UNIVERSITEIT·STELLENBOSCH·UNIVERSITY
jou kennisvennoot • your knowledge partner

CONTINUOUS PROCESSING OF VESICULATED BEADS

by

KAREN GOUS

Thesis submitted in partial fulfilment of the requirements for the degree of Masters of Science in Engineering (Chemical Engineering) in the Department of Chemical Engineering at the University of Stellenbosch

Study leader:
Prof. J.H. Knoetze
Department of Chemical Engineering

Stellenbosch
April 2003

DECLARATION:

I declare that this thesis is my own work, except where specifically acknowledged in the text. Neither this thesis nor any part thereof, has been submitted to any company or other academic institution.

.....

K. Gous

ABSTRACT:

OPSOMMING:

ACKNOWLEGDEMENTS:

I would like to thank the following people and institutions for their contributions during the project:

Prof. J.H. Knoetze, my supervisor, for his advice and guidance throughout this study.

Plascon (Pty.) Ltd, for their financial support.

Members of the *Plascon Research Institute*, in particular Mr J. Engelbrecht and Mr J.C. Terblanche for their help and advice as well as the entire analytical team.

The personnel of the *workshop* at the *Department of Chemical Engineering*, Mr J.M Barnard and Mr A.P. Cordier.

ACKNOWLEDGEMENTS:

I would like to thank the following people and institutions:

Prof. J.H. Knoetze for his guidance and support as my study leader throughout the project.

Plascon Research Centre Stellenbosch, in particular *Mr. J. Engelbrecht* and *Mr J.C. Terblanche* for their help and support.

Plascon (Pty.) Ltd. for their financial support.

Members of the Chemical Engineering Workshop, especially *Mr. J. Barnard* and *Mr. A. Cordier* for construction of my experimental equipment.

ABSTRACT:

Titanium dioxide (TiO_2) is extensively used as pigment in paint formulations, but due to the high cost associated with it, along with its' depleting natural resources, paint manufacturers are seeking substitutes that can at least partially replace this pigment.

Vesiculated beads have been successfully used in the past as a replacement for the TiO_2-pigment. These beads are spherical polymer particles that contain a multitude of aerated micro voids within the polymer shell. The aerated voids cause effective scattering of light inside the particles, presenting the beads with a white appearance. It was found that low levels of TiO_2 could be encapsulated in the particles as a means of increasing the whiteness and hiding power of the beads in the wet- and dry state. Because the beads are about two-thirds air by volume and contain only small amounts of TiO_2, it also presents a method of reducing the formula cost.

The beads are produced with an emulsification process where by an organic phase containing unsaturated polyester resin and styrene monomer is emulsified within an aqueous phase. This phase consists mainly of de-ionised water and stabilisers that assist in forming a stable emulsion of organic droplets in the continuous aqueous phase. A polyamine is also added to the system to achieve the uptake of water droplets inside the organic phase. It is this water that is replaced with air when it evaporates from the beads upon drying, and leaves the particles with air-filled vesicles.

Emulsification is currently achieved locally with the use of a Cowles disperser system or an emulsion reactor set-up with the application of a specified stirring speed for a specific period of time. These stirring specifications are manipulated so that the organic globules are subjected to a specific shear rate and consequently are broken down to the required particle size. The polymeric reaction is initiated with the addition of a free-radical initiator and redox activator and the product is left overnight to allow completion of the reaction and subsequent formation of slurry containing solid polymer particles.

In this study, homogenisation was investigated as a means of emulsifying and producing vesiculated beads in a continuous process. Homogenisation is defined as the act of breaking down globules into smaller particles under pressure and produces a product with evenly dispersed (homogeneous) fine particles. This process could therefore also be used to produce particles with a smaller average particle size than those obtained by the existing Cowles- and emulsion reactor manufacturing processes. These batch processes produce vesiculated beads with an average particle size between 3 and 10 micron on industrial scale. With the incorporation of the homogeniser in a continuous process it would be possible, not only to produce particles in the order of 1 micron required for the addition to gloss paint, but it would also have the added advantages of easy cleaning, higher production rates and the use of smaller equipment.

The most important operating parameters when using a homogenisation system were determined using a laboratory scale homogeniser set-up. These parameters included the geometry of the internals of the homogeniser, the number of passes and the flow rate. From the information and results obtained from the batch experiments a semi-continuous bench-scale homogeniser set-up was designed. This experimental set-up consisted of a homogeniser, high-pressure pump, continuous feed section for the initiator and a loop-reactor equipped with a heating mantle to facilitate continuous curing of the product. Vesiculated beads with properties similar to those obtained by the existing batch processes, but with an average particle size in the order of 1 micron, were produced successfully with this semi-continuous set-up. Although the beads were not entirely cured after leaving the loop-reactor it is believed that with increased heating and an increase in the length of the reactor, this problem can be addressed.

The results obtained with the semi-continuous process could be used in future in the design and construction of a continuous pilot plant for the production of vesiculated beads.

OPSOMMING:

Titaandioksied (TiO_2) word in groot hoeveelhede as pigment in verf gebruik, maar as gevolg van die hoë koste van hierdie pigment en die uitputting van die natuurlike bronne, is verfvervaardigers op soek na alternatiewe.

Polimeerpartikels met lugholtes daarin vasgevang, is in die verlede suksesvol as plaasvervanger vir die pigment gebruik. Hierdie partikels is sferiese polimeerpartikels met ‘n menigte klein lugholtes wat effektiewe verstrooiing van lig binne die partikels veroorsaak. Dit verskaf aan die partikels ‘n wit voorkoms en daar is gevind dat klein hoeveelhede TiO_2 binne die partikels vasgevang kan word om die witheid in die nat- en droë fase te verhoog. Omdat die partikels uit ongeveer twee derdes lug bestaan en slegs klein hoeveelhede TiO_2 bevat, word ‘n vermindering in produksiekoste verkry as dit in verf gebruik word.

Die polimeerpartikels word geproduseer met ‘n emulsifiseringsproses waarby ‘n organiese fase, bestaande uit onversadigde poliëster en stireen monomeer, in ‘n waterfase geëmulsifiseer word. Laasgenoemde bestaan hoofsaaklik uit gedeïoniseerde water en stabiliseerders wat die vorming van ‘n stabiele emulsie van organiese druppels in die kontinue waterfase bewerkstellig. ‘n Poli-amien word ook by die sisteem gevoeg om die organiese fase in staat te stel om water op te neem. As hierdie water dan van die partikels verdamp wanneer dit droog word, word dit deur lug verplaas en laat dit die partikels met ‘n menigte lugholtes agter.

In Suid-Afrika, word emulsifisering tans bewerkstellig deur die gebruik van ‘n “Cowles” menger of ‘n emulsiereaktorsisteem waar ‘n spesifieke roerspoed vir ‘n vasgestelde tydperk aangewend word. Hierdie roerspesifikasies word so gekies dat ‘n bepaalde skuifkrag op die organiese druppels uitgeoefen word en dit dus tot die verlangde partikelgrootte opgebreek word. As die bepaalde partikelgrootte bereik is, word die reaksie geïnisieer deur die byvoeging van ‘n vry-radikaal inisieerder en ‘n redoksaktiveerder. Die produk word dan oornag gelaat sodat die reaksie voltooi kan word en die soliede polimeerpartikels binne die kontinue waterfase gevorm kan word.

Tydens hierdie studie is homogenisering ondersoek as ‘n moontlike metode om emulisifisering te bewerkstellig en sodoende die polimeerpartikels te produseer. Homogenisering word gedefinieer as ‘n proses waartydens partikels afgebreek word onder hoë druk en gevolglik lei dit tot die vorming van ‘n produk bestaande uit klein partikels uniform versprei deur die produk. Die moontlikheid bestaan dus dat homogenisering in ‘n proses gebruik kan word om kleiner partikels te produseer as wat moontlik is met die bestaande Cowles- of emulsiereaktor prosesse. Hierdie enkelladingsprosesse word gebruik om polimeerpartikels met ‘n gemiddelde partikelgrootte tussen 3 en 10 mikron op industriële skaal te produseer. Deur die homogeniseerder in ‘n kontinue proses te gebruik sal so ‘n proses gebruik kan word nie net om partikels met ‘n grootte van ongeveer 1 mikron (noodsaaklik vir glansverf) te produseer nie, maar hou dit ook verdere voordele in soos hoër produksie, kleiner toerusting en die gemak waarmee so ‘n sisteem skoongemaak kan word.

‘n Laboratorium-skaal enkelladings homogeniseerder is gebruik om die belangrikste bedryfsparameters van ‘n homogeniseringsisteem te bepaal. Hierdie parameters sluit in die geometrie van die interne dele van die homogeniseerder, asook die vloeitempo en die aantal deurgange deur die homogeniseeder. Die resultate van die enkelladings eksperimente is gebruik om ‘n semi-kontinue loodsaanleg skaal opstelling met ‘n hoë druk pomp, homogeniseerder, kontinue toevoer seksie vir die inisieërder en ‘n kontinue buisreaktor om die volledige verloop van die reaksie te verseker, te ontwikkel.

Polimeerpartikels gevul met lugholtes is geproduseer met bogenoemde proses en produkeienskappe vergelykbaar met die van die bestaande enkelladingsprosesse is verkry. Die enigste verskil tussen die produkeienskappe van die verskillende prosesses was die gemiddelde partikelgrootte met die partikels geproduseer met die homogeniseerderproses in die order van 1 mikron en die van die ander prosesse veel groter.

Die resultate verkry met die semi-kontinueproses sal in die toekoms gebruik word vir die ontwerp en bou van ‘n ten volle kontinue loodsaanleg.

TABLE OF CONTENTS:

TITLE PAGE **I**

DECLARATION **II**

ABSTRACT **III**

OPSOMMING **V**

ACKNOWLEDGEMENTS **VII**

TABLE OF CONTENTS **VIII**

LIST OF FIGURES **XIII**

LIST OF TABLES **XVII**

NOMENCLATURE **XXI**

1. INTRODUCTION **1**

1.1. BACKGROUND 1

1.2. VESICULATED BEADS 1

1.3. COST SAVINGS USING VESICULATED BEADS 2

1.4. CONTINUOUS MANUFACTURING PROCESS 3

1.5. OBJECTIVES 4

2. DEVELOPMENT OF VESICULATED PARTICLES AND PRODUCTION PROCESSES **6**

2.1. INTRODUCTION 6

2.2. EMULSION POLYMERISATION 7

2.2.1. Process theory 7

2.3. SUSPENSION POLYMERISATION 9

2.3.1. Introduction 9

2.3.1. Process theory 9

2.4. SINGLE VOID POLYMER PARTICLES 10
2.4.1. Formulation 10
2.5. MULTI-VOID POLYMER PARTICLES 11
2.5.1. Spindrift® pigmented vesiculated beads 11
2.5.2. The importance of the degree of agitation: 16
2.5.3. Beads with reduced free monomer 19
2.5.4. Beads with reduced tendency to yellow 21
2.5.5. Beads with improved scattering efficiency 22
2.6. COST-SAVINGS USING VESICULATED BEADS 24
2.7. EXISTING BATCH PROCESSES 25
2.7.1. Formulation and component properties 26
2.7.2. Cowles process 27
2.7.3. Emulsion reactor process 29
2.8. HOMOGENISATION 30
2.8.1. Homogeniser valve and pump 30
2.8.2. Hand-operated homogeniser 32
2.8.3. Important operation principles 33
2.8.4. Homogeniser accessories 34

3. WATER AFFINITY TESTS 35
3.1. INTRODUCTION 35
3.2. EXPERIMENTAL 36
3.2.1. Test methods 36
3.2.2. Different polyester batches 37
3.2.3. Components that influence water up-take 38
3.3. RESULTS 39
3.3.1. Different polyester batches 39
3.3.2. Effect of DETA on water affinity of polyester 43
3.3.3. Effect of TWEEN on water affinity of polyester 46
3.3.4. Effect of stabilisers on water affinity of polyester 51
3.3.5. Effect of LMA on water affinity of polyester 52
3.4. PROPOSED MECHANISM 52
3.4.1. Special additives 55

4. EXPERIMENTAL AND ANALYTICAL PROCEDURES 57

4.1. INTRODUCTION 57

4.2. BATCH EXPERIMENTS 58

4.2.1. Laboratory scale 58

4.2.2. Bench scale 66

4.3. SEMI-CONTINUOUS EXPERIMENTS 69

4.3.1. Equipment 69

4.3.2. Process description 70

4.4. CONTINUOUS EXPERIMENTS 71

4.4.1. Equipment 71

4.4.2. Process description 72

4.5. ANALYTICAL PROCEDURES 75

4.5.1. Opacity 75

4.5.2. Average size and distribution 76

4.5.3. Total solids content 78

4.5.4. Viscosity 78

4.5.5. Unreacted monomer 79

4.5.6. Degree of vesiculation 81

4.5.7. Scrub resistance of paint 83

5. RESULTS OF BATCH EXPERIMENTS 84

5.1. INTRODUCTION 84

5.2. LABORATORY SCALE EXPERIMENTS 85

5.2.1. Plunger 1 85

5.2.2. Plunger 2 88

5.2.3. Plunger 3 90

5.2.4. Summary of the effect of operating parameters on product properties 91

5.2.5. Effect of plunger geometry on product properties 92

5.2.6. Effect of thickener and colloid stabiliser variations on viscosity 93

5.2.7. Repeatability 96

5.2.8. Effect of surfactant on product properties 97

5.2.9. Effect of hydrophobically modified monomer on product properties 98
5.2.10 Minimising free monomer (Styrene) 100
5.3. BENCH SCALE EXPERIMENTS 101
5.3.1. Effect of plunger geometry 102
5.3.2. Effect of number of plungers/sections 103
5.3.3. Effect of number of passes 103
5.3.4. Emulsification action of pump 106
5.3.5. Effect of surfactant 107
5.3.6. Effect of LMA 107
5.4. COMPARISON OF PRODUCT PROPERTIES 110

6. DEVELOPMENT OF CONTINUOUS PROCESS 111
6.1. INTRODUCTION 111
6.2. EXOTHERM DEVELOPMENT 112
6.2.1. Alternative initiating system 112
6.2.2. Manipulating the chp/fe^{2+} initiating system 113
6.2.3. Effect of heating on the development of the exotherm 114
6.3. ADDITION OF THE INITIATOR 121
6.3.1. Effect of mixing intensity 121
6.3.2. Effect of time 123
6.4. RESULTS OF SEMI-CONTINUOUS EXPERIMENTS 125
6.4.1. Effect of heating temperature on product properties 125
6.4.2. Effect of initiator flow rate and concentration on product properties 127
6.4.3. Effect of increased length of the reactor on product properties 128
6.4.4. Effect of an increased heating section on product properties 129
6.4.5. Effect of increased stabiliser concentration on product properties 131
6.4.6. Effect of static mixers in the loop-reactor 132

7. CONCLUSIONS AND RECOMMENDATIONS: 134

7.1. INTRODUCTION 134

7.2. CONCLUSIONS 134

7.2.1. Important operating parameters 134

7.2.2 Important chemical variations 136

7.2.3. Continuous process 136

7.2.4. Mechanism for particle formation 137

7.3. RECOMMENDATIONS AND FUTURE WORK 139

REFERENCES 140

APPENDICES 142

APPENDIX A: PROPERTIES OF DIFFERENT POLYESTER BATCHES 143

APPENDIX B: PLUNGER DIMENSIONS 147

APPENDIX C: REGRESSION RESULTS 150

APPENDIX D: EXPERIMENTAL DATA OF BATCH EXPERIMENTS 159

APPENDIX E: EXPERIMENTAL DATA OF SEMI-CONTINUOUS EXPERIMENTS 169

LIST OF FIGURES:

CHAPTER 2:

PAGE:

FIGURE 2.1: GRAPHIC ILLUSTRATION OF THE EMULSION POLYMERISATION PROCESS[12]. 8

FIGURE 2.2: HIGH SHEAR IMPELLER USED IN COWLES PROCESS. 27

FIGURE 2.3: COWLES PROCESS SCHEMATIC 28

FIGURE 2.4: IMPELLER USED IN EMULSION REACTOR PROCESS. 29

FIGURE 2.5: EMULSION REACTOR PROCESS SCHEMATIC. 30

FIGURE 2.6: CROSS SECTION OF A HOMOGENISING VALVE EQUIPPED WITH A BREAKER RING. 31

FIGURE 2.7: HOMOGENISER VALVE WITH SPRING. 32

FIGURE 2.8: HAND-OPERATED HOMOGENISER FOR LABORATORY WORK. 33

CHAPTER 3:

