderate temperatures. Both anionic and cationic polyurethanes containing unsaturated polyester polyols and polypropylene glycol in their backbone have often been used to graft acrylate monomers onto the main chain[94]. Though grafting is a useful technique by which to modify a polyurethane ionomeric dispersion, there are a limited number of polyurethanes which contain unsaturated polyester and polypropylene glycol segments.

Alternatively, polyurethane ionomeric dispersions can be modified by block copolymerisation. For this, NCO-terminated urethane prepolymers containing potential ionic groups are first capped with a reactive diluent, such as 2-hydroxyethyl acrylate (HEA) *via* polyaddition. The potential ionic groups are then neutralised and terminal HEA moieties are polymerised with various acrylate monomers, *via* a radical-polymerisation mechanism. The resulting block copolymers of polyurethane ionomers and polyacrylates are dispersed in water to obtain acrylate modified aqueous polyurethane dispersions.

2.9.2 Internal crosslinking

The properties of the films obtained from aqueous polyurethane dispersions can also be improved by internal crosslinking. Internally crosslinked polyurethane dispersions can be made by using polyfunctional amines as chain extenders[95,96]. Graft and block copolymerisation methods are most often employed. The properties of polyurethane dispersions can also be modified by blending and interpenetrating polymer network formation.

For the internal crosslinking of aqueous polyurethane dispersions by emulsion polymerisation, first vinyl-terminated aqueous polyurethane dispersions were prepared from aliphatic diisocyanate, polyol, ionic diol and hydroxy acrylate. Suitable vinyl monomers and initiator were added and polymerised to obtain crosslinked aqueous polyurethane dispersions[97-100].

2.9.3 Latex interpenetrating network (IPN) polymers

The internal crosslinking of polyurethane dispersions through IPNs can be carried out as follows. First, an aqueous dispersion of an hydrophilic, isocyanate-terminated prepolymer is prepared. Then a suitable initiator, monomer and its crosslinker are added and the system polymerised to give latex-based IPNs. IPNs of polyurethane-polymethylmethacrylate have recently been prepared to study metastable phase diagrams of IPNs[101].

2.9.4 Radiation curing of polyurethane dispersions

Compared to thermal curing, the ultraviolet (UV) curing of coatings saves energy and eliminates, or at least reduces, solvent emission. The UV-curing technique has therefore become commercially important in areas of protective coatings[102]. Most commercial UV-curing systems use acrylic-based monomers and resins, which are cured by a free-radical mechanism. Recently there has also been a growing trend in the area of water-based radiation curing of polyurethane dispersions[103]. The main reason for this is that the amount of acrylic monomer used as reactive diluent can either be greatly reduced or even eliminated. This implies that better physical properties of the derived cured systems are usually achieved. The low viscosity of aqueous polyurethanes is another advantage over the conventional, high viscosity, UV-curing type. The latter requires a very high proportion of reactive diluent to reduce workable viscosities, resulting in a corresponding decrease in physical properties.

To prepare the water-dispersible polyurethane acrylates, prior to emulsification, the -NCO-terminated polyurethane ionomer is reacted with a hydroxy acrylate. The mixture of emulsified polyurethane acrylate, reactive diluent and photoinitiator is then applied to the substrate and irradiated. Considerable work has recently been done to develop water-soluble and co-polymerisable photoinitiators for aqueous dispersions[104].

2.10 Polyurethane macroiniferters

Interest in block copolymers obtained from two different polymerisation techniques is a growing field, since block co-polymers exhibit a wide variety of physical and chemical characteristics. All block co-polymers cannot be synthesised in a single step since the one block is formed from a condensation product and the other block from addition polymerisation[105,106].

To incorporate the desired chain length and improve chemoselectivity, a new concept in "living" radical polymerisation using iniferters has been proposed. Two of the advantages of living radical polymerisation are that the Trommsdorff (auto-acceleration) effect does not occur since radicals formed during bulk polymerisation are mostly consumed by scavengers through primary radical reversible termination and, using iniferters, polymers can be synthesised at temperatures above their ceiling temperature.

An iniferter is an initiator, transfer agent and/or terminator in radical polymerisation[107]. According to the proposal made by Otsu and Yoshuda[108], an iniferter is an *ini*tiator and trans*fer* agent (inifer) or/and an *ini*tiator and *ter*minator (initer) and, since it is difficult to distinguish between the two, the combined term 'iniferter' was proposed. Tetraphenylethane and disulphide derivatives are typical iniferters for living radical polymerisations. Tetraphenylethane derivatives generate radicals through homolytic cleavage of their central ethane bond. Tharanikkarasu et.al[109] synthesised polyurethane iniferter using a diisocyanate and 1,1,2,2-tetraphenyl-1,2-ethane diol. This iniferter was used to polymerise vinyl monomers.

2.11 Properties and advantages of polyurethane dispersions

Dispersions of polyurethanes free of emulsifiers are insensitive to heat, shear forces and diluents and, as a result, the dispersion can be heated, stirred or mixed with organic solvents. This makes the use of polyurethane dispersions superior to that of any conventional emulsions as a pigment grinding medium in coatings and printing ink[110]. The film-forming abilities of polyurethane dispersions are good, even with hard polyurethanes, due to their small particle-size and surface hydration. Other advantages of polyurethane dispersions include: freedom from organic solvents, simple pigmentation, good abrasion resistance, elasticity, water vapour permeability, sorption behaviour and good tensile strength with elongation.

2.12 Applications of polyurethane dispersions

Aqueous polyurethane dispersions are predominantly used in areas where conventional solvent-borne polyurethanes are used. To reduce pollution, solvent-borne polyurethanes are being increasingly replaced by water-borne dispersions. The earliest application of aqueous polyurethane dispersions was for textile coating, which is still one of the largest market areas[111]. The nap side of woven or knitted fabric is coated using a direct- or transfer-coating process.

Textile fibres can be treated with aqueous polyurethanes to improve tensile strength and resistance to dry cleaning solvents[112] and aqueous detergent solutions[113]. Coagulation of films of aqueous polyurethane dispersions and subsequent lamination onto textiles result in poromerics. Poromerics are microporous plastics which are permeable to air and water vapour, but impermeable to water. Poromerics are used as coatings on split leather, and especially in the preparation of leather substitutes. Polyurethane dispersion coatings are used on leather because of their good gloss, flexibility, low temperature characteristics and scratch resistance[114]. Aqueous polyurethanes have also been known to provide shatterproof coatings for glass bottles and glass lamps[115] and cathode ray tubes[116]. Paper fibres are sized with aqueous polyurethanes to increase the strength of the paper as well as to reduce the tendency of ink to run on the surface[117]. Isocyanate- or blocked isocyanate-containing polyurethanes show excellent adhesion to cellulose materials. Wood coatings, especially for flooring, are made from aqueous polyurethanes as such or with waterborne acrylics. Polyurethane coatings provide high gloss, have high abrasion resistance and high fouling resistance. Organic solvents aggressively attack many plastic surfaces. To overcome this, aqueous polyurethane dispersions having good adhesion properties are used for plastic coatings. For adhesive applications, aqueous polyurethane dispersions have been used for a number of polymer substrates, usually in combination with other polymers to lower costs. Polyurethane ionomers have good adhesion to natural and synthetic rubber surfaces and can be used in the manufacture of footwear. Polyurethane ionomeric dispersions have been used as media in which monomers have been polymerised. This technique is known as latex interpenetrating polymer network, as mentioned in section 2.9.3, and is useful to control the phase separation. Cationic electrodeposition coatings are widely used for automotive metal primers, which provide excellent corrosion resistance to car bodies. Aqueous polyurethane dispersions are also used for wire coatings, metal coatings and as primers for coil coatings[118].

2.12.1 Coil coatings

In the history of coil coatings, the first coil-coating line was that of J. Hunter, constructed in 1935 to coat Venetian blind slats in a continuous process[119]. Today coil coating is one of the largest single users of paints and pre-treatment chemicals. It was in no way an invention nor a discovery but was developed from several well-known and well-established processes and techniques[120-123].

Roller coating, the paint-application method used almost universally in coil coating has become the standard method for coating at high speeds (150-250 m/min). It is an industrial pre-finishing process in which large coils of aluminium or steel strips are treated and fully finished with a baking enamel for subsequent fabrication into finished end products. It eliminates the need for the metal fabricator to perform a slow and costly finishing operation after the products have been shaped and assembled. Coil coating is a continuous process by which an organic coating (liquid or film) is applied to a sheet of metal. This technology is based on the simple fact that it is easier to pre-coat a flat surface than to post-paint an irregular-shaped component after fabrication. Coils of steel, often precoated with a metallic layer (e.g. zinc), or coils of aluminium weighing up to 20 tons are fed through purpose-built lines at speeds of up to 200m per minute where the substrate is chemically pre-treated before an organic coating system is applied to one or both sides of the strip. This results in a product of consistent quality, with excellent formability, durability, corrosion and weathering resistance[124]. Coil-coating development is one of the most important and difficult challenges that the coating industry has had to face and continues to encounter. The coil-coating process itself makes exacting demands on the application properties of the wet paint and the curing properties. In addition, the coating must survive coiling and uncoiling, and the cutting, forming and assembly of the coated metal without losing its appearance and resistance properties needed for uses such as building panels and domestic appliance coatings.

The typical sequence of a coil-coating line is usually:

- cleaning and pre-treatment of coil;
- application of primer by roller coater;
- stoving;
- application of top coat and baking coating;
- stoving;
- recoiling.

2.12.2 Coil coating requirements

Film flexibility is the overriding requirement for paints that are to be used in coil coatings. Post-forming can involve operations that are quite severe. Sometimes the coated metal may have to undergo embossing, roll forming, drilling, cutting, brake forming, drawing and stamping during the fabrication process. In some cases the coatings may be required to withstand deformation to nearly the limits tolerated by the metal. As at least 65% of the coated coil produced is destined for exterior application, hence durability is a further important requirement. This includes resistance to fading, chalking, gloss retention, erosion and dirt pick-up. Coating requirements for intended areas of application mean that great care must be taken in modelling studies for extreme situations such as in areas where the temperature of the coated steel exceeds 80°C during summer, as in most African countries. For example, a coated aluminium panel heated in the hot sun during the day and cooled during night shows significant dimensional changes because of the high heat-transfer coefficient of the metal (0.461g.cal/(sec)(cm^2)(°C/cm) at 0°C). The coating must therefore withstand these dimensional changes without cracking, losing adhesion, and without softening. Condensation of dew must also be taken into account. Most traditional coil coatings comprise solvent-borne epoxy primers and topcoats based on unmodified or silicone-modified solvent-borne polyester resins. Concern about the safety and toxicity of the solvents used is becoming an environmental issue. Legislation to limit VOCs is forcing the industry to develop a water-borne coating system which can substitute the present solvent-based formulations.

2.13 Health aspects and hazards of isocyanates

Isocyanates are generally considered as very toxic chemicals and great care must be exercised in handling them. Careless handling causes disastrous consequences. On the 3rd December 1984 water was pumped, mistakenly, into a bulk storage tank of methyl isocyanate in Bhopal, India. The released isocyanate cloud killed more than 3500 people in just one day.

Relatively low concentrations of isocyanates irritate the cylindrical epithelium of the respiratory tract, whereas, irritations of the squamous epithelium of the skin occur only after prolonged exposure to rather high concentrations of isocyanates. The digestive tract, with its squamous epithelium in the upper section and the high amount of digestive fluid, is highly resistant to larger amounts of isocyanate.

The toxicity of isocyanates when inhaled or in contact with skin varies considerably. Chemical reactivity and biological effects do not correspond. The more chemically reactive aromatic isocyanates, like TDI, cause less skin irritation than, say aliphatic HDI. Even in the isomeric family, the more reactive 2,4 isomer of TDI has less respiratory irritation than the less reactive 2,6 isomer. With the exception of HDI derivatives, the inhalation toxicity of modified isocyanates is generally lower than that of the monomer, due to the reduction in vapour pressure during modification. The maximum concentration that is considered to cause fatal death is in excess of 50ppm[2].

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Chapter 3

Experimental: Synthesis of self-assembling polyurethanes

3.1 Introduction

The synthesis of linear, segmented polyurethane resins for coatings applications requires that all reacting monomers, processing solvents and intermediates be free from moisture and primary carboxylic acids. This is because during polyurethane synthesis a number of competitive secondary side reactions take place. These include the formation of dimers and trimers, acylurea, allophanates, amide and carbamic acid derivatives. It is imperative that any traces of moisture be eliminated or at least minimised to below 0.1%. The reaction between a urethane group and an isocyanate, a typical competitive reaction in the preparation of linear segmented polyurethanes, is temperature dependent and can easily be controlled by processing at lower temperatures[1]. Whilst it is difficult to avoid side reactions, it is certainly possible to ensure that the reactants are free from acid groups and moisture. Processing polyester macroglycols to low acid values (generally below 5 mg KOH/gm) eliminates the presence of acids and subsequent drying of all monomers under vacuum will help to reduce the moisture content.

When a water molecule reacts with an isocyanate group, a primary amine and carbon dioxide are formed.

$$\text{R-NCO} + \text{H}_2\text{O} \longrightarrow \text{R-NH-COOH} \longrightarrow \text{R-NH}_2 + \text{CO}_2$$

This common major side reaction results in foaming, which is detrimental in bubble-free coatings and continuous surface coatings [2,3]. The amino groups formed can again react with other isocyanate groups and form urea linkages. This process continues until a three-dimensional network is formed, which cannot be used for coatings. In the following sections, the syntheses of different polyester macroglycols and linear, segmented polyurethanes will be described.

3.2 Synthesis of the soft segment macroglycols

Two types of polyester macroglycol soft segments will be synthesised. The synthesis procedures are outlined in sections 3.2.2 and 3.2.3.

3.2.1 Chemicals used

The chemicals used in the syntheses of the different macroglycols, to be used in the subsequent urethane-forming reactions, are listed in Table 3.1

Table 3.1 Chemicals used for the syntheses of the soft segment macroglycols

Chemicals	**Common Name**	**Suppliers**	**Supply form**
2,2-dimethyl propane diol	Neopentyl glycol	Perstorp Polyols, Sweden	Flakes
Hexanedioc acid	Adipic acid	ICI	Free flowing powder
5-(sodiosulfo)isophthalic acid	5-SSIPA	Eastman Chem. (USA)	Free flowing powder
1,4-cyclohexane dicarboxylic acid	CHDA	Eastman Chem. (USA)	Free flowing powder
1,2,4-phosphonobutane tricarboxylic acid	Bayhibit AM	Bayer Corporation	50% solution in water

3.2.2 Synthesis of a sulphonated polyester macroglycols

The synthesis of ion-containing polyester macroglycol soft segments requires the selection of monomers that can sustain melt condensation reaction temperatures for at least 10 hours without degrading and losing their ionic content and efficiency. Generally, co-reacting ion-containing monomers with carboxylic acids and glycols to form polyester resins in a melt condensation process is difficult due to the degradation of the ionic groups at high temperatures[4]. Some of the available ion-containing monomers cannot be easily esterified due to the absence of functional groups. Monomers with ionic groups attached to a thermally-stable phenyl ring are, in terms of thermal stability, the best candidates for making ion-containing macroglycols. 5-(sodiosulfo)isophthalic acid can easily be incorporated into a polyester backbone under standard reaction conditions of esterification through its dicarboxylic acids, to yield non-alkaline water-dispersible polyester resins.

The sulphonated polyester macroglycols used as the ionic soft segment component of segmented linear polyurethanes were synthesised by a conventional melt-condensation method. The mass percentages of the monomers used are tabulated in Table 3.2

Table 3.2 Compositions of the sulphonated polyester and control macroglycols

Chemicals	**Mass %**					
	MG-1	**MG-2**	**MG-3**	**MG-4**	**MG-5****	**MG-6****
2,2-dimethyl propane diol	45	45	45	45	45	45
Hexanedioc acid	50	45	40	25	50	45
5-(sodiosulfo)isophthalic acid	5	10	15	20	0	0
Isophthalic acid	0	0	0	0	5	10

**: Control, MG: Macroglycol

Table 3.3 The analytical values of the sulphonated polyester and control macroglycols

Analytical values	**MG-1**	**MG-2**	**MG-3**	**MG-4**	**MG-5****	**MG-6****
Acid value, mg KOH/gm	3.5	3.2	3.4	3.5	3.3	3.7
Final OH-number, mg KOH/g	85	87	90	88	82	80
Molecular weight, Mn	2200	2000	2000	2300	2000	2000
Polydispersity, Mw/Mn	1.83	2.10	1.98	2.15	2.31	2.25

**: Control, MG: Macroglycol

The above sulphonated polyesters and the control macroglycols were processed in a two-stage polycondensation reaction. Due to the electron-withdrawing nature of sodiosulfo groups, 5-(sodiosulfo)isophthalic acid is highly acidic, compared to isophthalic acid[5]. Therefore, it was important to first react 5-(sodiosulfo)isophthalic with excess 2,2-dimethyl propane diol to completely react the acid groups. The reaction was carried out in a standard 3L-reaction vessel equipped with a charging and sampling port, a nitrogen inlet and outlet, cooling and decanting ports. The reaction was carried at 200^0C for 5 hours, to bring the acid value to below 0.5mg KOH/gm, and then the batch was cooled to 145^0C and hexanedioc acid was added. The temperature was then raised to 220^0C and kept there until the acid value reached below 5 mg KOH/gm. The idealised structures of the sulphonated polyester macroglycol and the control are presented in Figures 3.1 and 3.2

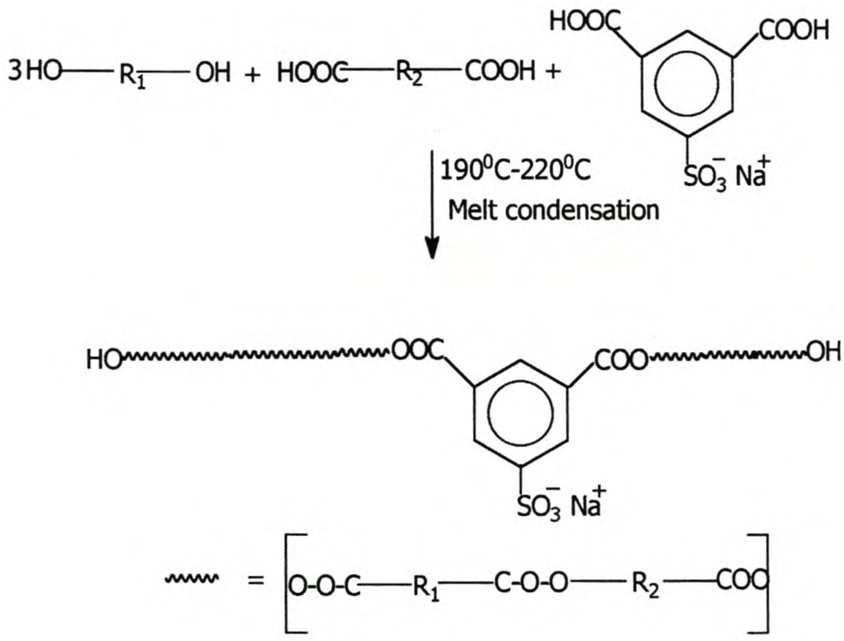


Figure 3.1 Idealised structure of the sulphonated polyester macroglycol

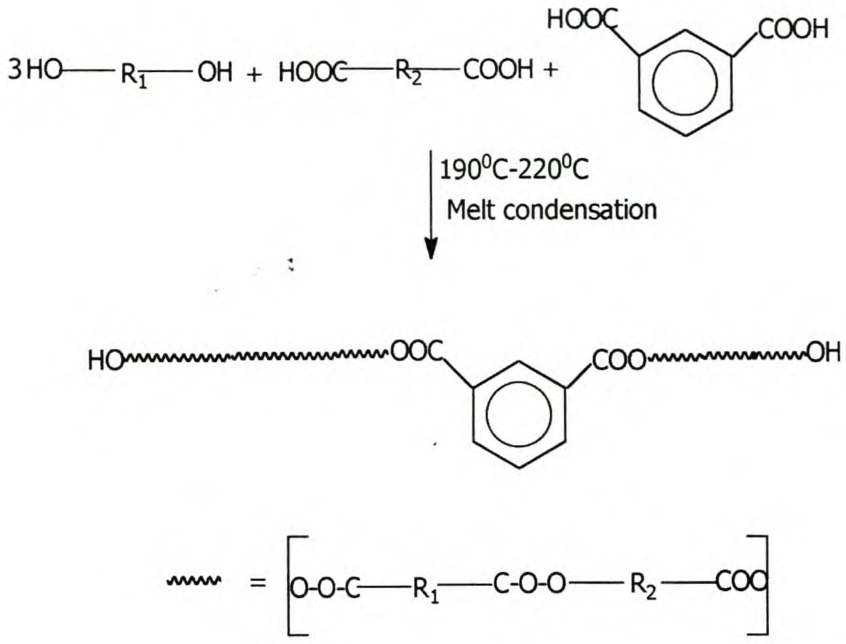


Figure 3.2 Idealised structure of the control polyester macroglycol

When isophthalic acid was used instead of 5-(sodiosulfo)isophthalic acid, all the raw materials were charged and heated to the desired esterification temperatures, 220^0C, until the reaction was completed.

3.2.3 Synthesis of a phosphated polyester macroglycols

The synthesis procedure for the phosphated macroglycols with different compositions is well documented by Mequanint and Sanderson[6]. The mass percentages of reactants used for the synthesis of phosphate-containing polyester macroglycols are listed in Table 3.4.

A typical reaction procedure involves charging a 3L- glass reactor with all the reactants and heating to the desired esterification temperature (ca 215-225^0C). During heating, the water from the 1,2,4-phosphonobutane tricarboxylic acid was first distilled at 105^0C and then the temperature was gradually increased by 10^0C/30 min until it reached 215-225^0C. In the reaction between a polybasic acid and a polyhydric alcohol to form esters, water is liberated as a by-product. It was important to remove this water to drive the reaction equilibrium towards the ester formation.

$$R_1\text{-}COOH + R_2OH \rightleftharpoons R_1COOR_2 + H_2O\uparrow$$

It was very difficult to remove the last traces of water from the product and a slight vacuum had to be applied to drive the forward reaction. From calculations based on the number of charged moles, a large decrease in reaction rate was observed below an acid number of 35-mg KOH/gm. When vacuum is applied during the synthesis, all the remaining water, any excess free diols and side-reaction products such as lower molecular weight ethers, ketones and aldehydes were distilled off. The phosphated-polyester macroglycols with terminal hydroxyl groups, synthesised as described above, were degassed at 90^0C and under reduced pressure then used for the synthesis of linear segmented polyurethanes.

Table 3.4 Mass percentages of the reactants used for the syntheses of phosphate-containing polyester macroglycols

Chemicals	**Mass % of the reactants**				
	*PMG-1	PMG-2	PMG-3	PMG-4	PMG-5
2,2-dimethyl propane diol	48	50	50	50	50
Hexanedioc acid	20	20	20	20	20
1,4-cyclohexane dicarboxylic acid	20	16	14	12	10
1,2,4-Phosphonobutane tricarboxylic acid	12	14	16	18	20

*PMG: phosphated macroglycol

Table 3.5 The analytical values of the phosphated polyester macroglycols

Analytical values	***PMG-1**	**PMG-2**	**PMG-3**	**PMG-4**	**PMG-5**
Acid value, mg KOH/gm	7	8	7.8	8.4	9.1
Final OH-number, mg KOH/g	100	105	110	95	104
Molecular weight, Mn	2500	2500	2550	2600	2500
Polydispersity, Mw/Mn	2.3	2.42	2.45	2.5	2.52

*PMG: phosphated macroglycol

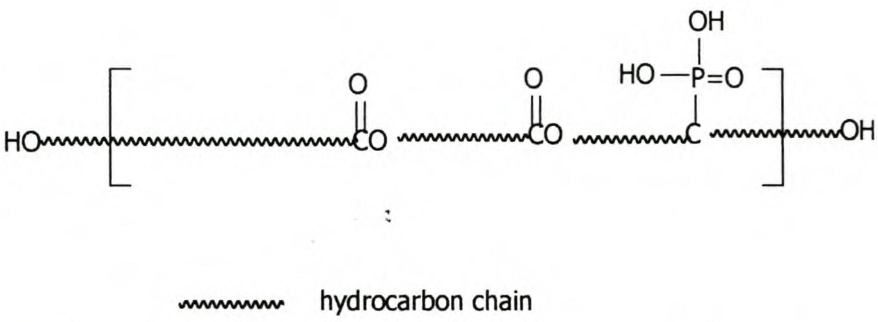
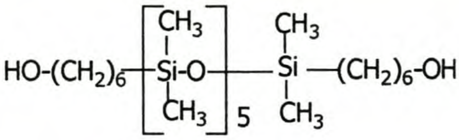


Figure 3.3 Idealised structure of the phosphated polyester macroglycol

3.2.4 Polydimethyl siloxane macroglycol

Silicone-based polymers are well known for their thermal stability and weatherability, good dielectric properties and low surface tensions. The silicone chains are non-polar and have very limited compatibility with polyesters/urethanes and other commercial polymers. α,ω-Diol polydimethylsiloxane, with the structure shown below, was used to synthesise self-assembling polyurethanes. The macroglycol has 5.6% OH corresponding to an OH number of 180mg KOH/gm.



$$\mathrm{HO{-}(CH_2)_6}\left[\mathrm{Si(CH_3)_2{-}O}\right]_5\mathrm{Si(CH_3)_2{-}(CH_2)_6{-}OH}$$

3.3 Synthesis of segmented polyurethanes

In general, the prepolymer and the solvent methods are available for synthesising segmented polyurethane ionomers intended for dispersion in water[7]. Each method has its own benefits and drawbacks, depending on what is required from the final dispersion. The prepolymer method results in more defined segmented polyurethanes and uses a small quantity of solvents, but the particle size distribution of the emulsion is generally broad[8]. The solvent method, on the other hand, permits the preparation of dispersions with uniform particles but the solvent resistance of the cast emulsion film is generally inferior and the recovery of large volumes of organic solvents is a problem.

3.3.1 Chemicals used

All the intermediate chemicals used for the synthesis of polyurethane ionomers are listed in Table 3.6. The polyester macroglycols were heated to 90^0C and degassed under reduced pressure for 1 h prior to use. Dicyclohexane-methane-diisocyanate (H_{12}MDI), 1,2-ethane diol, 2,2-hydroxymethyl propionic acid and all the neutralising bases were used as received. Butanone was dried over 4Å molecular sieve before use.

Table 3.6 Materials used to synthesise the segmented polyurethane ionomers

Chemicals	**Suppliers**
Sulphonated polyester macroglycol	Experimentally synthesised (section 3.2.2)
Phosphated polyester macroglycol	Experimentally synthesised (section 3.2.3)
α,ω-Diol polysiloxane macroglycol	Goldschmidt AG, Germany
2,2-Hydroxymethyl propionic acid	Perstorp Polyols, Sweden
1,2-Ethane diol	BASF
Dicyclohexane-methane-diisocyanate	Bayer AG, Germany
Trimethylamine	Merck
Triethylamine	Merck
Tripropylamine	Merck
Tributylamine	Merck
Triisobutylamine	Aldrich
Tripentylamine	Aldrich
N,N-dimethyldodecylamine	Aldrich
Morpholine	Aldrich
Lithium hydroxide	Saarchem
Sodium hydroxide	Saarchem
Potassium hydroxide	Saarchem
Butanone	Saarchem

3.3.2 Synthesis of segmented polyurethanes from sulphonated polyester macroglycols

The segmented sulphonated polyester-urethane ionomers prepared here are a special class of ionomers since the ionic groups are on the soft segment. In segmented polyurethane ionomers, the ionic groups are located on the hard segment[9] and their presence enhances phase segregation due to the increased polarity. Literature[10] revealed that ionisation of the polymer takes place in the hard domains because of the ease of incorporating the ionic moieties. Recently Wei *et.al*[11,12] synthesised polyoxylated amine and sulphonated polyether-based polyurethane ionomers. They focused their study on the solid-state ionic conductivity and dispersion in water was overlooked. In the present study of sulphonated polyester-urethanes, the ionic groups are bound to the soft segment.

The preparation of sulphonated polyester-urethane ionomers, where the ionic groups are located on the soft segment is described here. Dicyclohexane-methane diisocyanate and ethane diol were charged and heated to a temperature of 80^0C for 2 h to yield a urethane prepolymer with terminal isocyanates. The sulphonated polyester macroglycol, prepared as described in section 3.2.2, was then added into the reactor. Butanone (30% by weight) was added to reduce the viscosity, and the temperature maintained at 80^0C for 4h. The reaction progress was measured by the disappearance of the -NCO peak at 2265/cm from the infrared spectra. After 4h of reaction, the temperature was reduced to 60^0C and water was added to form the dispersion. As the viscosity increased during the addition of water, the stirrer speed needed to be increased. After the dispersion formed, butanone was removed by rotary evaporation under reduced pressure.

Polyurethane dispersions with hard segment contents of 20-50% and ionic contents of 3-8% on the soft segment were synthesised.

3.3.3 Synthesis of segmented polyurethanes from phosphated polyester macroglycols

A 1L-glass reactor equipped with a nitrogen inlet and outlet, condenser, mechanical stirrer, charging and sampling port, was charged with 2,2-hydroxymethyl propionic acid, 1,2-ethane diol and dicyclohexane-methane-diisocyanate. The reaction mixture was heated in an oil bath to 100^0C. The urethane-forming reaction proceeded at this temperature for 1½ h to form –NCO-terminated hard urethane segments. After 1.5 h, the temperature was reduced to 80^0C and a butanone solution of the phosphated polyester macroglycol, prepared as described in section 3.2.3, was added. The temperature was kept at 75-80^0C for a further 3 h. After the –NCO peak disappeared from the infrared spectra at 2265/cm, the reaction was cooled to 60^0C and a neutralising base was added. Dispersion into water was done at different temperatures (30-60^0C) and the butanone distilled off. Polyurethane ionomers with bound carboxylate ions on the hard segment were obtained. The hard segment content was 20-50% and the ionic content was 3-8%.

3.3.4 Synthesis of segmented polyurethanes from polydimethylsiloxane macroglycol

The method of synthesis, segment content and ionic content were the same as those described in section 3.3.3, except that the α,ω-diol dimethylsiloxane was used as the soft segment.

3.3.5 Synthesis of segmented polyurethanes from mixed macroglycols

A similar procedure described in section 3.3.3 was used for the synthesis of polyurethane from mixed macroglycols. Here the soft segments were mixtures of phosphated polyester macroglycols and α,ω-diol dimethylsiloxane, in different ratios. α,ω-Diol dimethylsiloxane to phosphorus-based macroglycol ratios of 95/5 to 5/95 were chosen.

3.4 Copolymerisation of acrylic monomers with phosphated and/or siloxane-based segmented polyurethanes

3.4.1 Introduction

Polymer modification to bring about specific properties is a growing field. Though polyurethanes do have good mechanical properties, modifications with acrylics can improve certain properties and may combine the best properties of the two polymers. Efforts made to copolymerise acrylic monomers with polyurethane ionomers will be described here. This technique of co-polymerising acrylic monomers onto a polyurethane ionomer can also eliminate the use of large volumes of organic solvent and the distillation process.

3.4.2 Chemicals used

The following chemicals were used for the preparation of acrylic-modified phosphated-urethane ionomers and/or phosphated-siloxane-urethane ionomers.

Table 3.7 Chemicals used to prepare of phosphated and/or siloxane-modified polyurethane acrylic dispersion

Chemicals	**Suppliers**
Phosphated polyester macroglycol	Experimentally synthesised as described in section 3.2.3
α,ω-Diol polysiloxane macroglycol	Goldschmidt AG, Germany
Dicyclohexane-methane-diisocyanate	Bayer, Germany
2,2-Hydroxymethyl propionic acid	Perstorp Polyols, Sweden
2-Hydroxyethyl methacrylate (2-HEMA)	Mitsubishi Rayon, Japan
Methylmethacrylate (MMA)	Mitsubishi Rayon, Japan
Ethylmethacrylate (EMA)	Mitsubishi Rayon, Japan
n-Butylmethacrylate (BMA)	Mitsubishi Rayon, Japan
Ethylene glycol dimethacrylate (EGDMA)	Inspec, UK

The macroglycols were degassed at 90^0C overnight under reduced pressure to remove any moisture. The other chemicals were used as received.