FIGURE 3.1: DEPENDENCE OF WATER AFFINITY ON FINAL LIQUID ACID VALUE OF THE POLYESTER. 41

FIGURE 3.2: DEPENDENCE OF WATER AFFINITY ON FINAL LIQUID ACID VALUE OF THE POLYESTER OUTSIDE THE RANGE SPECIFIED. 42

FIGURE 3.3: THE INFLUENCE OF DETA ON THE WATER AFFINITY OF THE POLYESTER AS DETERMINED WITH METHOD 1. 43

FIGURE 3.4: THE INFLUENCE OF DETA ON THE WATER AFFINITY OF THE POLYESTER. 44

FIGURE 3.5. SEM IMAGES OF MICROTOME SAMPLES 45

FIGURE 3.6: THE INFLUENCE OF TWEEN ON THE WATER AFFINITY OF THE POLYESTER. 46

FIGURE 3.7: THE EFFECT OF TWEEN ON THE WATER AFFINITY OF THE ORGANIC PHASE WITHOUT THE ADDITION OF DETA. 48

CHAPTER 4:

FIGURE 4.1: PNEUMATICALLY DRIVEN HOMOGENISER. 58
FIGURE 4.2: MECHANICAL DRAWING OF HOMOGENISER AND INTERNALS. 59
FIGURE 4.3: GEOMETRY OF PLUNGERS 1 AND 2. 60
FIGURE 4.4: GEOMETRY OF PLUNGER 3. 61
FIGURE 4.5: LABORATORY SCALE BATCH HOMOGENISER PROCESS SCHEMATIC. 62
FIGURE 4.6: ONE SECTION OF THE HOMOGENISER FOR THE BENCH SCALE SET-UP 66
FIGURE 4.7: PROCESS FLOW DIAGRAM FOR BENCH SCALE BATCH EXPERIMENTS. 68
FIGURE 4.8: PROCESS FLOW DIAGRAM FOR CONTINUOUS EXPERIMENTS USING A LOOP REACTOR 71
FIGURE 4.9: 20 ℓ REACTOR WITH HEATING MANTLE AND DIFFERENT OUTLETS. 72
FIGURE 4.10: PROCESS FLOW DIAGRAM FOR CONTINUOUS SET-UP. 74
FIGURE 4.11: SEM IMAGE WITH 8 PARTICLES COUNTED. 77
FIGURE 4.13: SEM IMAGE OF SAMPLE USED TO CALCULATE DEGREE OF VESICULATION. 82
FIGURE 4.14: WET ABRASION SCRUB TESTER. 83

CHAPTER 5:

FIGURE 5.1: THE EFFECT OF VARIATION IN THE HEC CONCENTRATION ON VISCOSITY. 94
FIGURE 5.2: THE EFFECT OF VARIATION IN THE HEC CONCENTRATION ON VISCOSITY. 95
FIGURE 5.3: SEM IMAGES OF VESICULATED BEADS PRODUCED WITH A VARIATION IN NUMBER OF PASSES (A) 1 PASS, (B) 3 PASSES. 104

FIGURE 5.4: VESICULATED BEADS PRODUCED WITHOUT THE USE OF PLUNGERS. 106
FIGURE 5.5: SEM IMAGES OF VESICULATED BEADS PRODUCED WITH A VARIATION IN LMA CONTENT. (A) 5 % LMA, (B) 10 % LMA. 109

CHAPTER 6:

FIGURE 6.1:DEVELOPMENT OF THE EXOTHERM AT ROOM TEMPERATURE COMPARED TO THAT OF 65 °C. 114
FIGURE 6.2: SEM IMAGE OF SAMPLE CURED AT ROOM TEMPERATURE. 115
FIGURE 6.3: SEM IMAGE OF SAMPLE CURED AT 65 °C. 116
FIGURE 6.4: SAMPLE CURED AT ROOM TEMPERATURE. 117
FIGURE 6.5: SAMPLE CURED AT 67 °C FOR15 MINUTES 117
FIGURE 6.6: EXOTHERM DEVELOPMENT FOR SAMPLES AT 65 °C FOR 1 HOUR AND AT 70 °C FOR 15 MINUTES COMPARED TO CURING AT ROOM TEMPERATURE. 118
FIGURE 6.7: SEM IMAGE OF SAMPLE CURED AT 35 °C WITH LMA FORMULATION. 119
FIGURE 6.8: SEM IMAGE OF SAMPLE CURED AT 77 °C WITH LMA FORMULATION. 119
FIGURE 6.9: PARTICLE DEVELOPMENT WITH TIME AFTER INITIATION OF THE REACTION. 121
FIGURE 6.10: DEPENDENCE OF EXOTHERM ON MIXING INTENSITY. 112
FIGURE 6.11: DEVELOPMENT OF THE EXOTHERM FOR SAMPLES WITH DIFFERENT ADDITION TIME OF THE INITIATOR. 124
FIGURE 6.12: SEM IMAGE OF SAMPLE WITH 2 MINUTES BETWEEN ADDITION OF COMPONENTS OF INITIATOR SYSTEM. 124
FIGURE 6.13: SEM IMAGE OF SAMPLE WITH 30 SECONDS BETWEEN ADDITION OF COMPONENTS OF INITIATOR SYSTEM. 124

FIGURE 6.14: SEM IMAGE OF SAMPLE CURED IN LOOP REACTOR. 133

LIST OF TABLES:

CHAPTER 2:

TABLE 2.1: TYPICAL PROPERTIES OF ROPAQUE. 10
TABLE 2.2: PARTICLE SIZE REQUIRED FOR DIFFERENT TYPES OF PAINT. 15
TABLE 2.3: FREE MONOMER AT DIFFERENT WATER TEMPERATURES. 21
TABLE 2.4: TYPICAL PRODUCT PROPERTIES FOR COWLES PROCESS. 28
TABLE 2.5: TYPICAL PRODUCT PROPERTIES FOR EMULSION REACTOR PROCESS. 30

CHAPTER 3:

TABLE 3.1: WATER CONTENT OF THE ORGANIC PHASE OF DIFFERENT POLYESTER BATCHES. 39
TABLE 3.2: WATER CONTENT OF THE ORGANIC PHASE AND OPACITY FOR DIFFERENT POLYESTER BATCHES USED TO PRODUCE VESICULATED BEADS WITH THE COWLES PROCESS AS DETERMINED WITH METHOD 2. 40
TABLE 3.3: WATER CONTENT AND OPACITY FOR DIFFERENT DETA LEVELS. 45
TABLE 3.4: TWEEN LEVEL, WATER CONTENT AND OPACITY. 47
TABLE 3.5: ADDITION OF TWEEN TO INCREASE THE WATER CONTENT. 49
TABLE 3.6: PROPERTIES OF BEADS PRODUCED USING DV 4696 WITH THE ADDITION OF TWEEN. 49
TABLE 3.7: WATER CONTENT OF ORGANIC PHASE OBTAINED WITH THE ADDITION OF TWEEN AND STABILISERS BEING OMITTED. 50
TABLE 3.8: DEPENDENCE OF WATER-AFFINITY ON THE PRESENCE OF THICKENER AND SURFACTANT. 51
TABLE 3.9: EFFECT OF LMA ON WATER UPTAKE. 51

CHAPTER 4:

TABLE 4.1: NUMBER OF GROOVES ON PLUNGERS 1 AND 2. 60
TABLE 4.2: DIFFERENT LEVELS USED FOR EACH FACTOR. 64

CHAPTER 5:

TABLE 5.1: ANOVA-TABLE. 85
TABLE 5.2: BETA-VALUES FOR THE PARTICLE SIZE AS DEPENDENT VARIABLE. 86
TABLE 5.3: STIRRING SPEED AND ADDITION TIME OF THE PRE-DISPERSION USED WITH PLUNGERS 2 AND 3. 88
TABLE 5.4: FACTORS THAT HAVE A SIGNIFICANT EFFECT ON PRODUCT PROPERTIES. 90
TABLE 5.5: FACTORS THAT HAVE AN INSIGNIFICANT EFFECT ON PRODUCT PROPERTIES. 91
TABLE 5.6: PARTICLE SIZE FOR DIFFERENT PLUNGER GEOMETRY. 92
TABLE 5.7: AVERAGE PRODUCT PROPERTIES OBTAINED WITH DIFFERENT PLUNGER GEOMETRY. 93
TABLE 5.8: VARIATION IN HEC– AND PVOH CONCENTRATION. 94
TABLE 5.9: CORRELATION COEFFICIENTS 96
TABLE 5.10: PARTICLE SIZE DATA TO INVESTIGATE REPEATABILITY. 96
TABLE 5.11. THE EFFECT OF TWEEN ON PRODUCT PROPERTIES. 97
TABLE 5.12: PRODUCT PROPERTIES OBTAINED WITH THE ADDITION OF LMA. 98
TABLE 5.13: PRODUCT PROPERTIES OF BEADS RE-INTRODUCED TO THE HOMOGENISER. 100
TABLE 5.14: FREE MONOMER RESULTS AT DIFFERENT CURING TEMPERATURES. 100
TABLE 5.15: FREE MONOMER RESULTS OBTAINED AT 70 °C WITH VARYING HEATING PERIODS. 101
TABLE 5.16: EFFECT OF PLUNGER GEOMETRY ON PRODUCT PROPERTIES. 102

TABLE 5.17: EFFECT OF THE NUMBER OF PLUNGERS ON PRODUCT PROPERTIES. 103
TABLE 5.18: EFFECT OF THE NUMBER OF PASSES ON PRODUCT PROPERTIES. 104
TABLE 5.19: 1 PLUNGER AND 2 PASSES VS. 2 PLUNGERS AND 1 PASS. 105
TABLE 5.20: PROPERTIES OBTAINED WITHOUT THE USE OF PLUNGERS. 106
TABLE 5.21: THE EFFECT OF TWEEN ON PARTICLE SIZE AND OPACITY. 107
TABLE 5.22: THE EFFECT OF LMA ON PRODUCT PROPERTIES 108
TABLE 5.23: PRODUCT PROPERTIES OF HOMOGENISER-, COWLES- AND EMULSION REACTOR PROCESSES. 110

CHAPTER 6:

TABLE 6.1: EXOTHERM DATA FOR AMOUNT OF CHP/FE^{2+} REQUIRED BY THE STANDARD FORMULATION. 112
TABLE 6.2: RESULTS OF EXPERIMENTS CONDUCTED WITH DOUBLE THE AMOUNT OF CATALYST. 113
TABLE 6.3: PRODUCT PROPERTIES OF BEADS PRODUCED WITH INCREASED INITIATOR CONCENTRATION. 114
TABLE 6.4: PRODUCT PROPERTIES OF SAMPLE CURED AT ROOM TEMPERATURE AND 65 °C. 115
TABLE 6.5: CURING AT DIFFERENT LENGTHS OF TIME AT ELEVATED TEMPERATURE. 116
TABLE 6.6: PRODUCT PROPERTIES OF SAMPLES PREPARED WITH 7.5 % LMA AND CURED IN A WATER BATH AT DIFFERENT TEMPERATURES FOR 15 MINUTES. 119
TABLE 6.7: EFFECT OF MIXING INTENSITY ON PRODUCT PROPERTIES. 122

TABLE 6.8: EFFECT OF ADDITION TIME BETWEEN INITIATORS ON PRODUCT PROPERTIES. 123

TABLE 6.9: EFFECT OF INCREASED TEMPERATURE OF WATER IN THE JACKET OF THE LOOP-REACTOR ON PARTICLE DISCREETNESS, OPACITY AND THE EXOTHERM. 126
TABLE 6.10: SAMPLES CURED IN WATER BATH AND NOT THROUGH LOOP-REACTOR 127
TABLE 611: EFFECT OF INCREASED FLOW RATE AND CONCENTRATION OF THE INITIATOR ON PRODUCT PROPERTIES. 127
TABLE 6.12: PROPERTIES OF EXPERIMENTAL RUN WITH INCREASED LENGTH OF THE REACTOR. 128
TABLE 6.13: PROPERTIES OBTAINED WITH AN INCREASED HEATING SECTION AT DIFFERENT SAMPLE POSITIONS IN THE PROCESS. 130
TABLE 6.14: LUMINOSITY VALUES OF THE WHITE- AND BLACK SURFACES. 130
TABLE 6.15: PRODUCT PROPERTIES OF RUNS PERFORMED WITH AN INCREASE IN STABILISER CONCENTRATION. 131
TABLE 6.16: EFFECT OF STATIC MIXERS ADDED TO THE LOOP-REACTOR ON PRODUCT PROPERTIES. 132

NOMENCLATURE:

CM	calibration mixture	[-]
df	degrees of freedom	[-]
d_i	diameter of i'th particle	[μm]
ISTD	internal standard	[-]
n	number of particles analysed	[-]
RRF	relative response factor	[-]
r_i	residual error in the regression analysis of the i'th experimental run	[-]
SEM	scanning electron micrograph	[-]
T	temperature	[°C]
x_n	number average particle size	[μm]
x_v	volume average particle size	[μm]
y_i	dependent variable in regression analysis of the i'th experimental run	[-]

GREEK SYMBOL:

β	regression coefficient	[-]

CHAPTER 1: INTRODUCTION

1.1. BACKGROUND:

The three main components of all surface coatings, including paint, are the resin, the solvent and the pigment [1]. These usually comprise about 95 % of paint with additives such as thickeners, dispersants, defoamers, and wetting agents completing the composition. During application of paint the solvent is responsible for smooth coating of the surface and when the coating dries, the solvent evaporates. The remaining film then consists mainly of the resin and the pigment that provides the required colour and hiding power (opacity). Titanium dioxide pigment is reported as having a good hiding power [2] and this together with the brilliant whiteness, excellent covering and resistance to colour change associated with the use of this pigment, makes it the preferred pigment for use as opacifier in the paint industry [3]. Considerable pressure however exists to reduce the level of titanium dioxide used in paint formulations since this component is generally the largest single contributor to the raw material cost of decorative paint [4].

Vesiculated beads have been found to be particularly useful as opacifiers and matting agents in paint and can be used to partially replace some of the expensive titanium dioxide pigment [5]. An example of this is the use of Spindrift vesiculated beads produced commercially by Dulux Australia that gives rise to 10 – 20 % savings in raw material cost of the paint and therefore increases profitability [2].

1.2. VESICULATED BEADS:

Vesiculated beads are manufactured by a process where an organic phase is emulsified in an aqueous phase. The organic globules that form and are suspended in the aqueous phase are polymerised with the addition of an initiator. With the completion of the reaction the product remains as slurry of solid polymer beads in water. During this process the organic granules are filled with aqueous droplets that irreversibly diffuse out of the granules and are filled with air when left to dry. The

dry product then consists of spherically shaped polymer particles that contain variable-sized air voids.

The vesiculated beads possess the ability to internally reflect and scatter incident light due to the difference in refractive index between the polymeric shell of the beads and the air-voids. This presents the beads with a white appearance and hiding power (opacity). To increase the opacity of the beads in the wet state (when the voids are still filled with water), small amounts of titanium dioxide are added to the organic phase.

It is possible to introduce the beads to different types of paint by changing properties such as the average particle size. For instance, beads of approximately 1-micron average particle size can be used in gloss paint; where as beads of up to 500 micron can be introduced to textured paint [6]. In these instances the vesicles may occupy a range of 5 to 75 % of the total bead volume depending on the opacifying effect required.

1.3. COST-SAVINGS USING VESICULATED BEADS:

Titanium dioxide pigment is the largest contributor to raw material cost. Although a short-term surplus of supply could continue until 2003, the longer-term outlook indicates a growing shortage of suitable quality feedstock for TiO_2 pigment production [3]. This will result not only from growth in pigment consumption, but also from a decline in production of titanium minerals due to depletion of mineral resources. These concerns together with the fluctuating import costs (about R 29 per kilogram) associated with the pigment have forced paint manufacturers to consider using vesiculated beads as synthetic opacifiers.

It has been found that the introduction of vesiculated beads to paint does not adversely affect paint properties, but leads to significant cost savings. This is mainly due to the fact that the beads are about two thirds air by volume and therefore are less expensive (about R 3.70 per kilogram) than equivalent volumes of titanium dioxide [2].

1.4. CONTINUOUS MANUFACTURING PROCESS:

Vesiculated beads are produced locally on commercial scale using paint mixing vessels as part of a batch process. Two different manufacturing processes are used. The one utilises a Cowles disperser blade to achieve emulsification of the organic phase in the aqueous phase, whilst the other is performed in emulsion reactors commonly found in paint plants. With the growing demand for vesiculated beads as an economical alternative to pigment, their volume limits production of beads with the batch processes. According to literature [7] the production of paint was estimated at 24 million tonnes for the year 2001 across the globe, with the production of decorative paint in the order of 40 % of this volume [8]. This represents the production of approximately 10 million tonnes of paint, of which the water-based paint market share is 60 %. If vesiculated beads would be incorporated in the production of the water-based paint at about 10 % by weight, the potential world market would require the production of 0.6 million tonnes of vesiculated beads per year. Even if only 10 % of this potential market for vesiculated beads were realised, such production volumes would be unattainable with the existing equipment and batch processes and certainly suggest the use of a continuous process to cope with the high demand.

It was therefore decided to investigate the development of a continuous process to produce vesiculated beads. Such a process would have the advantage of producing larger volumes per annum as well as the added advantages of easy cleaning and possibly better repeatability when compared to the batch processes.