3.4.3 Copolymerisation of acrylic monomers using the phosphated polyurethane dispersion as the 'seed' in the aqueous dispersed phase

A 3L-glass reactor equipped with a mechanical stirrer, a charging and sampling port, a nitrogen inlet and outlet was charged with the phosphated polyester macroglycol and/or α,ω-diol polysiloxane macroglycol and excess dicyclohexane-methane-diisocyanate. The reaction took place at 95^{0}C over 1½ h. This temperature was maintained to avoid any competitive secondary reactions, as highlighted in Chapter 2. After 1½ h, 2,2-hydroxymethyl propionic acid was added and allowed to react with the –NCO for 1h. The temperature was reduced to 60^{0}C and methylmethacrylate (ethylmethacrylate, n-butylmethacrylate and ethylene glycol dimethacrylate were also used) was added to reduce the viscosity. Finally, 2-hydroxyethyl methacrylate was added and allowed to react with the –NCO for 2h, to complete the reaction. The reaction temperature was kept to 60^{0}C to prevent thermal polymerisation of C=C. The acid groups of the 2-hydroxy ethylmethacrylate-terminated polyurethanes were neutralised and water was added to form the dispersion. Internally crosslinked phosphated-polyurethane-acrylate particles were obtained by adding an aqueous solution of 0.5% potassium persulphate (based on the total solids content) into the aqueous dispersion over 1hr at 65^{0}C. The emulsion polymerisation reaction was carried out for 5h.

3.4.4 Ultraviolet (UV)-curable polyurethane-acrylic dispersions

The above phosphated polyurethane-acrylic dispersions (section 3.4.3) before, emulsion polymerisation, were cured by means of UV. The aqueous dispersion and a photoinitiator were mixed and the metal substrate was coated and cured under UV light.

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Chapter 4

Experimental: Characterisation of self-assembling polyurethanes

4.1 Introduction

Characterisation of self-assembling phosphated and siloxane-modified polyurethane dispersions prepared for coatings applications requires an understanding of the mechanism by which the dispersion is formed and the subsequent properties of the self-assembling coatings. It is not often that a single characterisation technique can reveal full information on a specific property profile; and a number of complimentary techniques have to be used to obtain adequate understanding of the dispersion characteristics and the interface properties of the coatings obtained from the dispersions.

In this study a number of characterisation techniques were employed to understand the dispersion properties and the self-assembling properties of the novel multi-component phosphated and siloxane-modified polyurethane dispersion coatings intended for metal protection.

4.2 X-ray Photoelectron Spectroscopy (XPS)

X-ray photoelectron spectroscopy (XPS) employs soft x-rays to detach electrons from a film or powder surfaces. The difference in energy between the incident x-rays (*hν*) and the kinetic energy of the emitted electron (E_{kim}) is equal to the binding energy (E_B) of the electrons.

$$E_B = h\nu - E_{kim} \text{............equation 4.1}$$

During XPS analysis, two types of electrons are emitted: those from the inner core and the more loosely held valence electrons. When the photon ejects the inner electron (photoionisation), the effective increase in nuclear charge causes a reorganisation of the valence electrons, resulting in the excitation of these electrons from an occupied to an unoccupied level and the loss of valence electrons. The emitted electrons can be analysed by an electrostatic analyser at 10^{-10} - 10^{-7} torr to preclude electron scattering. Since XPS plots intensity against binding energy of the inner core electrons, it provides surface mapping. However, if surface characterisation deeper than 50Å is required then sputtering has to be used.

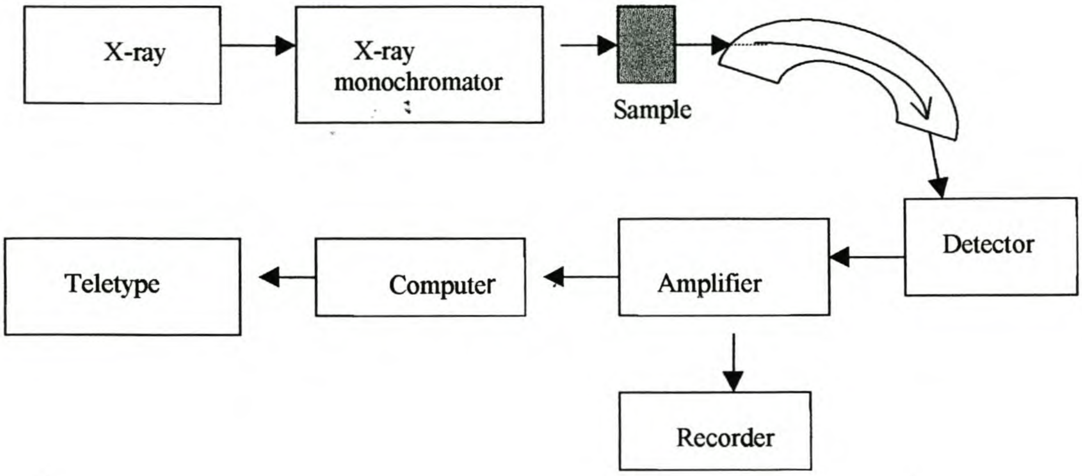

Figure 4.1 Basic principle of XPS [1]

4.2.1 Sample preparation and instrumentation

Coatings were prepared in very thin layers (2-3µ) by dipping the hot-dipped galvanised steel into 5 % aqueous dispersions of the phosphated and siloxane-modified polyurethane and drying at 60^0C for 1h. 1cm x 1cm samples were cut and loaded into the Quantum 2000 Intro chamber, which was then evacuated. Narrow spectra of the samples were recorded by using Quantum 2000 Scanning ESCA Microprobe (PHI). The source of X-rays was monochromated Al kα (1486.6eV), 15kV. Quantitative data was calculated from the peak areas for each element. Depth distributions were obtained by changing the take-off angle from 5 to 90 degrees. For information on depths greater than 70 Å, samples were Ar^+ ion-sputtered (2kV Ar^+ ions, sputtering rate 14nm/min) to remove approximately 30nm of the top surface. After the sputtering step, narrow spectra of the samples were recorded and quantitative data was calculated from the peak areas of each element. This was repeated several times to obtain a depth profile.

4.3 Energy Dispersive X-ray Spectroscopy (EDX)

Energy Dispersive X-ray Spectrometry relies on the proportional property of a suitable detector to give a distribution of photon energies from the sample[2]. The major components of energy dispersive X-ray spectrometry are the primary X-ray source (primary X-ray tube sealed and powered by a high voltage generator), the spectrometer itself and the detector. The critical factor in assessing the ability of an energy-dispersive instrument to separate one energy from another is its resolution, R, which is related to energy, E, by

$$R=(K_1+K_2E)^{1/2} \quad \text{............equation 4.2}$$

where, K_1 is the noise level of the instrument and

K_2 is the true statistical function of the Si(Li) detector.

The instrument is particularly suitable for rapid qualitative analysis and is non-destructive. As the electrons from the filament hit the sample, it excites the inner shell electrons into a higher energy level. The electrons at the higher energy level are, however, not that stable and spontaneously return to the lower energy level by losing energy. The energy difference is then emitted in the form of X-rays.

4.3.1 Sample preparation

While XPS provides information on self-assembly at the coating/air interface and depth distributions, EDX was primarily used to characterise the self-assembly at the metal/coating interface and study the formation of metal phosphate by the polymer and the untreated metal. Samples for EDX analysis were prepared by dipping the metal plate into a 5% aqueous dispersion of phosphated and siloxane-modified polyurethane and dried at 75^{0}C for 12h under vacuum. The coatings did not contain any crosslinker and the dispersions used here were linear polymers that were soluble in tetrahydrofuran (THF). As a result, the coating was also soluble in THF. The metal phosphate so formed was evaluated after the coating layer was fully etched by THF for 6h. To prove the solubility of the polymer in THF after drying at 75^{0}C, a separate sample was kept in an aluminium dish for 12h at 75^{0}C, then re-dissolved in THF and filtered. No gel formation on filtration was detected.

EDX analysis of the interface was done with a Topcon ABT-60 Link model 5079, using a 25kv beam equipped with a 0.008 Be window. The detector area was 10mm^2. Data was analysed and plotted using an AN 10000 Software X-ray analyser.

4.4 Dynamic Contact Angle Analyser (DCA)

Currently, one of the best methods available by which to characterise solid surface energies is by measuring the contact angles that a series of probe liquids make with the surface of interest. A Wilhelmy-type wetting force is used to measure advancing and receding contact angles. This method, which involves measurement of the wetting force of a probe liquid up and down on the surface of any flat solid samples give true advancing and receding contact angles. The more commonly used, non-moving sessile drop method does not adequately cover the polymer surface and a small amount of evaporation of the drop can also rapidly change the contact angle[3]. In this study, a CAHN DCA-322 analyser operating at 25^{0}C, with velocities ranging from 40μm/sec to 150μm/sec, was used to evaluate the self-assembly nature of the phosphated and siloxane-modified polyurethane coatings by contact angle measurements. The hot-dipped galvanised steel panels were cut to 1.5cm by 1.5cm size and dipped into a mixture of aqueous dispersions of approximately 10 % wt and a melamine crosslinker. The coatings were then hooked with a spring and suspended in a curing oven. Curing was done at 230^{0}C peak metal temperature for 20 seconds. In some instances, curing was not done and films were simply dried at 80^{0}C for 30min.

4.5 Fourier Transform Infrared Spectroscopy (FTIR)

Fourier Transform Infrared Spectroscopy (FTIR) was used to characterise emerging and disappearing functional groups in the synthesis of self-assembling phosphated and/or siloxane-modified polyurethane dispersions and ultraviolet (UV)-cured coatings of the polyurethane acrylate dispersions. The samples for infrared analysis were prepared by solution casting of the polymer onto KBr pellets.

Infrared spectra were obtained with a Fourier Transform Infrared Spectrophotometer (SHIMADZU FTIR, model 8101M) and recorded by averaging 32 scans at a resolution of 1/cm. For the cured coatings, a FTIR Nicolet Nexus with ATR (attenuated total reflectance) transmission-mode was used.

4.6 Dynamic Thermogravimetry (TGA)

Thermogravimetric Analysis (TGA) is especially useful for studying polymers and composite materials. It measures the amount, and rate, of change in the weight of a material as a function of temperature or time in a controlled atmosphere. TGA measurements are used primarily to determine the composition of materials and to predict their thermal stabilities at temperatures up to 1000^0C. TGA can characterise materials that exhibit weight loss or gain due to decomposition, oxidation or dehydration. Results of TGA analysis provide information on the composition of multi-component systems, the thermal and oxidative stability of materials, their estimated lifetime and decomposition kinetics.

TGA analyses of the phosphorous-containing polyurethanes were carried out using a TGA-50 SHIMADZU Thermogravimetric instrument with a TA-50WSI thermal analyser connected to a computer. 10-15mg samples were degraded in nitrogen or air (flow rate 50mL/min) at a heating rate of 2.5-10^0C/min.

4.7 Gel Permeation Chromatography (GPC)

Gel Permeation Chromatography (GPC) analyses, to determine the molecular weights of uncured polyurethane dispersions, were performed periodically to evaluate their hydrolytic stability. The molecular weight and the polydispersity of the macroglycols were also measured. Samples of the polyurethane dispersions were dried at 90^0C for 12h then dissolved in tetrahydofuran (THF) to the required concentrations. Two different GPCs were used for these analyses (due to availability at different times). The models and analytical conditions were as follows.

- GPC 1: Waters GPC equipped with RI detector (Waters 410), UV detector (Waters 486), Autosampler TSP AS 100, and Pump (Waters 515). The column temperature was 30^0C. The sample flow rate was 1ml/min and polystyrene standards were used to measure the molecular weight.
- GPC 2: Spectraphysics Model 3.90 with IR detector, 4 columns in series of pore sizes 100 Å, 500 Å, 1000 Å and 10000 Å. The sample flow rate was 1.25ml/min. The column temperature was 35^0C and polystyrene standards were used.

4.8 Measurements of conductivity

The conductivity measurements of the polyurethane ionomers, during the dispersion process of the ionomers, were measured in a digital conductivity probe Model TESTRONIX-15 from Manish Instruments and Chemicals, India. The instrument had a digital display unit, a progressive printout screen, and a 1000 HZ frequency Ac source. The probe was dipped into the ionomers before addition of water and conductivity change was recorded accurately.

4.9 Measurements of rheological properties

The rheological properties of the acrylic-modified phosphated and/or siloxane-based polyurethane solutions and dispersions were measured with a Brookfield viscometer, model LVTDV-II, over the prescribed temperature range. The viscometer was equipped with a small sample adapter that allows temperature control by means of a circulating water bath. Calibration was done with a viscosity standard supplied by Brookfield. The temperature of the solution was varied from 15-60^{0}C and the shear rate varied from 0-200/s, in increments of 40/s

4.10 Determination of viscosity changes during the dispersion stage

Changes in viscosity of the polyurethane ionomers, during neutralisation and addition of water, were measured by a Brookfield synchro-lectric viscometer with spindles LUT number 1-4.

4.11 Particle-size measurements

Particle-size measurements of the dispersions were done using Malvern Zetasizer Model 3000HS at 25^{0}C.

4.12 Atomic Force Microscopy (AFM)

AFM images were compiled on an Explorer TMX 2000 Atomic Force Microscope using a silicon tip (high-resolution) at a force constant of 30-80 N/m in the non-contact mode.

4.13 Measurements of gel content to determine the extent of crosslinking during UV curing

The gel contents of samples of cured films were determined by Soxhlet extraction using toluene as solvent. The solvent was refluxed for 6h and the insoluble material was dried under vacuum at 1mm Hg pressure and 90^0C overnight. The gel contents of the cured films were calculated from the differences in weight of sample before and after extraction experiments using the equation:

$$\text{Gel content (\%)} = \frac{W}{Wo} \times 100 \quad \text{.................equation 4.3}$$

where W is the weight of samples after extraction

W_o is the weight of samples before extraction

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Chapter 5

Structure-property relationships of polyurethane dispersions

5.1 Introduction

Due to their outstanding resistance to solvents and chemicals and good weather stability, polyurethane dispersions have been used extensively for coatings applications. Aqueous polyurethane dispersions continue to become industrially and economically more important as high quality coating polymers. They are environmentally compatible and safe to work with. Formulation of coatings without wetting agents is now also possible[1] since their pigment wetting properties are excellent.

Polyurethane dispersion ionomers are superior to those products in which conventional surface-active agents are used for emulsifying non-ionic hydrophobic polyurethanes. High and low molecular weight polyurethane ionomers are also good emulsifiers for emulsion polymerisation. Since the introduction of aqueous polyurethanes into the class of ionic polymers in the 1960s, research work has focused on their end uses rather than obtaining an understanding of their property relationships, especially the possibility of self-assembly.

In emulsion polymerisation, the role of each component, the mechanism of the reaction, including the kinetics, are well understood. However, there is very little information available on structure-property relationships of polyurethane ionomers for commercial applications. There is a gap between understanding traditional emulsion technology and polyurethane ionomers. Cooper et.al[2-6] have done extensive work on polyurethane ionomers but their characterisation studies were done mainly on solid-state sulphonated ionomers with the sodium salts attached, which is undesirable for coatings applications.

Whilst the end use of polyurethane dispersion ionomers in high quality coating systems has been driven by their outstanding performance over many of the waterborne dispersions and emulsions, basic property-relationships of these fascinating polymers are not well understood. As a result of this, it was deemed necessary to obtain a clear understanding of the mechanism of dispersion formation, the effects of the neutralising base on the stability and other properties, such as swelling, of these ionomers.

5.2 Emulsification mechanisms

Special methods are necessary for the production of polyurethane dispersions because of the thermodynamically unstable nature of these two-phase systems. A simple application of the well-known emulsion polymerisation techniques[7] for the preparation of isocyanate-based emulsion polymers is not possible, due to the reactivity of the NCO-group with water. Generally, it is the extreme water sensitivity of all polyurethane preparation procedures which often call for complete absence of water, that was a deciding factor for using the different emulsification method described here.

Unlike traditional emulsion polymerisation or even those so-called new generation emulsion polymers obtained from co-polymerisable surfactants and surface-active initiators, polyurethane emulsions are quite different due to the absence of water during their synthesis. They are prepared by a polyaddition reaction with or without organic solvent. The polymerisation locus is not the 'micelle' as the polymer is in discrete solution. However, post-polymerisation modifications allow these polymers made by polyaddition reactions to become water-dispersible emulsions.

The emulsification or phase-inversion of the polyurethanes in this study, from organic solution phase to aqueous phase, was found to take place in three stages. These are discussed below.

5.2.1 Stage one: Changes in viscosity during neutralisation

During this stage the polymer was fully reacted in an organic solvent (butanone). When calculated stochiometric amounts of the neutralising amine, triethylamine, was added to form the ionomers, the viscosity increased as shown in Figure 5.1

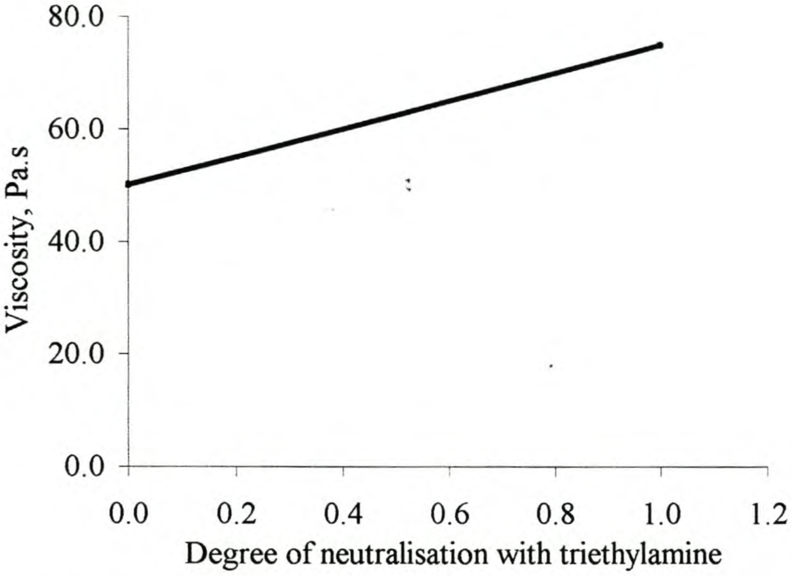

Figure 5.1 Increase in viscosity of phosphated-polyurethane resin upon neutralisation, 30% in butanone

However, neutralisation of the acid groups to convert the polyurethane into ionomer had no effect on molecular weight increase and the increase in viscosity was attributed to the formation of micro-ionic lattices. Micro-ionic lattices form as a result of inter- and intra-molecular coulombic interactions between the carboxylate groups, formed upon neutralisation of the acid groups of the stabilising monomer, and the positive counterions. Inter- rather than intra-molecular ion clustering is more likely because of the repulsion of the negative charges along a single chain[8]. Thus, as in the solid state where the ion association leads to pseudo-crosslinking and elasticity, the same phenomena was responsible for the anomalously high viscosity. This phenomenon was proved by the addition of small quantities of a high dielectric solvent, for example water, to the ionomers, which resulted in a sharp decrease in viscosity to below that before neutralisation. Ionic association is reversible and any water present solvated the ionic clusters and reduced the viscosity. This situation is shown in Figure 5.2

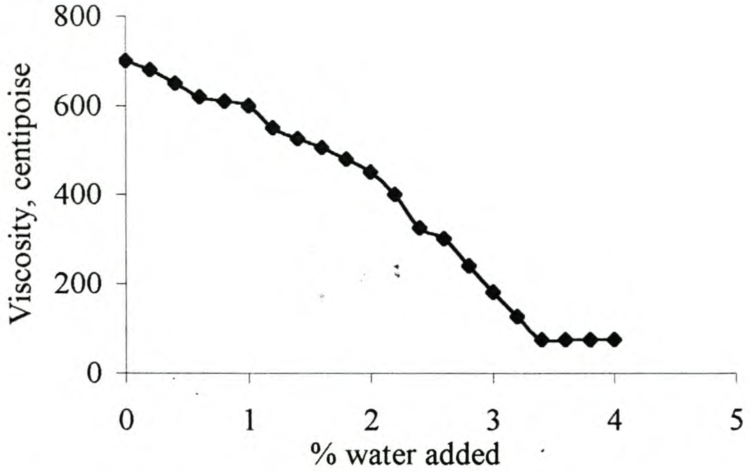

Figure 5.2 Decrease in the viscosity of a 10% solution of an anionic polyurethane in butanone on addition of water

5.2.2 Stage two: Changes in viscosity as concentration is reduced

As the agitation (stirrer) speed was increased and more water added, the viscosity again increased although the solids content decreased. Since the butanone concentration was reduced, the solvation sheath of the hydrophobic segments was also reduced. During this stage the viscosity increased to a maximum, as shown in Figure 5.3. At this stage as water was added, it was adsorbed by the carboxylate anions situated on the surface of the hard segment micro-ionic lattices, causing a separation of neighbouring chains and aggregates. Each micro-ionic lattice, which is considered to form in the organic medium, is an aggregation of unsolvated salt segments stabilised by coulombic forces[9]. As the amount of water was increased, it started to enter the interior of the more disordered hard segment micro-ionic lattices and, subsequently, the soft segment forms aligned hydrophobic aggregates, which eventually became the dispersed phase.

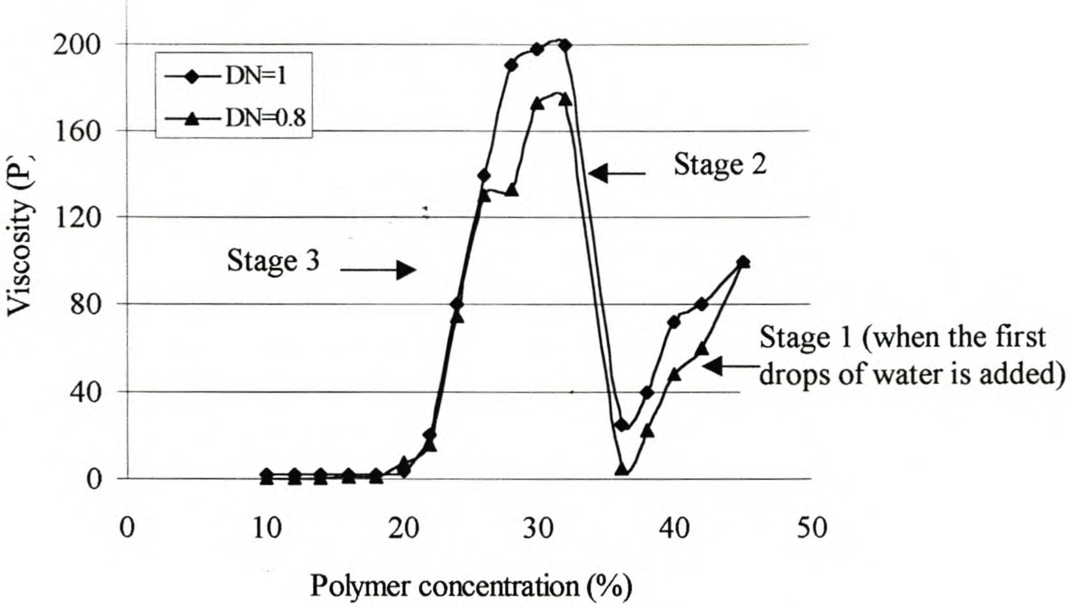

Figure 5.3 Change in viscosity of TEA-neutralised phosphated-polyurethanes during the dispersion process at 30^{0}C

5.2.3 Stage three: Particle formation

In stage one and two discussed above, the solution was clear since the ionomers were molecularly dispersed. As the last portion of water was added, turbidity which was an indication of the formation of a dispersed phase, was observed. During this stage turbidity reached a maximum and the viscosity dropped sharply due to the rearranging of the aggregates to form microspherical particles (Figure 5.3 stage 3). In this stage a discontinuous phase of polyurethane was dispersed in a continuous aqueous phase. When butanone was removed by distillation, a polyurethane ionomer emulsion in water was obtained. The three stages of emulsifications are schematically shown in Figure 5.4.

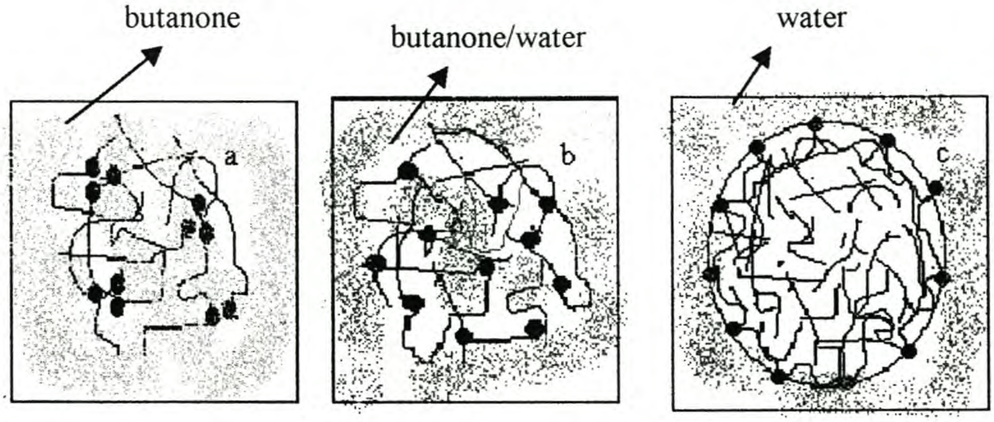

Figure 5.4 Schematic representation of the three stages in the emulsification of polyurethane ionomers: (a) ionic association during stage 1 (b) interchain association of hydrophobic segments during stage 2, and (c) rearrangement of the hydrophobic chains into microspheres in stage 3

5.3 Conductivity measurements during the dispersion

Conductivity measurements during the phase inversion (emulsification) of polyurethane ionomers can be used to determine the end point for the dispersion process. The conductivity of polyurethane ionomers during dispersion, at two dispersing temperatures, are shown in Figure 5.5. As can be seen, the conductivity increased during the dispersion stage then levelled off. The beginning of the constant conductivity reading was taken as the end point of the dispersion. Conductivity is highly temperature-dependent due to the high mobility of the ions in a low viscosity medium (Figure 5.5). At higher dispersion temperatures and higher degrees of neutralisation, water enters more easily into the hard segments. The temperature effect of conductivity could also be explained in terms of hydrogen bonding, which dissociates at 40-60^{0}C[10]. At the dispersion temperature of 50^{0}C most of the hydrogen bonds would be disrupted and more water could enter into the hard segment and increase the ionic mobility and hence the conductivity. The effect of the degree of neutralisation upon the conductivity at the same dispersion temperature was due to the number of ions generated upon neutralisation. It is well known that polymers with bound ions and free counter ions have better conductivity during solvation if sufficient ions are present in the solution[11].

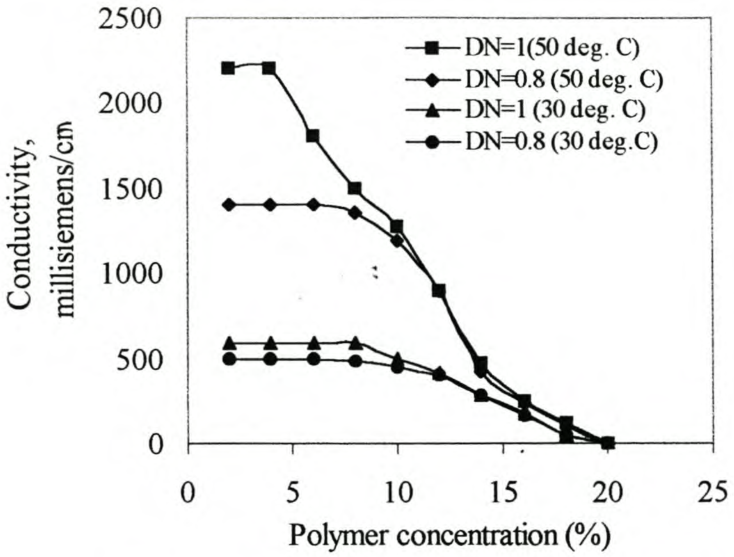

Figure 5.5 The effect of dispersion temperature and DN on conductivity of polyurethane ionomers (3.5% ionic)

5.4 Particle-size control during dispersion

In polyurethane ionomers, the particle number, particle size and particle-size distribution are directly related to the amount of bound carboxylic acid/ sulphonate groups in the polymer. Dispersion temperature, the ratio of organic solvent to water, the stirrer speed, the NCO/OH ratio (in cases where the prepolymer process is used) have also been cited to contribute to the size of the particles[12]

5.4.1 The effects of the neutralising cation on the dispersibility and stability of polyurethane ionomers

The neutralising cation has a profound effect on the dispersion and mechanical properties of ionomers. The mechanical properties of the early known ionomers of ethylene and methacrylic acid were strongly dependent upon the neutralising cation[13]. The mechanical properties of polyurethane ionomers neutralised by different metal salts have also been investigated[5]. Whereas the effect of the neutralising cation on the film properties of polyurethane ionomers is well documented, its effect on dispersion properties such as dispersibility, particle-size and dispersion stability has been overlooked.

In this study, phosphated polyurethane resins were neutralised with wide ranges of neutralising bases and results of particle sizes are given in Table 5.1. The phosphated polyurethanes studied had 70% soft segment, 30% hard segment and 4% 2,2-dihydroxymethyl propionic acid, which was fully neutralised.

Table 5.1 The effect of the neutralising cation on the particle-size and formation of stable dispersions

Neutralising base	**pK_b**	**Particle size (nm)**
Triethylamine	3.24	55
Tripropylamine	3.35	200
Tributylamine	3.11	400 (Dispersible and stable only for 1 day)
Triisobutylamine	3.68	Not dispersible
Tripentylamine	-	Not dispersible
Morpholine	-	62
LiOH	-	40
NaOH	-	45
KOH	-	50

As seen in the table, the metal cations produced smaller particles than the corresponding ammonium cations. This was due to the ease of hydration during the addition of water. In cases where higher substituted alkyl tertiary amines were used, stable dispersions were not possible. In the extreme cases of triisobutylamine and tripentylamine, the ammonium cations were too hydrophobic to be dispersed in water and no dispersions were possible, irrespective of the amount of the carboxylic acid groups. Dispersibility was also not possible when the soft segments were composed of only the polysiloxane macroglycol in excess of 60%, due to the surface activity of the siloxane side chains at the water/air interface. The smaller particles obtained from the lower alkyl amines seemed to be correlated with their increased water solubility. The short-chain alkyl amines are soluble in water but those amines having more than 5 carbon atoms are insoluble at higher temperatures but sparingly soluble at lower temperatures[14]. To verify the effect of temperature on hydration of the ammonium cations, dispersions were prepared at 5^{0}C, 10 ^{0}C, 20^{0}C, 30^{0}C, 40^{0}C, 50^{0}C, 60^{0}C and 65^{0}C for the tributylamine series. As can be seen from Figure 5.6, the lower temperatures favour dispersibility with lower particle sizes. This result was actually unexpected, since it has been reported[15] that higher dispersion temperatures disrupt hydrogen bonding and separation of the chains into smaller particles was possible, without considering the effect of the counter ion. The temperature effect of the neutralising amine was very striking if considered for making paints to be used at higher service temperatures. This is because complete hydrophobicity is obtained, unlike other waterborne systems where blistering due to hydrophilicity is a limiting factor. Though primary particle sizes are smaller for the metal cations in the order of Li < Na < K, the presence of metal cations was not desirable for dispersions intended for use in coatings due to the non-volatility during curing and thus water sensitivity.

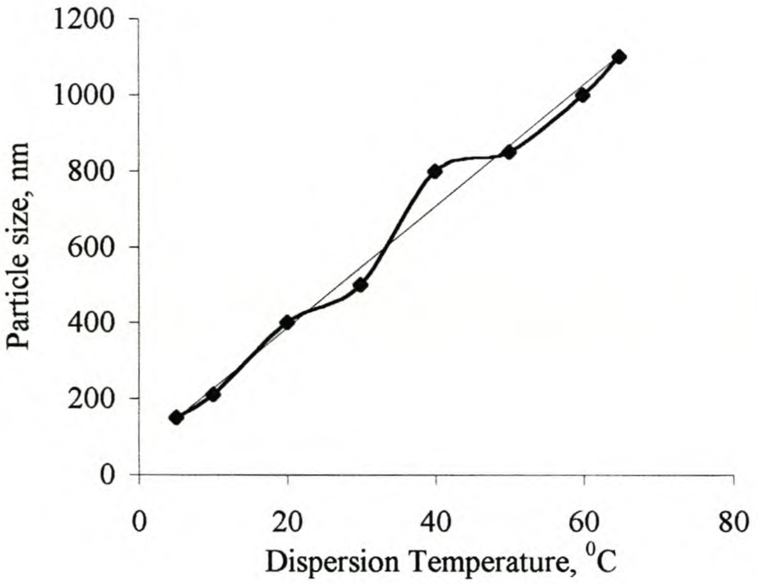

Figure 5.6 The effect of temperature on dispersion formation and particle size of the tributylamine- neutralised dispersions

From the range of amines used, morpholine showed a good balance between non-toxicity and dispersibility. It also has a low boiling point (128^{0}C) and can be easily dissociated upon curing. Morpholine is a secondary amine, which can also react with isocyanates. During this study complete consumption of the charged isocyanate was verified before neutralisation was effected.

5.4.2 Effects of ion concentration on particle number

All ion-containing polymers are not water dispersible[16]. A minimum ionic content with choice of favourable counter ions has to be met for water dispersibility and storage stability. While ionic groups associated in polymers in the solid state act as crosslinkers and improve mechanical properties[17], their role in a dispersion is different; they need to stabilise the dispersed phase in the presence of water. Dispersibility is governed by the hydration of the neutralising cation, and the hydrophilicity of the chains. As mentioned in section 5.4.1, stable emulsions are not possible when the polysiloxane macroglycol is used as a soft segment and the soft segment is more than 60%, irrespective of the ionic content (up to 7% w/w) and the neutralising cation. Under favourable conditions, the increasing amount of ionic groups in a dispersion leads to smaller particles and hence, more particles. The relationship between ion concentration and number of latex particles formed, Nc, was calculated from the mean particle diameter, D_T, obtained from light scattering measurements and using the relationship:

$$Nc = \frac{m_p}{4/3\pi r_u^3 d_p} \quad \text{..............equation 5.1}$$

where: m_p is the mass of the polymer,

r_u is the radius of the particle and

d_p is the density of the polymer.

However, since particles formed from polyurethane dispersions are polydisperse, the calculated value of Nc is smaller than the actual value. A plot of Nc versus concentration of bound stabilisers is shown in Figures 5.7 and 5.8. The line of the linear relationship does not pass through the origin. The slope of the graph gives information on the efficiency of the bound ionic groups for dispersion formation and the intercept is the minimum amount of ionic groups required for the formation of stable dispersions, below which no stable dispersion could ever be formed. The slope for the carboxylate ion (Figure 5.7) is lower than that for the sulphonate ion (Figure 5.8), which indicates the high efficiency of the sulphonate ions for dispersion formation (high slope corresponds to high efficiency). The odd distribution of data points in Figure 5.7 is coincidental and based on experimental deviation. There appears to be to be no reason for the data points pattern.

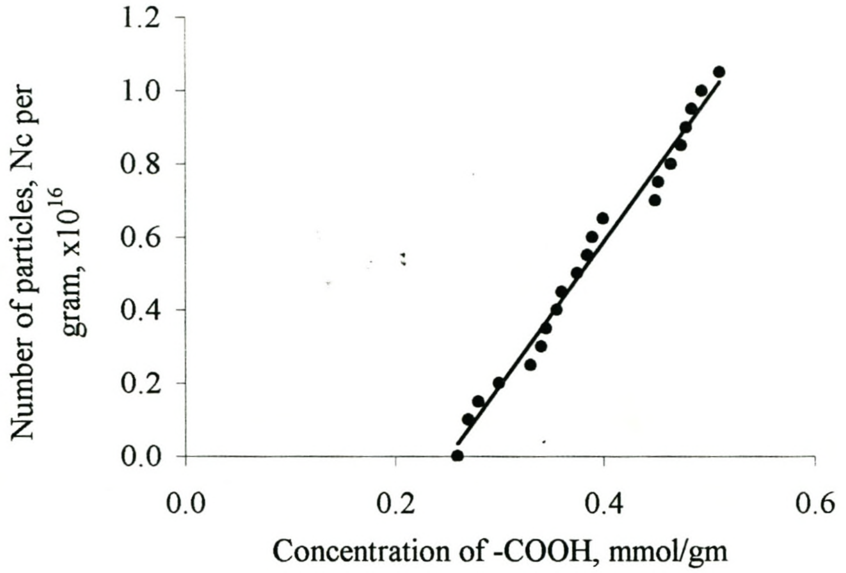

Figure 5.7 Number of latex particles, Nc, versus carboxylate ion concentration

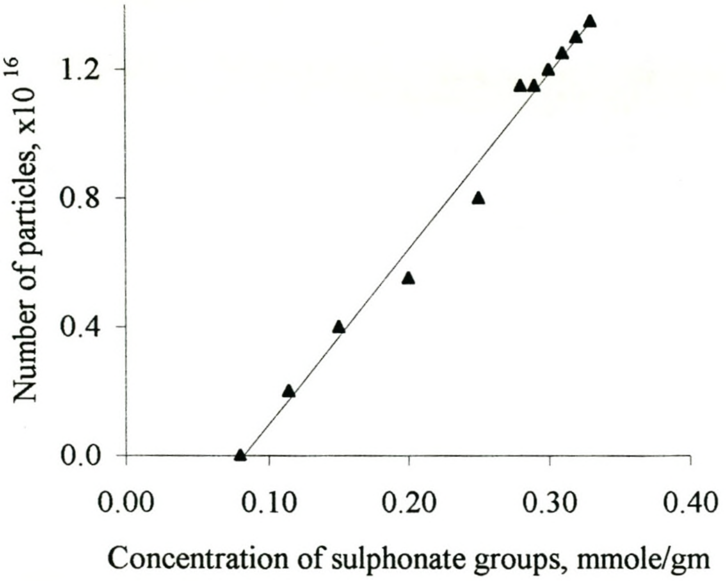

Figure 5.8 Number of particles, Nc, versus sulphonate groups

5.4.3. Effects of the degree of neutralisation (DN) on particle size and particle number

The degree of neutralisation has a direct effect on the particle size of the dispersions, as shown in Table 5.2. As the degree of neutralisation increased, particle size decreased, due to the hydrophilicity of the neutralised carboxylate ions, and dispersion viscosity increased due to the hydrodynamic volume of the finer particle size and swelling of the droplets.

Table: 5.2 Variation in particle-size and viscosity of phosphated polyurethane dispersions with the degree of neutralisation

Composition of the ionomer	**Degree of neutralisation** $^{(a)}$	**Particle size, nm**	**Viscosity,** $^{(b)}$ **cps**
Phosphated polyester-urethane 70% w/w soft segment and 30% hard segment 0.45mmole g^{-1} COOH	0.70	210	40
	0.80	135	55
	0.85	110	70
	0.90	80	120
	0.95	55	200
	1.00	40	310
	1.20	40	350

(a): triethylamine was used as a neutralising agent; (b): Brookfield viscometer at 20^0C

The effect of the carboxylate ion concentration on the number of particles formed is presented in Table 5.3. As the concentration of the carboxylate ion increased, the particle number also increased.

Table 5.3 Effect of carboxylate ion concentration on the number of particles formed during emulsification

-COOH mmole g^{-1}	**Number of Particles $x10^{15}$**
0.27	1.02
0.30	2.22
0.35	3.11
0.40	4.37
0.45	7.83
0.50	9.02
0.55	12.06

5.4.4 Mechanism of acrylic copolymerisation in the dispersed phase of polyurethane

The copolymerisation of acrylic and methacrylic esters with polyurethane dispersions is a classical seeded system. Such a system, as the name indicates, is polymerisation of acrylic monomers in the presence of the preformed particles. In a typical emulsion polymerisation system with added surfactant, the seeded polymer has to be subjected to ultrafiltration to remove extra surfactants and initiator decomposition products and then further polymerised by the addition of monomers. In aqueous dispersions of polyurethane seed, ultrafiltration of the seeded particles was not required. The reason for this is that the dispersion is surfactant-free and the stabilising effect arose from the built-in carboxylic groups. Furthermore, the seed polymer was also free from any residual initiator fragments due to the polyaddition nature of the seed preparation. In the context of the present study, the word 'seed' is meant to be the phosphated and/or siloxane-based polyurethane dispersion particles that are used to copolymerise acrylic monomers.

During the addition of the acrylic monomer into the seeded polyurethane particles in the presence of potassium persulfate, the monomer diffused into the latex particles. If sufficient monomer was added, monomer droplets would also be formed, so that equilibrium concentration of monomers in the particle is attained[7]. The polyurethane seed was stable to secondary nucleation and to flocculation over the initiator concentration range used. Particle growth occurred in the absence of secondary particle formation. In most of the experiments, a maximum of 30% acrylic monomers was polymerised into the seed before the particle became too large to be stabilised by the charged carboxylate ions and coagulation began to take place.

5.4.4.1 The effect of the seed neutralising cation on acrylic copolymerisation

A number of papers have been written describing the more beneficial properties of hydrophobic emulsion polymers containing chemically bound hydrophilic stabilisers than the blended surfactants used in current emulsion polymerisation[18,19]. Studies[18,19] have shown that particle charge derived from copolymerised monomer is more effective against mechanical shear coagulation than is absorbed charge because of differences in the ability of charges to move about the surface of the particle. Among the prominent advantages of the use of chemically-bound stabilisers were: higher mechanical stability, better water resistance in paper, textile and other coatings applications, increased ageing resistance and no surfactant migration.

At high pHs, the copolymerised acid (DMPA) of the present study was very effective in promoting colloidal stability. However, to place an acid monomer on the surface of a latex particle without it being buried was difficult, and a two-step polymerisation had been used. First, a carboxyl functional, phosphated-polyester and/or siloxane-based polyurethane was synthesised. The acid groups were then neutralised and the pH raised to 8-9. In the presence of water the ionised carboxylic acids stabilise latex particles, which in turn provide conventional loci for further emulsion polymerisation. The charged carboxylate ions remain on the surface of the particle, near to the aqueous environment.

The stabilising effect of the neutralising base during acrylic copolymerisation in the dispersed phase has been studied. The amount of the acrylic monomer used was 30% based on the seed. Table 5.4 lists the neutralising bases used and the % coagulation during methylmethacrylate copolymerisation process.

Table 5.4 Effects of neutralising cation on coagulation (grit) formation using a polyurethane seed latex

Neutralising base	**% of grits during methyl methacrylate copolymerisation**
LiOH	2
NaOH	4.5
KOH	5
Triethylamine (TEA)	6.1
Morpholine	7.3
Tripropylamine (TPA)	Instant coagulation
Tributylamine (TBA)	Instant coagulation

It is clearly seen that small, highly solvated cations were required for stabilising the emulsion during copolymerisation in comparison with large and less solvated cations. For the amine series, as the size of the alkyl increased, the resulting cation became too hydrophobic and grit formation was much higher.

5.4.4.2 The effect of acrylic monomers on the particle-size of the phosphated and/or siloxane-modified polyurethane acrylic dispersion

Particle size measurements of the phosphated-polyester and/or siloxane-based polyurethane seed were carried out before the acrylic monomers were added. When the acrylic monomer was added into the system, the monomers swelled the seed particles and as a result the particle sizes increased, as shown in Figure 5.9. There was a difference between the swollen radius of the monomer-saturated particles and the unswollen radius. It is also known[7] that due to the hydrophilicity of the initiator radical it is insoluble in the organic phase and might not enter the particles. The primary radicals can react with the monomers in the aqueous phase until they form a less hydrophilic surface-active radical that can irreversibly enter into the particle. In homogeneous nucleation theory[7], the oligomeric free radicals in the aqueous phase were believed to propagate, precipitate, swell with monomer and form particles. However, charged groups from the initiator impart colloidal stability that does not last long and the particles can undergo irreversible coagulation[7].

During radical polymerisation in the dispersed phase, the particle-size decreased to below the particle-size of the swollen particles but was above that of the seed particles. One reason for this was the shrinkage of the particle upon polymerisation. A second reason was that the newly grown particles, in the presence of acrylic monomers, are more hydrophobic than the swollen particles before polymerisation and expelled water from the particles, as shown in Figure 5.9.

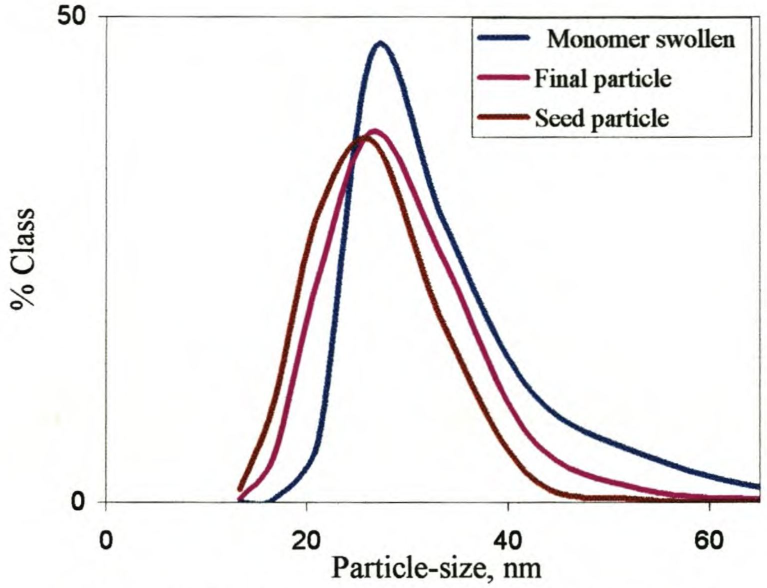

Figure 5.9 Particle-size distribution of phosphated polyurethane during polymerisation of acrylic monomer

In general, the copolymerisation of monofunctional and multifunctional acrylic monomers into phosphated and/or siloxane-based polyurethane dispersions resulted in a decrease in viscosity and an increase in particle size, as shown in Figure 5.10

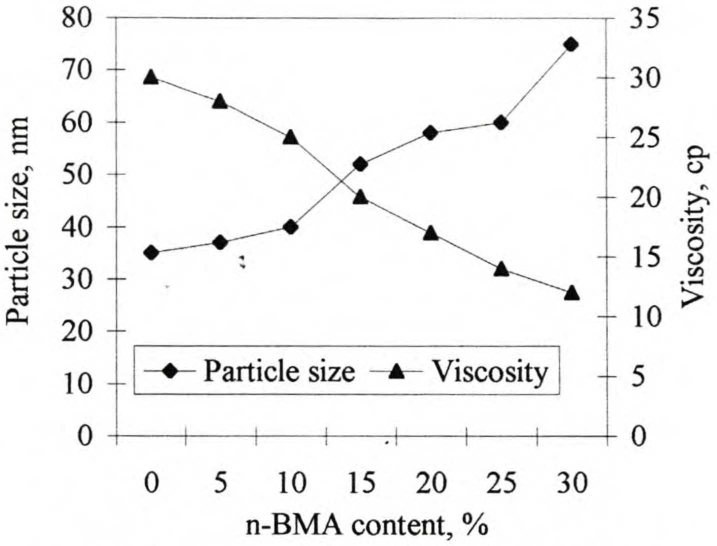

Figure 5.10 Particle size and viscosity variation during n-BMA copolymerisation

5.5 Swelling studies

5.5.1 Introduction

One of the disadvantages of polyurethane dispersion films is their hydrophilicity that arises from the neutralised carboxylic groups or the built-in sulphonate groups when compared with their solvent-borne counterparts. It has been shown in section 5.4.1 that the neutralising cation has a profound effect on particle size during the dispersion. Water swellability of polyurethane dispersion films depends largely on the amount of the ionic groups, the chain length, and the ease of hydration by water molecules.

5.5.2 Experimental

Specimens for swelling tests were prepared by weighing small amounts of the dispersions (4-5g) in an aluminium dish and evaporating the water in an oven above 100^0C. The resulting films were then removed from the dish, cut into appropriate sizes and accurately weighed to ±0.001 mg. Their thickness was about 2-5mm. The specimens were suspended on a copper wire and completely submerged in distilled water at 20 ± 1^0C. The relative water-absorption masses were determined by weighing the specimens after they had been dried with filter paper, and subtracting these value from values of the initial mass.

$$\text{Swelling (\%)} = \frac{Ws - Wd}{Wd} \text{ ....equation 5.2}$$

where: Ws is the weight of the swollen sample and Wd is the weight of the dried sample.

5.5.3 Results and discussion

The time-dependent percentage of swell for the polyurethane ionomers, where the ions are on the soft segment (case 1) and on the hard segment (case 2), at varying ionic contents is shown in Figure 5.11

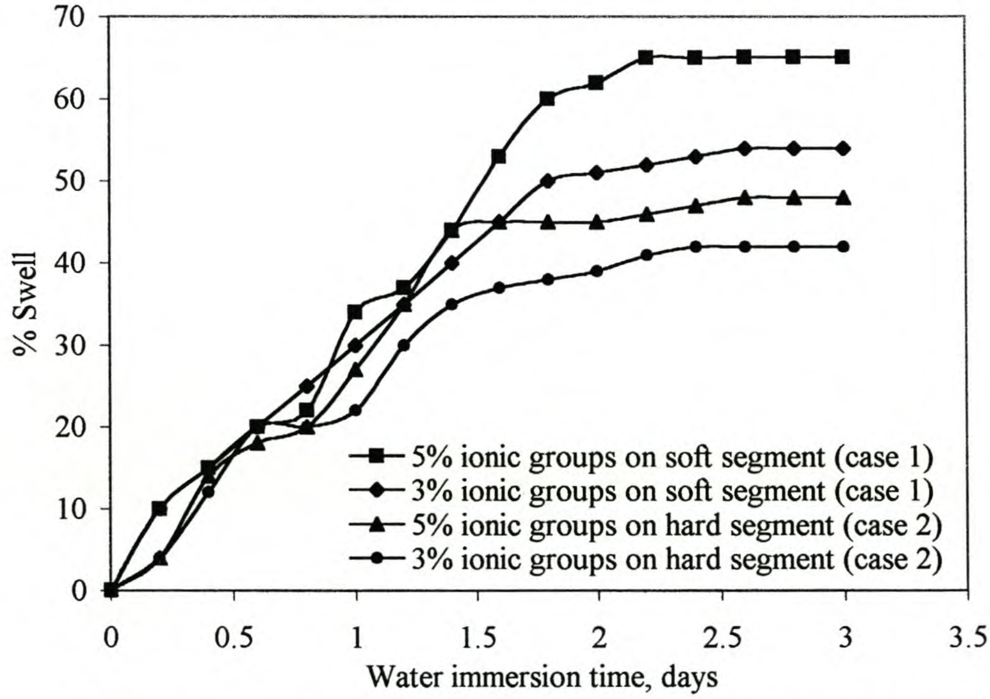

Figure 5.11 Water swell of uncured polyurethane ionomers (70:30 soft segment to hard segment) at 20^{0}C.

It can be seen from the graph that the location of ionic groups at different segment positions changed the swelling properties of the films. Those films cast from segmented polyurethane ionomers with ions located on the soft segment showed greater swelling than the hard segment counterparts. This is explained by the ease with which water enters into the soft segments compared to the ordered hard segments. Inter-urethane hydrogen bonding could also contribute to lower water uptake[20].

As water molecules are strongly hydrogen bonded they are likely to be absorbed in polymeric films that have polar groups. Absorption is governed by the degree of ordering of the polymer chains, the accessibility of the polar groups in the polymer to water, and by the strength of the intermolecular forces between water/polar groups and water/water interaction[21]. All the films absorbed water until equilibrium was established.

5.6 The effect of the neutralising base on swelling

The effect of the neutralising base on the water uptake of uncured polyurethane ionomer films has been studied. This study was done on ionomer films cast from butanone. Figure 5.12 shows that those ionomers neutralised with longer chain amines, which have lower water solubility than short chain amines, had the least water absorption due to the hydrophobic nature of the counter ions. The water swell decreased as we moved from morpholine, to tripropylamine (TPA), tributylamine (TBA), and triisobutylamine (TIBA). There was little change in swelling when N,N-dimethyldodecylamine (DMDCA) was used as neutralising agent compared with results obtained from the unneutralised film. The use of metal cations resulted in most swell, increasing in the order of lithium, potassium and sodium.

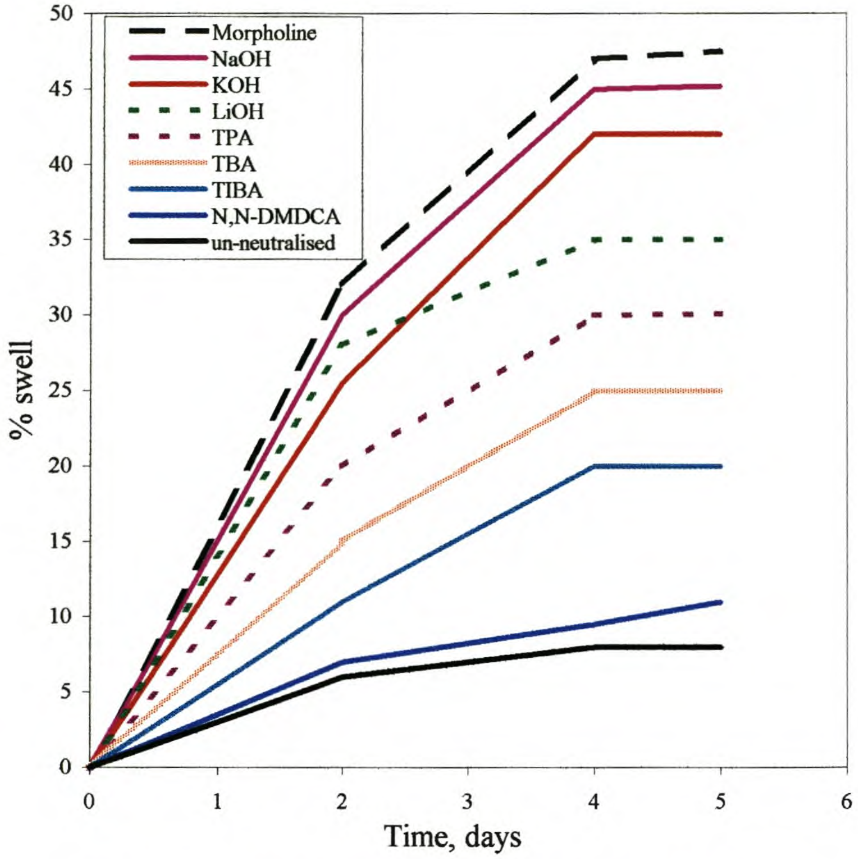

Figure 5.12 Effect of the neutralising base on the time-dependent swelling of phosphated polyester-urethane ionomers (70% soft segment, 30% hard segment and 4% DMPA)

5.7 Surface-tension and wetting properties of acrylic-modified phosphated polyurethane ionomers

The effect of varying the 2,2-dihydroxymethyl propionic acid (DMPA) concentration on the surface tensions of the polyurethane ionomer dispersions are presented in Table 5.5. The surface tensions of the ionomer dispersions decreased as the amounts of DMPA in the polyurethane increased. This indicated that the more carboxyl groups the dispersions contained, the finer were the particles that were formed. It was interesting to note the surface activity of the polyurethane dispersions. As the % of the carboxyl groups increased, the surface activity of the dispersion increased, as is known for other surface-active agents.

Table 5.5 Surface tensions of phosphated polyurethane-acrylic dispersions

% of carboxylic acid in the aqueous polyurethane	**Surface tension, N/m**
3	50
4	44
5	39
6	34

5.7.1 Water contact angle studies

Advancing and receding contact angle measurements of the phosphated polyurethane could provide more information on the hydrophilicity of the emulsion cast films and hence the wettability. A better understanding of the hydrophobicity of the films could be obtained from dynamic contact angle studies than from swelling studies. The water contact angles increased as the amount of acrylic monomers copolymerised were increased. The increased contact angles in water meant that the films showed poor wetting with increased acrylic content, as shown in Figure 5.13. The increase in advancing contact angle widened from methylmethacrylate to ethylmethacrylate and ethylene glycol dimethacrylate.

5.7.2 The effect of temperature treatment on contact angles

As outlined in Chapter 3, ionic polyurethanes are made by neutralising the pendent carboxylic acids with tertiary amines which have relatively high boiling points. When films are cast from these emulsions and dried at room temperature for 24 h, all the amines will not be dissociated and therefore they will not fully volatilise, leaving behind the hydrophobic polymer chains. To study the effect of the retained amines (in this case triethylamine and tributylamine) on the film during sample preparation for contact angle studies, the same samples used for Figure 5.13 were heat treated at 100^0C, for 5min. The films were then cooled to room temperature and the contact angles were measured. Results of water advancing contact angles of the cast films before and after the heat treatment are given in Table 5.6.

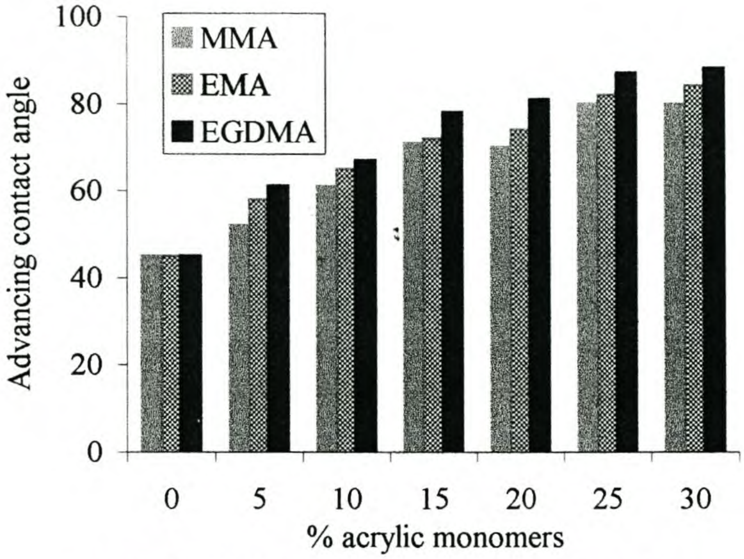

Figure 5.13 The effect of the type of the acrylic monomers copolymerised on contact angles of the polyurethane emulsion films

Table 5.6 Advancing contact angles of phosphated polyurethane ionomer films before and after heat treatment

	% modification							
	0%		**10%**		**20%**		**30%**	
Monomers	θ_{adv} before	θ_{adv} after	θ_{adv} before	θ_{adv} after	θ_{adv} before	θ_{adv} after	θ_{adv} before	θ_{adv} after
MMA	45	46.90	60.9	64.2	70.2	74.5	80	83.2
EMA	45	46.90	65.3	68.7	74.1	77	83.8	87.1
EGDMA	45	46.90	66.1	69.8	79.9	82.5	84.7	88.9

Table 5.6 clearly shows that temperature treatment at 100^0C for a short period of 5min increased the contact angle (reduced wetting by water). As discussed in Section 5.4.1, the higher-alkyl substituted amines lost their solubility at higher temperatures in the hydrophilic medium and were easily removed, resulting in a change in the surface properties of the films.

5.8 Hydrolytic stability of uncured polyurethane ionomers

5.8.1 Introduction

Many polymers are produced by condensation reactions such as esterification or acidification during which water is released. Under extreme conditions, this process can be reversed, leading to a reduction in molecular weight and greater water sensitivity due to the presence of an increased number of hydroxyl and carboxylic acid groups. If such polymers are used in adhesives or coatings, early adhesion failure will be observed due to the lack of chain entanglements and the negative hydroxyl ion gradient[22]. The OH^- ions produced by the reduction reaction caused by the cathodic protection of organic coatings are a key factor in the loss of adhesion from steel substrates. As the OH^- ion concentration increases, the pH of the whole system also increases, which results in the saponification of the polymer due to the migration of the OH^- ions between the coating and the substrate. This is also true for vinyl- or acrylic-ester polymers, which are known to break down more rapidly under conditions of damp and high humidity.

One of the main research objectives of the coatings industry is to improve the performance of water-dispersible coatings. Coatings or materials for any application formulated from water-dispersible polymers, have poor storage stability. This problem is generally attributed to hydrolysis of the ester linkages of the resin. Turpin[23] has suggested that both steric hindrance and an Anchimeric effect play roles in hydrolysis. Increased alkyl substitution at the alpha and beta carbons on either side of the ester group can improve hydrolytic stability. Nucleophiles, such as carboxy compounds, act as intramolecular catalysts for ester group hydrolysis. Water-dispersible polymers are often formulated at pHs above 7 and a small degree of hydrolysis generates –COOH groups, causing a downward drift in the pH.

In polyesters, the acid groups present (released) exert, moreover, an autocatalytic effect. Residual esterfication catalysts, if present in the polyester, also accelerate hydrolysis. With hot, dilute acids or bases, the saponification process can be driven to the point of complete breakdown of polyester-based polymers into the starting components[24].

5.8.2 The effect of the ionic groups on the hard segment on hydrolysis resistance

The first (case 1) uncured polyurethane ionomers studied had the ionic groups on the soft polyester segment (see section 3.3.2) and the second (case 2) had the ionic groups on the hard segment (see section 3.3.3), as diagrammatically shown in Figure 5.14.

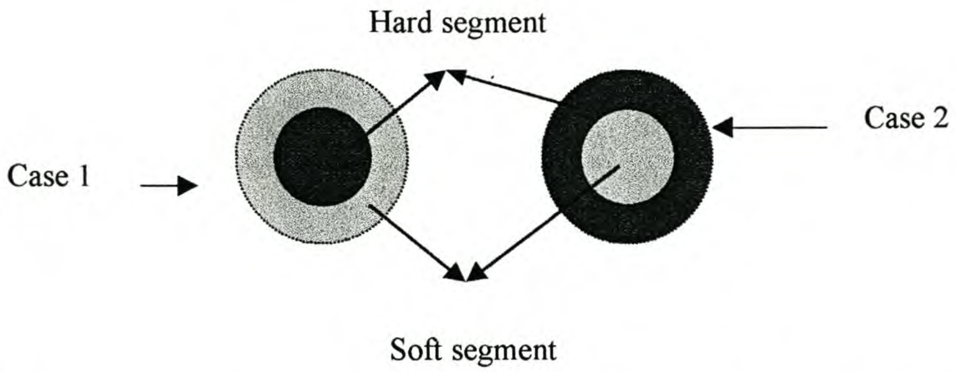

Figure 5.14 Diagrammatic representation of the two types of polyurethane ionomer particles

Measurements of molecular weight changes were carried out periodically for 2 years to check the hydrolytic stability of the dispersions. Results from GPC measurements for the two cases of polyurethanes are shown in Figure 5.15. From the graph it was seen that for those dispersions where the ionic groups were on the hard segment (case 2), the molecular weight remained fairly constant over the time under investigation compared with those dispersions where the ionic groups were on the soft segment (case 1). Upon increasing the urethane groups (higher hard segment content) from 30 to 50%, hydrolytic stability increased. For the samples prepared from a higher proportion of polyester soft segment, an induction period of 50 weeks was observed before molecular weight decreased.