To develop a continuous process an alternative method of emulsification had to be found. By keeping in mind that the emulsification must be applied in a continuous process, homogenisation was investigated as such a possible alternative. This technique can be employed with the use of a high-pressure pump and valve system to obtain emulsification. It is achieved by forcing the two phases, i.e. the organic- and the aqueous phase used to produce vesiculated beads, through a minute orifice under pressure [9]. The shear force resulting from this movement causes the organic

globules to be worn and broken down and to be uniformly dispersed within the aqueous phase.

Homogenisation could possibly also be used to produce vesiculated beads that can be incorporated into gloss and semi-gloss paint. These should be in the order of 1 micron and have not yet been produced with the existing Cowles or emulsion reactor processes.

1.5. OBJECTIVES:

Initially the main objective of this study was to produce vesiculated beads that could be incorporated into gloss paint. An average particle size in the order of 1 micron and with other properties similar to that obtained with the Cowles- and emulsion reactor processes would be required of these beads. However, it soon became apparent that the homogeniser could be included in a continuous process for the production of vesiculated beads.

The objectives of this project with the main aim of developing a continuous process then were to:

- Determine the important operating parameters when using homogenisation to produce vesiculated beads.

- Establish the product properties obtainable first with a laboratory scale homogeniser and then with a bench scale homogeniser.

- Produce vesiculated beads using the bench scale set-up to establish the effect of different process parameters including recycling, different geometry of the internals, flow rate, method of catalysis and heating on the product properties such as average particle size, particle size distribution, opacity and viscosity.

- Design a bench-scale continuous process incorporating those conditions (geometry of internals, catalysis, heating, etc) most suitable to such a process.

- Perform production runs using the continuous set-up to produce vesiculated beads with product properties comparable to those obtained from existing batch processes, but with smaller average particle size.

During the development of the continuous process it also became necessary to investigate the mechanism by which the vesicles inside the particles are formed, as well as the factors that influence its' development. This study had the following objectives:

- To link the amount of water entrapped and consequently the degree of vesiculation within the particles to the raw material properties and consumption.

- To optimise and possibly manipulate product properties by manipulating the factors influencing the water uptake of the organic phase and the degree of vesiculation.

CHAPTER 2: DEVELOPMENT OF VESICULATED PARTICLES AND PRODUCTION PROCESSES.

2.1. INTRODUCTION:

Since the 1970's air-void technology has been used in conjunction with the concepts of emulsion- and suspension polymerisation processes to develop synthetic opacifiers for application in the paint industry. Developments in this field include vesiculated beads (Spindrift®) commercially produced by Dulux Australia and Ropaque® Opaque Polymer manufactured by Rohm & Haas Company in the USA. The latter comprises polymer particles containing a single void and an average size particle of about 0.5μm, whilst Dulux's invention entails the formation of multiple voids together with small amounts of encapsulated pigment inside the polymer shell. These beads are also larger than the ones produced by Rohm & Haas and have an average particle size of 11 - 14μm. Both of the inventions rest on the ability of the particles to bring about internal reflection and scattering of light because of the difference in refractive index between the hard polystyrene polymer in the shell and the air in the void(s) [2].

The sections that follow give an overview of the principles of emulsion polymerisation as well as previously patented processes to produce vesiculated beads.

Since this study was focussed on producing vesiculated beads using homogenisation some literature concerning this technique is also presented together with a discussion of the Cowles- and emulsion reactor processes used to produce vesiculated beads on industrial scale.

® Spindrift and Ropaque are registered trade names.

2.2. EMULSION POLYMERISATION:

Emulsion polymerisation is described as a process with which unsaturated organic carbon compounds are polymerised [10]. This chemical process is carried out in a liquid medium, almost always aqueous, and produces a milky fluid called latex. The latex consists of an intimate mixture of two immiscible liquids – one, named the dispersed phase existing as discrete droplets dispersed throughout the other, named the continuous or aqueous phase [2].

According to **Penboss** [11], four basic components are needed to achieve emulsion polymerisation. These include the following:

- the monomer
- the dispersion medium (continuous phase)
- an emulsifier (surface-active agent, surfactant)
- an appropriate initiator

When correct amounts of these components are mixed together, with sufficient contact between the different phases and within a certain temperature range an emulsion of monomer droplets is formed in the continuous dispersion medium [12].

2.2.1. PROCESS THEORY:

A simplified outline of the emulsion polymerisation process is presented together with a graphic illustration [12] (Fig 2.1).

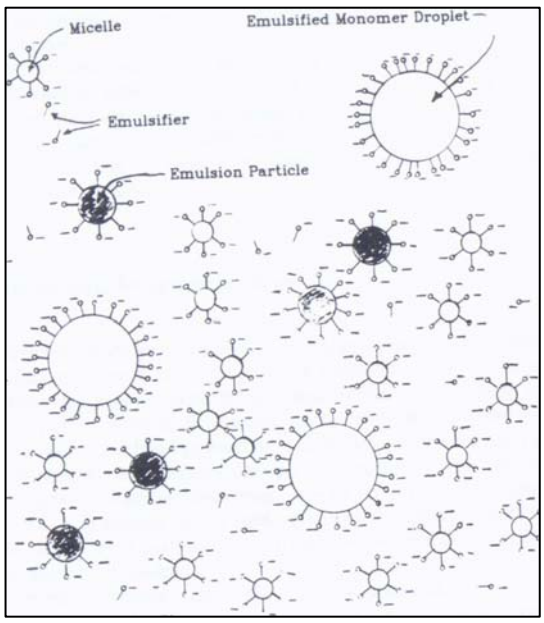


Figure 2.1: Graphic illustration of the emulsion polymerisation process [12].

The aqueous phase contains the species represented in the illustration. With the application of mechanical agitation the monomer phase is broken up into small droplets. These droplets are held in suspension by the collective action of the agitation and the stabilisation achieved with the surfactant molecules.

In many cases the monomer is only slightly soluble in water and the surfactant actually increases the solubility of the monomer in the water phase. This increased solubility is achieved by the formation of micelles, which are groups of surfactant molecules clumped together. These are orientated in the same fashion as the surfactant molecules with the hydrophobic ends clumped together around the surface of the monomer droplets and the hydrophilic ends in the water phase. The micelles therefore contain a large hydrophobic region that attracts the monomer droplets.

With the emulsion of the monomer phase in the water established, and the presence of the micelles presumed, the *initiator* is added and it degrades with the formation of charged radicals. These radicals react with monomer molecules inside the micelles to form new radicals that combine with other monomer molecules through addition polymerisation.

The next step of polymerisation is termed *propagation*. As the monomer molecules in the micelles combine with one another, more will migrate from the droplets through

the water to the micelles. The micelles therefore grow from small groups of surfactant and monomer molecules to larger groups of polymer chains, held in emulsion by the surfactants located on the exterior surface. With time all of the micelles will disappear and the monomer droplets will shrink in size.

Termination of the process occurs when all of the monomer molecules in the suspension have migrated and are attached to the polymer chains, with basically all of the surfactant molecules also attached to it.

2.3. SUSPENSION POLYMERISATION:

2.3.1. INTRODUCTION:

Just as emulsion polymerisation follows a free-radical reaction, suspension polymerisation occurs with the same type of reaction, but with a unique mechanism. In the latter the polymerisation occurs in the organic- or the monomer phase, while in the case of the emulsion polymerisation the reaction takes place in the water phase [13]. Another difference is the use of a polymeric stabiliser such as poly vinyl alcohol to stabilise the dispersed droplets in the suspension process as opposed to the surfactants used in the emulsion polymerisation process [11].

2.3.2. PROCESS THEORY:

The monomer droplets are dispersed within the continuous aqueous phase and kept in suspension with mechanical agitation. These droplets each behave as small batch reactors, with the monomer reacting to produce the polymer. For suspension polymerisation to take place an oil-soluble initiator is needed to ensure that the initiator does not enter the water phase and that polymerisation will therefore occur in the monomer (or oil) phase [12].

2.4. SINGLE-VOID POLYMER PARTICLES:

Ropaque Opaque Polymer particles are formed using an emulsion polymerisation process that causes the entrapment of water within the core of the particles [2]. The product liquid is of a milky white appearance like any other emulsion. When the particles are left to dry out in a coating film, the water irreversibly diffuses out of the core. The result is an opaque, white powder containing spheres that consist of a hard polymer shell with a hollow air-filled core that cannot be filled with water again. Since the particles have no film forming ability it is treated as part of the pigment when incorporated into paint formulations.

Since the beads are formed through an emulsion polymerisation process the average particle size and the size distribution can be controlled quite accurately. Typical product properties are given in the table below.

Table 2.1: Typical properties of Ropaque [2].

Solids content [%]	37 - 38
Dry relative density	0.741
Wet relative density	1.038
Average particle size [micron]	0.4
Viscosity [cps]	100

2.4.1. FORMULATION:

The efficiency with which light is scattered by a pigment is related to the hiding power achieved [2]. Therefore hiding power should increase linearly as pigment concentration is increased. However it is found that at pigment levels above the critical pigment volume concentration (CPVC) flocculation and aggregation of pigment particles occur and the hiding power subsequently decreases. Single-void particles however retain the ability to scatter light at all pigment volume concentrations making it possible to formulate paints at a range of PVC's with the introduction of beads without any drop in opacity.

With the introduction of the beads to a paint formulation a reduction in the amount of titanium dioxide required is achieved. This leads to extensive savings in raw material cost and a subsequent increase in profitability (see section 2.6).

2.5. MULTI-VOID POLYMER PARTICLES:

2.5.1. SPINDRIFT® PIGMENTED VESICULATED BEADS:

Gillian and Kershaw [6] filed a patent in 1969 describing a process by which vesiculated polymer granules with a pre-determined size can be formed and can successfully be introduced as opacifying components in surface coatings and particularly water-based paints. These beads have an average particle size between 0.1 micron and 500 micron, with the vesicle diameter ranging from 0.01 micron to 5 micron.

Preparation method:

The beads are prepared using a double emulsification process consisting of the following steps:

- Making up a solution of the base (such as polyamines or metal oxides) and the pigment in water (first aqueous phase).
- Dispersing droplets of the water solution into the polyester solution (polyester and monomer).
- Making up a second aqueous phase containing water and surfactants.
- Suspending the polyester solution in the second aqueous phase, in the presence of a base, by applying mechanical agitation.
- Initiating the reaction by the addition of a free radical initiator or by exposure to ultra-violet radiation.

With this process a suspension of polyester globules in the aqueous phase is formed, with each globule containing droplets of aqueous liquid. The droplets inside the globules will diffuse out of the produced polymer particles when left to dry in air.

This leads to the formation of air-filled vesicles that occupy between 5 % and 75 % of the bead volume.

The components that make up the formulation are described below.

Components:

The beads produced by this particular invention [5] utilise the following components:

- Unsaturated polyester resin

The resin should be prepared as condensation products of polybasic acids and alcohols and should posses carboxylic groups that will react with and will be at least partially neutralised by the base. Such a resin should also have a viscosity greater than Gardner-Holdt S and an acid value of 5 – 75 mgm KOH per gm resin.

- Pigment

To increase the opacifying effect of the product, especially in the wet state, the resin can be pigmented. This pigment should be water-insoluble and should not prevent free radical polymerisation. It should be noted that the hiding power of the pigment is related to its ability to scatter and/or absorb light. If all the incident light is either scattered or absorbed and no light is reflected to the observer, the object covered by the pigment will be completely hidden. *Titanium dioxide* is regarded as having the best hiding power because of its high scattering efficiency and is therefore recommended by the patent writers as the preferred pigment to use.

- Unsaturated monomer

The monomer should also be water-insoluble and can be used as a single monomer or as a mixture together with other water-insoluble monomers. Preferred monomers are *styrene*, *vinyl toluene* and *divinyl benzene*.

- Base

A strong base that is able to at least partially neutralise the carboxylic groups of the resin is proposed. This component will give a stable dispersion of polyester within

the aqueous phase if the dissociation exponent is less than 5. Examples of such bases include polyamines (e.g. *diethylenetriamine*) and solid metal oxides.

The amount of base required to form a stable dispersion is related to the number of free carboxylic groups of the resin with the best results achieved at about 0.7 to 3 equivalents of base per carboxyl group.

- Surface active agent (Stabiliser)

As mentioned in the section on suspension polymerisation surfactants that stabilise oil-in-water suspensions such as *poly vinyl alcohol* may be used as steric stabilisers in suspension polymerisation processes. These stabilisers form part of the aqueous phase and typically have a molecular weight in the order of 100 000. With insufficient quantities of the stabiliser present the suspension may become unstable, where as an excess of stabiliser will lead to a loss in discreteness of the globules and a consequent loss in discreteness of the beads in the final product.

- Thickener

A thickener is also added to the aqueous phase as a means of increasing the viscosity. This prevents the settling of suspended globules and contributes to the production of small particles. Suitable thickeners include water-soluble ethers of cellulose (*hydroxy ethyl cellulose*) used at concentrations of 0.02 – 14 % by weight of the aqueous phase.

Typical example of the preparation method:

1. An unsaturated polyester resin is prepared as a condensation product of fumaric acid, phtalic anhydride and propylene glycol in the molar ratio of 3:1:4. This resin has an acid value of 44 mgm KOH per gm polyester and a Gardner Holdt viscosity of T as a 70 % solution in xylene.

2. A solution of 18 parts of the resin, 0.5 parts of benzoyl peroxide and 12 parts of styrene is prepared as the oil phase.

3. The aqueous phase consists of the following:

hydroxy ethyl cellulose	4.06 parts

poly vinyl alcohol*	7.28 parts
water	719 parts
diethylene triamine	2 parts

* poly vinyl alcohol with 20 % residual vinyl acetate and molecular weight of about 110 000

The resin solution prepared in step 2 is added to the aqueous phase (step 3) at high stirring speed. A suspension of globules of polyester containing droplets of aqueous liquid is formed with the globules being about 15 micron in diameter. These are then polymerised by heating the suspension at 95 ºC for 3 hours. After the heating is completed, the suspension is diluted with 4000 parts of water and left overnight to allow for the sedimentation of the concentrated beads. These can then be separated from the bulk of the water and the product properties can be obtained.

The beads produced by the process described here has the following product properties:

average particle size	15 micron
average vesicle size	2 micron
vesicle volume	75 %

Manipulating particle- and vesicle size:

The average particle size of the product is determined by the size of the suspended globules in the aqueous phase and by applying either of the following the particle size can be reduced:

- higher stirring speeds
- increased viscosity of the aqueous phase

According to Gillian and Kershaw [6] the vesicle size can also be manipulated by changing the composition and concentration of the base and/or adjusting the viscosity and acid value of the polyester. With a higher concentration of the base they found that the concentration of the vesicles increased to a maximum where after further increases had little effect on the vesiculation. If the viscosity of the polyester is increased and a subsequent decrease in the acid value of the polyester occurs, a

decrease in the degree of vesiculation and a consequent decrease in opacity are observed.

Uses:

The vesiculated beads produced by the invention of Gillian and Kershaw [6] are reported to be useful as low-density fillers and opacifiers in plastic mouldings, polymer films and paper. For these purposes the beads can comprise up to about 25 % of the total volume of the final product.

If the beads are used as *fillers* it should preferably have an average particle size of 5 micron to ensure the optimum opacifying effect.

For the use of beads in *plastics mouldings* for building sheeting it should have an average particle size of 2 – 3 mm with a vesicle content of about 80 % of the total bead volume. This also presents the articles with the added advantage of exceptional lightness.

Furthermore, the beads can be used as matting and opacifying agents in different *paints*. These are prepared by stirring the beads into a conventional paint formulation at concentrations of 55 % for gloss and semi-gloss paints and up to 95 % for matt paints.

The following table shows the different applications using different particle size ranges:

Table 2.2: Particle size required for different types of paint.

	Bead diameter [micron]
Textured paint	50 - 500
Matt/semi-gloss paint	1 - 100
Gloss paint	1

It should be noted that the optimum light scattering effected by the vesicles and consequently the optimum opacifying effect is achieved with a vesicle diameter of 0.2 to 0.5-micron diameter. The small vesicle diameter is also related to the use of a

polyamine as base and confirmed with the results achieved when experimental runs were performed without the presence of the amine. These runs produced beads with vesicles of substantially larger diameter at 1 – 5 microns.

2.5.2. THE IMPORTANCE OF THE DEGREE OF AGITATION:

In 1972 **Gunning et al.** [13] filed a patent in which they describe the importance of the degree of agitation applied in the different stages of the process of preparing vesiculated pigmented granules. They state that although the granules prepared by the process as described by Gillian and Kershaw [6] are satisfactory for application for some purposes it has been observed that if the granules are used as matting agents in paints it shrinks considerably as the paint dries. This leads to cracking of the paint film and the particles are termed dimensionally unstable.

A test method was therefore developed by which the dimensional stability of the vesiculated bead slurry can be tested and if such a slurry exhibits less than a 5% shrinkage as determined by the test, the beads are termed stable. The incorporation of these beads to a paint film either eliminates cracking completely or substantially overcomes the problem.

It is also reported that the product prepared according to the invention described above [6] exhibits undesirable fluctuations in quality where agglomerates of particles are formed. These, if incorporated in a paint film, will cause defects known as bittiness and flip. The inventors of this patent have however found that the defects can be avoided by slight modifications to the process developed by Gillian and Kershaw [6].