Polyurethane dispersions made about four years ago were found to be stable and showed little change in molecular weight[25]. The presence of hydrophobic polyester bonds explains the fact that films and coatings deposited from aqueous polyurethane sols (case 2) are insoluble in water as well as the fact that such sols do form. It is interesting that the hydrolytic stability of aqueous polyester-polyurethanes increased when the ions were on the hard segment. Polyester-polyurethane ionomers in which the ions are solely bonded to the soft segment ester groups (case 1) suffer hydrolytic degradation, while ionomer dispersions with hydrophobic soft segments show little molecular weight reduction after 2 years. Other authors have reported similar results[26].

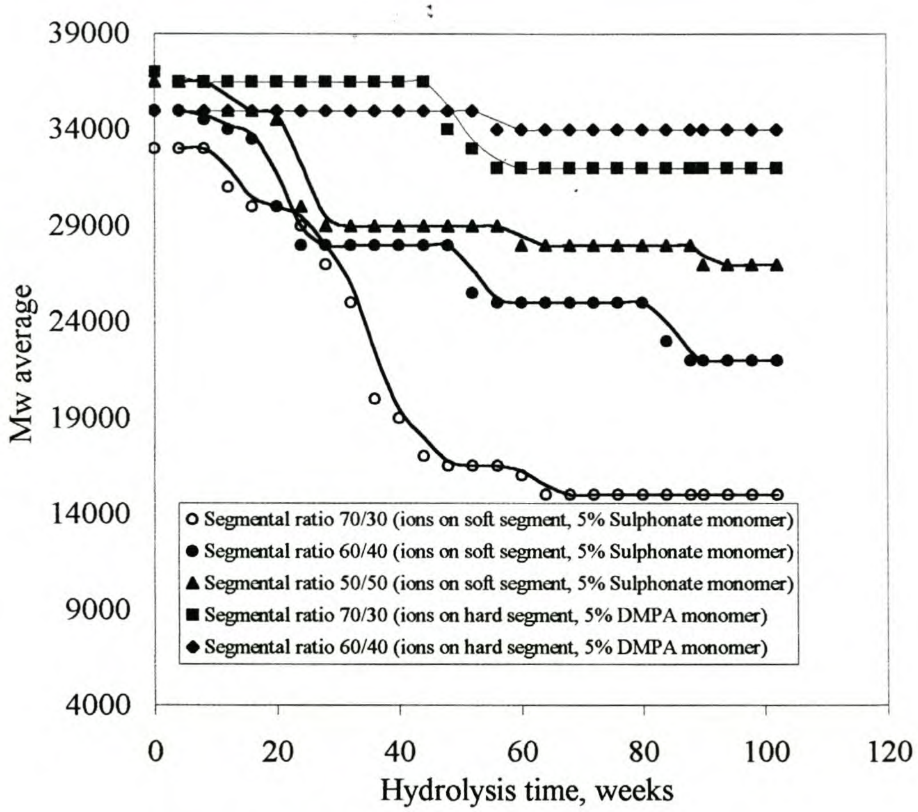

Figure 5.15 Hydrolysis resistance of model uncured polyurethane ionomers

5.8.3 The effect of the ionic groups on the soft segment on hydrolysis resistance

The effect of ionic groups on the soft segment had a profound effect on the hydrolytic stability of the resulting polyurethane ionomer dispersions. During the dispersion stage, the non-ionic urethane groups were coiled inside the particles and the polyester chain that had the bound ions was the shell with direct contact with the aqueous phase. It can be said that polyurethane chemists have been avoiding water not only because of its undesirable reaction with isocyanates, to form crosslinked polyurethanes, but also hydrolytic degradation of polyester urethanes may occur. The first polyester-based polyurethane elastomers were relatively sensitive to hydrolysis and the use of special stabilisers such as carbodiimides was necessary[26]. The hydrolytic degradation of the polyester segments increased with increasing hydrophilicity of these segments. Water-soluble products were completely hydrolyzed within a few days[26].

Figure 5.15 shows the effects of ions on the soft segments on the hydrolysis of the polyurethane. As expected, molecular weight decreased very rapidly. It is also clearly seen that with a decreasing soft segment content from 70% to 50%, the resistance of the polyester to hydrolytic attack increased. Because the acid number increases at an accelerating rate during longer storage periods, especially at higher temperatures, additions of acid acceptors such as carbodiimides or epoxides as hydrolysis stabilisers have been reported[26]. For this reason polyesters made from long chain starting components were more stable than those made from short chain components.

Thus, the surprising hydrolytic stability of the aqueous dispersions of polyurethanes in Figure 5.15 are a good example of the completely different properties achieved by a two-phase dispersed system in comparison with the corresponding one-phase systems.

If, on the other hand, the ester groups are situated close to the ionic groups, as is the case in polyurethanes made from ionic polyester macroglycols (Figure 5.14, case 1), sols prepared from these substances undergo hydrolytic degradation within a short time. They are not much different from a one-phase system as the polyester segments are in contact with the aqueous phase.

Under well-defined conditions, ionic urethanes yield stable emulsions in the absence of emulsifier, and these have many practical applications. The hydrolytic stability is derived from the fact that unsolvated hydrophobic polyester segments are packed in the interior of sol particles while the strongly hydrated urethane segments with mutually repelling carboxylate ions are situated on the outside surface of the particle. The polyester groups are thus protected against hydrolysis as effectively as in the dry solid form.

5.9 Monoacrylates and diacrylates as diluents: A new process for preparing polyurethane-acrylic dispersions

Most commercial polyurethane dispersions are prepared either by the solvent or pre-polymer process[27]. In the case where a high molecular weight polymer is prepared in an organic solvent (acetone or butanone), so as to reduce the viscosity of the reaction mix, distillation of the organic solvent after dispersion is required. The amount of solvent used is generally high (40-60%), due to the low temperatures of the urethane-forming reactions resulting in high viscosity. If the acetone distilled after the dispersion process is to be used for a subsequent batch, it has to be recycled to remove all traces of water. Overall, the solvent process yields a low reactor volume product. Polyurethanes prepared by the pre-polymer process, on the other hand, though free from solvents, have higher viscosities and dispersing requires the use of powerful mixers. The chain extenders used in the aqueous phase of the pre-polymer method are also limited to highly nucleophile amines due to their fast reaction velocity with the isocyanate in the presence of water. The present study investigated a new process for preparing polyurethane dispersions that are free from organic solvent and that does not require the use of powerful mixers.

Figure 5.16 shows the viscosities of fully reacted phosphated polyurethane ionomers prepared with different quantities of reactive diluents. The viscosity of the 2-hydroxyethyl methacrylate-terminated phosphated polyurethane was reduced by an order of magnitude during processing. This means that the process of synthesising polyurethane dispersions free of organic solvents was made possible by the use of these reactive diluents. The reduction in viscosities brought about by the acrylates was in the order of methylmethacrylate (MMA), ethylmethacrylate (EMA), n-butylmethacrylate (BMA) and ethylene glycol dimethacrylate (EGDMA).

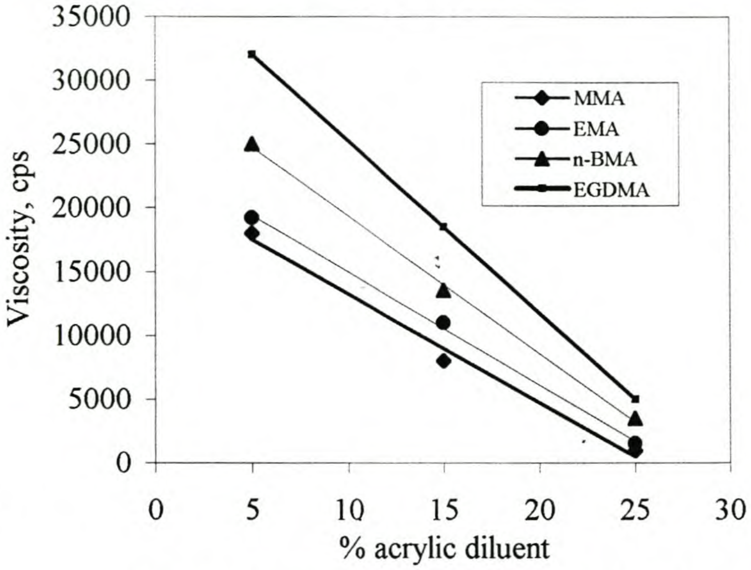

Figure 5.16 The effect of the acrylate diluent on the viscosity of phosphated polyurethanes, 70/30 soft to hard segment content

The reduction in viscosity upon addition of these monocrylates is directly proportional to the viscosity of the pure acrylate type, as shown in Table 5.7. The viscosity of n-alkyl methacrylates increases with chain length and as a result n-BMA gave slightly higher resin viscosity than ones with EMA and MMA at the same concentrations. The resin viscosity with the diacrylate (EGDMA) was generally higher than the monoacrylates studied due to the higher viscosity of the diacrylate.

Table 5.7 Solubility and viscosity of the acrylate monomers and the reduced viscosity of the phosphated polyurethane resin

Monomers	**Solubility in water at 25^0C**	**Viscosity of the acrylate, monomer, cps**	**Viscosity of the phosphated polyurethane polymer, (80/20 soft to hard segment and 80% solids) cps, at 20^0C**
MMA	1.72	0.56	950
EMA	0.46	0.62	1500
n-BMA	0.04	0.92	3500
EGDMA	-	-	5000

5.10 Rheological behaviour of polyurethane-acrylic dispersions

Figures 5.17 and 5.18 show the rheological profiles of the phosphated urethane acrylics before and after dispersion in water, respectively. Because of the wide range of the viscosities of the dispersions, different shear rates were necessary to keep within the range of the viscometer. A least-squares fit to the power law[28] was used when necessary to extrapolate the viscosity to $1 s^{-1}$.

According to the power law,

$\eta = m\gamma^{n-1}$..............................equation 5.3

where: η is the measured viscosity and,

γ is the shear rate

m and n are empirically determined parameters for a given system.

For Newtonian fluids, n equals 1 and then m becomes the viscosity.

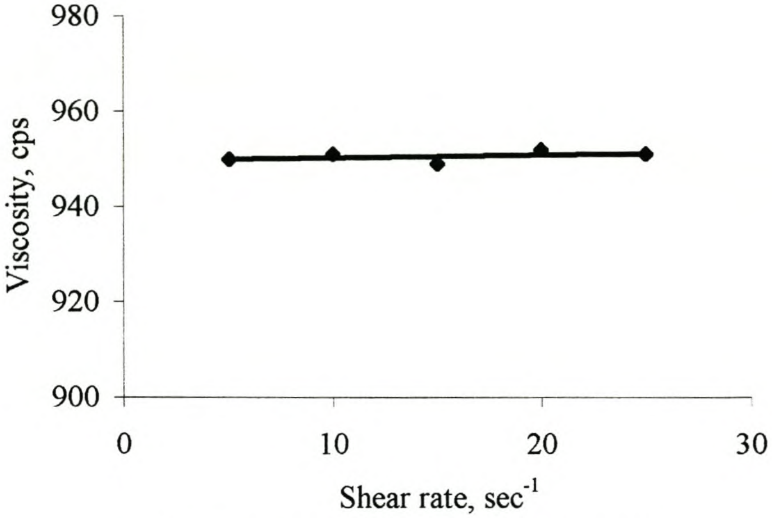

Figure 5.17 The effect of shear rate on the viscosity of a phosphated polyurethane before dispersion, 20% MMA

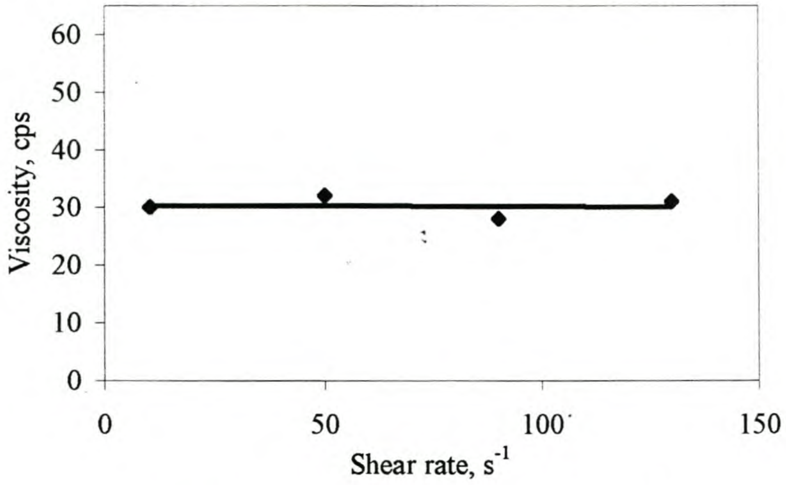

Figure 5.18 The effect of shear rate on the viscosity of a phosphated polyurethane acrylic dispersion; 20% MMA, 35% solids in water

For all the systems depicted in Figures 5.16 and 5.17, n was calculated to be between 0.96 and 1, indicating Newtonian behaviour.

The viscosity of a polymer solution including a water-dispersible system depends on temperature[29], the polymer fraction[30], and polymer molecular weight[31]. In the coatings field, the polymer fraction and temperature are major factors in ensuring proper film thickness and ease of application. In the present study, the viscosity behaviour of the waterborne phosphated polyurethane-acrylate dispersions was studied with respect to polymer fraction and temperature.

Figures 5.19 and 5.20 show the shear stress versus shear rate of the phosphated polyurethane dispersions at different polymer concentrations and temperatures, respectively.

All the graphs are linear, indicating that the shear stress is independent of both shear rate and temperature. It was not possible to measure the dependence of shear stress on shear rate above 60^0C due to the thermal polymerisation of the acrylic monomer that invalidates the data.

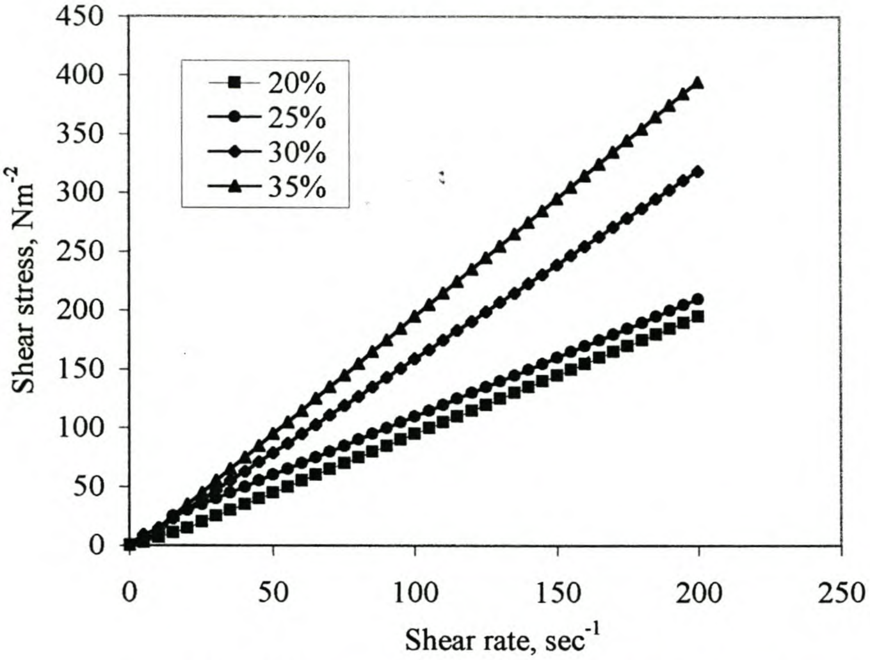

Figure 5.19 Shear stress versus shear rate for phosphated polyurethane acrylic dispersions of different concentrations at 25^{0}C

All the phosphated polyurethanes, before the addition of water, show a Newtonian fluid behaviour and the lower viscosity generally permitted easy dispersion into water. The dispersions also showed Newtonian behaviour. This result is an added benefit to phosphated polyurethane dispersions made from phosphated polyester macroglycols. The high shear stability without agglomeration could make them a very useful pigment-grinding medium.

Huang et.al[32] recently used polyester-based, anionic polyurethane dispersions as pigment grinding media under standard grinding conditions using a ball-mill. Their findings suggested the possible use of these ionomers for pigment grinding, provided that they are shear stable.

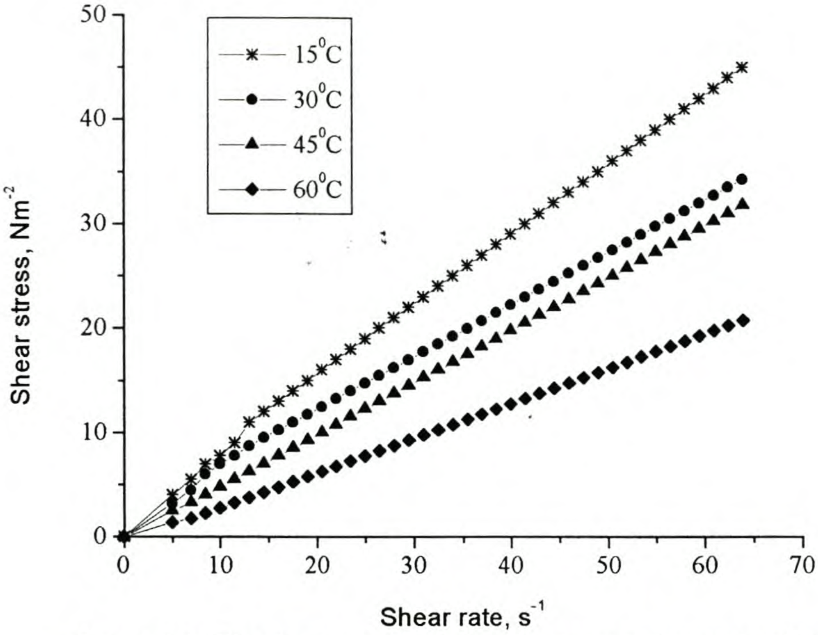

Figure 5.20 The dependence of shear stress on shear rate of 35% phosphated polyurethane acrylic dispersions at various temperatures

In another study, Wang et.al[33] found the shear thinning and pseudoplastic behaviour of polyurethane dispersions synthesised from polyethylene oxide glycol and dimethylol propionic acid which could not be used as pigment grinding medium. In a separate study, Mequanint and Sanderson[1] have described the use of phosphated polyester-based urethane ionomer as pigment grinding medium in emulsion paints. This finding has already been commercialised[1].

In the present study the calculated rheological equation of state for the phosphated and acrylated polyurethane ionomers did comply to Newtonian behaviour, as presented in Figures 5.19 and 5.20. Non-Newtonian behaviour is associated either with pseudoplastic or thixotropic flow. The former is caused by the agglomeration of particles due to destabilisation and the latter when a pre-existing structure, such as that caused by hydrogen bonding, is disturbed.

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Chapter 6

Self-assembling metal coatings from phosphated and siloxane-modified polyurethane dispersions

6.1 Introduction

The behaviour of macromolecules near surfaces and interfaces of organic coatings often plays a vital role in numerous properties and applications of the coatings. Therefore an understanding of interfaces responsible for durability, adhesion and mechanical properties, on a molecular level, are important in the development of new generations of organic coatings. A common feature of all multiphase polymers is the presence of large interface areas. The properties of the interface are central to the properties of coatings and the ability to understand the interface is regarded as a key feature in developing and optimising improved coating materials. The coating interface may be with air, another coating or with an inorganic surface, such as a metal.

Interfaces involving polymers are generally of finite thickness. Thus, polymers adsorbed to a substrate or to a coating/air interface may differ from the bulk of the polymer. It is important to determine interface properties but they are generally difficult to characterise; and reliable information is neither easily obtained nor readily available. The interface may have been formed in a process that had not reached equilibrium and kinetics and thermodynamics must be taken into account[1]. For instance, diffusion of species towards or away from the interface may be slow, relative to the time-scale of coating, and a non-equilibrium composition profile may be kinetically trapped as temperature drops or as crosslinking increases.

6.2 Wetting and adhesion

Wetting is the extent to which a liquid makes contact with a surface. This is characterised by the degree of direct interfacial contact and the ease with which it is achieved. Adhesion is the intimate sticking together of surfaces so that stress can be transmitted between the phases. It can be quantified by the amount of work required to pull the interface apart, from two surfaces. Wetting is quantified by determining the contact angle of a liquid on a surface at equilibrium, by the Young's equation[2].

$\gamma_{SV} = \gamma_{SL} + \gamma_{LV} \cos\theta$................equation 6.1

where; γ_{SV} is the solid surface energy,

γ_{SL} is the solid/ liquid interfacial energy,

γ is the liquid surface tension and

θ is the contact angle.

This equation follows from the requirement that the sum of the horizontal components of interfacial forces acting on the point of three-phase contact be zero at equilibrium, as shown in Figure 6.1. In the case of low molecular-weight liquids, a more rigorous treatment replaces γ_{SV} with the surface energy of the solid on which equilibrium adsorption of the vapour from the liquid phase has occurred, and both γ_{SV} and γ_{LV} refer to surfaces relative to which the gas phase is at equilibrium vapour pressure. However, in the case of polymers with zero vapour pressure, equation 6.1 is sufficient[1].

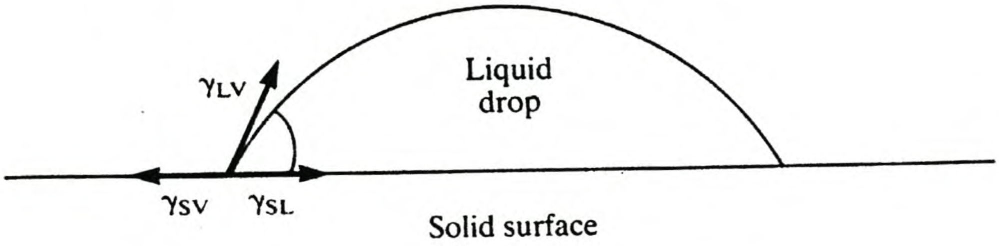

Figure 6.1 Force balance at the point of three-phase contact.

For complete wetting θ should ideally be zero, and as θ decreases the driving force for wetting increases. However, in systems where θ is higher (i.e. poor wetting) more work is necessary to penetrate and wet the surface.

Equation 6.1 indicates that θ can be reduced and wetting improved by increasing γ_{SV} or reducing either γ_{LV} or γ_{SL}. Young's equation describes wetting at equilibrium, the rate of which depends on the balance between the driving force for wetting and viscosity.

However, when the liquid advances over the solid, θ is higher than when the liquid recedes from the solid[1]. This difference between the advancing contact angle and the receding contact angle is the contact angle hysteresis.

In this chapter the self-assembling nature of the phosphated and siloxane-modified polyurethane dispersion coatings is studied and discussed.

6.3 Experimental

The experimental conditions used for preparing the coatings were described in Chapter 4, section 4.4. Different coating compositions were made with different polysiloxane contents. Coatings were cured according to the coil-coating process requirements.

6.4 Results and discussion: Self-assembly at the coating/air interface

6.4.1 Velocity dependence of dynamic contact angle

Dynamic contact-angle determinations were made under dynamic conditions, that is, at constant velocity of the moving platform during the dipping and retraction motions and were therefore velocity dependent. In the study of contact angles, velocity dependence has been a source of controversy. No general conclusion as to the velocity dependence of the contact angles has yet been reached, though most researchers agree that the receding contact angle is somehow velocity independent[3-5]. A number of workers have claimed that at low velocities the contact angle is independent of velocity, whereas the velocity should be taken into account above a velocity of 100μm/sec[6,7]. In the present study, the dynamic contact angles of water on phosphated and polysiloxane-modified polyurethane acrylate coatings were measured as a function of velocity and results are presented in Figure 6.2.

It was found that receding contact angles were less sensitive to velocity than advancing contact angles. This difference was attributed to the way the liquid interface recedes compared with the way it advances. When the liquid advanced, the three-phase boundary moved in 'jumps' and when the three-phase boundary receded, the recession started at one edge and moves across the slide like a zipper. Accordingly, the wetting force curve is 'ragged' for advancing than for receding, as shown in Figure 6.3. Moreover, the smoother movement of the three-phase boundary during recession caused the energy barrier to be less for receding than for advancing angles. This accounts for the lower dependence of receding contact angles on the three-phase velocity.

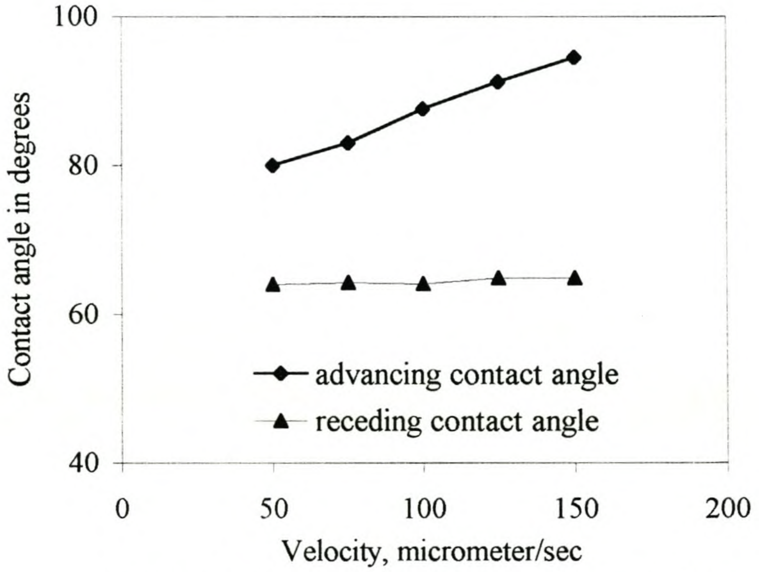

Figure 6.2 The velocity dependence of dynamic contact angle experiments

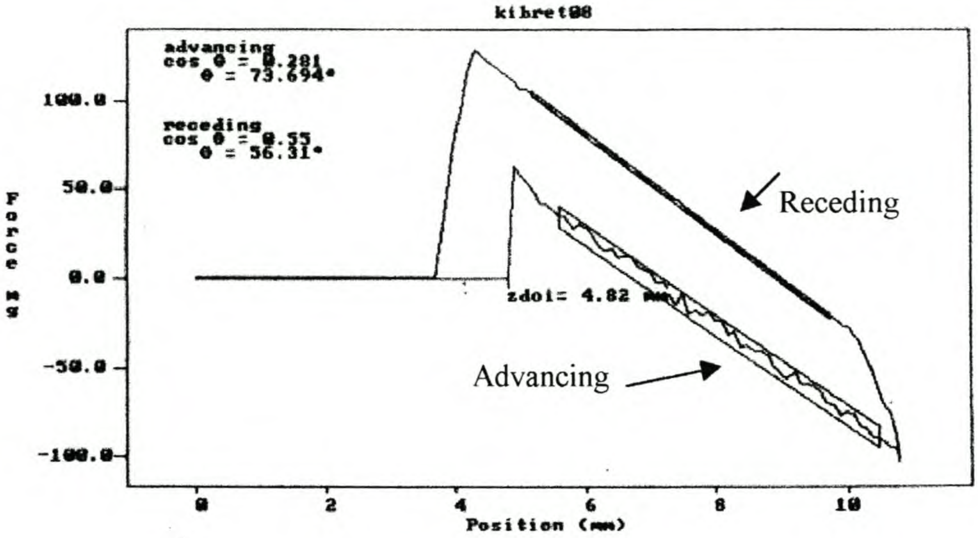

Figure 6.3 The 'ragged' nature of an advancing contact angle compared with a receding contact angle

6.4.2 The effect of the polysiloxane segments on wettability of phosphated and siloxane-modified polyurethane coatings

It has long been known[8] that the surface composition of a multi-component polymer may differ substantially from the bulk composition. This phenomenon is associated with surface energy, where the surface is enriched with lower energy components. The effect of the polysiloxane segment in crosslinked and uncrosslinked coatings on the wettability of the coatings is shown in Figure 6.4.

Both the cured and uncured coatings showed an increase in advancing contact angles with an increase in the polysiloxane segment concentration in the film. Curing seemed to decrease advancing contact angles slightly. This was due to chain entanglements caused by network formation that hinder the free rotation of the siloxane chains to move into the coatings/air interface. Another reason for the slight decrease in water contact angle of the cured films was the presence of the rigid melamine ring used as crosslinking agent that hindered free rotation. Hirayama and Urban[9] studied the effects of the melamine crosslinker on the surface enrichment of polyester-melamine coatings. They found that self-condensation of the melamine at the coating/air interface caused melamine enrichment and deterred flexibility.

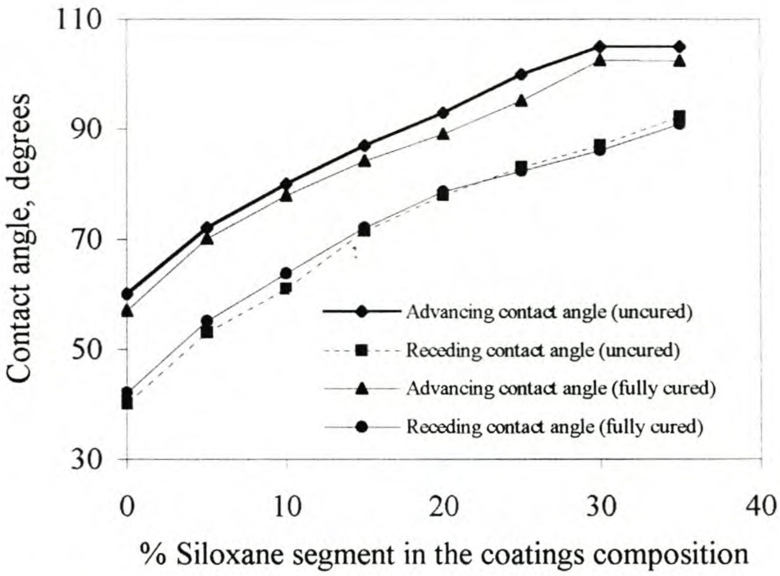

Figure 6.4 Advancing and receding contact angles of water on cured and uncured phosphated and siloxane-modified polyurethane dispersion coatings

The effect of differences in the types of melamine resin used to cure the system on the phase enrichment of the coatings was unfortunately not reported. Hence, not much emerged from their study of the hexamethoxymethyl melamine resin (HMMM). It is widely acknowledged[10-12] that HMMM does not self condense, even in the presence of strong acid catalysts such as derivatives of sulphonic acid, whereas melamine resins containing a substantial amount of both hydroxy methyl and secondary amino groups self-condense easily. Calbo[13] studied the reaction of HMMM with hydroxylated polymers and found that self-condensation was much slower than transesterification. Self-condensation increased as the concentrations of NH and NCH_2OH increased and became dominant, even in the presence of primary hydroxyl-containing polymers. The reaction proceeded either between the two hydroxy methyl (methylol) groups or between the secondary amino (NH) and methylol groups, to form methylene bridges[14]. In the light of the results of the above detailed studies of melamine self-condensation, melamine enrichment at the film/air interface of the polyester-HMMM film studied by Hirayama and Urban[9] could not be explained by self-condensation. Hamada et.al[15] proposed a diffusion model on surface segregation of the melamine crosslinker to and away from the surface, due to a concentration gradient. This model is plausible and relevant to the present work.

When coated on polar surfaces such as metal, polydimethylsiloxane chains in the polyurethane coatings change from a random coil to a "spread chain" conformation, in which the urethane groups are oriented towards the bulk and the siloxane methyl groups are oriented away from the bulk. The spreading coefficient is high because of the low interchain cohesive energy density of polydimethylsiloxane. Consequently, when polydimethylsiloxane contacts high-energy substrates, surface films form readily. The new surface presented by the siloxane methyl groups is of significantly lower energy[16]. Consequences of the free orientation of polymer chains are low cohesive energy density and low surface energy, resulting in poor wetting of the coatings as the siloxane content increased.

The effects of the incorporation of acrylate groups, such as ethylmethacrylate into the siloxane-based phosphated polyurethane coatings on water contact angles are shown in Figure 6.5.

Comparing Figure 6.4 with Figure 6.5, it is clear that the presence of the ethylmethacrylate on the polar urethane groups added hydrophobicity to the coatings. The wettability of the acrylic-based phosphated and siloxane-modified polyurethane coatings decreased quite rapidly at lower siloxane contents and above 20% siloxane content, the presence of the acrylic groups did not impart a significant additional hydrophobicity. It is seen in Figure 6.5 that 5% polysiloxane in the acrylic urethane coating had an advancing contact angle of 88^0 while in Figure 6.4 the same composition without the acrylic had an advancing contact angle of 72^0.

It is noted that the only polymers having lower surface energy than polydimethylsiloxane are some of the highly fluorinated polymers such as poly(hexafluoropropylene), as presented in Table 6.1[17]. The low surface energy of polydimethylsiloxane is maintained not only in coatings but also when reinforced with fillers having different surface energy values[18].

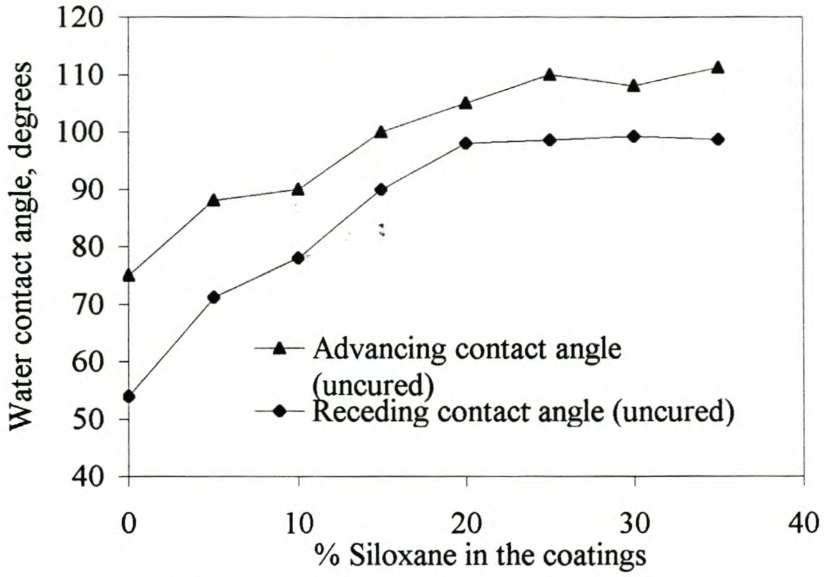

Figure 6.5 Wettability of phosphated and siloxane-modified polyurethane acrylic coatings by water

Table 6.1 Surface energies of some common surface-coating polymers[17]

Coating polymer	Surface tension, N/m
Melamine resin	57.60
Polyester-melamine cured resin	44.90
Polymethylmethacrylate	41.00
Poly butylmethacrylate	34.60
Polydimethylsiloxane	21.5
Polytetrafluoroethylene	18.5
Polyhexaflouropropylene	16.5

6.4.3 Reversible nature of the dynamic contact angle on self-assembling coatings

The dynamic contact angles of water on the coatings discussed above showed constant hydrophobicity with time under standard atmospheric conditions. Phosphated polyurethane coatings on galvanised steel with 20% siloxane segments had an advancing contact angle of 93^0 shortly after curing. The water contact angle of this specific coating was checked periodically. The results, presented in Figure 6.6, were fairly constant for the duration of the investigation. This indicated that under normal atmospheric conditions the contact angle did not change.

The phosphated and siloxane-modified polyurethane coatings discussed above were made from hydrophilic-modified carboxylic acid co-monomer, which had particle sizes below 100nm, as discussed in Chapter 5 section 5.4. The coatings derived from water dispersible polymers were therefore expected to be hydrophilic and have lower water contact angles. However, the coatings had poor wetting properties due to the assembly of silicone-rich components in the surface and the polar and hydrophilic components were buried in the film. The driving force that causes the burying of hydrophilic groups in siloxane-based polyurethane coatings, as shown by poor wettability, is the thermodynamic requirement of minimising the interfacial tension of the coatings.

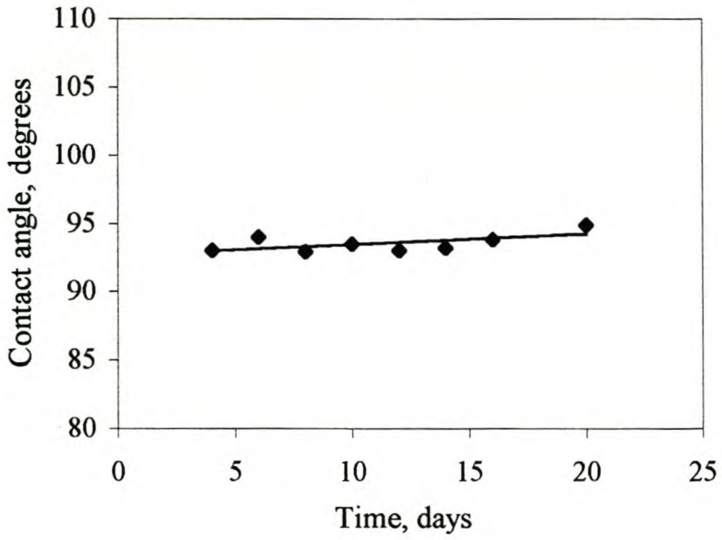

Figure 6.6 The effect of atmospheric conditions on the wettability of phosphated and siloxane-modified polyurethane coatings

Under certain conditions, the buried hydrophilic and/or polar groups should, due to thermodynamic requirements, be reversed when the surrounding phase is changed[17]. For this reason coatings were immersed in a 5% aqueous solution of ammonium chloride for 15 days and contact angle measurements were done 15 minutes after the samples were taken from the solution, to avoid time-dependent hydrophobic recovery.

As shown in Figure 6.7 (P-Si-U means phosphated and siloxane-modified polyurethane coatings and P-Si-Ac-U means phosphated and siloxane-modified polyurethane acrylic coatings), significant decreases in water contact angles were observed after the samples were exposed to an ionic solution of ammonium chloride for 15 days. The decrease in contact angles with immersion in the aqueous ammonium solution was thought to be due to the leaching out of some of the loosely attached, low-surface energy components or by the detachment of some hydrophobic moiety through chemical reaction with the solution. In an effort to prove this assumption, the same samples were rinsed with deionised water and kept at 30^{0}C. The contact angles were then measured as a function of time. It was found that the hydrophobicity had completely recovered, as shown in Figure 6.8. The cyclic loss and recovery of the dynamic contact angles lead to the rather fundamental finding that the change in contact angles was due to the surface dynamic change of the self-assembling coatings rather than the previously mentioned assumption of leaching or detachment.

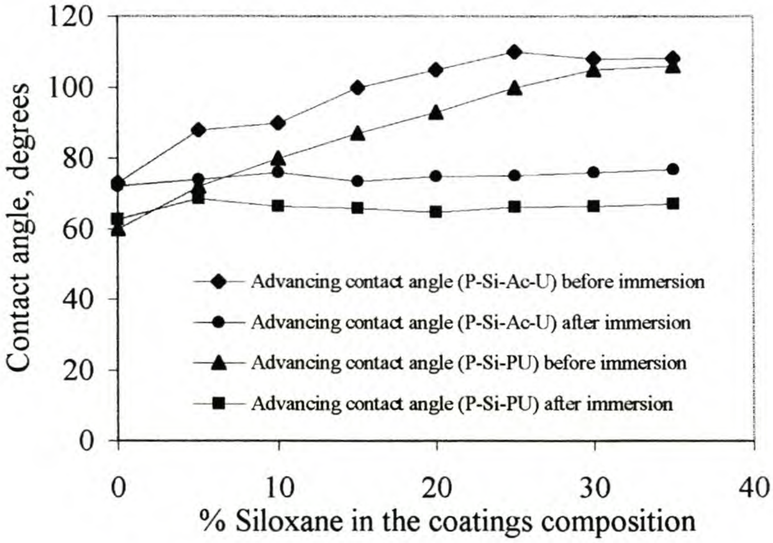

Figure 6.7 The effect of ammonium chloride solution on the wettability of phosphated and siloxane-modified polyurethane coatings

The results in Figures 6.7 and 6.8 highlighted the rotational and diffusional migrations of the hydrophobic siloxane chains away from the polar liquid/ film surface upon immersion in ammonium chloride solution. Such migrations could be anticipated, due to the amorphous nature of the coatings to give coatings a high gloss finish and low glass transition temperature, since the overriding criterion for coil coatings is film flexibility. However the migration of the chains to and away from the surface may be hindered by the presence of the crystalline phases in the polymer. For plasma fluorine-treated polyethylene terephthalate (PET) and Nylon 6, on immersion in water, Yashuda et.al[19] reported a decrease in diffusion-controlled hydrophobic recovery, as crystalinity increased.

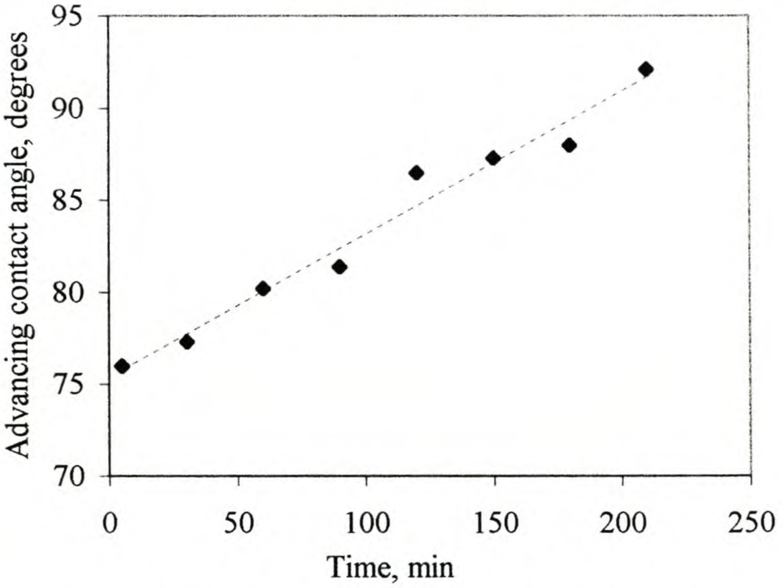

Figure 6.8 Hydrophobic recovery of phosphated and siloxane-modified polyurethane-acrylic self assembling coatings; 10% siloxane in the coatings, 93^0 and 76^0 before and after immersion, respectively

Macromolecules at a polymer surface have a high degree of freedom in determining their conformation according to the immediate neighbouring phase. Considerable mobility and the specific arrangement of functional groups of macromolecules at a surface are dictated by environmental conditions to which the surface is exposed. Consequently, changes in environmental conditions, such as immersion in ionic solutions, can cause considerable changes in the surface characteristics, compared with the characteristics evaluated under atmospheric conditions (Figure 6.7).

The effect of water on the surface dynamic nature of the coatings was also studied by immersing the coatings in distilled water for 15 days and measuring the contact angles 10min after removing from the distilled water. No quantifiable change in contact angles of the coatings were observed, based on the disappearance and reappearance of the siloxane groups on the coatings, as shown in Figure 6.9. Many workers[20-22] have reported decreased contact angles for some polymers when they were brought into contact with water. Better wettability of polymer surfaces after exposure to water in the cited literature was mainly due to the use of water-soluble polymers and highly hydrophilic surfaces like poly (hydroxy-ethylmethacrylate). In the present study the coatings were made hydrophilic by neutralising the pendent carboxylic acid with volatile amines and once the coating were cured the amines were lost and the polymer was no longer highly hydrophilic and wettable by water. In addition, the polar groups were buried under the self-assembling surface.

Thus, the contact angle of water on the surface of the phosphated and siloxane-modified self-assembling polyurethane coatings depended on whether the polar moieties of the polymer molecules were oriented towards the air interface or towards the bulk of the solid, but not on the total polarity and, short-range rotational mobility of a polymer molecule has major influence on contact angle[8].

The difference in wetting behaviour of the coatings after exposure to ammonium chloride solution was explained in terms of polarity. While the coatings were in contact with the solution, the polar groups oriented towards the surface. As the polar components diffused into the coating/solution interface, the polar urethane groups were the components that came to the surface and gave better wetting (lower contact angle) with water. Though the polar groups moved into the outer surface, the urethane groups are hydrolytically stable in the presence of water (Chapter 5, section 5.8) and no coating failure was observed.

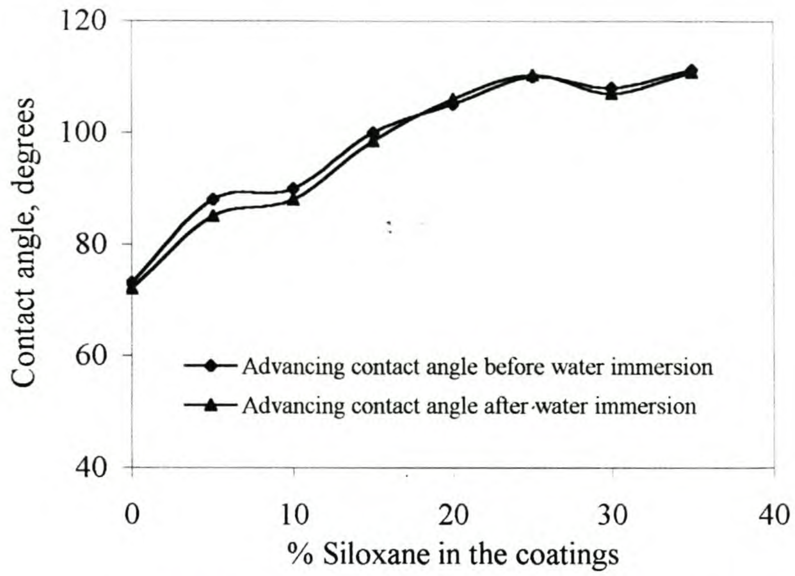

Figure 6.9 The effect of water immersion on the advancing contact angle of phosphated and siloxane-modified self-assembling polyurethane coatings, immersed for 15 days in distilled water and dried at ambient conditions for 10min

There has been a growing interest in self-assembling coatings for many applications, particularly anti-fouling to eliminate toxic copper compounds that adversely affect non-targeted organisms in the sea[23]. In an attempt to achieve this, Brady et.al[23] studied self-assembling fluoro-coatings and characterised their fouling properties in seawater. They used dynamic contact angles to measure the surface dynamics of the coatings after immersion in seawater. It should be noted from the present study that ionic solutions attracted the polar component into the coatings/air interface and reduced the contact angle of siloxane-based coatings and the same may be expected from fluoropolymers[19]. However, Brady et.al[23] reported that the dynamic contact angle was almost the same before and after immersion into seawater. The study may be criticised for failing to address the time-dependent contact angle recovery after the samples were withdrawn from the sea. If contact angle measurements were taken soon after withdrawal, then an even lower contact angle should have been obtained. As contact angle measurements are sensitive to the very top layer of the coatings and since re-assembly can take place with time, studies of self-assembling coatings under specific conditions need careful attention.

6.4.4 Correlation of contact angle reversibility with chemical reactions

The extent to which self-assembling coatings disappear from the surface during the immersion of the coatings in ionic solutions can be empirically related to diffusion-controlled chemical reactions. The diffusion-controlled reaction parameter in polymer matrices, where the extent of reaction is proportional to the contact angle of water before and after immersion, has been reported as a parameter to explain the losses of hydrophobicity in contact angle studies[19].

For a coating sample immersed in an ammonium chloride solution for time t, the hydrophobic "decay" after 't' time, (A_t), A_t was related to the parameter of the original sample before immersion (A_o) by,

$$A_t = A_o t^{-k} \quad \text{..........................equation 6.2}$$

or, taking the logarithm,

$$\text{Log } A_t = \log A_o - k\log t \quad \text{...........equation 6.3}$$

Typical disappearance of hydrophobic character expressed as log contact angle (θ) for the coatings as a function of immersion time t on a log scale is shown in Figure 6.10. There is a linear relationship with immersion time. The k parameter is an indication of the mobility of the molecule away from the surface.

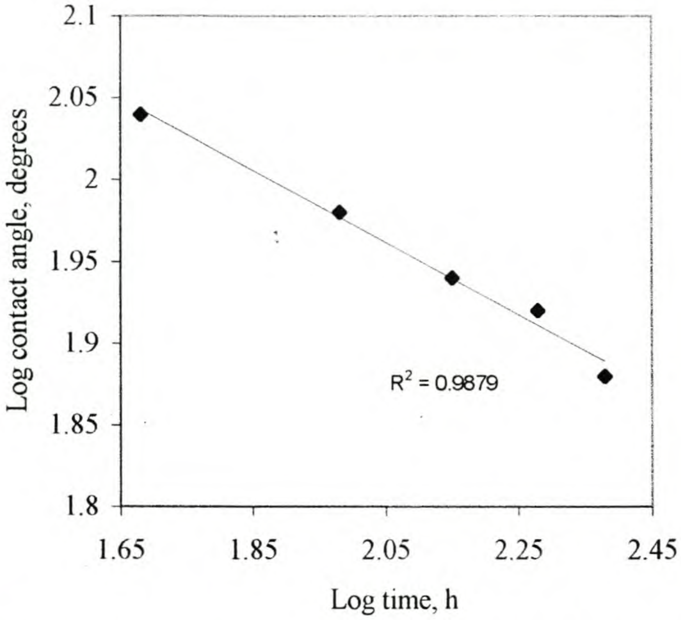

Figure 6.10 The loss in hydrophobicity of coatings as a function of immersion time in ammonium chloride solution

6.4.5 Adhesion of coatings to metal, based on thermodynamic surface matching

In surface coatings, with the exception of powder coatings and ultraviolet curing coatings, paints are supplied in suitable carrier solvents. Consequently, the interpretation of wetting is difficult because of preferential adsorption. Further complications arise since the solvents used to dilute the paint are of different molecular species with different adsorption properties[24]. The lower surface tension of the solvent compared with that of the actual polymer will result in instantaneous preferential adsorption of the solvent to the metal interface and it may appear as if the contact angle is zero or at least near zero. As the solvent evaporates during the curing or drying time, wetting can change because of the multiple attachments of which polymers are capable. Therefore a more systematic method of thermodynamic surface matching to the solid substrate, to exclude solvents, was used to study adhesion. This was based on advancing and receding contact angle measurements of both the solid polymer and the solid metal. If a series of randomly chosen probe liquids of known surface tensions are used to wet the polymer and the metal, independently, and the hysteresis graphs are plotted, adhesion between the two surfaces can be predicted by visual comparison[14]. From thermodynamic compatibility considerations, those surfaces that had similar hysteresis spectra correlated with better adhesion since solids with similar hysteresis graphs have similar surfaces.

Table 6.2 Surface tensions of probe liquids used for thermodynamic matching of surfaces (N/m)

Liquid	**Surface tension (N/m)**
Water	72.8
N-methyl pyrollidone (NMP)	40.7
Dimethylformamide (DMF)	37.3
Propylene glycol mono methyl ether acetate (PMA)	28.2
o- Xylene	30.1
Hexane	18.7

The results of the contact angle study are shown in Figure 6.11. Each graph represents one spectrum for each liquid. The bottom of each spectrum is cos θ_a and the top of each spectrum is cos θ_r. In this contact-angle study of the phosphated and siloxane-modified polyurethane coatings only two immersions were done to avoid swelling and large hysteresis. The Y-axis is the cosine of the contact angle. The X-axis is an ordered list of probe liquid surface tensions. The length of each spectrum is the measure of the contact-angle hysteresis.

There is close similarity between the spectra of the metal and the phosphated-polyurethane confirming that the steel substrate and the coating film were thermodynamically compatible and there was good adhesion between the polymer and the metal.

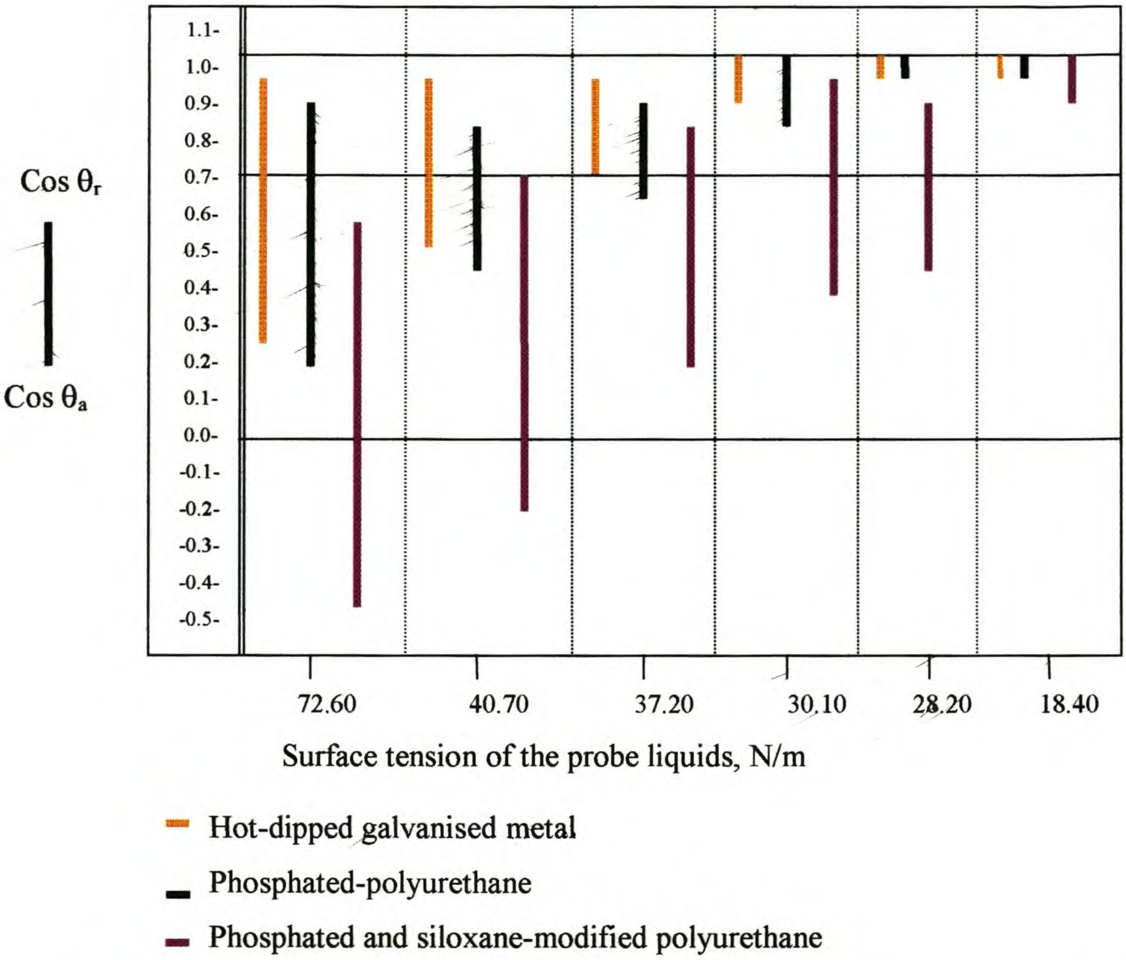

Figure 6.11 Hysteresis spectra of the hot-dipped galvanised steel and the phosphated coatings with and without siloxane

The effect of the self-assembling silicone coatings on surface energies of a coating is also shown in Figure 6.11. When comparing the spectra of the phosphated and siloxane-modified polyurethane with the phosphated polyurethane and the bare metal, it is seen that the surface of the phosphated siloxane-modified polyurethane coatings is drastically modified. For all the probe liquids used, both θ_a and θ_r were decreased, indicating poor wettability of the surface of the phosphated and siloxane-modified polyurethane coating. The reduction in the surface energy of the coating layer, due to the assembly of the coatings, resulted poor wettability by all solvents used as probes. This is not surprising, since contact-angle measurements are highly sensitive to the chemical characteristics of the outermost part of a solid surface. The solvents used here were carefully chosen, to cover almost all solvents with surface tensions ranging from 18 to 72N/m, used in the paint industry. The only exception in Figure 6.11 is the hysteresis graphs of the phosphated siloxane-modified polyurethane coatings when hexane was used as the probe liquid. Here improved wetting of the coating was observed due to the low surface tension of hexane. The surface tension of hexane is below the critical surface tension of polydimethylsiloxane, as shown in Tables 6.1 and 6.2, and from the critical surface tension concept hexane is expected to wet polydimethylsiloxane. In section 6.5.3 it will be seen that metal phosphate is formed at the metal/coating interface for good adhesion, irrespective of whether the coatings contain silicone or not. Although the thermodynamic surface matching between the metal and the phosphated and siloxane-modified polyurethane dispersion coatings, from Figure 6.11 is far from close, self-assembly of the phosphate groups at the metal interface and self-assembly of the siloxane at the air interface were the driving factors for the observed good adhesion[14]

6.4.6 Contact angle hysteresis

Contact angle hysteresis, the difference between the equilibrium advancing contact angle and the equilibrium receding contact angle, is a frequent observation in dynamic contact angle studies. In this study θ_a was much greater than θ_r for the high surface tension liquids, such as water, while for the lower surface tension liquids θ_a approaches θ_r and in some cases it has been observed that $\theta_a = \theta_r$. It should, however, be mentioned that $\theta_a = \theta_r$ does not mean that the contact angle is zero as $\theta_a = \theta_r$ happens at $\theta>0$[25].

It was more accurate to relate the length of each spectrum to hysteresis due to roughness and heterogeneity of the bare metal, as evidenced by atomic force microscopy (Figure 6.12). A crystalline metal has a high molecular or atomic density, and hence different surface free energies. The structure of the grain boundary at the zinc layer has a profound effect on hysteresis. Because of the grain difference, the surface is rough and heterogeneous and has a different wetting property. On heterogeneous surfaces the advancing contact angle is sensitive to the less wettable surface (low surface energy) while the receding contact angle is more sensitive to the more wettable part. This means that the advancing contact angle "directly" shows the surface energy condition whereas a receding contact angle shows the surface energy condition of the already wetted surface[26].

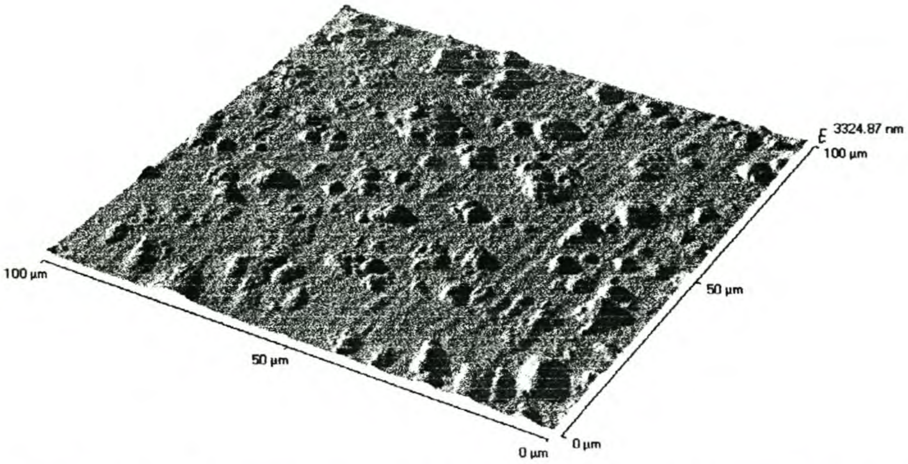

Figure 6.12 3-dimensional AFM image of a galvanised steel surface showing surface roughness

Surface roughness was not the primary cause of hysteresis of the coatings in the present study since atomic force microscopy did not reveal any roughening of the surface of the coatings that could cause large hysteresis (Figure 6.13).

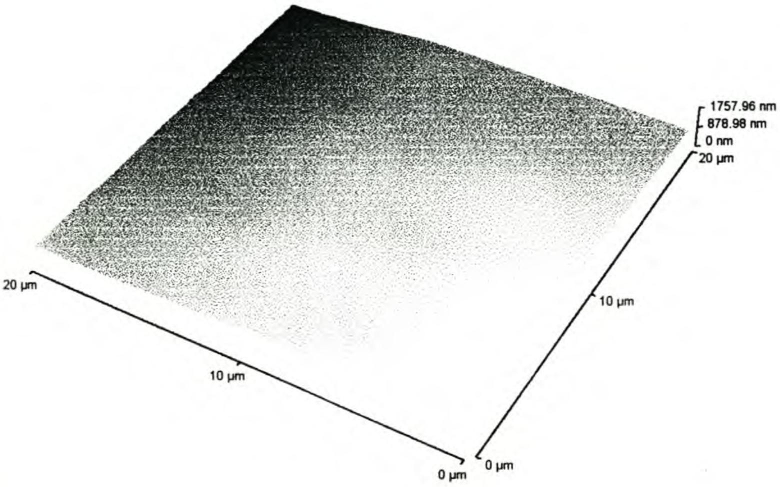

Figure 6.13 3-dimensional AFM image of a coating on galvanised steel showing a smooth surface

Time-dependent dynamics and swelling of the polymer surfaces were also assumed to be primary causes of contact angle hysteresis[22]. However, the coatings prepared did not swell during contact angle studies as evidenced by the smooth force reading during immersion and withdrawing. Furthermore, the self-assembly property of the coatings did not change with time under normal conditions, as shown in Figure 6.6. For the coatings, only surface heterogeneity would explain the hysteresis differences shown in Figure 6.11. In section 6.4.2 it was described that the contact angle increased with the content of the siloxane in the coatings formulation, indicating that the top surface was not fully enriched with the low-surface tension siloxane and some polar groups were present in 'patches'. Thus, the advancing contact angle 'sees' the siloxane/air interface whereas the receding angle 'sees' the polar 'patches' at the interface, and large hysteresis is obtained.

6.5 Self-assembly of phosphate groups at the metal/coatings interface

6.5.1 Introduction

Phosphating is the most widely used metal-treatment process for the surface finishing of ferrous and non-ferrous metals. The surface phosphating treatment of steel prior to the application of paints or adhesives, to improve adhesion and inhibit corrosion, is a conventionally used industrial practice. The phosphate conversion coating results in a non-conductive layer of metal phosphate in its crystalline form that insulates the metal from corrosion and provides enhanced adhesion for subsequent coatings. The quality of finish required by the industry determines the degree to which the pretreatment and phosphating are carried out. In a traditional multi-step process, the metal surface is cleaned several times and by several means, phosphated and then sealed before it is dried with hot air and is ready for painting. Since industrial phosphating does not cover 100% of the metal surface[27], the unphosphated area becomes a pore and sealing is normally done with a chromate solution. The conversion coating (pretreatment) of zinc yields insoluble hydrate films of $Zn_3(PO_4)_2.4H_2O$. The use of chromate pretreatment for aluminium or the use of it as a seal for phosphated metals is however, expected to be banned (in some countries it is already banned) since hexavalent chromium (Cr^{6+}) is a known carcinogen[28]. In most commercial treatment lines oxidizing agents and accelerators are added for fast production output and increased line speed. Disposal of all this toxic waste is becoming a serious problem. Thus the idea of combining the metal phosphate and the organic coating in a single process, by means of self-assembling coatings, is a novel idea that could eliminate the existing multistep process and health threat

6.5.2 Experimental

Coatings were prepared as described in Chapter 4, section 4.3.1. The dried coating samples were soaked in THF for 6h to remove any soluble layer. The metal interface obtained was rinsed with de-ionised water and dried at 70^{0}C for 30min.

6.5.3 Results and discussion

To ensure that the formation of metal phosphate on the hot-dipped galvanised steel surface was from the phosphated and siloxane-modified polyurethane coatings and not from any previous treatments, it was necessary to obtain the EDX spectrum of the metal as a reference. Figure 6.14 shows the EDX spectrum of the bare, hot-dipped galvanised steel. Its only peaks are those of zinc, as labelled by the instrument. Figure 6.15 shows the EDX spectrum of the metal interface after it was dip-coated with the phosphated and siloxane-modified polyurethane dispersions.