Test method to quantify shrinkage of beads:

The test method developed by Gunning et al. entails diluting a drop of the bead slurry with water and spreading it on a microscope slide for inspection under a microscope with a calibrated eyepiece. As soon as the movement of beads stops, at least 10 beads are selected and monitored. The microscope is then used to measure the diameter of the selected granules, which should be in the order of 10 – 20 micron,

at a magnification of about 400X. After the beads have dried out the measurement is repeated and the average shrinkage of the 10 beads calculated as a percentage of reduction in diameter.

Improved process:

Dimension stability of the beads can be increased by the use of a base having dissociation constant in water of 8.5 – 10.5 and at a concentration of about 0.3 –1.4 amine groups per carboxyl group of the resin. Compare this to the dissociation constant of less than 5 and concentration of 0.7 – 3 amine groups per carboxyl group reported by Gillian and Kershaw [6].

The improved process further consists out of the following steps:

- Dispersing pigment in water in the presence of a non-flushing pigment dispersing agent such as sodium hexametaphosphate (first aqueous phase).
- Suspending the water and pigment solution in an unsaturated polyester resin and monomer solution, in the presence of a water-soluble polyamine with the concentration mentioned above using mechanical agitation.
- Applying sufficient agitation until the size of the dispersed particles is reduced below 1 micron.
- Dispersing the above emulsion in the second aqueous phase containing water, surfactant and thickener with continuous mechanical agitation limited to the intensity below the threshold at which coalescence of the dispersed globules will occur.
- Initiating the polymeric reaction whilst at the same time controlling the agitation at a level as to not exceed the critical shear rate at least until a sample of the curing granules is insoluble in methyl ethyl ketone.
- Continuing agitation until a specified maximum level of unreacted monomer is reached.

Typical example of the preparation method:

The following solutions/mixtures are prepared:

1. A polyester resin manufactured from phtalic anhydride, fumaric acid and propylene glycol with mole ratios of 1:3:4.4 and acid value of 22 mg KOH per gm polyester is dissolved in styrene. The resulting mixture has a concentration of 70 % by weight and viscosity of Gardner – Holdt Z3.

2. Colloid solution A is prepared by dissolving 1.8 parts of hydroxy ethyl cellulose in 326.2 parts of water and colloid solution B is prepared by dissolving 7.5 parts of partially hydrolysed poly (vinyl acetate) in 92.5 parts of water. The partially hydrolysed poly (vinyl acetate) has an approximate molecular weight of 125 000 and a viscosity of 35 – 45 cPs.

3. An aqueous mill-base is prepared by blending together the following:

titanium dioxide pigment	208 parts
sodium hexametaphosphate	0.8 parts
water	104 parts

The first emulsion is then prepared by vigorously stirring a mixture of 230 parts of the aqueous mill-base and 1.2 parts of diethylene triamine into a mixture of 123 parts of polyester resin (as prepared in 1 above) and 54.5 parts of styrene. This emulsion is then immediately poured into a mixture of 446 parts of colloid solution A, 80 parts of colloid solution B and 2.7 parts of 70 % cumene hydroperoxide. It is stirred until the particle size of the globules is about 20 micron (the peripheral speed of the blade should not exceed 15 m/s).

The stirring rate is then reduced to 5 m/s and a mixture of 60 parts of water, 0.4 parts of diethylene triamine and 0.03 parts of ferrous sulphate heptahydrate is added. Stirring is stopped after the addition of the mixture described above and the batch is allowed to cure under its' natural exotherm.

The product produced by this method has the following properties:

average particle size	30 micron
vesicle volume	70 %
shrinkage	4 %

2.5.3. BEADS WITH REDUCED FREE MONOMER:

It was found that vesiculated beads prepared by processes such as those published up to the early 1980's might be incompletely polymerised and consequently contain un-reacted free monomer. This presents the product with an objectionable odour, for example of styrene, and gives rise to reduced conversion, waste of expensive monomer and high VOC. In 1981 the **Tioxide Group LTD** [14] filed a patent in which they propose an improved process whereby the disadvantages discussed above are eliminated.

The processes described in the prior art introduce the initiator during the formation of the emulsion and this may lead to premature curing of the organic phase. In such a case the quality of the beads may be affected adversely with an increase in the level of free styrene also occurring.

The Tioxide Group LTD [14] suggests the addition of hot water to increase the temperature of the final emulsion to at least 45 ºC before the initiator is added. The temperature of the mixture will then rise even further due to the exothermic nature of the reaction and the temperature of the mixture is maintained above 50 ºC for at least two hours. According to the patent writers this leads to a reduction in free monomer from approximately 3 % to about 0.3 % on the total weight of the slurry.

Typical example of the preparation method:

1. An unsaturated polyester resin is manufactured by condensing together fumaric acid, phtalic anhydride and propylene glycol in the molar ratio of 3:1:4.5. The resin is diluted with styrene to a mixture containing 70 % resin by weight with an acid value of 24 mgm KOH per g of resin and a viscosity of 25 cPs (at 250 ºC).

2. A pre-milled aqueous phase is prepared containing the following:

water	114 parts
5 % solution of CALGON PT	20.5 parts
titanium dioxide pigment	267 parts
diethylene triamine	2.5 parts

3. An oil phase is prepared consisting of 50 % resin as prepared in step 1 and 50 % styrene.

309 parts of the oil phase is then added to the pre-milled aqueous phase with high speed stirring and an emulsion is formed. 177 parts of this first emulsion is then added under high speed stirring to a second aqueous phase containing the following:

hydroxy ethyl cellulose	0.54 parts
90 % hydrolysed polyvinyl acetate	2.55 parts
water	171 parts

This second emulsion is kept under agitation until the oil globules have an average size of approximately 12-micron. The heated water of 131 parts at 90 ºC is then added to the second emulsion and the final emulsion has a temperature of about 46 ºC.

Curing of the beads is initiated by the addition of

cumene hydroperoxide	1.25 parts
2 % aqueous solution of DETA	10 parts
0.9 % aqueous solution of $FeSO_4$	2 parts

and the beads are left overnight to allow for curing to be completed.

The product exhibits a free styrene content of 0.2 % on the total weight of the slurry.

The table below shows the free monomer content obtained from different samples with the heated water at different temperatures:

Table 2.3: Free monomer at different water temperatures.

	Water T [C]	Free monomer [weight %]
Sample 1	90	0.2
Sample 2	60	0.4
Sample 3	55	0.7
Sample 4	10	2.9

2.5.4. BEADS WITH REDUCED TENDENCY TO YELLOW:

Goldsbrough and Hodge [15] filed a patent in 1982 in which they claim the development of a process that produces vesiculated polymer beads with a reduced tendency to yellow. This invention applies a double emulsification process without the necessity of a polyamine or a solid metal oxide in the first aqueous phase as required by the invention of Gillian and Kershaw [6].

Instead of using the above-mentioned substances in the first aqueous phase, Goldsbrough and Hodge use a strong base (alkali metal hydroxides, alkali metal salts of weak acids or ammonium salts of weak acids) together with a water-soluble inorganic salt such as sodium chloride. If the product produced by this process is compared to that produced using the invention described in section 2.5.1 a reduction in yellowing is achieved without any adverse effects on the other product properties.

Typical example of the preparation method:

1. An unsaturated polyester resin is prepared as a condensation product of maleic anhydride, phtalic acid and propylene glycol in the molar ratio of 3:1:4.5. The resin has an acid value of 24 mg KOH per g of polyester and a viscosity of 2.5 Pa.s as a 70 % solution in styrene.

2. The oil phase is prepared by dispersing 178 parts of titanium dioxide pigment in 166 parts of a 50 % solution of the resin prepared in step 1 in styrene. A further 41 parts of styrene is added.

3. The first aqueous phase consists of the following:

sodium hydroxide	0.6 parts
sodium chloride	0.12 parts
water	129 parts

385 parts of the oil phase prepared in step 2 is added to the phase discussed above under high-speed agitation. This forms the first emulsion.

The second emulsion is prepared by addition of 192 parts of the first emulsion to the second aqueous phase containing:

hydroxy ethyl cellulose	0.45 parts
90 % hydrolysed poly vinyl acetate	2.25 parts
sodium dihexyl sulfosuccinate	0.5 parts
water	180 parts

The emulsion is submitted to further agitation until the polyester globules reach an average size of approximately 12-micron. 177 parts of hot water is then added to give a final emulsion with a temperature of about 50 ºC, where after polymerisation is initiated by the addition of the following:

cumene hydroperoxide	1.25 parts
2 % aqueous solution of DETA	10 parts
0.9 % aqueous solution of $FeSO_4$	2 parts

2.5.5. BEADS WITH IMPROVED SCATTERING EFFICIENCY:

In 1984 **Karickhoff** [16] filed a patent in the USA claiming that he developed a process by which vesiculated beads, each containing more than one vesicle, with improved scattering efficiency and resistance to shrinkage (less than 5 % shrinkage upon drying) can be produced. This process follows the same basic steps as the invention described in section 2.5.1 developed by Gillian and Kershaw [6] where a double emulsification process is used to form the beads.

The improvement claimed by Karickhoff is brought about by the following:

- Using a base (polyamine) concentration outside of that taught by Gillian and Kershaw. The aforementioned inventors required a base concentration of 0.7 to 3 equivalents of base per carboxyl group to form a stable dispersion, but Karickhoff reports using between 2 and 10 equivalents of base per carboxyl group. According to him this leads to an increase in scattering efficiency if compared to beads produced by prior inventions as well as less shrinkage. The patent also reports an increase in scattering efficiency resulting in an increase in the opacity of the product.
- Using an unsaturated polyester resin with an acid value of 8 to 20, and preferably between 8 and 14 mgm KOH per gm polyester as opposed to 5 – 75 mgm KOH per gm polyester proposed by Gillian and Kershaw [6]. Karickhoff claims that a higher scattering efficiency is achieved using polyester batches with the lower acid values.

Typical example of the preparation method:

1. The first aqueous phase is prepared as a mixture of 10 parts ice, 11.08 parts water, 2.2 parts of a 75 % solution of sodium sulgated dioctylsuccinate in butanol, 0.32 parts of ethanol and 0.79 parts of defoamer using a high speed disperser and a Cowles blade. The titanium dioxide pigment at 53.2 parts is added to this aqueous solution over a period of 3 minutes and kept under agitation for a further 15 minutes. The speed of the agitator is then reduced and 1.04 parts of the base, diethylene triamine, and 6.66 parts water added and mixed for a further 2 minutes.

2. The unsaturated polyester resin (49 parts), formed as a condensation product of propylene glycol, fumaric acid and isophtalic anhydride in a mole ratio of 4.72:3.11:1 is mixed with 18.52 parts of styrene under low speed agitation. The polyester has an acid value of 12.4 as a 58 % solution in styrene. The first aqueous phase is added to this polyester and styrene mixture still under low speed agitation. This mixture has approximately 4.8 amine groups per carboxyl group of the resin and is agitated for about 3 minutes at increased stirring speed, where after emulsification is completed at a lower stirring speed for 15 minutes.

3. The second aqueous phase contains the following:

hydroxy ethyl cellulose*	43.23 parts
polyvinyl alcohol†	47.97 parts
water	110.27

* 1.5 % hydroxy ethyl cellulose solution in water

† 7.5 % polyvinyl alcohol solution in water

These components are mixed together at low stirring speed and the first emulsion (prepared in step 2) added over a period of 4 minutes. Agitation is increased and maintained for 20 minutes, where after the speed is reduced and 102.57 parts of hot water at 52 ºC is added.

Initiation of the reaction is achieved with the addition of 0.921 parts of cumene hydroperoxide, 0.159 parts of a 10 % solution of diethylene triamine in water and 1.05 parts of a 1 % ferrous sulphate solution. Stirring is continued for 2 minutes and then stopped. The temperature of the emulsion increases to approximately 52 ºC and it is allowed to stand overnight to achieve complete curing of the beads.

The beads produced by this process exhibit a good scattering efficiency with shrinkage of less than 3.1 %.

Product properties:

The vesiculated beads produced with this invention [16] have an average particle size range of 0.1 to 500 micron and with vesicle diameters ranging between 0.01 and 5-micron. When the beads are intended as opacifying agents the vesicle diameter should however be between 0.03 to 1 micron and it should comprise 65 to 80 % of the bead volume. These properties compare well to the ones reported in the invention described in section 2.5.1 but with added improvements.

2.6. COST-SAVINGS USING VESICULATED BEADS:

A range of paints can be formulated with a variation in the concentrations of latex, TiO_2, extender, binder and vesiculated beads [11]. Therefore cost-savings on almost all types of paint can be achieved with the introduction of the beads. However with low-

quality paints containing low levels of TiO_2 and latex and relatively high levels of extender cost-savings are more difficult to achieve. This is due to the higher cost associated with the vesiculated beads if compared to the extenders and cheap extenders would essentially be replaced in part by the more expensive beads.

Significant formula cost-savings can however be achieved using Spindrift beads through reformulation of high quality and standard quality paints formulated with higher levels of TiO_2. It is reported through literature [2] that production savings derived from using vesiculated beads instead of equivalent volumes of *pigment* in paint are in the order of 10 – 20 % on the raw material cost per liter. With the use of the beads instead of huge volumes of pigment powder, a reduction in health risks associated with the handling of these fine powders also occurs. The beads are produced as aqueous slurries that are readily transported through the paint factories by pumping of the liquid, without requiring any manual handling.

Furthermore, if some of the e*xtender* is replaced by the low-density vesiculated beads a reduction in density of the paint is obtained. This implies that for a given weight of paint a higher volume is achieved and will translate to savings because the paint is sold by volume.

Because the vesiculated beads also posses some film forming ability, it is possible to reduce the level of the expensive *binder* used in the paint formulation. This then gives rise to further cost-savings.

2.7. EXISTING BATCH PROCESSES

Currently two batch processes are used to produce vesiculated beads locally. These processes have been developed by a local member of the Nova Club with technology released to companies within the Club by a Mexican counterpart. This company attempted the production of vesiculated beads in the 1990's with a *double emulsification* process as described through the patents but found it difficult to produce the beads on industrial scale due to the sensitivity of the process to certain

process parameters. The local member continued research on the technology and has succeeded in producing vesiculated beads with a *single emulsification* process on industrial scale using Cowles dispersers and emulsion reactors readily available in paint factories.

The two manufacturing processes differ mainly in the type of impellers used and the temperature applied during curing of the beads. The difference in magnitude of the shear force exerted on the particles (resulting from the different types of impellers) leads to different particle size ranges produced and therefore both processes have an application in industry. A process diagram and a short discussion of each of the processes are given in subsequent sections.

2.7.1. FORMULATION AND COMPONENT PROPERTIES [17]:

For both of the processes the following preparation method is used with slight variations to accommodate the differences in equipment used.

The unsaturated polyester resin is prepared as a condensation product of maleic anhydride, phtalic anhydride and propylene glycol and mixed with styrene to form a 70 % solution of polyester in styrene. This mixture should have an acid value of 16 – 19 mg KOH/ g polyester and a viscosity of 900 – 1100 cPs.

The pigment is first dispersed within the polyester in the following relation:

unsaturated polyester resin	14.98 parts
titanium dioxide pigment	0.86 parts

where after the organic phase is prepared by the addition of styrene and the polyamine to the resin:

styrene	6.54 parts
polyamine (diethylene triamine)	0.21 parts

The organic phase is added to the aqueous phase containing:

thickener (hydroxy ethyl cellulose)*	10.44 parts
surfactant (polyvinyl alcohol)†	13.27 parts

polyamine	0.06 parts

* 2.5 % hydroxy ethyl cellulose solution in water

† 10.7 % polyvinyl alcohol solution in water

After emulsification is achieved the following is added:

de-ionised water	52.29 parts
organic peroxide	0.12 parts
redox initiator	0.01 parts
fungacide	0.18 parts
surfactant	0.85 parts

2.7.2. COWLES PROCESS:

The Cowles process utilises a simple flat-bottomed reactor with a flat disc impeller with slanted teeth (see figure 2.2. below). This induces fierce turbulent motion especially at high stirring speeds and therefore a high velocity at each tooth tip of the blade is instigated. A high shear force, resulting from the high velocity, is therefore exerted on the pigment being dispersed or the organic phase being emulsified within the vessel, resulting in fairly small particles being produced. Because the Cowles disperser can be operated at high rotational speed it is also possible to use it in producing dispersions with a high viscosity.

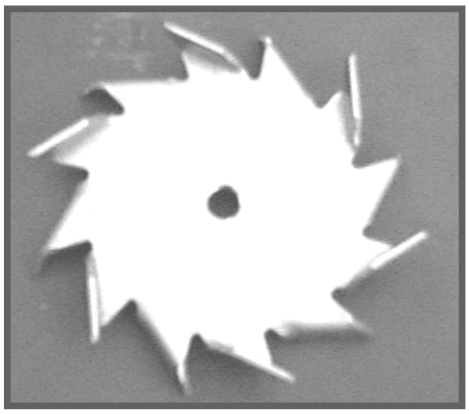


Figure 2.2: High shear impeller used in Cowles process.