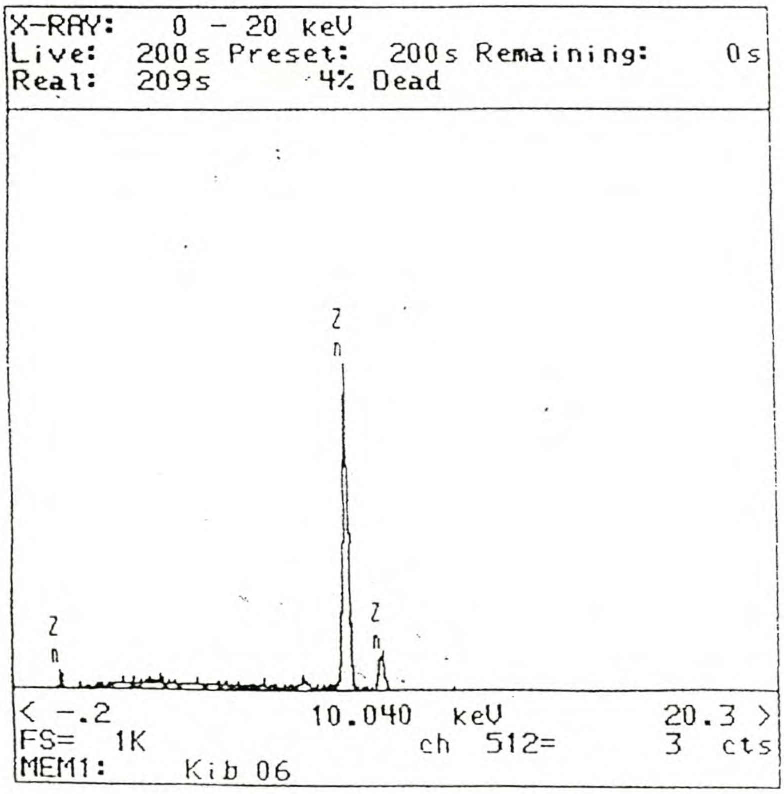

Figure 6.14 EDX spectrum of the bare, hot-dipped galvanised steel

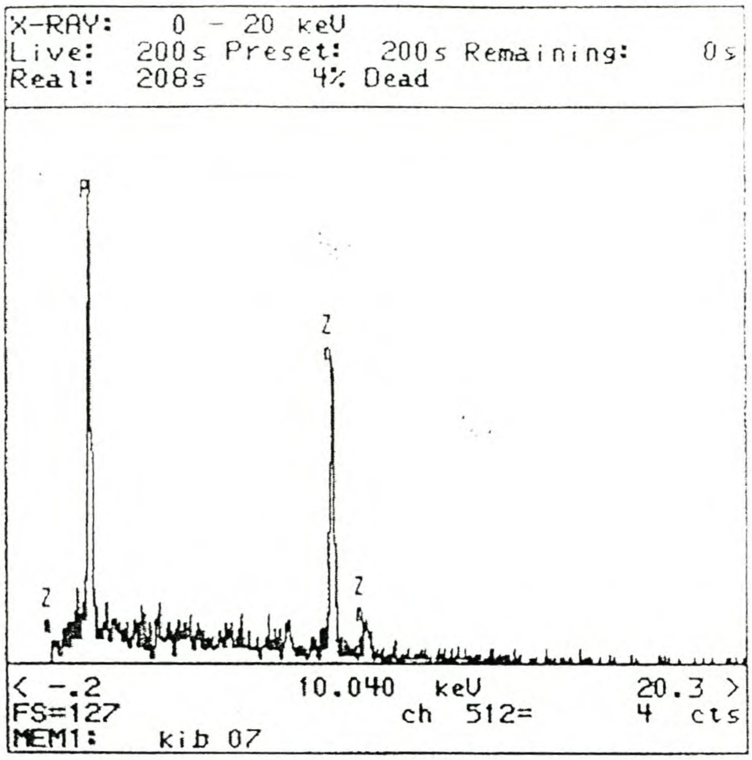

Figure 6.15 EDX spectrum of the metal interface after dip-coating with the phosphated and siloxane-modified polyurethane dispersions

The appearance of zinc (Zn) at the principal emission line of 8.60KeV and phosphorus (P) at 2.02KeV in the energy dispersive spectrum indicated that the insoluble zinc phosphate was indeed formed at the interface. (Note that the value 10.04 keV in Figures 6.14 to 6.16 is the value of the cursor from the instrument and not the principal emission line for zinc). The high peak intensity of phosphorus with respect to zinc in the same sample and identical counts (200 counts) indicated the thickness of the phosphate layer. Very thick crystalline metal phosphate layers are, however, not required for certain applications. Some microcracking of the phosphate layer has been observed underneath a flexible primer coat when thick coatings were subjected to 180^0 bend (0-bend) in clear coats prepared by coil coating[14]. In this above case[14], the clear coat was deformed without cracking but only the metal phosphate was cracked. However, when the coating was prepared from a low phosphate-content polyurethane dispersion, EDX peaks were obtained with lower phosphorus to zinc peak ratios, as shown in Figure 6.16.

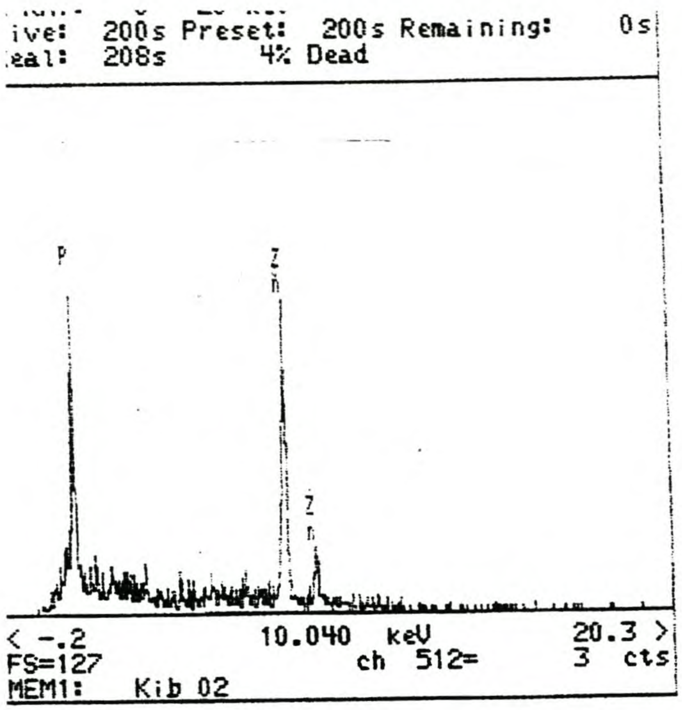

Figure 6.16 Zinc phosphate formation from phosphated and siloxane-modified polyurethane dispersions (low phosphorus content)

In all the cases the formation of insoluble metal phosphate at the interface dictated that when phosphated polyurethane dispersions were applied on a clean metal, like galvanised steel, the phosphoric acid groups diffused into the metal and assembled at the interface by forming metal phosphate.

6.5.3.1 The effect of the neutralising base on the formation of insoluble metal phosphate

The polyurethane dispersions described in the present study were made hydrophilic and dispersible in water by neutralising the pendent carboxylic acid groups with bases. In Chapter 5, the effects of the neutralising bases on the physical properties were discussed. The neutralising bases also affect the coating properties. Wicks and Chen[29] and Ferrell et.al[30] have reported amine transesterification with a melamine crosslinker when amino-alcohols were used as a neutralising bases. The present author found[14] a drastic reduction in the dynamic mechanical properties of the melamine-cured polyurethane dispersions when high boiling amino-alcohols were used to neutralise the resin. These all show the deterrent properties of the neutralising amines.

The effect of the neutralising base on the metal phosphate formation is evidenced by comparing Figure 6.15 with Figure 6.17. In Figure 6.15 the neutralising amine was triethylamine and in Figure 6.17 it was diethanolamine. When EDX analysis of the interface was done for dispersions neutralised by diethanolamine, no phosphorus (P) at 2.05KeV was detected and only peaks corresponding to zinc were identified.

The fundamental reason for the phosphorus not being detected, as an indication of metal phosphate formation at the interface, was due to the neutralising amines. In the phosphating process the functional groups involved are the P=O and POH groups of the polymer. The presence of these groups can be seen in the FTIR spectra of the 1,2,4-phosphonobutane tricarboxylic acid (PBTCA)-derived macroglycol in Figure 6.18.

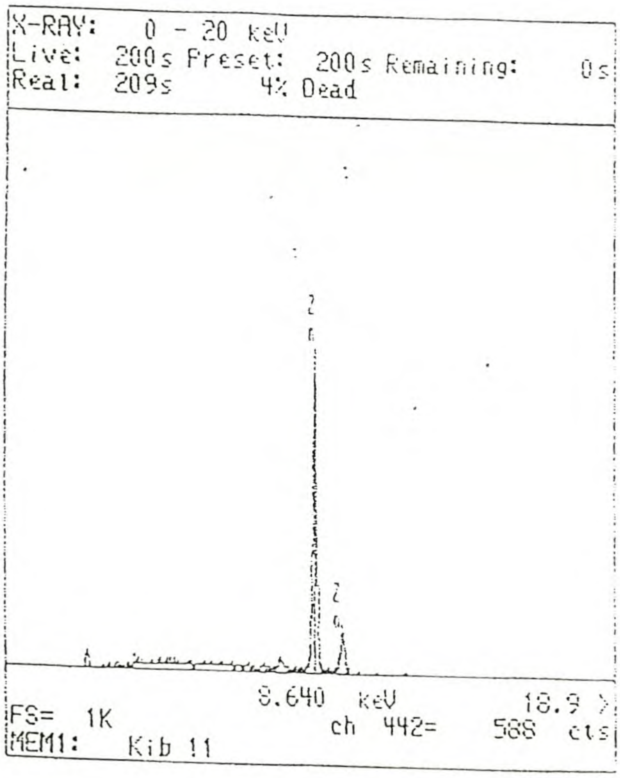

Figure 6.17 EDX spectrum of phosphated and siloxane-modified polyurethane coatings showing the effect of the neutralising amine on the formation of metal phosphate

The macroglycol was chosen instead of the final polymer to avoid any overlapping peaks due to the additional functional groups of silicone, urethane and acrylic combinations.

Figure 6.18 shows two bands at 1005 and 1041 cm^{-1}, which are the P=O stretching vibration, and an absorption at 1168 cm^{-1} which indicates the aliphatic nature of the P=O stretching[31], since the monomer used is aliphatic. A medium-strength absorption is observed in the range 1610-1700 cm^{-1} for the P=O(OH) groups[32]. The hydrogen bonded phosphoryl (P=O) group has a characteristic absorption in the region of 1250-1260 cm^{-1}[32]

For the formation of insoluble metal phosphate, the P-OH must dissociate into PO$^-$ ions and the metal phosphate has to be crystalline. Both dissociation and crystallisation processes require water[34]. Phosphated polyurethane dispersions have the added advantage since the solvent is water.

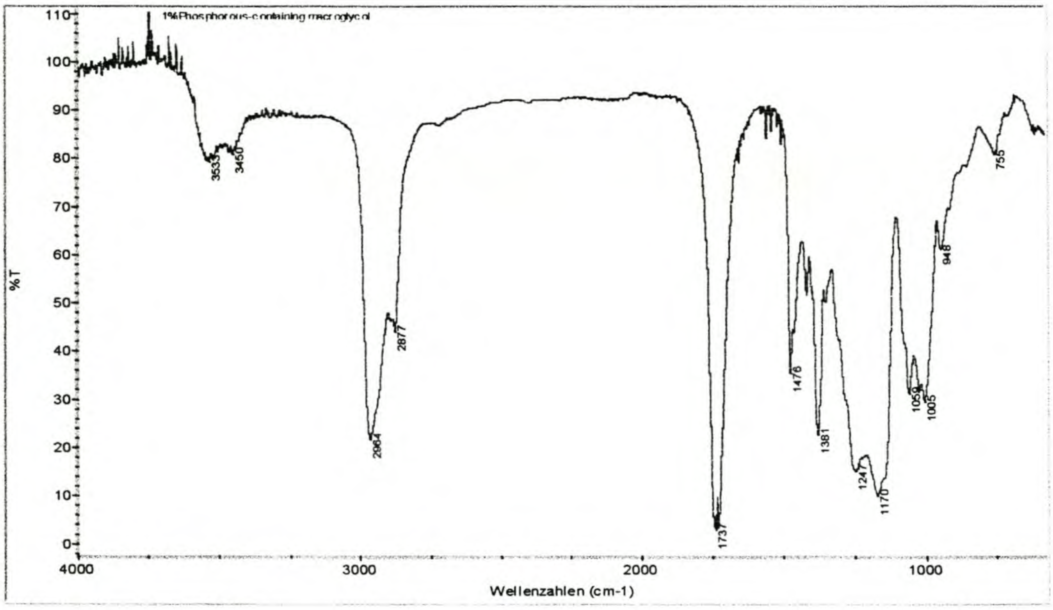

Figure 6.18 FTIR spectrum of a phosphorus-containing macroglycol

The last important point is the pH of the solution, which has to be acidic for metal phosphate formation. Thus, for metal phosphate formation the dispersion must be slightly acidic, if not strongly acidic. The requirement of the coating composition to be acidic means that the neutralising amines that exist in equilibrium with the free acid and free amine must be dissociated.

$$\text{R-CO}\overset{-}{\text{O}} + \text{HN}\overset{+}{\text{R}}_3 \rightleftharpoons \text{R-COOH} + \text{NR}_3$$

At drying temperatures of 75^{0}C, under vacuum, triethylamine is likely to dissociate and evaporate due to its low boiling point compared to that of diethanolamine. The amines act as complexing agent for the P-OH groups and the coating film remains alkaline as long as the amines are not dissociated. Therefore metal phosphate could not be formed in this case and during the etching process by THF; all the coating layers were dissolved and no phosphorus was detected by EDX. Thus, when the neutralising amine had a lower boiling point and low basicity, it dissociated at lower temperature and favoured metal phosphate formation. In fact, for paints intended for use in coil coatings and provided that the curing proceeded thermally, most amines would dissociate and the coatings would become acidic due to the high curing temperature (220^{0}C peak metal temperature in most cases) required. Lastly, the acidity of the coatings upon amine dissociation generates carboxylic acids and these act as a weak catalyst for the melamine crosslinking, as described in a previous study of polyurethane dispersions by the author[14].

It is concluded from EDX studies that the formation of insoluble metal phosphate at the interface was evidenced by the appearance of the phosphorus (P) peak at 2.02KeV and the zinc at 8.64KeV. Phosphorus has been successfully assembled under favourable conditions at the interface. The nature of the metal phosphate depended on the temperature required to dissociate the amine. Silicon was not detected at the interface, proving that the silicone-rich components assembled at the coating/air interface and not at the metal/coating interface as expected.

6.6 X-ray Photoelectron Spectroscopy (XPS) investigation of the self-assembling coatings

6.6.1 Introduction

X-ray Photoelectron Spectroscopy (XPS) is one of the most popular and useful methods to analyse the surface composition of coatings. XPS probes a layer to a depth of about 7nm.

Angle-resolved XPS is a technique whereby, by tilting the sample to change the angle of the surface with respect to the detector, a thin layer can be probed[34]. At small 'take-off' angles the detector will only collect electrons emitted from the shallow region near the surface. At high 'take-off' angles, the detector will collect electrons emitted from both the shallow region and the deeper layers, as presented schematically in Figure 6.19. Therefore, by changing the take-off angle, a concentration depth profile can be obtained. Low-angle XPS can provide improved depth resolutions to about 0.5nm. This is the top surface to which advancing and receding contact angles in surface tension studies are sensitive.

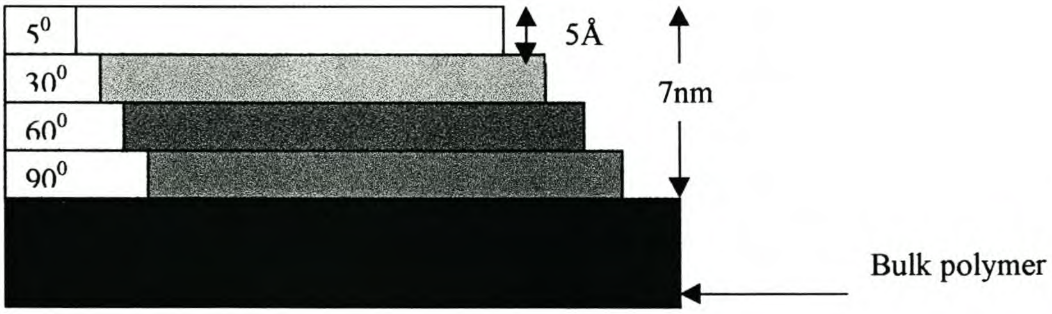

Figure 6.19 Schematic representation of the surface layer of coatings analysed by angle-dependent XPS

6.6.2 Results and discussion

The methods of sample preparation and the analytical XPS instrumentation used were described in Chapter 4, section 4.2.1. The elemental compositions of the coatings were calculated from the integrated peak areas and the sensitivity factors for each element (see Table 6.3), which result from the silicon 2p, phosphorus 2p, carbon 1s, nitrogen 1s, and oxygen 1s core level electrons, using the equation:

$$Cx = \frac{Ix/Sx}{\sum(Ii/Si)} \quad \text{.............equation 6.4}$$

where; Cx is the concentration fraction of element X

Ix is the real integrated area for element X

S is the sensitivity factor (see Table 6.3),

i is the total number of elements present in the sample.

Table 6.3 Sensitivity factors of the elements in the coating composition[35]

Element	**Sensitivity factor**
Carbon (C1s)	0.314
Oxygen (O1s)	0.733
Nitrogen (N1s)	0.88
Silicon (Si 2p)	0.368
Phosphorus (P2p)	0.525

The elemental compositions of the phosphated and siloxane-modified polyurethane dispersion coatings determined at different take-off angles are presented in Tables 6.4 and 6.5.

Table 6.4 Elemental composition of phosphated and siloxane-modified polyurethane coatings where 20/80 ratio of polysiloxane-macroglycol to phosphated-macroglycol were reacted *in-situ* with the isocyanate to obtain phosphated and siloxane-modified polyurethane dispersions with 70% soft segment and 30% hard segment.

Take-off angle **% Element**	**5^0**	**30^0**	**60^0**	**90^0**
Carbon	57.02	60.75	63.00	66.00
Oxygen	24.91	24.48	24.15	20.10
Silicon	18.07	14.77	10.23	10.19
Nitrogen	0.00	0.00	2.33	2.39
Phosphorus	0.00	0.00	0.29	0.32

Table 6.5 Elemental composition of phosphated and siloxane-modified polyurethane coatings where the polysiloxane-based polyurethane dispersion was blended into a phosphated polyurethane dispersion

Take-off angle % Element	5^0	30^0	60^0	90^0
Carbon	51.40	66.00	75.73	78.70
Oxygen	23.12	15.45	13.11	10.00
Silicon	25.48	16.55	3.06	0.20
Phosphorus	0.00	0.00	2.20	4.20
Nitrogen	0.00	0.00	5.90	6.80

As can be seen from both tables, phosphorus and nitrogen were not detected in all the samples at lower take-off angles (5^0 and 30^0) indicating that the polar urethane groups and phosphorus were not on the surface of the coatings. In Table 6.4, the silicon decreased as the take-off angle increased. This was accompanied by a decrease in oxygen from 5^0 to 90^0. Further, as we moved from 5 to 90^0, the carbon increased. Small amounts of both nitrogen and phosphorus were detected at higher angles (higher depths). The decrease in silicon with depth is an indication of the assembly of the silicon at the very top surface (less than 15 angstroms).

The assembly of the silicon can be explained by looking at the oxygen content that showed a similar trend with silicon content. The decrease in oxygen with decrease in silicon content is related to the presence of the Si-O-Si bond of the polysiloxane chain. Thus, as the amount of silicon decreased towards the bulk of the polymer, so did the oxygen. As discussed in section 6.4.3, the poor wettability of the self-assembling coatings was due to the lower surface tension of the polysiloxane chains, which the XPS result confirmed. It was also mentioned in section 6.4.3 that the polar urethane group accounted for the improved wettability of the coatings after exposure to ionic solutions. As can be seen from Table 6.4, the urethane groups were not present (no nitrogen) in the surface-sensitive region of the dynamic contact angle tests under normal storage conditions. Thus the polar groups were buried in the bulk until they came into contact with ionic solutions.

The effect of the method of incorporating the siloxane groups into the dispersions on self-assembly is presented in Table 6.5. In Table 6.5 the siloxane-based dispersion was blended into a phosphated-polyurethane dispersion whereas in Table 6.4 the dispersions were obtained by *in-situ* polymerisation of the siloxane and the phosphated macroglycols with the isocyanate. However, both coatings had the same percentage of siloxane groups.

The significant difference between the two coatings is seen in the silicon content in the 5 and 30^0 angles when we compared Table 6.4 with Table 6.5. In Table 6.5 a 40% increase in silicon was observed at 5^0 compared with Table 6.4, indicating that the coatings from the blend enriched the surface with more silicon than did the coatings from the *in-situ* reaction product. The silicon content of the coating prepared from the blend dispersion is close to that of the pure siloxane. In the pure siloxane segment, the silicon % is 26.92 compared to 25.48 % observed in the coating at 5^0.

The silicon enrichment seen in Table 6.4 is explained in terms of phase separation between the two dispersions, due to solubility differences between the phosphated-polyurethane and the siloxane-polyurethanes. Pascault and Camberlin[36] have studied block co-polymers of polydimethylsiloxane-polyurethanes and found that the solubility differences between the segments were responsible for the silicon enrichment at the film/air interface. Tezuka et.al[37] investigated the wetting properties of poly (vinyl alcohol)-poly (dimethylsiloxane) grafts and found that the air/polymer surface was essentially covered with pure siloxane segment.

The silicon content at different take-off angles in Table 6.5, however, is explained by the ease with which the siloxane segments move independently from the phosphated polyurethane chains. Polymer chains in a blend move much more freely than they do in covalently bonded and crosslinked polymers. For coatings prepared by *in-situ* polymerisation of the siloxane and the phosphate-containing macroglycols with the isocyanate, the siloxane groups are covalently linked with the whole chain. Thus, though the silicone chains try to move to the outer surface, they will be restricted by the covalent bond together with the rest of the chain that contains phosphate. Thus, when the depth is increased, the silicon content of the *in-situ* reaction is substantially higher than that of the blend, where the silicon is almost negligible (0.2% compared to 20.19% at 90^0)

Detection of the nitrogen 1s electrons at a binding energy of 400eV indicates the presence of the urethane hard segments since the urethane groups are the only nitrogen-containing functional groups. The silicon 1s electron at 150eV and 2p electrons at 102eV binding energies are only from the polysiloxane groups. The carbon and oxygen 1s electrons are from all the segments (the polyester, the urethane and the siloxane). Thus, the ratio of silicon to nitrogen was used to characterise the surface. Results of the ratio of silicon to nitrogen versus depth are presented in Figure 6.20.

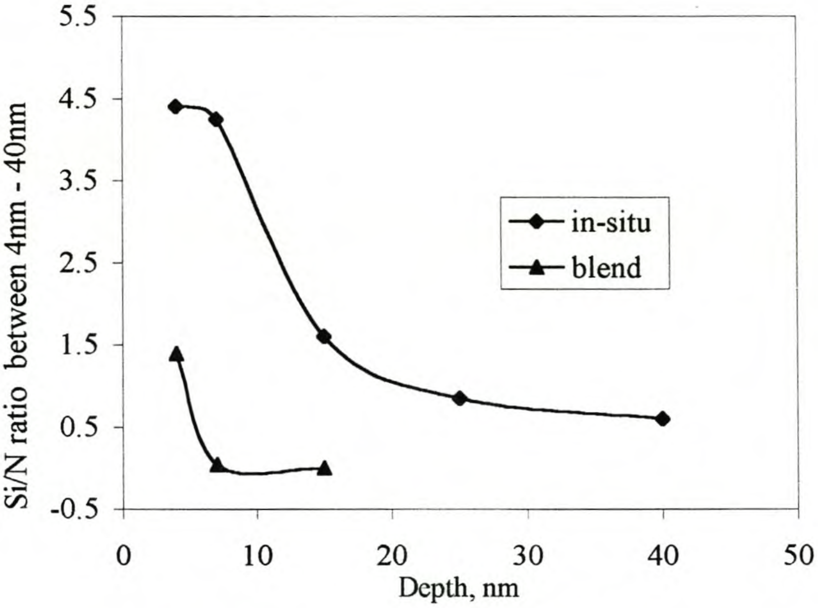

Figure 6.20 The dependence of the Si/N ratio between depths of 4nm and 40nm on the method of incorporating the siloxane chains into polyurethane dispersions

The Si/N ratio of the coatings prepared from the *in-situ* reaction remained high, even at depths greater than 40nm, and the Si/N ratio for the blend dropped to zero after 9nm depth. Since nitrogen was not observed at the lower angles (Si/N becomes meaningless), Figure 6.20 shows values of Si/N ratios obtained for 60^0 and 90^0 and those obtained by sputtering to depths of 40nm.

Sputtering was done to obtain a relative indication of elemental composition. The exact values of each element may be higher since some degradation can take place due to the high energy used to sputter the samples. Nevertheless, the elemental composition values in Tables 6.4 and 6.5 were sufficient to conclude the self-assembly of the coatings without sputtering.

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Chapter 7

Ultraviolet (UV)-curing of phosphated polyurethane acrylic dispersions

7.1 Introduction

The use of ultraviolet (UV) to cure vinyl-terminated coatings is well established and documented[1]. The primary advantages of using UV for curing are the high cure speeds that can be used and the fact that the coating formulations are 100% solids. Most commercial UV-curing coatings use acrylic-based monomers and resins, which cure by a free-radical mechanism. However, the high level of the acrylic diluent used to reduce the viscosity has an adverse effect on the cured film. UV curing is generally accompanied by shrinkage, because non-bonding distances between the monomers are converted to shorter bonding distances in the polymers. Following the onset of polymer network formation, shrinkage may lead to internal stresses because of restricted relaxation process. This problem is further exacerbated in rapid-curing systems, in which relaxation processes may not keep pace with polymerisation[2,3]. 8-20% shrinkage occurs during the polymerisation of monofuctional acrylates and methacrylates. Internal stresses generally have adverse effects on the mechanical properties of coatings and their adhesion to substrates. Relatively small volume changes and even expansion may occur during polymerisation of monomers which undergo ring-opening reactions, as a consequence of bonding distances being converted into longer non-bonding distances in the ring-opening process.

From the health point of view, the use of high proportions of acrylic monomers is unacceptable, particularly for spray applications. Low-molecular-weight diluents can easily be adsorbed into the substrate (if porous) during the time between application and curing. The part of the diluent being shielded from the UV light would not be polymerised and could cause failure of the coatings and an unpleasant odour. It is not only the monomers but also the photoinitiators that, due to the high content of initiator extractables after cure, are considered to be a potential threat in the packaging industry. Hence the ‘once best, volatile organic compound free technology’ is under new scrutiny[4,5].

Most photoinitiators absorb in the 300-430nm region. The medium-pressure mercury arc lamp offers maximum UV output within this range. In addition to the lamps, complete UV-assemblies for commercial coating lines require: a power source, lamp reflectors, suitable shielding to reduce UV leakage, adequate cooling and ventilation. In practice, multiple lamps are mounted perpendicular to the moving conveyer, which is placed a few centimeter away from the coating.

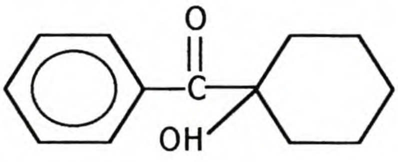
Waterborne UV curing has recently become increasingly important[6] and a substantial amount of work is being done to develop co-polymerisable photoinitiators to minimise the extractables[7,8] In this chapter, phosphated-polyurethane acrylic dispersions are investigated as candidates for UV curing applications.

7.2 Experimental

Water-based dispersions of the phosphated-polyurethane acrylates were prepared from a phosphate-containing polyester (molecular weight 2000) macroglycol, dimethylol propionic acid, 2-hydroxyethyl methacrylate and the reactive diluents as described in Chapter 3, sections 3.4.3 and 3.4.4. Dispersions of the phosphated-polyurethane acrylates were crosslinked with UV, as a source of radiation, when a photoinitiator was added to the system.

7.2.1 Photoinitiator

Hydroxy-cyclohexyl-phenyl-ketone (Irgacure 184, CIBA-GEIGY Corporation) was used as photoinitiator. It is a highly efficient UV- curing agent, used to initiate the photopolymerisation of the phosphated polyurethane-acrylic dispersions. 2% concentrations were used.



Hydroxy-cyclohexyl-phenyl-ketone

7.2.2 Substrate preparation

All the substrates used in this study were products of ISCOR and Hulett. Of the possible substrates available for coil coating, only the hot-dipped galvanised steel and aluminium were used. The panels were cut to sizes of 10cm x 20cm. Their thickness was approximately 0.6 mm. Before application of the coating, all the panels were first dried at 120^0C for 5min in an oven to remove any traces of moisture adsorbed during transportation and storage. After cooling to room temperature the panels were coated immediately.

7.2.3 Film applicator

A wire-wound drawdown bar was used to apply the coating to the substrate. Since the diameter of the wire wound on the bar controlled the thickness of the wet film, the choice of the bar was important in controlling dry-film thickness. In the coil-coating line, coating thickness is controlled by varying the pickup or applicator roll speed and nip adjustments. The wire-wound drawdown bar resembled a roller.

7.2.4 Preparation and curing of coatings

The UV-cured coatings were obtained by depositing a mixture of the phosphated and/or siloxane-modified polyurethane acrylic dispersion and photoinitiator onto the substrates. Before applying the coatings, proper homogenising of the photoinitiator with the dispersion was done at 40^0C for 10min. The phosphated and/or siloxane-modified UV-curable polyurethane dispersions were mixed with the photoinitiator, coated onto the substrate and irradiated using a medium-pressure mercury lamp (of varying intensities), equipped with semi-elliptical reflector. The distance between the sample and the lamp was 30mm and the films obtained were 5-30microns thick. The conversions (polymerisations) of the C=C bonds were studied by FTIR spectroscopy.

7.3 Results and discussion

7.3.1 Verification of complete UV curing

The UV-curing reactions are radical polymerisations involving the vinyl groups of the 2-hydroxylethyl methacrylate and the acrylate diluent. Complete reactions were verified by the FTIR absorption bands of the acrylate C=C at 820/cm and 1635/cm, prior to and after irradiation. Figure 7.1 shows the FTIR spectra of the C=C absorption before and after irradiation of the coatings. As can be seen, the C=C bonds diminished after irradiation.

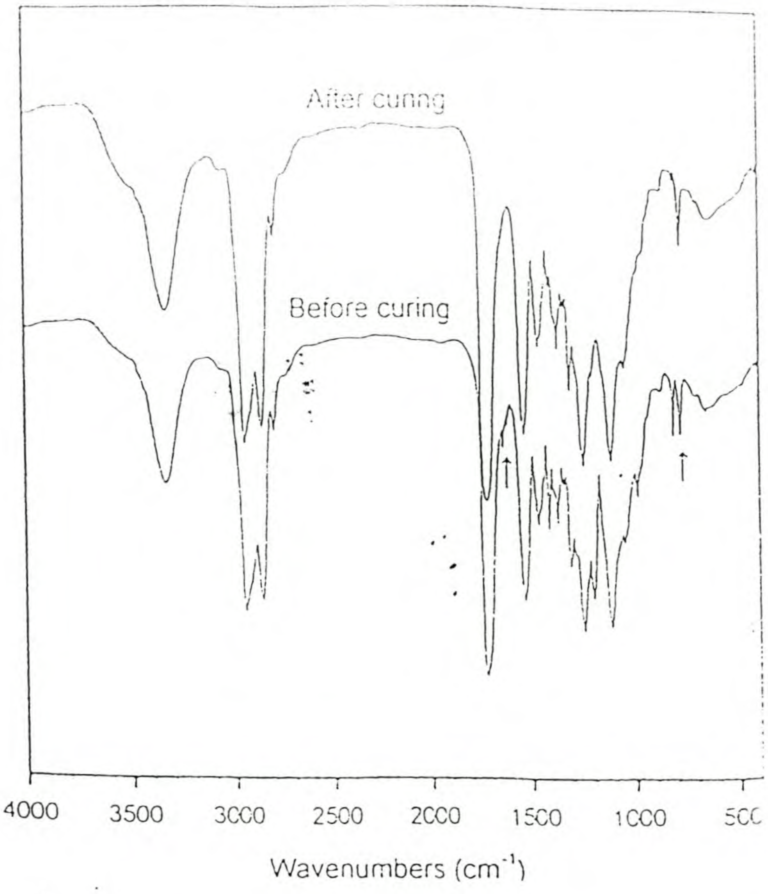


Figure 7.1 FTIR spectra of the coatings before and after UV curing

7.3.2 The effect of light intensity on polymerisation

One of the unique advantages of light-induced reactions is that the initiation rate can be easily varied by the intensity of the UV-beam that impinges on the sample. When the light intensity (I_0) was increased, the polymerisation was found to develop more rapidly from the increased rate of initiation. The profiles of the conversion of the C=C bonds versus UV exposure time for the phosphated-polyurethane acrylic dispersions exposed to UV radiation of various intensities (I_0) are presented in Figure 7.2. After a short induction period, due to the inhibitory effect of oxygen dissolved in the formulation, the rate of polymerisation increased sharply to a maximum value and later decreased before it levelled off. The polymerisation reaction was found to develop faster as the light intensity was increased to a certain value, above which it did not increase any further.

The effect of the light intensity on conversion was twofold. At first, conversion increased with light intensity (I_0). This is attributed to the inability of shrinkage to keep pace with the polymerisation and crosslinking, resulting in the creation of free volume, thereby facilitating reaction and enhanced conversion. At higher intensities, conversion was found to be reversed or, at least, it remained constant owing to increasing radical-radical termination reactions. Since radical concentration increases with I_0, termination reactions, which are second order in radical concentration, are expected to increase more rapidly than chain propagation reactions which is first order in radical concentration[9]. Decker et.al[10] recently proposed that a decrease in initiation rate, rather than termination, was responsible for the levelling off of the polymerisation rate. According to their study, a given number of radicals must be generated by photolysis of the initiator to consume the oxygen dissolved in the formulation and, accordingly, the reciprocal of the induction time was found to vary linearly with light intensity. This proposal, however, needs more clarification before general acceptance. Initial conversion increases with I_0 and only high conversion is decreased at higher I_0. Thus, a decrease in the number of initiating radicals at higher light illumination is not a plausible explanation for the observed decrease in conversion.

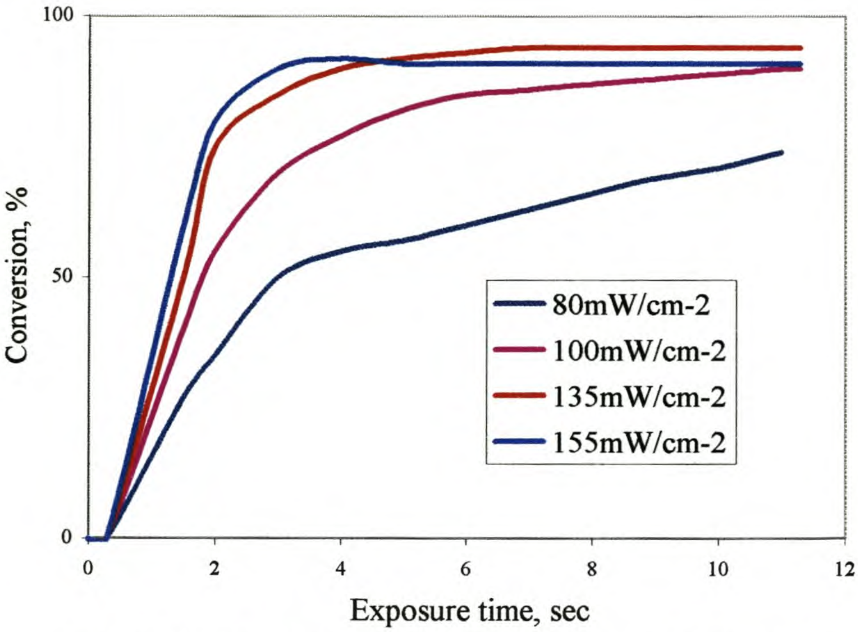


Figure 7.2 Influence of the UV light intensity and exposure time on the photopolymerisation of phosphated-polyurethane acrylic dispersions

7.3.3 The effect of temperature on UV curing

During high-speed UV polymerisation, because of the great amount of heat evolved from reacting C=C double bonds in addition to the heat emitted by the UV-lamp, the temperature of the sample increases rapidly. UV-cured coatings were therefore, in reality, not polymerised at room temperature. To quantify the real polymerisation temperature, it was measured just after switching on the lamp. The time-dependent temperature build up under the UV-lamp is plotted in Figure 7.3. It clearly shows the temperature increase with time, as would be expected if continuous curing is carried out by conveying successive samples through the UV-chamber at an exposure time of say, 12s for each coating.

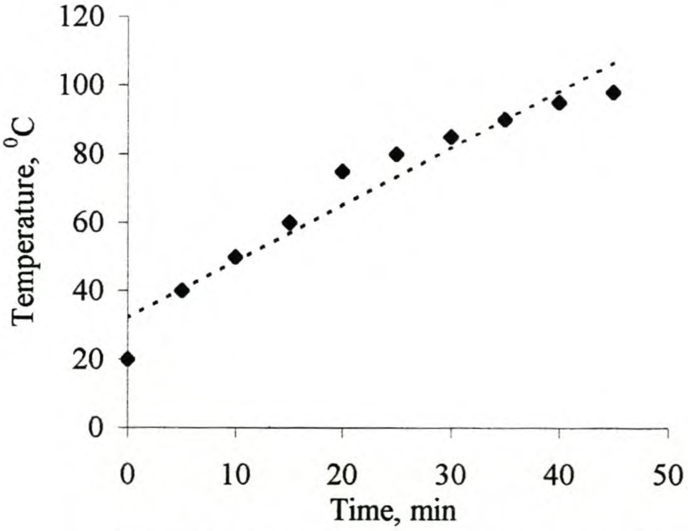


Figure 7.3 Time-dependent temperature increase under the UV lamp during UV-curing

Though the practical commercial UV-curing set-up is normally ventilated and therefore temperature increase may be less than in the experimental conditions of Figure 7.3, temperature has a direct effect on the rate of polymerisation.

The instantaneous average chain length ν of a polymer formed during UV curing is given by [11],

$$\frac{dR_p}{dT} = (E_p + {}^{E_d}\!/_2 - {}^{E_t}\!/_2)/RT^2 \qquad \text{(equation 7.1)}$$

$$\frac{dv}{dT} = (E_p - {}^{E_d}\!/_2) - {}^{E_t}\!/_2)/RT^2 \qquad \text{(equation 7.2)}$$

where E_d, E_p and E_t correspond to activation energies of the initiator decomposition, propagation and termination rates. The effect of a small change in temperature during the curing could thus be estimated. Since Ed ≈ 0 and Ep-Et/2 ≈ 20 KCal mole^{-1}[11],

$$\ln\frac{R_p(T_2)}{R_p(T_1)} = \ln\frac{v(T_2)}{v(T_1)} = -20x10^3 \Big/ R(1/T_2 - 1/T_1) \qquad \text{(equation 7.3)}$$

Thus a change in temperature from 30^{0}C to 40^{0}C induced a 25% increase in the polymerisation rate, R_p, of the phosphated polyurethane dispersions.

The heat generated from the reaction, excluding the heat emitted by the UV lamp, started to rise as soon as the polymerisation began. It reached a maximum value once the reaction slowed down, because of gelation, and decreased later as air cooling became predominant over the small amount of heat evolved in the latter stage, as shown in Figure 7.4. For the sample that contained no photoinitiator, the temperature increase from the lamp was low during a 15 s exposure (from 25 to 43^{0}C).

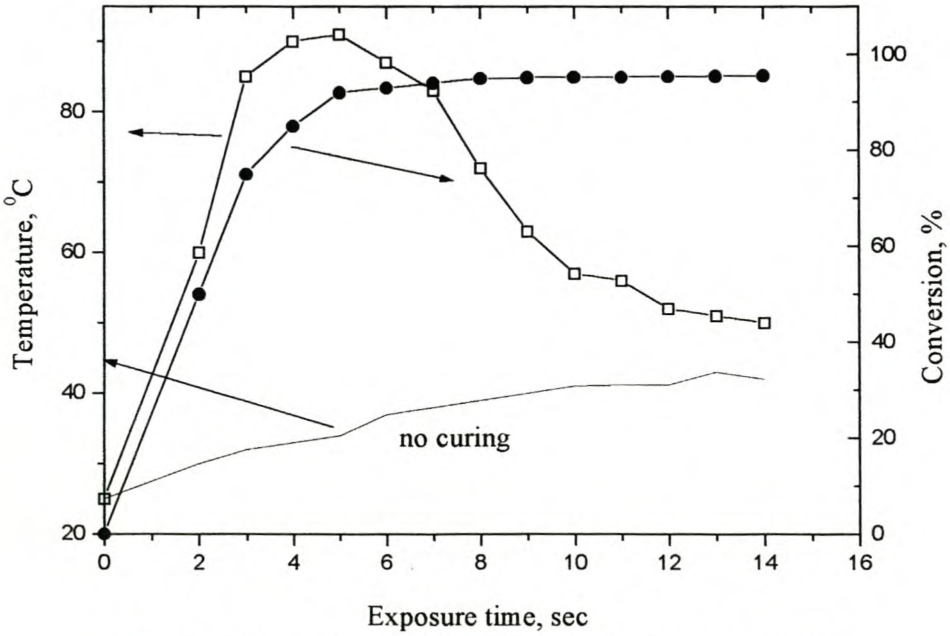


Figure 7.4 Temperature and conversion profiles for UV curing of phosphated polyurethane acrylates

A linear relationship existed between the increase in temperature and the maximum rate of polymerisation $(R_p)_{max}$, calculated from the slope of the conversion versus time curve in Figure 7.2, as shown in Figure 7.5.

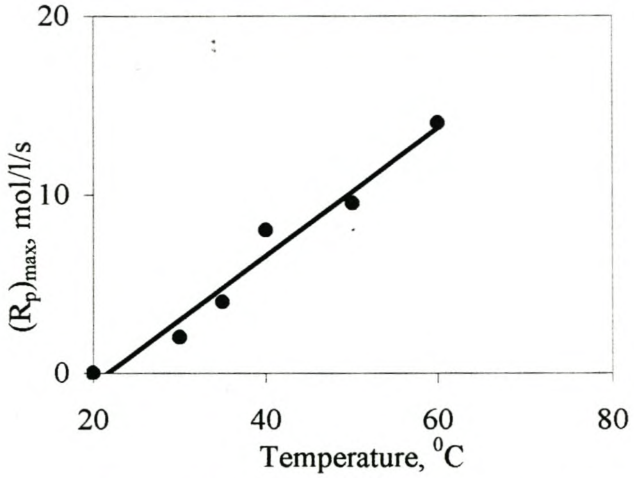


Figure 7.5 Dependence of $(R_p)_{max}$ with temperature

The maximum temperature (T_{max}) reached upon UV exposure was also found to increase with the film thickness of the coatings, as shown in Figure 7.6. This is explained by considering that the total amount of heat evolved upon polymerisation increased with increase in the sample weight (film thickness).

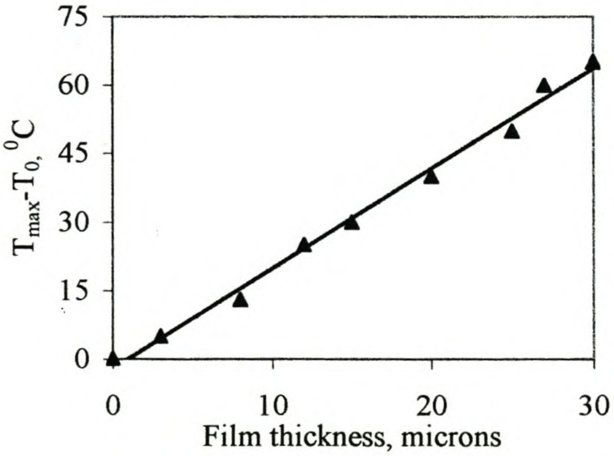


Figure 7.6 Dependence of temperature increase upon UV exposure with film thickness of the coatings

The heat transfer co-efficient of the substrate also showed a significant increase in temperature and hence rate of polymerisation. The specific heat transfer coefficient of aluminium is much higher than that of the steel or galvanised steel.

Figure 7.7 shows the temperature increase with time for the two substrates used. The aluminium surface reached a higher temperature because of the high heat transfer of the metal.

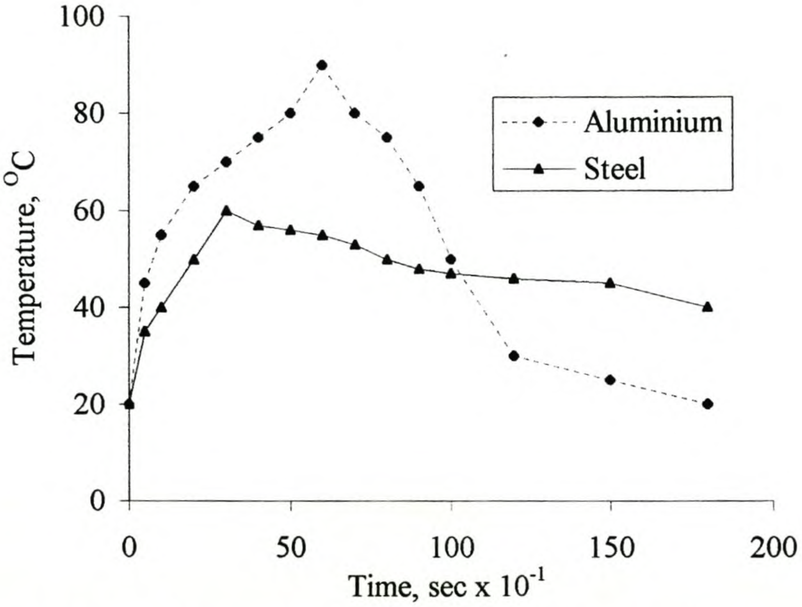


Figure 7.7 Effect of substrate on heat transfer during UV-curing of polyurethane dispersion coatings

7.3.4 The effect of soft segment content on conversion

The conversions versus exposure times for phosphated-polyurethane dispersions (as formulated in Table 7.1) with different soft segment contents but the same quantity of acrylic monomer, are presented in Figure 7.8.

Film thicknesses, the drying conditions to evaporate the water, the curing conditions and all the other conditions were the same for all coatings.

Table 7.1 Coating compositions of phosphated-polyurethane dispersions

Soft segment content (gm)	**Hard segment content (isocyanate, DMPA, 2-HEMA), (gm)**	**EGDMA content (g)**	**% soft segment**
60	40	20	50.00%
65	35	20	54.16%
70	30	20	58.33%
80	20	20	66.66%

As seen in Figure 7.8, the coatings with high soft-segment content had improved conversion with exposure time. The improved conversions with time in Figure 7.8 were found to be related to the chain flexibility caused by the low glass transition temperature of the soft segment.

When crosslinked networks are formed by low-temperature UV polymerisation, incomplete conversion of the monomer into polymer are observed[12]. This, caused by vitrification, is also true for step growth reactions involving, for example, the curing of epoxy resins with polyamines below the Tg of the cured polymer[13]. During UV crosslinking, the glass transition temperature of the composition increases. The reduction in the mobility caused by increasing viscosity and crosslinking first suppresses the termination process, then later the mobility of the monomer. The radical is also suppressed and the polymerisation rate becomes diffusion controlled. On further crosslinking, the diffusion coefficient is decreased and so is the rate of polymerisation. Therefore, the assumption advanced by early researchers that the same polymer can be made at room temperature by photopolymerisation as were formerly made at higher temperature, does not hold true[12]. The reason for the bumpy pattern on the conversion curves in Figure 7.8 is not understood. Such non-steady pattern should not have been observed.

Phosphated-polyurethane coatings with higher soft-segment content lead to crosslinked coatings that are elastomeric, where mobility restrictions are expected to be less pronounced than those with low soft-segment content. Thus as crosslinking progressed, coatings with low soft-segment content became less mobile before high conversion was achieved. It can also be seen from Figure 7.8 that the trapped immobilised radicals were essentially inactive after continued irradiation.

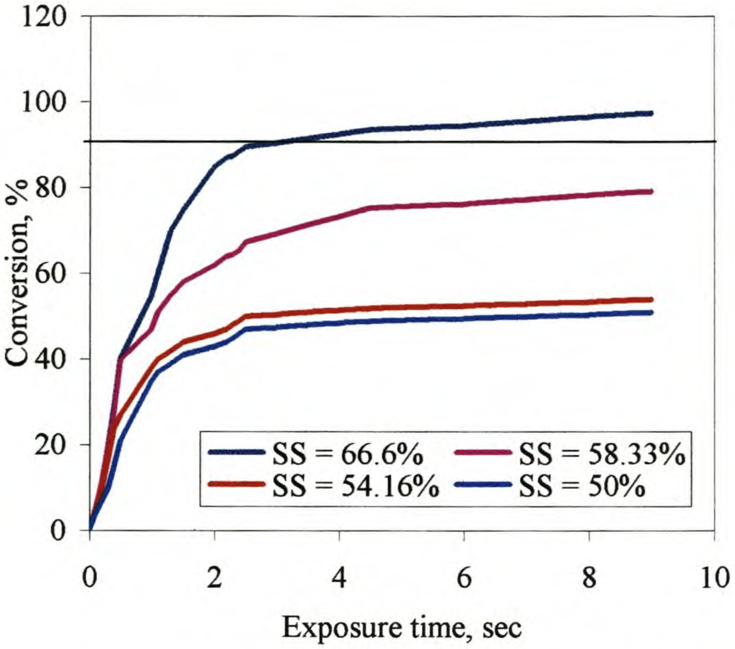


Figure 7.8 The effect of the soft segment (SS) content on the conversion of phosphated polyurethane dispersions

One of the limitations of conventional UV-curing coatings is the presence of high levels of reactive diluents used to reduce the viscosity. Such reactive diluents are mainly multifunctional acrylates and, as a result, the crosslink density of the coatings is very high. This in turn leads to properties of films that are not required for coating flexible surfaces. Koshiba et.al[14] found that increasing the reactive diluent content to more than 20% lead to the development of a second high glass transition temperature, that lead to decreased conversion due to mobility restrictions. However, a 20% reactive diluent is normally not enough to bring the viscosity of the polymer to application viscosity, such as for spray and roller coatings.

When EGDMA (in Table 7.1) was substituted with MMA, EMA and BMA, the conversions with exposure time were found to increase in order of MMA < EMA< BMA, directly related to the mobility caused by the lower Tg of the diluent and the overall resulting polymer.

7.3.5 Comparison of UV-cured coatings with coatings from internally crosslinked dispersions

As mentioned in Chapter 3, crosslinked dispersions were made from the phosphated-polyurethane dispersion 'seed' by copolymerising monofunctional and difunctional acrylate monomers in the dispersed phase. The UV-curable dispersions have the same compositions as the crosslinked dispersions. When coatings prepared by UV curing were compared with those of the crosslinked counterpart dispersions, significant property differences were observed. The main one was the flexibility of the coatings, as determined from impact tests, as shown in Figure 7.9. The results of an impact test are expressed by kg/m, that is, the height required to produce cracking on the deformed area using an 1.8kg mass at 25^0C.

Internally-crosslinked phosphated polyurethane dispersions are typical core-shell polymers with a low glass-transition temperature soft segment core and a hard shell that contains the urethane and the acrylic groups. Since polymerisation is carried out in the dispersed phase stabilised by carboxylic acid monomer, particle growth occurs in the absence of secondary nucleation and no homopolymer formation of the acrylic monomer is observed. Thus, coatings from internally crosslinked dispersions show better impact resistance due to the fact that the applied energy is absorbed by the soft and flexible soft segments. However, homopolymersation of the reactive diluent under UV curing conditions is very likely and homopolymers of the acrylic diluents are brittle. Since the homopolymer chains are less chemically bonded to the phosphated polyurethane particles, they may act as weak areas for poor flexibility. Shrinkage of the coatings during UV exposure, that could develop internal stress of the coatings, may also be responsible for the low impact resistance of the UV-cured coatings.

Another possible reason for the observed difference in flexibility may be non-homogeneity of the acrylate phase caused by the high speed UV curing. In UV curing, the light is mounted perpendicular to the coating surface and crosslinking begins at the outer layer. This is because photoinitiators at the interface absorb light faster than those in the deeper layer to initiate the crosslinking. Thus the acrylate diluent may diffuse to the reaction site, causing non-homogeneity[9].

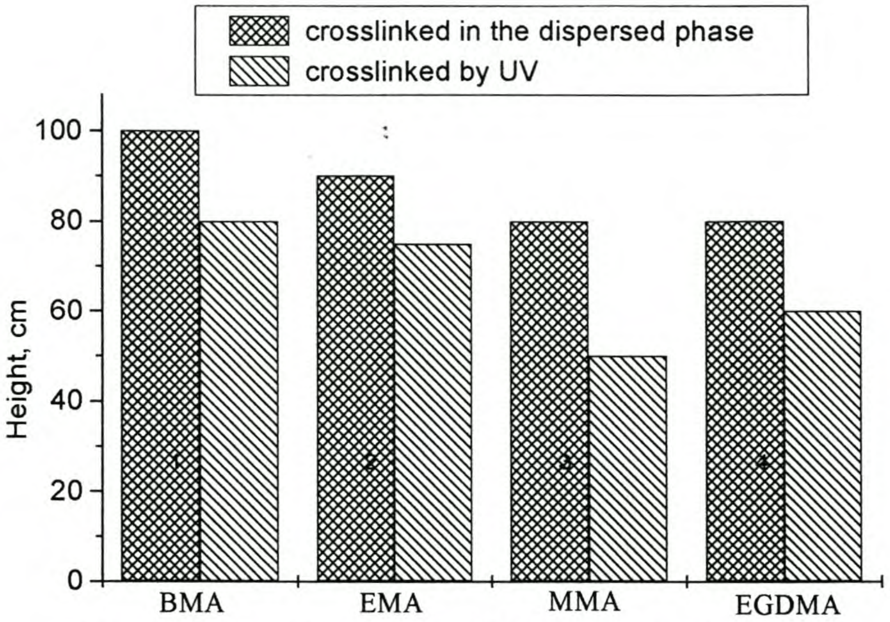


Figure 7.9 The effect of the crosslinking method on impact resistance of phosphated polyurethane-acrylic coatings

7.3.6 The effect of water on UV curing

For a UV curing system, it is important that all water be removed (by evaporation) before irradiating, for increased network formation. The effect of residual water on gel content was significant for samples that were irradiated without water evaporation. Figure 7.10 shows that when the flash-off time between coating and curing was 3 min, gel content was low. In a commercial application, water evaporation is normally done either by an infrared lamp or in a hot oven at a temperature of 80^0C, before curing. It must be emphasised, however, that loss of the photoinitiator at the drying temperature may also occur. Davidson[7,15] and Anderson et.al[16] studied the use of polymeric photoinitiators to avoid the potential loss of low-molar mass photoinitiators during the water evaporation stage at elevated temperatures and reported reduced volatility during flash-off time. Studies by Catalina et.al.[8] on the use of copolymerisable photoinitiators to overcome photoinitiator losses have also shown reduced steam volatility.

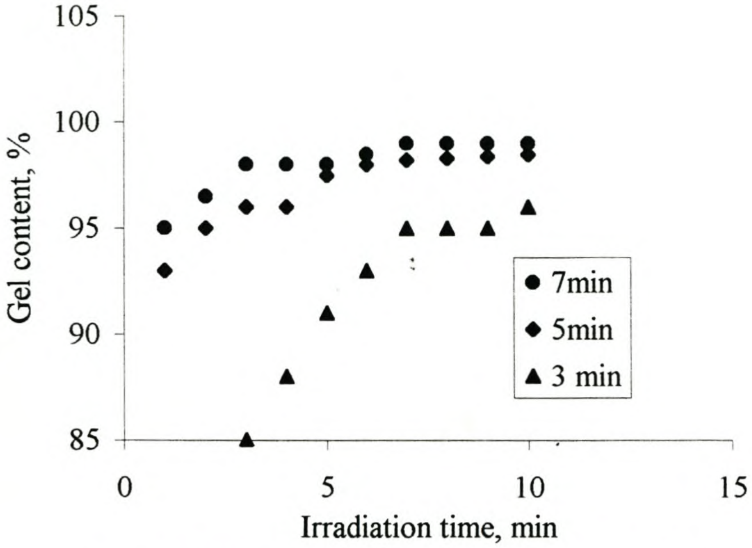


Figure 7.10 The effect of water on gel content of the UV-cured coatings of phosphated polyurethane acrylic dispersions

The gel content of coatings irradiated after all the water had been completely removed at 80^0C is presented in Figure 7.11. It is clearly seen that an UV exposure time of only 1.5 sec was adequate to crosslink 80% of the dispersion coatings.

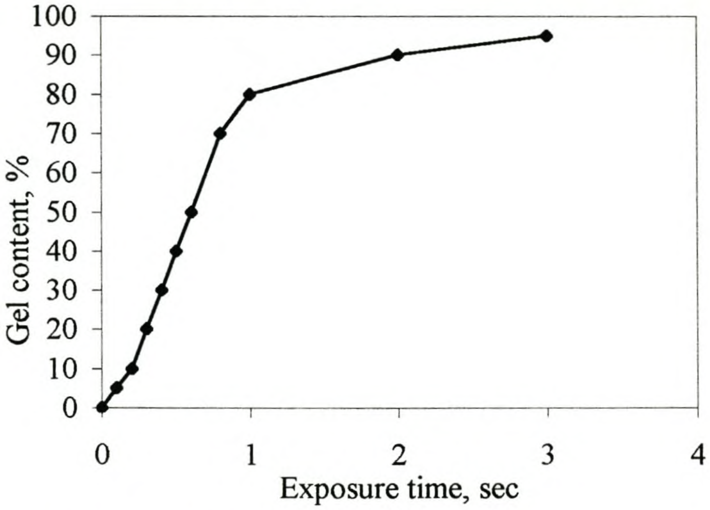


Figure 7.11 Gel content versus irradiation time for a completely dried dispersion coating

On the other hand, water, can have a positive contributing factor for polymers cured by UV. For example, a non-reactive diluent can be added into the acrylic monomer before irradiating to decrease the glass transition temperature of the growing polymer during polymerisation and to drive the polymerisation to completion at room temperature. It has been reported[17] that the addition of polar solvents, like water, have a plasticising effect on the UV curing of acrylic monomers and the polymerisation rate is fast. On the basis of this, the effect of water on the gel content of the UV-cured phosphated polyurethane dispersions was not directly related to lack of conversion of the reactive diluent to polymer, since FTIR studies showed the complete C=C bond consumption of the dispersions irradiated before water evaporation.

For waterborne dispersions used in UV curing, it is essential to have initial film formation before curing commences. This means that the water must be evaporated from the particles to allow the particles to coalesce and form a coherent film. If no film formation is obtained before irradiation, then crosslinking will occur inside the individual particles separated by water, and a coherent film will not be obtained. Another possibility for the low gel content is that homopolymerisation of the diluent could take place and the base dispersion may not be crosslinked. Thus, gel content, as determined by toluene and acetone extraction may decrease as a result of incomplete crosslinking and not necessarily due to incomplete conversion. Network formation requires that the growing chains be in close proximity, which, in this case, they were not. They were separated by water molecules and the water must be removed for crosslinking to take place.

Waterborne UV curing, like any other curing techniques, is not without limitation particularly, the slow curing resulted from the need to evaporate the water. Nevertheless, some striking advantages of the UV-curable phosphated polyurethane acrylic dispersions are: their low viscosities at high molecular weight, that allows thin-film coatings, easy control of the rheology, tack-free coatings before cure, ease of application (spray, roller coatings, curtain coatings) and easy cleaning of the application equipment.

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Chapter 8

Thermogravimetric study of polyurethane ionomers

8.1 Introduction

Phosphate-containing compounds are frequently used as fire-retardant additives for polyurethanes[1,2]. Their influence is partly associated with their effect on the thermal decomposition of the polymer. Thermal decomposition also determines the inflammability and toxicity of the volatile products, the quantity and the physical nature of the residue which may play an important role in the overall characteristics of the burning process. When phosphate-containing compounds are in the form of additives, they are highly susceptible to loss by evaporation, leaching out by solvent or water and migration either in storage, compounding or during application or after application. All these disadvantages can be overcome if the phosphate compound is part of the polymer structure.

Phosphate-containing polyurethanes are proposed for coatings application due to their improved adhesion to metal. Curing is mostly done by heat and most applications require curing temperatures in excess of 150^0C and curing times between 40 seconds and 1hr, depending on the curing mechanisms. If the application is destined for high-speed curing like coil coating, the cure time may be as low as 40 seconds and curing temperature as high as 240^0C. Furthermore, in a multiple coating system, if the phosphate-containing polymer is designed as a primer, it may be subjected to a second cure with the topcoat and thus to heating again. During the curing cycle, loss of flexibility and yellowing of the clear coat is observed[3]. The term "over-bake" resistance test, frequently quoted by paint technologists, indicates the degradation of the polymer to some extent upon prolonged exposure to heat.

In the present study, the thermal stability of phosphate-containing polyurethane dispersions was investigated. Special emphasis is given on the initial weight loss kinetics and the overall activation energy.

8.2 Experimental

TGA analyses of the phosphate-containing polyurethanes were carried out using a TGA-50 SHIMADZU Thermogravimetric instrument with TA-50WSI thermal analyser, connected to a computer. Samples (10-15mg) were degraded in flowing nitrogen or air (50mL/min) at a heating rate of 2.5-10^{0}C/min. The reactive polyurethanes (samples for TGA analyses) were prepared by solution casting of the polymer from a 40% solution of butanone into a Teflon mold, followed by drying at room temperature for 24 h. The samples were further treated in a vacuum oven at 90^{0}C for 72 hours. Atmospheric moisture and any traces of solvents in the film are known to affect the TGA profiles of the degradation process. Complete drying of the samples was verified by analysing the TGA data between 30 to 110^{0}C. No weight loss on the TGA curves in this temperature range, is used as guideline for having achieved complete drying.

8.3 Results and discussion

8.3.1 Qualitative information from TGA

In a complex compound like a polyurethane, the onset degradation is governed by the weakest link in the chain, whereas the most frequent chain and the environment of the given groups are the dominant factors for overall thermal stability. Polyurethanes with different backbone structures have different thermal stabilities[4]. The primary TGA curves for a representative phosphate-containing polyurethane, at different heating rates in nitrogen, are shown in Figure 8.1, and the rate of weight loss is shown in Figure 8.2.