Process description:

Vesiculated beads are produced with a single emulsification process following the concepts of suspension polymerisation discussed in section 2.3. To facilitate this reaction the reactor is first charged with the aqueous phase to which the organic phase is then added over a specified period of time and with the application of a specific stirring speed (*addition* step). After the addition step, the *emulsification* step follows, again over a specified period of time and at a specific stirring speed. When the required particle size of the polyester globules have been formed, additional water is added to achieve the required solid content. Changes in the time periods and stirring speeds allowed for each step would result in differences in the average particle size together with a variation in other measured properties of the product produced [18].

As soon as the emulsification has been completed the *initiator* is added and the product is left overnight to *cure* at ambient temperature. *Post treatment* and recovery then commences the following morning.

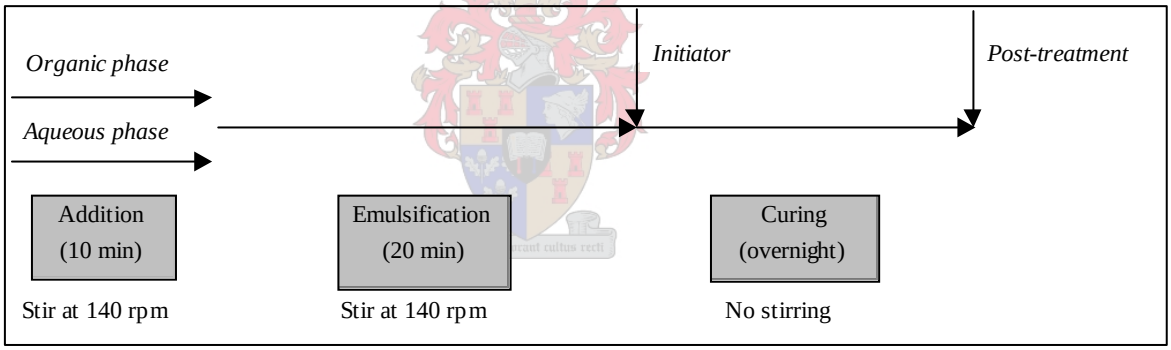


Figure 2.3: Cowles process schematic (stirring speed reported for a 457 mm diameter impeller in a 990 mm diameter reactor typical to industry).

Product properties:

Typical product properties obtained using the Cowles process are shown in the table below:

Table 2.4: Typical product properties for Cowles process.

Average particle size [micron]	2 - 4
Opacity	0.93 min

2.7.3. EMULSION REACTOR PROCESS:

As stated above one of the main differences between the emulsion reactor and the Cowles process is the type of impeller/disperser used. For the emulsion reactor process a turbine-type impeller (shown in figure 2.4) is used at moderate stirring speeds (49 rpm using a 45° axial-flow turbine impeller of 1100 mm diameter) to produce a slightly larger average size particle than that produced by the Cowles process. This is mainly due to the lower mixing intensity and shear force experienced by the particles.

As for the equipment the following differences also exist between the two batch processes.

1) The Cowles reactor has a flat-bottomed end versus the spherically shaped bottom-end used in the emulsion reactor process.
2) The emulsion reactor is jacketed to facilitate heating during the curing step.
3) Baffles are incorporated in the emulsion reactor to increase the mixing intensity.

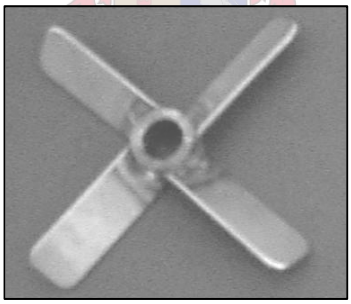


Figure 2.4: Impeller used in emulsion reactor process.

Process description:

The production of beads using the emulsion reactor follows the same steps as that described for the Cowles process up to the addition of the initiator. After the initiator is added the stirrer is stopped for 30 minutes to allow absorption of the initiator in the organic phase [17]. This is followed with *ramping* of the temperature to 50 °C under agitation. The batch is then *held* at 50 °C for four hours after which the *post-treatment* is done.

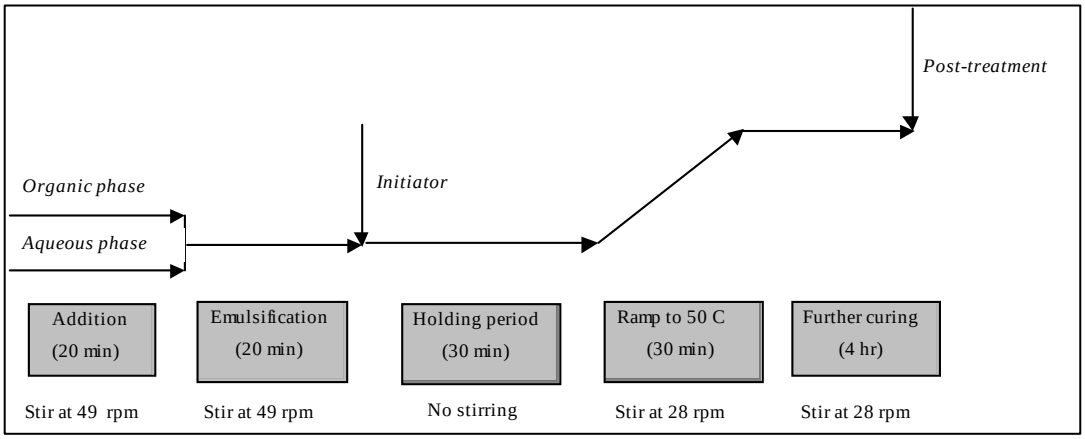


Figure 2.5: Emulsion reactor process schematic (stirring speed reported for a 1100 mm diameter impeller in a 2265 mm diameter reactor typical to industry).

Product properties:

The table below shows some measured properties of the vesiculated beads produced using the emulsion reactor process.

Table 2.5: Typical product properties for emulsion reactor process.

Average particle size [micron]	5 - 10
Opacity	0.93 min

2.8. HOMOGENISATION:

Homogenisation in its simplest form is the breaking down of globules into smaller particles under pressure. This is done by forcing liquid through a minute orifice and then releasing the pressure to produce a homogeneously dispersed product of smaller particles.

2.8.1. HOMOGENISER VALVE AND PUMP:

Homogenisers can be referred to as high-pressure pumps fitted with a minute orifice through which fluids are forced at high pressure [9]. This configuration causes a

marked change in the physical properties of the fluid treated and produces a very intimate mixture of the ingredients of the fluid.

According to **Farrall** [9], the homogeniser valve is the heart of the homogeniser. The valve could take on various shapes and sizes, with the poppet-type valve equipped with a secondary part, termed a breaker ring, being the most widely used. The breaker ring surrounds the main homogenising valve so that the fluid strikes the inner surface of the ring at right angles as it leaves the orifice formed by the conical shaped valve and seat (see figure 2.6). Apart from the shape of the valve, the size of it is just as important. If the valve is too large it may cause excessive clustering, where as a too small valve may not give the proper break-up of particles and may also cause clustering.

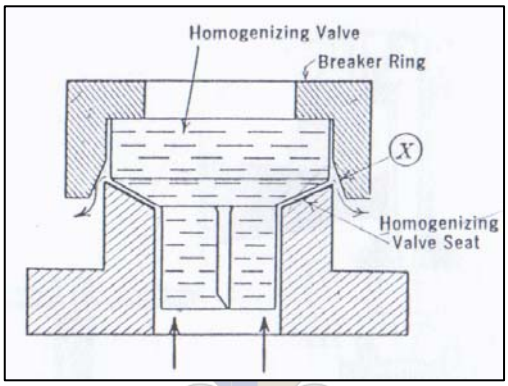


Figure 2.6: Cross section of a homogenising valve equipped with a breaker ring.

In operation, the valve as shown in figure 2.6 is kept down by a heavy spring having adjustable tension (see figure 2.7). As the fluid pressure (3.45-34.5 MPa [19]) comes against the valve, the spring is compressed and the valve rises to form a narrow annular orifice through which the fluid moves. The emulsification is then obtained by forcing the two phases past the spring-seated valve [19].

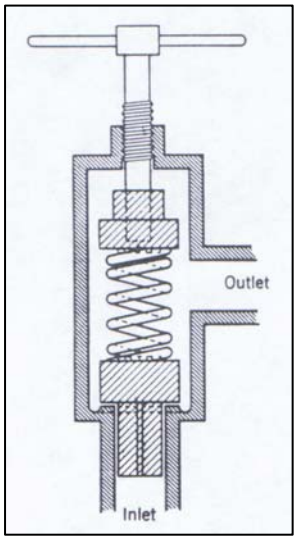


Figure 2.7: Homogeniser valve with spring.

The emulsification achieved by the homogeniser occurs as a result of a shearing action between the globules as they flow through the narrow passage at high velocity, much as rocks are sheared and worn by the action of a fast-moving river [9]. The faster the flow and the narrower the passage, the greater is the shearing action. Particles are however not only worn and broken down by the shearing action but also by a disruption action due to the impact experienced when the high-velocity stream strikes a solid surface such as the breaker ring.

Kirk-Othmer [19] reports the use of more than one stage of emulsification by employing successive relief valves. This is of great value when high-pressure homogenisation causes clumping of the fine particles in the first stage. The second stage of emulsification, at a slightly lower pressure then breaks up the clumps and produces a product with a lower viscosity. This is particularly useful in systems where a high-viscosity product is formed and the homogeniser can be applied as a post-treatment to reduce the viscosity.

2.8.2. HAND-OPERATED HOMOGENISER:

Ormerod Engineers' publication [20] of the homogenisers they manufacture, contain a robust hand operated homogeniser/emulsifier (see figure 2.8). This particular

homogeniser is reported as being ideal for the preparation of test samples in laboratories, and is also used extensively by pharmacists.

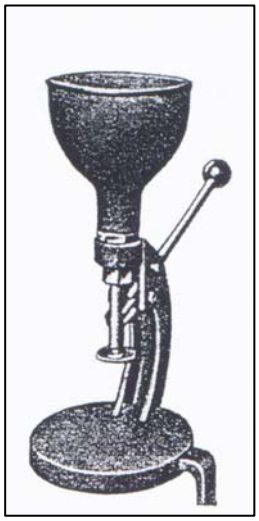


Figure 2.8: Hand-operated homogeniser for laboratory work.

Just as the homogenisers described in section 2.8.1 this hand-operated model consists of a movable impinger/plunger kept in place by a heavy spring. If the fluid pressure comes against the spring, the plunger is moved and fluid is allowed to flow through a narrow passage. This movement causes the shear force that breaks down the particles and supplies the emulsification action.

It has been shown that a hand-operated homogeniser such as the one above can be used to produce vesiculated beads [21]. This homogeniser produces vesiculated beads with a smaller average particle size, in the order of 1-micron, than that obtained with the Cowles process. Furthermore, the study showed that the particle size is dependent on the pressure and the number of passes through the homogeniser. An upper limit however exists for the application of these operating parameters. If this limit is exceeded the beads tend to agglomerate and to loose discreetness. This results in a loss of homogeneous dispersion and is also reported by Farrall [9].

2.8.3. IMPORTANT OPERATION PRINCIPLES:

The following pointers are given to the homogeniser operator [9]:

- An increase in the homogeniser pressure, leads to finer break-up of globules, but also leads to an increased tendency to form clusters or clumps.
- If the pressure is too high an excessive viscosity can be encountered.
- High-temperature homogenisation reduces the risk of clustering, gives better break-up and reduces viscosity.
- An irregular pulsating pressure may reduce the efficiency of the homogeniser.
- Minute imperfections in the homogeniser valve will allow large particles to slip through, causing a reduction in efficiency.

2.8.4. HOMOGENISER ACCESSORIES:

To ensure proper and safe operation of the homogeniser the use of the following accessories are advised [9]:

- Inlet strainer to prevent coarse particles from entering the homogeniser and blocking the flow passage.
- Pressure relief valve with the relief pressure set slightly above the operating pressure in order to protect the homogeniser.
- Pressure gauge to monitor and record the homogeniser pressure.

CHAPTER 3: WATER AFFINITY TESTS

3.1. INTRODUCTION:

During this study vesiculated beads were produced from different polyester batches using the homogeniser process. All of these polyester batches exhibited properties within the specifications given by the vesiculated bead manufacturers. However, some of the beads produced using these polyester batches showed a considerable variation in some product properties. The same tendency was observed with the Cowles- and emulsion reactor processes with some polyester batches producing vesiculated bead products with collapsed particles as well as with a significant variation in opacity and viscosity from batch to batch. Since all the other raw materials were kept constant during the experimentation some property, either unmeasured or without close monitoring, of the different polyester batches was contributing to the problem.

According to Gillian and Kershaw [6] the diameter and consequently the volume comprised by the vesicles inside the vesiculated particles are related to product properties such as the opacity [6]. With this in mind it was decided to study and try and acquire a better understanding of the mechanism by which the vesicles are formed in an attempt to explain the varying properties mentioned above. Because the vesicles are formed by the presence of water inside the particles a variation in the amount of water taken up inside the bead particles could possibly influence the degree of vesiculation obtained. A larger amount of water taken up might lead to a higher degree of vesiculation, which in its turn could have an influence on the opacity and the viscosity of the product. It was therefore decided to study and investigate the water affinity of the different polyester batches as well as the factors that could possibly influence this property of the polyester. If the water affinity of the polyester and consequently product properties such as degree of vesiculation, opacity and viscosity could be manipulated using these factors it could provide a method of optimising the usage of certain components in the formulation as well as optimising product properties.

3.2. EXPERIMENTAL:

3.2.1. TEST METHODS:

Method 1:

A water affinity test for the polyester had to be developed under the conditions present when the actual vesiculated beads are produced. This would ensure that the results obtained with such a test are also applicable to bead production. Consequently all the components of the vesiculated bead formulation (except for the initiator) were charged to a plastic container in the relation prescribed by the formulation. No stirring was done with the addition of the components and it was added in the following order:

- polyester
- monomer
- amine
- stabilisers (surfactant and thickener)
- water

The container was sealed to prevent leakage and then placed on a set of rollers that provide slow mixing of the different phases without emulsification occurring. It was removed from the rollers after adequate contact (usually after approximately 2 hours) between the aqueous- and the organic phases were achieved and the polyester was allowed to take up water from the aqueous phase. The samples were then emptied into a measuring cylinder and left overnight to allow for any separation between the phases to occur. A fraction of the water that was not taken up by the polyester phase and subsequently separated from it by the following morning formed a top layer in the measuring cylinder. The volume of this water was then read off from the cylinder and used to calculate the mass of water entrapped within the polyester (see equation below).

$$Water\ in\ organic\ phase[\frac{g}{g}] = \frac{Total\ aqueous\ phase[g] - Water\ in\ top\ layer\ (not\ taken\ up)[g]}{Total\ organic\ phase[g]}$$

[3.1]

Method 2:

A more scientific method than that of method 1 for the determination of the water up-take was developed as the project progressed. This method followed the same steps as method 1 for the addition and mixing of the phases, but instead of leaving the sample in a measuring cylinder overnight, it was left in a separation funnel for about 12 hours. A sample was then taken from the bottom layer (organic phase containing polyester and water taken up) in the funnel and introduced to a Karl-Fischer titration instrument to determine the percentage of water present in the organic phase.

$$Water\ affinity = Percentage\ of\ water\ present\ in\ organic\ phase \qquad [3.2]$$

The results achieved using the methods developed for the water affinity test would also be compared to trends and results reported in literature to establish the accuracy of these methods.

3.2.2. DIFFERENT POLYESTER BATCHES:

The water affinity test (method 2) as described in section 3.2.1 above was performed using different polyester batches supplied by different manufacturers. These batches were supplied together with the following specifications:

Specifications of the polyester in itself

- batch time
- processing temperature
- final melt viscosity
- final acid value
- total inhibitor concentration

Specifications of the final liquid (polyester with added monomer):

- acid value
- viscosity
- stability @ 120 °C

- relative density
- gel time
- peak exotherm
- gpc analysis including molecular weight

The following polyester batches were subjected to water affinity tests (see appendix A for complete list of properties for each batch):

- Plant batches DV 2721, DV 4696 and DV 5008 produced by company A and all within specification.
- Laboratory batches A, B, C and D produced by company B and all within specification
- Laboratory batch I produced by company B with the final liquid acid value outside the specified range.

3.2.3. COMPONENTS THAT INFLUENCE WATER UP-TAKE:

Since it is known through the patents that an increase in the concentration of the base, in this case the polyamine, leads to an increase in the vesicle volume [6] it was decided to investigate the influence of the base (in this case diethylene triamine, DETA) on the amount of water taken up by the polyester. Different levels of DETA was used with the same batch of polyester (DV 2721) and with all the other components of the formulation kept constant. This was done not only to determine the effect of DETA on water up-take but also to determine if the methods used produced results comparable to that mentioned in literature [6].