At a lower heating rate, the time required for the polymer to reach a given temperature was longer than at higher heating rates, which resulted in higher degradation (conversion) and better resolution of the degradation data. Thus, the rate of weight loss at a lower heating rate is lower than that at a higher heating rate, as shown in Figure 8.2. A higher heating rate shifts the weight loss rate curve, which is the change in weight per given time (dW/dt), to a higher temperature and the peak is also higher. There are three distinct stages of degradation for the phosphate-containing polyurethane observed in Figure 8.2. The onset and maximum temperatures of the first step, T_{1on} and T_{1max}, the second step, T_{2on} and T_{2max}, and the third step, T_{3on} and T_{3max} illustrate the three qualitative degradation steps. This process ends with the loss of all volatile fractions and a char mass that does not change much after 500^{0}C. The multistage degradation of phosphate-containing polyurethane indicates the complexity of the process[5]

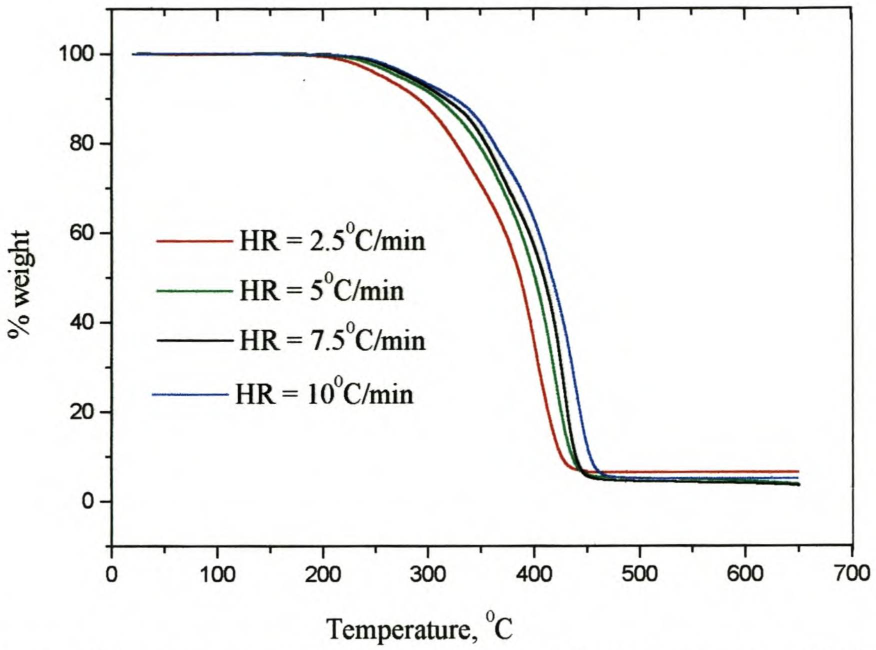

Figure 8.1 TGA curves of phosphate-containing polyurethane at different heating rates (HR) in N_2 (0.5% P)

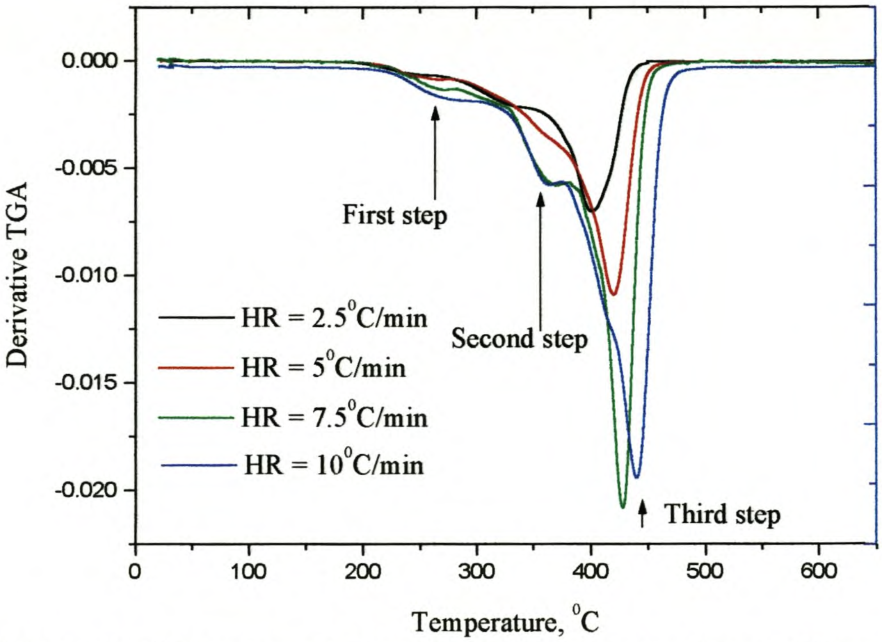

Figure 8.2 Derivative TGA curves of a phosphate-containing polyurethane at different heating rates in N_2

The effect of the phosphate groups (expressed as phosphorus content) on the weight loss of the polyurethanes is shown in Figure 8.3. The phosphate-containing polyurethanes exhibited an initial weight loss around 180^{0}C, which is below the curing temperature of the coil-coating process. The maximum degradation temperature for all the phosphate-containing polyurethanes was, however, higher than the curing temperature. When the phosphorus content in the coatings was increased, the decomposition residuals (char) were high and thermally stable up to a temperature of 700^{0}C (the maximum temperature used in the experiments). The initial weight-loss temperature of these phosphate-containing polyurethanes was lower than that of the phosphate-free polyurethanes. Initial weight loss of the polyurethanes without phosphate groups was not observed below 245^{0}C, as shown in Figure 8.3. The low thermal stability of the phosphate-containing polyurethanes was also reported by others[6,7]. Such behaviour characteristics of phosphate-containing polyurethanes are attributed to the relative ease of degradation of the phosphate-containing segments, that further contribute to the yellowing of the films during prolonged and cyclic curing schedules at 225^{0}C peak metal temperature.

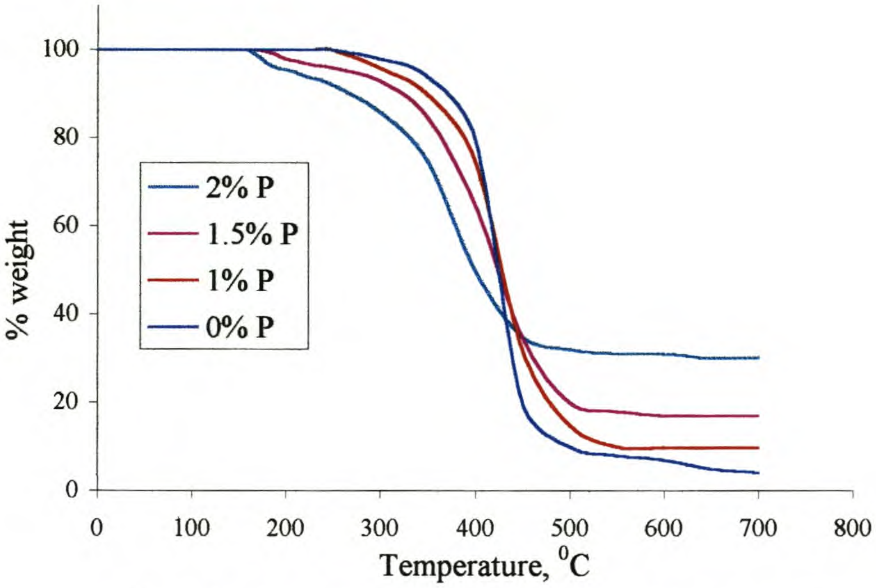

Figure 8.3 The effect of phosphorus on TGA curves of polyurethane coatings (heating rate 10^{0}C/min in air)

The weight loss of the phosphate-containing polyurethane dispersions was dependent on the neutralising base used. Coating films prepared from dispersions neutralised by triethylamine showed no differences in the TGA curves since the amine dissociated during the sample preparation stage. A significant difference in weight loss was, however observed, when the neutralising bases were metal hydroxides, eg. NaOH, as presented in Figure 8.4. This was attributed to the non-volatile degradation product of the metal carboxylate[8]. Although the coating formulation neutralised by NaOH showed enhanced thermal stability, all coatings showed loss of flexibility (especially 0-bend) and yellowing, irrespective of the nature of the neutralising base. Some polymers were found to lose their important properties without a weight loss and TGA results were somewhat disappointing due to the fact that the degradation of polymers is not always accompanied by a weight loss[9]

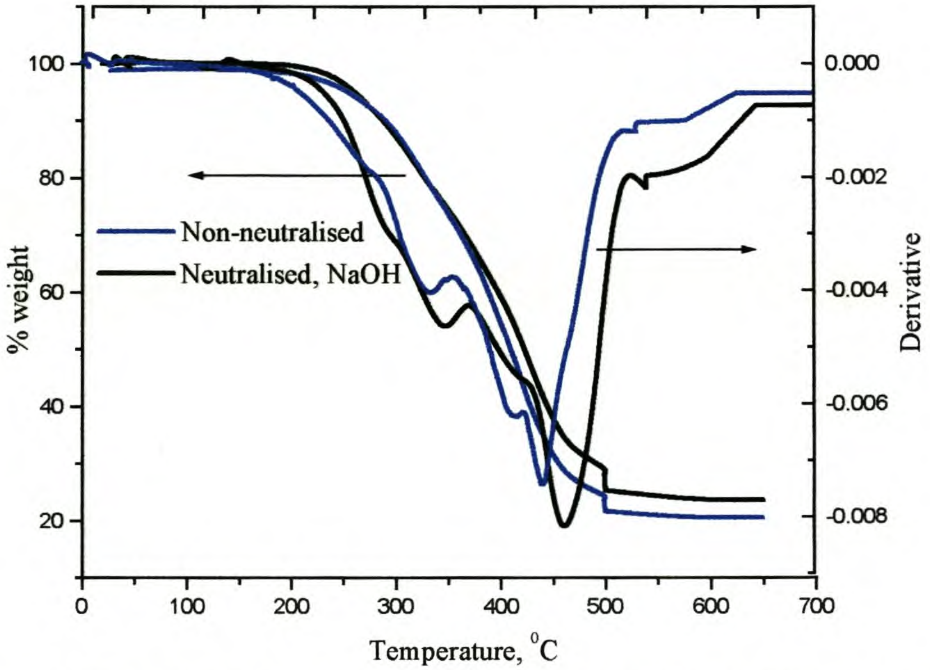

Figure 8.4 The effect of the metal hydroxide neutralising base on the TGA curves of phosphate-containing polyurethanes (heating rate 10°C/min in N_2 and 2% P)

The presence of phosphate groups in polyurethanes does not improve the onset temperature of the thermal degradation either in an inert atmosphere or under oxidising conditions (O_2), as presented in Table 8.1 and Figure 8.5. However, the percentages of char (residue) yield for phosphate-containing polyurethanes were found to be higher than those of polyurethanes without phosphate.

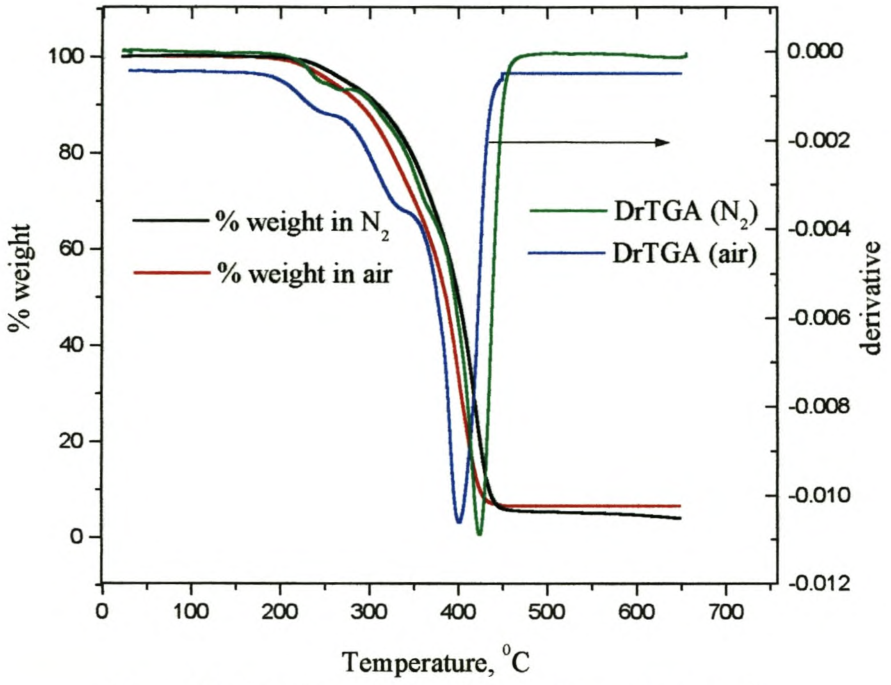

Figure 8.5 The effect of N_2 and air on the weight loss of phosphated polyurethanes (heating rate 10^0C/min)

Table 8.1 Char yield of phosphate-containing polyurethanes degraded in air

% Phosphorus in the coatings	% Char yield at 650^0C
0	2.03
0.5	7.2
1.0	9.5
1.5	15.71
2	25.3

8.3.2 Correlation of char yield with fire retardance

Char formation is a major factor in flame retardancy[10]. There are several ways to improve the yield and integrity of char for producing barrier layers containing elements other than carbon[10]. Van Krevelen[11] studied the relationship between char yield and flame retardant properties of some polymers. One approach to reduce the burning of polymers was to add a char-forming additive, such as phosphates, into non-char-forming polymers, such as polyolefins, to reduce the flammability of the polymers. Lyon[12] developed a mechanistic model of fire retardancy from char-forming polymers, using TGA data. It is generally accepted that increased char yields as determined from TGA experiments in air, is an indirect way of measuring the fire retardant properties of polymers[13].

Char formation in a fire limits the amount of volatile fuel that can be produced by the burning polymer. It provides a thermally-insulating layer at the surface to reduce heat transmission into the material and acts as a diffusion barrier to combustible gasses. The charred layer of cellular foam on the surface of the burning polymer provides resistance to heat and mass transfer, giving good insulation to the underlying combustible polymer. The higher char yield of the phosphate-containing polyurethane coatings can thus be related to its fire retardant properties (Table 8.1). It is seen in Figure 8.3 that the initial weight-loss temperature of the phosphate-containing polyurethanes is low. The maximum degradation peak temperature (the temperature at which a major fraction decomposes) of the phosphate-containing polyurethanes was also low, indicating a probable tendency for slow burning. This is expected, since the presence of the phosphate promotes carbonisation and inhibits combustion. Polymers that form a carbonaceous char during burning have lower ignitability and a lower heat-release rate than non-char-forming polymers[14].

This phenomenon introduces a flame-retardant effect to the polymer. On the other hand, the thermal degradation of phosphate-containing polyurethanes in air is almost similar to that in nitrogen, as shown in Table 8.2.

Table 8.2 Thermal degradation of phosphate-containing polyurethanes in air and in nitrogen

% Phosphorus	**$T_{on\ (air)}$, ^{0}C**	**$T_{on(N2)}$, ^{0}C**	**$T_{max\ (air)}$, ^{0}C**	**$T_{max(N2)}$, ^{0}C**	**dw/dt at T_{max}, mg/min**
0	233	240	370	430	1.12
0.5	214	218	323	343	0.41
1	201	209	308	311	0.38
1.5	192	190	312	315	0.35
2	180	183	309	303	0.37

The presence of oxygen did not change the onset degradation temperature of the phosphate-containing polyurethanes significantly since the ratio of $T_{on\ (air)}$, ^{0}C to $T_{on(N2)}$, ^{0}C varied between 0.97 to 1.00. The maximum degradation temperature of the polyurethane without phosphate was modified by the type of gas used during the pyrolysis. Whilst the ratio of $T_{max\ (air)}$, to $T_{max(N2)}$ was between 0.94 and 1.02 for the phosphate-containing polyurethanes, it was 0.86 for the non-phosphated polyurethanes. The rate of weight loss at T_{max} for the non-phosphated polyurethanes was also very high (1.12mg/min) compared to three-fold lower values when phosphate groups were incorporated into the coating formulation. The higher char yield of the phosphate-containing polyurethanes is attributed to the fact that phosphate promotes carbonisation and inhibits combustion simultaneously[15].

The high char yield resulting from thermal degradation of the phosphate-containing polyurethanes in air indicates the fire retardant behaviour of the coatings. It has been reported by many workers[16,17] that char formation from TGA results correlates well with the Limiting Oxygen Index (LOI) tests for fire retardancy. Liu et.al.[16] found an increased char yield and increased LOI values for polyurethanes made from phosphate-containing isocyanates. Liaw and Lin[17] investigated the flame-retardant properties of phosphate-containing polyurethanes prepared by N-alkylation. Their results have shown a linear relationship between the char yield in a pyrolysis experiment and LOI with increase in phosphate content.

8.3.3 Quantitative information (kinetics of degradation)

The derivation of kinetic data for polymer degradation from dynamic TGA data has received considerable criticism[18] and kinetic parameters are strongly dependent on the method of calculation. Nishizaki et.al[19] used several different methods of calculation to measure the kinetic parameter of polystyrene degradation from primary TGA data. Their results were strongly dependent on the methods used to calculate the parameters. There was, however, a close relationship between the results of each method used, provided that the experiment has a simple reaction mechanism, a single reaction order and a single activation energy. This is however not the case with polymers. It is therefore not surprising that the determination of meaningful kinetic parameters for phosphate-containing polyurethanes from the degradation process is very complex, due to the presence of different types of segments with different modes of degradation.

8.3.3.1 Methods for calculating kinetic parameters from TGA data

The methods used for calculating kinetic parameters from TGA data are classified into two groups: integral and differential methods. The most suitable method has however not yet been clarified[19]. For both methods, the basic equation for the fraction of conversion, α, for a weight loss system, is given by

$$\alpha = \frac{(w_0 - w)}{(w_0 - w_f)} \quad \text{........equation 8.1}$$

where w is the weight of sample and the subscripts 0 and f refer to values at the beginning and the end of the weight loss event of interest.

The rate of conversion, $\frac{d\alpha}{dt}$, for dynamic TGA is determined by multiplying the thermogram slope by the constant heating rate, $\beta = \frac{dT}{dt}$, and may be expressed by

$$\frac{d\alpha}{dt} = \beta \frac{d\alpha}{dT} = f(\alpha)k(T) \quad \text{.........equation 8.2}$$

where $f(\alpha)$ and $k(T)$ are functions of conversion and temperature, respectively. Further,

$$f(\alpha) = (1-\alpha)^n \quad \text{.......... equation 8.3}$$

On the other hand, $k(T)$, the temperature dependence of the rate of weight loss, is often modelled successfully by the Arrhenius equation,

$K(T) = A\exp(-E/RT)$ ....equation 8.4

where E is the activation energy, A the pre-exponential factor and R the gas constant. Insertion of equations (8.3) and (8.4) into equation (8.2) gives

$d\alpha/dt = \beta d\alpha/dT = (1-\alpha)^n A \exp(-E/RT)$..............equation 8.5

Both the integral and derivative methods use equation 8.5 as a base expression.

The Ozawa method is one of the most frequently quoted integral forms of equation 8.5[20]. This method requires several TGA curves at different heating rates for each degree of conversion (α). α is defined as the weight loss at a given temperature divided by total weight loss. When the logarithm of the heating rate in ^{0}C is plotted against 1/T (where T is the absolute temperature) a straight line is obtained from which activation energy is calculated from the slope using:

E_a = -Slope x R/0,457 ....equation 8.6

where R is the gas constant.

The dependence of the logarithm of the heating rate versus 1/T for the phosphate-containing polyurethanes is shown in Figure 8.6.

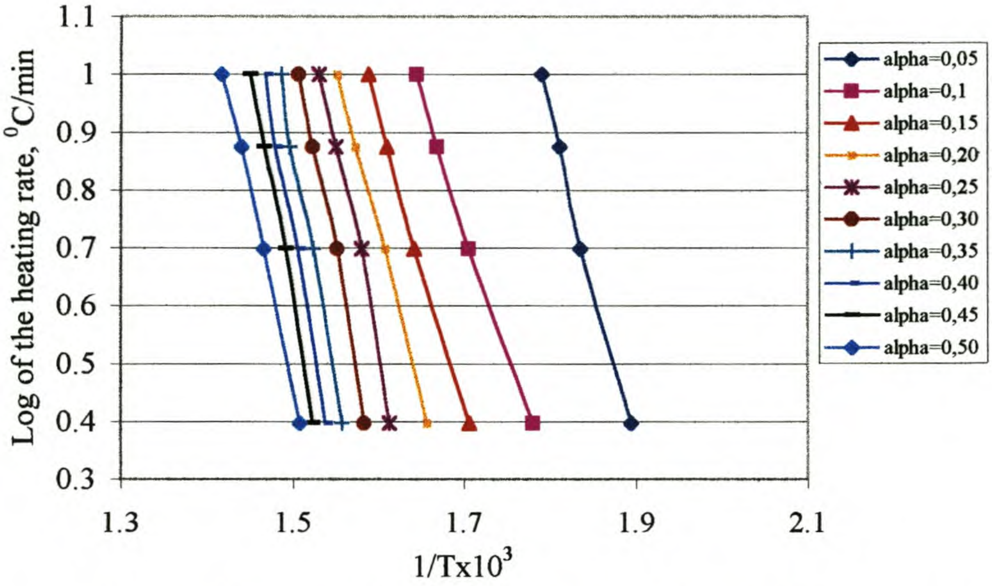

Figure 8.6 The dependence of the logarithm of the heating rate on 1/T for phosphate-containing polyurethanes

8.3.3.2 Analysis of weight-loss kinetics at low conversion

Rates obtained at the initial stage of weight loss are valuable in relating curing-induced degradation kinetics. Initial weight-loss data is useful for the formulation of thermally-cured coatings. In many cases, polymers lose their desirable properties during the first few percent of weight loss. The properties such as flexibility and adhesion, which are directly related to natural ageing, deteriorate early in the degradation. Thus activation energies and other kinetic parameters calculated from these early data are more meaningful in predicting the thermal stability of polyurethanes than the latter values are.

Differentiation of equation 8.5 with respect to α gives an expression for the slope of the line obtained from a plot of $T^2 d\alpha/dT$ vs α[21]

Slope $= d/d\alpha[T^2(d\alpha/dT)]$

$= E/R + 2T + T^2 [f'(\alpha)/f(\alpha)]\, d\alpha/dT$..................equation 8.7,

where $f'(\alpha)$ is the derivative of $f(\alpha)$ with respect to α.

For $\alpha \ll 1$, the last part of equation 8.7 can be neglected and one obtains for the slope,

Slope = E/R+2T or E= R(Slope)-2RT......................equation 8.8,

where R is the gas constant and T is the average temperature at which the slope is taken.

This method, proposed by Flynn and Wall[21], is applicable at low conversion (maximum degradation 10%). The plot of $T^2(d\alpha/dT)$ versus α should give a straight line, from which activation energy is calculated by using equation 8.8. Since the value of T at low conversion is difficult to assign, the integrated rate equation for the term $T^2(d\alpha/dT)$ was found to be equal to $-d\alpha/d(1/T)$[21]. Thus a plot of $-d\alpha/d(1/T)$ versus α should afford a linear relationship with slopes exactly the same as in equation 8.8. These are shown in Figure 8.7.

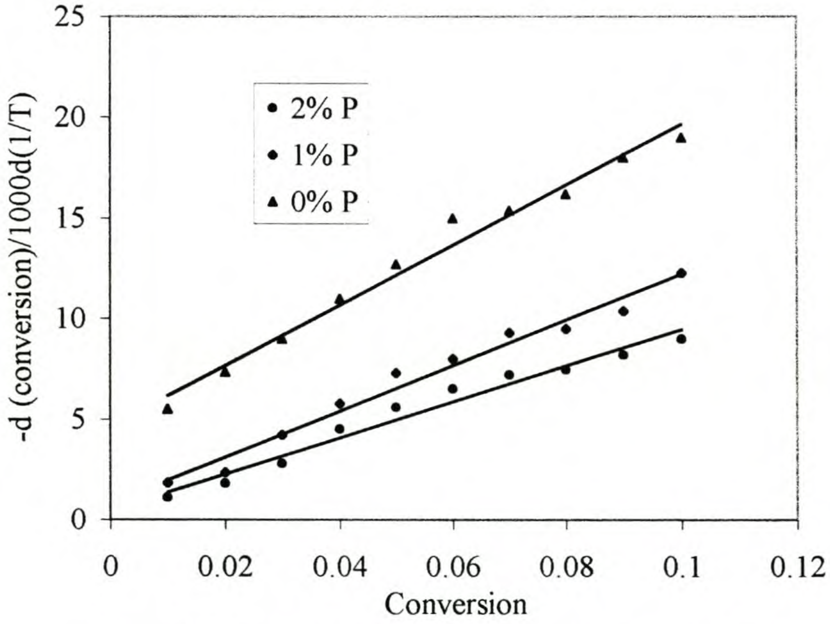

Figure 8.7 The dependence of -d(conversion)/d(1/T) on conversion of polyurethanes having different phosphorus contents

The activation energies calculated from the linear lines gave: 250KJ/mole for 0% P, 145KJ/mole for 1% P and 134KJ/mole for 2% P. Calculation of the kinetic parameter at the initial stage of weight loss ($\alpha = 0.1$ max) showed a decrease in activation energy for the polyurethanes with increased phosphate content. This indicated that degradation commenced at the chain that contained the phosphate groups. In the present study, the phosphate groups were incorporated on the soft segment polyester macroglycol. Such studies have not been reported in any literature to date and it is plausible to conclude that degradation started at the soft segment of the polyurethanes. This is unexpected, since other workers[22-24] have reported that thermal degradation of polyurethanes begins at the hard segment, since the urethane group is not stable above 230^{0}C. For phosphate-containing polyurethanes where the phosphate is on the hard segment, Grassie and Mackerron also concluded that the degradation started at the hard phosphate-containing segment[25]. Therefore, it may be said that in segmented polyurethanes, the location of the phosphate determines where the degradation starts. The low thermal stability of phosphate-containing segments is also reflected in the calculated values of activation energy presented in Figure 8.8, where the activation energy decreased with phosphorus content.

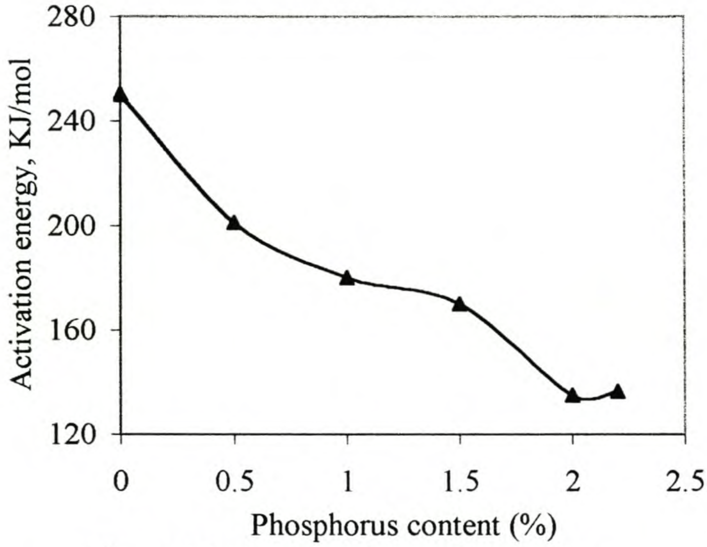

Figure 8.8 The dependence of activation energy on phosphorus content of polyurethane coatings

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Chapter 9

Conclusions

9.1 The synthesis of phosphate-containing nano-particle polyurethane dispersions

Phosphate-containing macroglycols of molecular weight 2000 have been synthesised from a new phosphate-functional carboxylic acid monomer. The macroglycols were used as a soft segment for the preparation of segmented polyurethane dispersions. Phosphate-containing polyurethane dispersions were made by phase inversion from the organic solvent after the carboxylic acid groups were neutralised. During phase inversion, there were three stages, namely:

9.1.1 Stage one: Change in viscosity of phosphated polyurethane during neutralisation

During the first stage after synthesis the polymer was fully reacted in an organic solvent (butanone). When calculated stochiometric amounts of the neutralising amine, triethylamine, were added to form the ionomers, the viscosity of the resin increased. However, neutralisation of the acid groups to convert the phosphated polyurethane resin into ionomers did not lead to an increase in molecular weight. The sharp increase of the viscosity of phosphated polyurethane resin was attributed to the formation of micro-ionic lattices. Ionic association is reversible and any water present solvated the ionic clusters and reduced the viscosity.

9.1.2 Stage two: Change in viscosity of the phosphated-polyurethane ionomer as concentration of the polymer is reduced

As more water was added to the resin the viscosity again increased, although the solids content decreased. Since the butanone concentration was reduced, the solvation sheath of the hydrophobic segments was also reduced. At this stage the phase-inversion, water was adsorbed by the carboxylate anions situated on the surface of the hard segment micro-ionic lattices, causing a separation of neighbouring chains and aggregates.

9.1.3 Stage three: Particle formation

As the last portion of water was added, turbidity, which was an indication of the formation of a dispersed phase, was observed. During this stage turbidity reached a maximum and the viscosity dropped sharply due to the rearrangment of the aggregates to form microspheres. During this stage a discontinuous phase of polyurethane was dispersed in a continuous aqueous phase. When butanone was removed by distillation, a polyurethane ionomer emulsion in water was obtained.

The three stages of the phase inversion of the phosphated polyurethane to form a dispersion were also studied by conductivity measurements during the phase inversion.

Results of particle-size analyses and particle-number determinations have indicated that the dispersions were highly dependent on the neutralising base used. It was also shown that the hydration properties of the higher alkyl ammonium cations were reduced as the dispersion temperature was increased.

9.2 The synthesis of phosphated and siloxane-containing polyurethane acrylic dispersions

The organic solvent used (butanone) to synthesise the polyurethane dispersions was replaced by acrylic monomers as a diluent to reduce the viscosity. The phosphate-containing polyurethane dispersions were then used as a ‘seed’ to polymerise these acrylic monomers in the dispersed phase. Results have shown that the carboxylated phosphated-polyurethane particles can be used as the polymerisation loci for acrylic monomers. The polymerisation of acrylics in the aqueous dispersed phase occurred in the absence of secondary nucleation. However, the seed neutralising cation was found to affect the acrylic polymerisation substantially. Small and easily hydrated cations were necessary to obtain stable dispersions. In the present work, monoacrylates and diacrylates have been polymerised with the polyurethane dispersion to obtain cross-linked dispersions. Phosphated and siloxane-modified polyurethane dispersions were also synthesised.

The phosphated polyurethane acrylic dispersions were found to have Newtonian behaviour with respect to sheer rate and temperature, hence they could be used as a pigment grinding media.

9.3 Ultraviolet (UV)-curing of phosphated polyurethane acrylic dispersions

Phosphate-containing polyurethane dispersions were successfully cured by ultraviolet radiation. There were two significant advantages of these UV-curable phosphated polyurethane acrylic dispersions:

1. The reactive diluents lead to low solution-viscosities of phosphated polyurethane resin during the synthesis of phosphated polyurethane dispersions; hence the use of an organic solvent as synthesis medium for the preparation of polyurethane dispersions could be eliminated.
2. After the dispersions were formed, the low viscosities of the polyurethanes meant that thin-film and tack-free coatings, before UV curing, could be obtained.

9.4 Self-assembling coatings

Two-directional, self-assembling coatings were formulated; namely, assembly at the metal/coating interface and assembly at the coating/air interface.

On the one hand the presence of phosphate groups in the dispersion formed an assembly at the metal surface to form an insoluble metal phosphate, as evidenced by EDX analysis. The phosphate groups were indeed assembled at the metal interface by forming a non-conductive layer of metal phosphate. The assembly of the phosphate groups to the metal interface depended on the neutralising amine and its boiling point, due to its competitive complexing effect.

On the other hand, the polysiloxane groups of phosphated and siloxane-modified polyurethanes assembled at the coating/air interface. The low surface tension of the silicone groups resulted in very poor wetting properties of the coating. Advancing and receding dynamic contact angle studies have shown time-independent silicon enrichment under standard atmospheric conditions. However, when these coatings were exposed to an ionic solution, the silicone groups were found to move away from the surface. When the coatings were removed from the ionic solution, a full hydrophobic recovery with time was observed. This observation was interpreted in terms of surface dynamics. Angle-resolved XPS studies have also shown silicon enrichment on the top surface compared with the bulk of the polymer, complimenting the dynamic contact angle (DCA) results.

9.5 Thermal degradation of phosphate-containing polyurethane dispersions

Thermogravimetric studies of the thermal degradation of phosphate-containing polyurethanes have shown that their activation energies were lower than the polyurethanes which contained no phosphate. The char yield of the former was higher than that of the latter. Char formation in a fire limits the amount of volatile fuel that can be produced by the burning polymer; it provides a thermally-insulating layer at the surface, to reduce heat transmission into the material, and acts as a diffusion barrier to combustible gasses. It can therefore be said that coatings obtained from phosphate-containing polyurethane dispersions are fire retardant.