Previous work also showed that the addition of surfactants such as *Tween* generally cause an increase in the opacity of the product [18]. Since the opacity is dependent on the reflection and scattering of light caused by the vesicles [2], it should also be dependent on the water taken up inside the particles to form the vesicles. Therefore the influence of Tween on the water affinity of the polyester was investigated by varying the levels of Tween.

Furthermore, the effect of *laurel methacrylate* (LMA), a hydrophobically modified monomer, on the water affinity of the polyester was also investigated. LMA is used to increase the water resistance of the vesiculated beads.

3.3. RESULTS:

3.3.1. DIFFERENT POLYESTER BATCHES:

Water content of the organic phase and opacity:

The following values were obtained for the water content of the organic phases of the respective samples.

Table 3.1: Water content of the organic phase of different polyester batches.

Polyester batch	% Water
DV 2721	58.63
DV 4696	47.46
DV 5008	51.61
A	26.564
B	49.59
C	33.63
D	45.89

From table 3.1 it is seen that the highest water content (at about 60 %) was measured for polyester batch DV 2721. Seeing that batch DV 2721 generally produced a vesiculated bead product with a higher opacity if compared to the other batches (see table below), it seems as though a water content of about 60 % on mass is desirable to achieve an acceptable opacity. Given that the density of the water and that of the organic phase containing the polyester and monomer are comparable (water density ≈ 1000 kg/m^3; polyester and monomer density ≈ 1080 kg/m^3) a mass percentage of 60 % corresponds with a volume percentage of approximately 60 %. This suggests that the accompanying degree of vesiculation achieved with batch DV 2721 and used, as a target value should be in the order of 60 %. This compares to literature stating that the vesiculated beads are about two thirds air by volume [2]. If a new batch of

polyester is tested and its water affinity determined using experimental method 2, it seems as though it should therefore be about 60 % to ensure acceptable opacity.

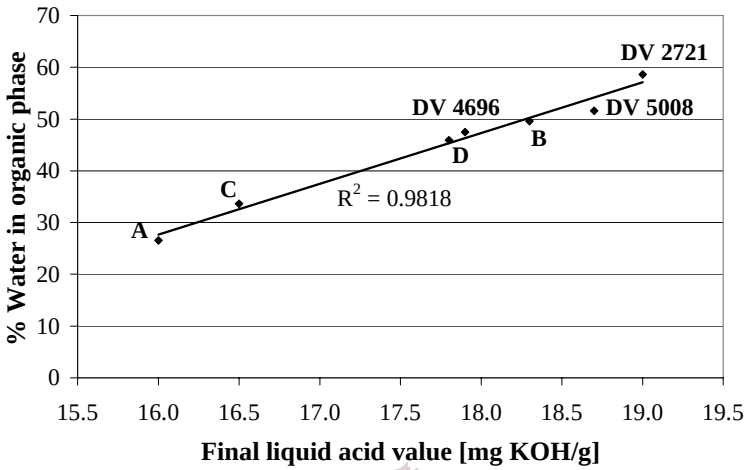
Table 3.2: Water content of the organic phase and opacity for different polyester batches used to produce vesiculated beads with the Cowles process.

Polyester batch	% Water	Opacity
A	26.56	0.91
C	33.63	0.89
D	45.89	0.76
DV 4696	47.46	0.88
B	49.59	0.89
DV 2721	58.63	0.96

Although the highest water content was associated with the polyester batch producing the highest opacity, no simple correlation exists between the opacity and the water content of the organic phase if all the data of the batches tested are inspected. The amount of water present in the organic phase is therefore not the only measure of the opacity of the product. It could also be dependent on the actual average size of the vesicles and not only on their total volume. For example a sample containing a high proportion of vesicles of small diameter could induce higher scattering and reflection of light leading to a higher opacity than a sample with only a few vesicles of large diameter. The patent submitted by Gillian and Kershaw [6] confirms the dependence of opacity on the vesicle diameter by stating: "it was seen that dried films of the paints comprising granules in which the vesicles had sub-micron dimensions were of higher opacity than those made with more coarsely vesiculated granules." This patent also mentions the importance of the relation between the amount of base required and the free carboxylic groups of the resin. It reports the base to be about 0.7 equivalents of base per carboxyl to prevent the aqueous phase from becoming unstable. It could therefore be that the correct amount of DETA was not incorporated into the formulation for each polyester batch tested and that this also influenced the amount of water taken up and the subsequent opacity of the product. According to the patent the number of unsaturated carboxylic groups for each batch of polyester should therefore be determined accurately and the DETA level determined accordingly.

Water content of the organic phase and acid value of the polyester:

During the investigation of the water affinity of the different polyester batches a linear correlation between the water content of the organic phase and the final liquid



(polyester with added monomer) acid value of the polyester was found. This is shown by the graph below.

Figure 3.1: Dependence of water affinity on final liquid acid value of the polyester.

The different polyester batches shown in the graph had final liquid acid values in the range of 16 – 19 mg KOH per g polyester. This is the specification given by the vesiculated bead manufacturers. From the graph it can be seen that the higher values of the final liquid acid value produced organic phases with a higher water content. This trend is supported by literature [6] that reports a reduction in the degree of vesiculation achieved with a consequent drop in acid value of the polyester from 43 mgm KOH per gm polyester to 4 mgm KOH per gm polyester. Therefore it seems as though the final liquid acid value can be used as a measure of the water affinity of a particular batch of polyester and it could be possible to use the correlation found to predict the water affinity. It also suggests that by manipulating the acid value of the polyester, the water up take can be manipulated.

The water affinity of a polyester batch with a final liquid acid value above 19 mg KOH per g polyester and outside the range normally specified was also studied. For this purpose laboratory batch I was manufactured by company B with a final liquid

acid value of 20.1 mg KOH per g polyester. This batch produced an organic phase with a water content of 50.4 %. If this value together with the acid value is compared to those shown in the graph of figure 3.1, it appears as though a final liquid acid value higher than 19 mg KOH per g polyester produces an organic phase with less water than achieved at 19 mg KOH per g polyester (DV 2721). The correlation shown above is therefore only valid for the range of acid values specified and shown on the graph. If the properties of batch I is added to that of the batches shown in figure 3.1, the correlation changes from a linear- to a polynomial dependency of the water uptake on the final liquid acid value. This correlation shows the optimum range of final liquid acid value for water uptake to be in the region of 18 to 20 mg KOH per g polyester.

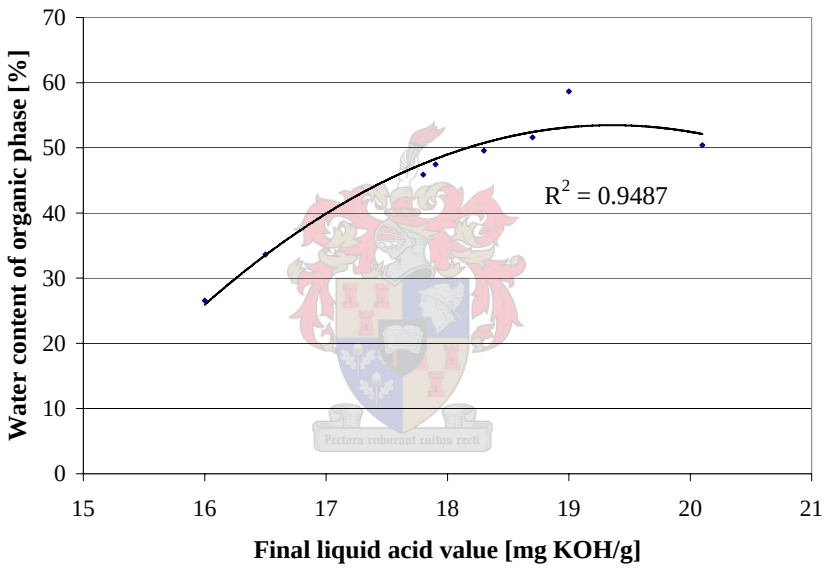


Figure 3.2: Dependence of water affinity on final liquid acid value of the polyester outside the range specified.

However more polyester batches (with final liquid acid value both within and outside the specification) should be tested to draw definite conclusions concerning the range of acid value specified. If these experiments yield results that support the correlation shown in figure 3.2 for the water content of the organic phase and acceptable values for opacity and other properties are achieved, the range of final liquid acid value specified to the polyester manufacturers should be adjusted accordingly.

The results presented, whether within the specification or outside of the range of final liquid acid value specified, however show the dependence of the water content of the organic phase on this property of the polyester.

3.3.2. EFFECT OF DETA ON WATER AFFINITY OF POLYESTER:

Experimental method 1:

Experiments were conducted using method 1 described in section 3.2.1. with a variation in the amount of DETA added to the bead formulation. This was done to investigate the influence of DETA on the water affinity of the polyester.

From the graph (figure 3.3 below) the dependency of the water affinity of the polyester on the presence of DETA can clearly be seen. This should be expected as discussed in section 3.2.2. With an increase in the amount of DETA a consequent increase in the water affinity of the polyester containing organic phase is obtained, until a maximum value is reached. From this point forward, at about 1.25 % DETA/polyester, a further increase in the amount of DETA does not significantly influence the water affinity of the polyester.

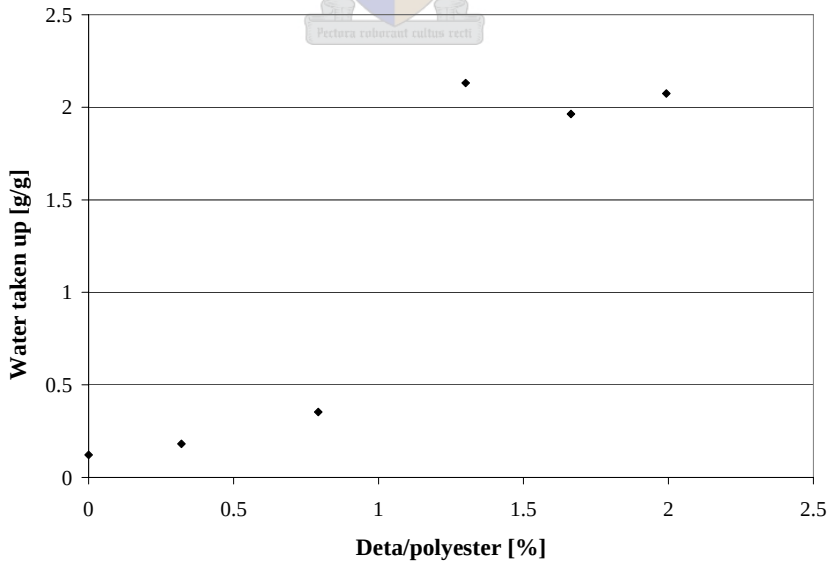


Figure 3.3: The influence of DETA on the water affinity of the polyester as determined with method 1.

The graph suggests that the maximum amount of water the organic phase is able to entrap is about 2 g of water per g of organic phase and therefore the water constitutes

about two thirds of the total mass of the particles. This again is supported by literature that reports the vesiculated beads to be about two thirds air by volume.

If the standard level of DETA is used (1.79 % DETA/polyester) as prescribed by the formulation the maximum water content attainable with this experimental method is achieved. This value does seem a bit high seeing that the same water content is obtained if about 1.25 % DETA is used. A reduction in DETA-level may also lead to a reduction in the yellowing of the beads produced or at least contribute in finding a solution to this problem. Therefore it is suggested that vesiculated beads are produced using this reduction in DETA-level and the properties of the product be compared to that achieved with the formulation as is. If the reduction in DETA does not adversely affect product properties, the formulation should be adjusted accordingly.

Experimental method 2:

The influence of the DETA on the water affinity of the polyester was also investigated applying the more scientific method 2 described in section 3.2.1. As with method 1 discussed above a variation in the DETA-level was applied to investigate the effect of this component on the amount of water taken up by the polyester.

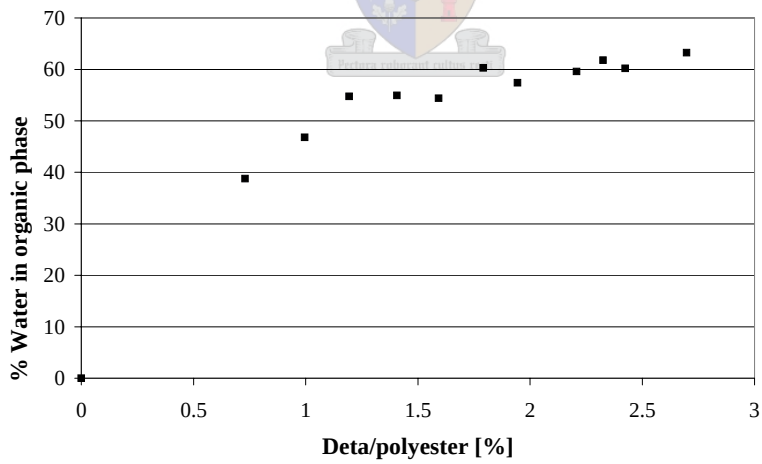


Figure 3.4: The influence of DETA on the water affinity of the polyester as determined with method 2.

If the result obtained with method 2 and shown in figure 3.4 above is compared to that of method 1 (shown in figure 3.3) the same basic trend for the relation between the water affinity and the DETA can be seen. With an increase in the amount of DETA a

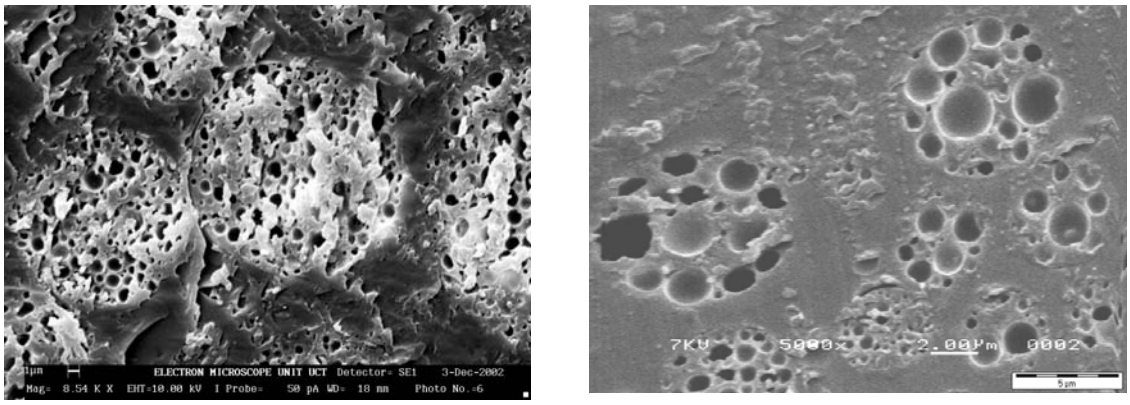
subsequent increase in the amount of water taken up by the organic phase is obtained. Again the organic phase seems to become saturated with water at the point where it contains approximately 60 – 65 % of water. This method however shows that the amount of DETA required to achieve an organic phase with a 60 % water content should be maintained at 1.79 % DETA/polyester as prescribed by the formulation.

Again it should be noted that a high water content is not necessarily a guarantee for acceptable opacity of the vesiculated beads produced. This is supported by the results shown in the table below.

Table 3.3: Water content and opacity for different DETA levels.

DETA/Polyester [%]	Opacity	% Water
1.005	0.76	46.84
1.808	0.89	59.36
2.399	0.97	57.43

The opacity values were measured for vesiculated beads produced using the hand-operated homogeniser shown in chapter 4. The result shows that the highest water content (59.36 %) is <u>not</u> associated with the highest opacity and that a water content of slightly less (at 57.43 %) is in fact associated with an excellent opacity of 0.97. This may be due to a difference in the shape and the average size of the vesicles of the different samples. The SEM images of the samples shown below confirm this theory.



(a) *(b)*

Figure 3.5. SEM images of microtome samples.

(a) Opacity = 0.94, (b) opacity = 0.87.

From the images it can clearly be seen that the vesicles of sample (b) retain a larger volume than that of sample (a) and therefore would possess a higher water content than sample (a). The individual vesicles of sample (a) however are much smaller in size and this sample then also exhibits a higher opacity. *This confirms that the size of the vesicles is important in achieving an acceptable opacity and not only the amount of water in the organic phase.*

Although method 1 is not as scientific as method 2 the result obtained using method 1 compares well to that of method 2 and with the trends in the literature and both methods can therefore be used with confidence.

3.3.3. EFFECT OF TWEEN ON WATER AFFINITY OF POLYESTER

Tween and DETA:

As mentioned in section 3.2.3. previous work [18] has shown that the addition of surfactants, such as Tween, cause an increase in the opacity of the product. To investigate the influence of Tween on the water affinity of the polyester the more scientific method 2 described in section 3.2.1 was used and all the components of the formulation, except the initiator, was added. As with the investigations concerning the effect of the DETA-level on the water up-take, a variation in the Tween-level was applied and the consequent percentage of water taken up by the organic phase was measured in each case.

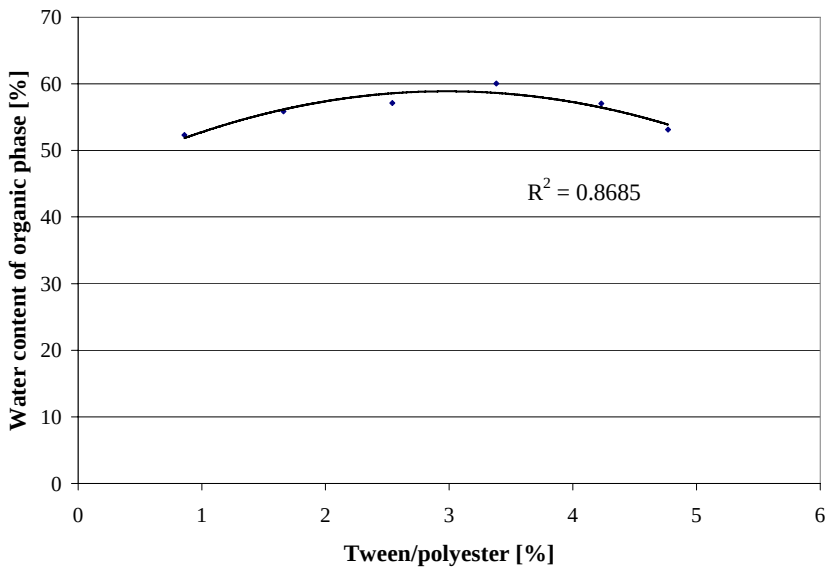


Figure 3.6: The influence of Tween on the water affinity of the polyester.

It seems as though an increase in the amount of Tween causes an increase in the water content of the organic phase until a maximum value is reached. The maximum water content achievable with the addition of the Tween again is in the region of 60 % as was obtained with the variation in the DETA-level discussed above. It therefore seems that the water uptake of the polyester and probably the degree of vesiculation can be increased with the addition of Tween. With the increase in degree of vesiculation, the opacity may also increase. This is supported by literature that shows the use of Tween to cause an increase in opacity [18].

The standard level of Tween used in the production of vesiculated beads is at 3.4 % (mass) Tween per polyester. This value corresponds with the maximum water content of the organic phase shown in figure 3.5 and is therefore believed to be sufficient for the particular batch of polyester (DV 2721) used in the water affinity test. Because of the differences, such as the acid value, that exist between different batches of polyester, it may be necessary to verify the optimum amount of Tween used to obtain the required water content of the organic phase (see table below for Tween levels introduced to polyester batch DV 5008).

Table 3.4: Tween level, water content and opacity.

Tween/polyester [%]	Opacity	% Water
0.040	0.92	53.96
0.514	0.94	61.45
3.388	0.89	59.36

From the table it is evident that the required amount of Tween at 3.4% (mass) Tween per polyester does not produce the highest water content or an acceptable opacity for the product produced using batch DV 5008. This is in contrast with the result obtained using batch DV 2721 shown in figure 3.5 above, where the required Tween level produced the organic phase with the highest water content. In this set of experiments however, the highest water content did correspond with the highest opacity, unlike the results obtained with a variation in the DETA level (table 3.3). As

with the discussion of the DETA-level it should also be noted here that the actual shape and average size of the vesicles formed should be taken into account.

Tween WITHOUT DETA:

Experiments were also conducted to determine if Tween could be used without DETA to achieve water uptake by the organic phase. For these experiments experimental method 1 was used and all the components comprising the vesiculated beads formulation was added, with the exception of the initiator and the DETA. The figure below shows the result.

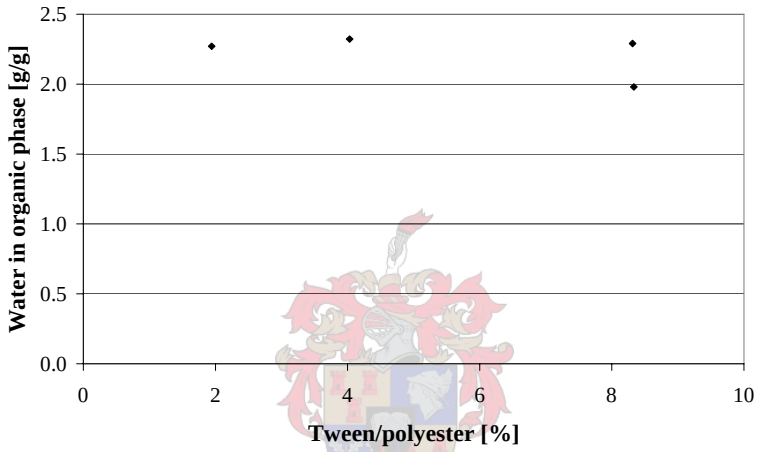


Figure 3.7: The effect of Tween on the water affinity of the organic phase without the addition of DETA.

Although only a few experiments were done it is clear that the addition of Tween does in fact cause the organic phase to take up water even without the addition of DETA. The graph also shows the maximum amount of water present in the organic phase (2 g of water per g of organic phase) to be comparable to that achieved with the addition of DETA only (section 3.3.2).

Unfortunately when these results were applied to the actual production of vesiculated beads (adding Tween without DETA) catalysis could not be achieved and further water affinity experiments where the DETA is omitted were abandoned.

Using Tween to increase the water uptake as well as opacity:

The organic phase containing polyester batch DV 4696 was used as an example in studying the manipulation of the water affinity of the polyester in an attempt to improve product properties, such as opacity. For this particular batch of polyester a water content of 47.46 % was measured for the organic phase without the addition of Tween and it produced beads with an opacity of 0.88. With the addition of different amounts of Tween, this percentage of water was increased to approximately 60 % (also the water content of the organic phase containing polyester batch DV 2721 and used as a target value).

Table 3.5: Addition of Tween to increase the water content.

Water [%]	Tween/polyester [%]
47.46	0
58.11	0.343
59.24	0.751
STD	3.4

It was found that the addition of extremely small amounts of Tween – between 1 % and 3 % - of that required by the formulation lead to an increase in more than 10 % of the water content of the organic phase. Seeing that a 59.24 % water content compares to that achieved with batch DV 2721 it was thought that the opacity of the beads produced using DV 4696 together with the Tween level (0.751 % Tween per polyester), used to obtain this water content, should also be comparable to the 0.96 opacity achieved with batch DV 2721. Experiments were therefore conducted using the pneumatically driven batch homogeniser (see chapter 4) to investigate this theory. The results obtained by the incorporation of different amounts of Tween are shown below.

Table 3.8: Properties of beads produced using DV 4696 with the addition of Tween.

Tween/polyester [%]	Opacity
0	0.88
0.526	0.94
0.947	0.92

The addition of the Tween levels suggested by the water affinity test and shown in table 3.5 did in fact lead to an increase in the opacity of the beads produced. Although this opacity is not as high as that achieved with batch DV 2721 at 0.96, it shows that by manipulating the water content of the organic phase, the opacity can subsequently be increased. This result again shows that the opacity of the product is not entirely dependent on the total volume of water (degree of vesiculation) achieved, but that the average diameter of the vesicles probably also play an important role (see discussion in section 3.3.1).

Table 3.6 shows that the total amount of Tween required by the formulation may not always be necessary to achieve acceptable opacity values. In the case of batch DV 4694, only 15 % (0.526 % Tween/polyester) of the required amount of Tween was needed and in fact, when more than this (0.947 % Tween/polyester) was added, an adverse effect on the opacity was noted. This was also found to be true for batch DV 5008 where 0.514 % Tween per polyester produced an organic phase with a water content of 61.45 % and opacity of 0.94 (see table 3.4). It is therefore suggested that the optimum Tween level for production of vesiculated beads with an acceptable opacity and water content be determined for each new batch of polyester.

Pectora roborant cultus recti

3.3.4. EFFECT OF STABILISERS ON WATER AFFINITY OF POLYESTER

During the experiments studying the effect of Tween on the water affinity of the polyester it was found that the stabilisers used in the vesiculated bead manufacturing have a distinct effect on the water uptake. When these components of the formulation are omitted, no water is found within the organic phase. This was seen with a variation in the amount of Tween added together with the required amount of DETA.

Table 3.7: Water content of organic phase obtained with the addition of Tween and stabilisers being omitted.

Tween/polyester [%]	Water [%]
0.997	0
2.506	0
4.537	4.67

This result indicates that it is actually the affinity of the polyester for the water *phase* and not its' affinity for pure water that is important in vesicle formation. It therefore also shows that the vesiculation is not only dependent on the presence of DETA but also on the presence of the stabilisers. Without the stabilisers the aqueous phase probably becomes unstable [6] inside the organic phase and separation of the phases occurs.

Further experimentation was done to determine which of the stabilisers (the surfactant or the thickener) have the predominant effect on the water uptake or if both are equally important in achieving vesiculation.

Table 3.8: Dependence of water-affinity on the presence of thickener and surfactant.

	Water content [%]
Standard formulation	51.61
Thickener and surfactant replaced by water	0
Thickener replaced by water	22.63
Surfactant replaced by water	10.20

It was found that the absence of the surfactant (surfactant replaced by water) resulted in the largest reduction in the amount of water present in the organic phase. This suggests that the surfactant plays a predominant role in the formation of the vesicles inside the beads. Although the experiment where the thickener was omitted produced an organic phase with a larger water content than that where the surfactant was omitted, it still does not compare to the water content achieved with the standard formulation. Therefore the one component cannot be replaced by the other.

3.3.5. EFFECT OF LMA ON WATER AFFINITY OF POLYESTER:

Laurel methacrylate (LMA) is incorporated in the vesiculated bead formulation to increase the water resistance of the beads. To investigate the effect of the LMA on the water uptake of the polyester, batch DV 5549 (with properties within the

specifications) was used. The table shows the effect of LMA on the water affinity of the polyester [*].

Table 3.9: Effect of LMA on water uptake.

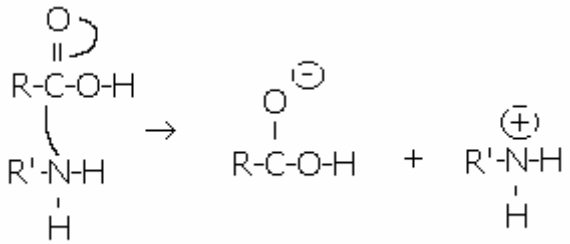
Without LMA [% water]	5 % LMA/Styrene [% water]	10 % LMA/Styrene [% water]
63.22	59.32	51.61

As seen from the result shown in table 3.9 the incorporation of LMA in the formulation leads to a decrease in the water content of the organic phase when compared to that of the standard formulation, as was expected. This decrease in the water content may lead to a decrease in the opacity of the final product and it is suggested that small amounts of Tween could be added to rectify the problem.

3.4. PROPOSED MECHANISM:

From the results obtained and discussed above it seems as though the mechanism by which the vesiculated particles are formed could be summarised as follows:

As discussed in chapter 2 the *organic phase* is prepared as a dispersion of titanium dioxide pigment in the unsaturated polyester resin with added unsaturated monomer (such as styrene). The polyamine, a strong base that is also water-dispersible, is added to the polyester solution to neutralise the carboxylic groups of the resin [6] by the following reaction.



The polyester, containing several carboxylic groups (now ionised) orientates itself with the negative charges in the direction of the positively charged amine ions. These

[*] Experimental work done by Plascon Research Centre, Stellenbosch.

tend to group together with the negative-charged polyester chains orientated around it to form a more stable macro-molecular structure, i.e. micelle [18] (see figure 3.8).

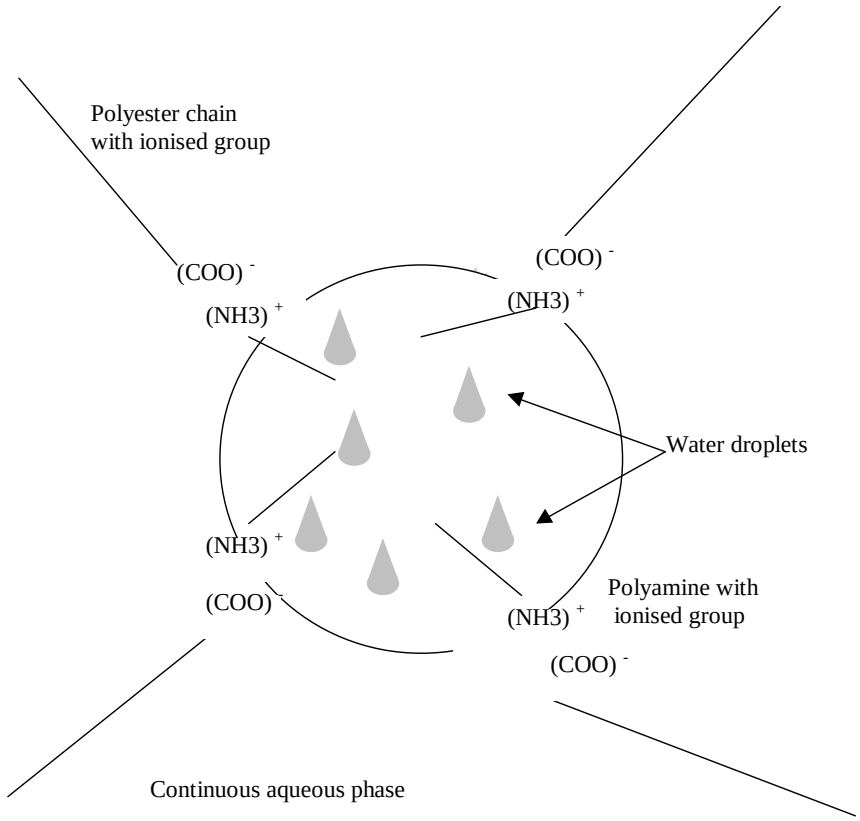
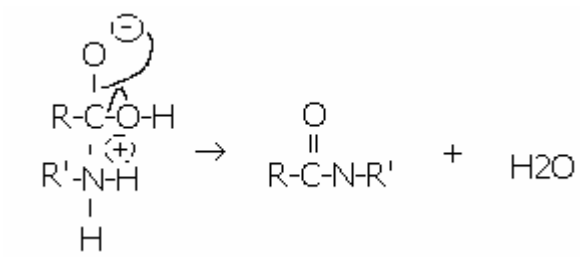


Figure 3.8: Micelle formation of polyamine and polyester chains.

The amine groups in the centre of the micelles present it with hydrophilic character that will attract and stabilise the water formed with the binding of some of the charged ions following the mechanism shown below.



During the above reaction energy is dissipated and it can be observed through the increase in the temperature of the solution after the addition of the amine.

This organic phase is added to the *aqueous phase* under agitation that breaks up the organic phase and evenly disperses it through the aqueous phase. The latter contains water, steric stabilisers that act as a surfactant, thickener and a small amount of amine. This amine is added to prevent the system from experiencing a pH-shock when the polyester with its' neutralised carboxylic groups is added.

Because of the hydrophilic centre of the amine and polyester micelles, the organic phase becomes more "soluble" in the aqueous phase and additional water is able to migrate from the aqueous phase to the organic phase just as the monomer droplets migrate to the micelles discussed in the section on emulsion polymerisation. Here the *amount of amine* present in the organic phase plays an important role in the amount of water "attracted" to the organic phase. If the amount of amine is increased, more carboxylic groups will be neutralised. This will result in an increase in the amount of water formed through the reaction as well as an increase in the volume of the hydrophilic centre of the micelles. The greater the hydrophilic centre, the more water will probably be accommodated and may migrate from the aqueous phase until a saturation point is reached. Therefore an increase in the amount of amine, leads to an increase in the amount of water inside the polyester globules. This is confirmed by the results shown in section 3.3.2.

The organic phase, now existing as globules of polyester with entrapped water inside the aqueous phase are stabilised by the thickener and the steric stabiliser (partially hydrolysed polyvinyl acetate) acting as surfactant. The acetate orientates itself with the hydrophilic end in the aqueous phase and the hydrophobic end on the surface of the polyester globules. This ensures that the water present inside the polyester globules are repelled by the hydrophobic end of the stabiliser situated on the surface and that it is does not migrate back to the aqueous phase again.

The effect and in fact the *importance of the partially hydrolysed polyvinyl acetate* on the entrapment of the water inside the organic phase was discussed in section 3.3.4 above. In the case where no stabiliser was present, the water that migrated to the centre of the micelles because of the ionised-amine groups probably migrated back to the aqueous phase. This may be due to the absence of the hydrophobic force located on the surface of the organic droplets (supplied by the stabilising surfactant) that maintains the water inside the polyester.

3.4.1. SPECIAL ADDITIVES:

With the addition of *Tween* as a supplementary surfactant an increase in the water content of the organic phase as well as a subsequent increase in the opacity of the beads produced using polyester batch DV 4696 occurred. This may be explained through the reduced surface tension between the organic- and aqueous phase brought about by the addition of the surfactant. With this tension reduced, it is easier for water to migrate to the polyester globules and more water can therefore be found in the resulting organic phase. It was also shown that water could be found in the organic phase without the presence of the amine, but with Tween added. This supports the theory that the Tween assists in the migration of the water from the aqueous phase to the organic phase. A saturation point for the amount of water in the organic phase however exists. When this point is reached the addition of further amounts of Tween does not increase the water content and in fact leads to a reduction in water uptake. This could be ascribed to instability occurring inside the polyester globules because of the volume of water present.

Laurel methacrylate, a long chain monomer possessing hydrophobic character, can be added to increase the water resistance of the vesiculated beads. With the addition of this monomer a reduction in the water content of the organic phase is obtained (section 3.3.5). Because it is not quite sure where the LMA positions itself with relation to the polyester globules (inside it or on the surface) it is difficult to explain exactly how this component contributes to the water uptake and vesicle formation. If the long chains of the monomer align itself on the surface of the particles it would prevent the uptake of water because of its hydrophobic character as soon as the

particles are “covered” with it. This would confirm the results achieved with the addition of this component where the water content decreased.

It is also important to determine where exactly in the production process this monomer should be added. If it is added and aligned before a sufficient amount of water is present in the organic phase and further entry of water is prevented, it could adversely affect product properties dependent on the degree of vesiculation.

CHAPTER 4: EXPERIMENTAL AND ANALYTICAL PROCEDURES

4.1. INTRODUCTION:

Homogenisation was initially investigated as a means to produce small particles for application in gloss paint, but it was soon realised that homogenisation offers an alternative method of production that could lead to a continuous process. The continuous process had to be developed using the principles known and applied in the Cowles and emulsion reactor batch processes and therefore investigations were started with homogenisation as a batch process on laboratory scale. For these experiments existing homogeniser equipment was used to determine the important operating parameters concerning homogeniser operation. With the operating parameters and its influence on process conditions and product properties known, a bench scale batch process where these parameters were applied could be developed. From here the process would be developed into a semi-continuous set-up using continuous catalysis and curing and from there a fully continuous process (with continuous feed) would be constructed.

The experimental set-up and accompanying equipment had to be changed throughout the project to provide for the developments from a batch process to a continuous process. These developments are summarised below:

- <u>Batch</u> experiments performed on
  - *laboratory scale* (500 mℓ) with a pneumatically-driven homogeniser
  - *bench scale* (10 ℓ) using a high-pressure pump and homogeniser set-up
- <u>Semi-continuous</u> experiments performed on *bench scale* using the same set-up as above together with a loop-reactor for continuous curing

- Continuous experiments performed on *bench scale*
  - using a loop-reactor, and
  - using several conventional reactors in a cascade-type set-up to facilitate continuous curing

The sections that follow show the different experimental set-ups schematically together with mechanical drawings of the equipment and the experimental procedures followed in each case.

The analytical procedures used to analyse and test the product samples are also given.

4.2. BATCH EXPERIMENTS:

4.2.1. LABORATORY SCALE:

Equipment:

For the laboratory scale experiments a homogeniser similar to the one discussed in section 2.8.2 *(chapter 2)* but with a pneumatically driven handle (instead of the hand-operated model) was used. This model is fairly compact and easy to operate in comparison with other existing power driven homogenising equipment. The power driven equipment is generally large, expensive and it has a high capacity that generally makes it unsuitable for laboratory work [20].

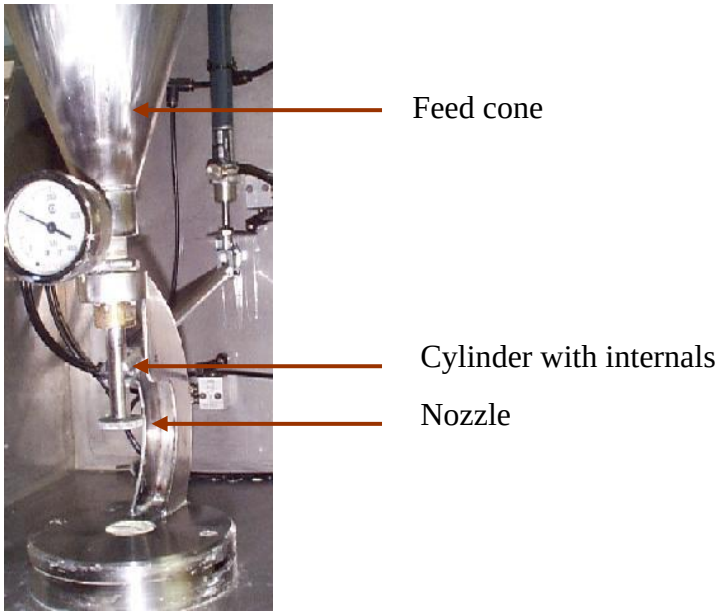


Figure 4.1: Pneumatically driven homogeniser.

The homogeniser could not accommodate more than 500 mℓ at a particular time and was therefore used to produce 500 mℓ samples. Figure 4.2 below shows the homogeniser together with its internals.

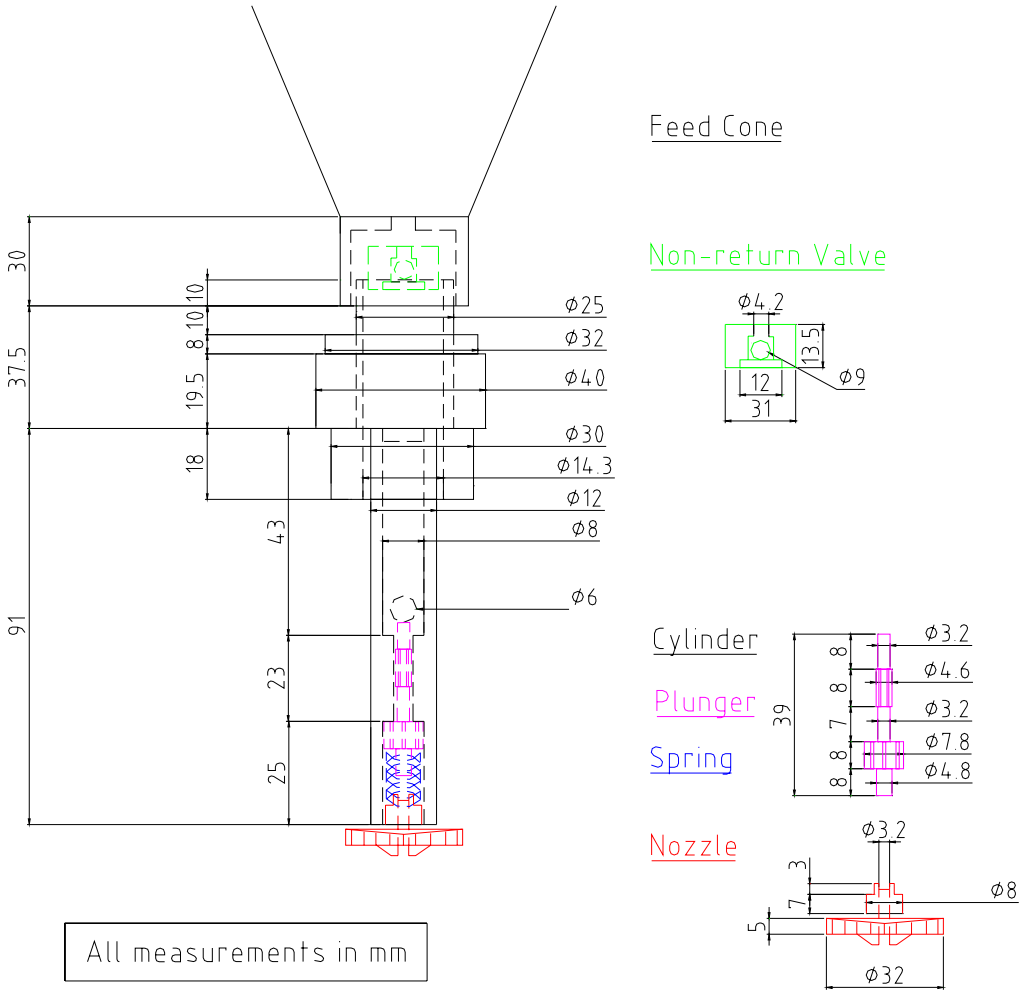


Figure 4.2: Mechanical drawing of homogeniser and internals.

The plungers used in the laboratory scale batch experiments were designed in such a way that the changes in geometry would have an effect on the average particle size of the product. These changes included the number of grooves and sections present on the plunger and were chosen in an attempt to vary the shear force exerted on the particles. The figures and table below describe the different plungers used.

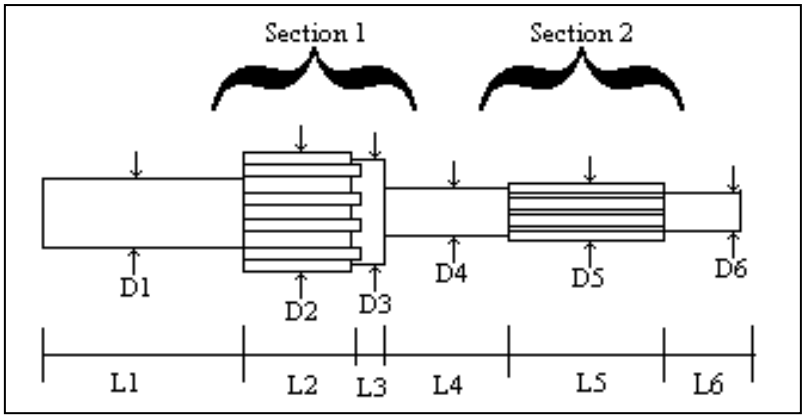


Figure 4.3: Geometry of plungers 1 and 2.

Both plungers 1 and 2 have the geometry shown above, with the only difference being the number of grooves present in section 1 and 2. The table below lists the difference between the plungers:

Table 4.1: Number of grooves on plungers 1 and 2.

	Number of grooves in:	
Plunger type	Section 1	Section 2
1	6	4
2	4	2

It was thought that by decreasing the number of grooves present in plunger 1, the flow area would also be reduced. At a constant flow rate the shear rate and consequently the shear forces applied to the particles would also increase. Therefore the reduction in number of grooves should lead to a reduction in the average particle size of the product.

For plunger 3 a different geometry to that of plungers 1 and 2 was chosen (see figure 4.4 below). Here an extra section was added to the plunger in an attempt to increase the shear force exerted on the particles. The grooves (number and depth) on plunger 3 were designed to be the same as those on plunger 1.

(See Appendix B for a complete list of the plunger dimensions.)

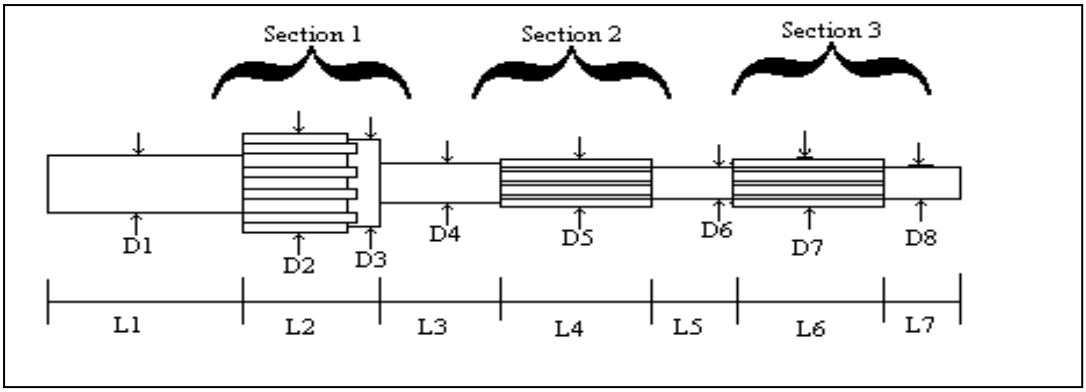


Figure 4.4: Geometry of plunger 3.

Equipment operation:

Fluid is introduced to the homogeniser through the feeding cone and with downward movement of the cylinder drawn into it through a non-return valve. This valve is a ball type valve situated at the base of the feed cone. A fixed volume of fluid is constantly drawn into the cylinder, which ensures that all the fluid particles in the batch are subjected to the same conditions and a uniform product is produced. The fluid is trapped within the cylinder by the plunger and spring that tightly fit inside it (position shown by figure 4.2).

When the cylinder moves upwards the pressure created forces the spring to compress and fluid can flow through the cylinder and exit through the nozzle. With the presence of the plunger the fluid is in fact forced through the grooves in it and the movement causes a shearing action to be exerted on the particles. The particles are consequently broken down and the mixture of two phases completely emulsified. The particles (beads) are then expelled from the cylinder through the nozzle where it undergoes a sudden drop in pressure. This release in pressure produces a uniform dispersion of particles.

Process description:

All the laboratory scale experiments were conducted using the first generation vesiculated beads formulation (without the addition of special additives such as Tween or LMA as discussed in section 3.4.1) with a 24 % total solids content. Slight modifications to the formulation used in the Cowles and emulsion reactor processes were however made to accommodate the homogeniser application. These changes included changes in the stirring speed and addition- and mixing times and were

brought about because of the smaller batches (500 mℓ) produced and because the emulsification is achieved with the homogeniser and not with agitation (compare schematic shown below with the Cowles process schematic – *chapter 2*). This is also the reason for the use of only one turbine type stirrer in the feed tank (lab stirrer) instead of high shear impellers. The homogeniser process however follows the same basic steps as those described in *chapter 2* for the Cowles process. These steps include the following:

- addition of the organic phase to the aqueous phase
- emulsification
- addition of the initiator
- curing overnight

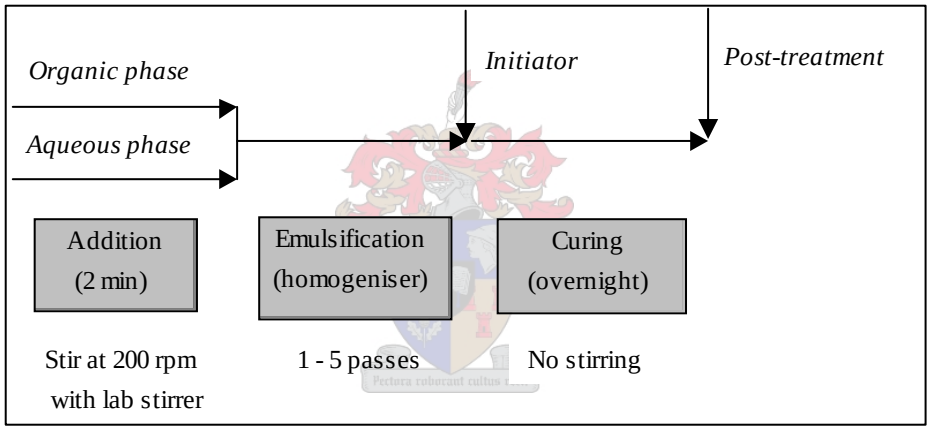


Figure 4.5: Laboratory scale batch homogeniser process schematic.

The organic phase, containing the polyester, monomer and polyamine, is added to the aqueous phase at a constant rate over a period of 2 minutes. This is done under constant agitation at fairly low shear. After the addition stage, the material is introduced to the homogeniser where emulsification is achieved under high shear. The shear forces are produced when forcing the liquid through the small grooves in the plunger and a homogeneous product is produced.

As the particle size of the product produced by the Cowles process is manipulated using different stirring speeds [18] (and consequently applying different magnitudes of

shear), the shear forces exerted by the homogeniser can be altered by either of the following:

- increasing the number of passes through the homogeniser
- altering the dimensions of the grooves in the plunger

Upon leaving the homogeniser, the cross-linking polymeric reaction is initiated by the addition of the initiator, again under the lab stirrer at 200 rpm. The sample is then left overnight to cure.
In this process no stirring is done overnight and no heating is required.

Experimental design:

As mentioned before the main objective of the laboratory scale batch experiments was to determine which factors/variables associated with homogeniser operation mainly influence the average particle size and size distribution of the product. The influence of these factors on other product properties, such as opacity and viscosity, was however also monitored. With these objectives in mind statistical methods were used to generate an experimental design for the experiments and to analyse the results obtained.

Parameters associated with homogeniser operation were identified in an earlier study [15] and each applied at high- and low levels to determine which factors significantly influence the particle size of the product. These parameters are given below:

- plunger geometry
- adjustment of the nozzle (manipulating the homogeniser pressure)
- the rate at which the handle of the homogeniser works (flow rate through the homogeniser)
- the number of passes

The material is pre-mixed before introducing it to the homogeniser, therefore it is known from the Cowles process that

- the addition time of the organic phase to the aqueous phase,

- the stirring speed
- the addition of the water (either together with the stabilisers before addition of the organic phase or just before catalysis after emulsification) and
- the curing temperature

influence product properties [18], these parameters completed the list of factors investigated for their effect on particle size.

It was decided to do different sets of experiment for each plunger whilst varying the other factors. These factors were applied at two levels – high and low – for each factor and the product properties obtained with the use of the different plungers compared to each other. The plunger geometry was therefore not entered into the statistical software package as a variable, whilst all the other factors were treated as variables applied at the levels shown in table 4.2.

Table 4.2: Different levels used for each factor.

	Low	High
Stirring speed [rpm]	150	300
Addition time [min]	1	4
Nozzle [no of turns open]	0.5	3
Passes	2	5
Water	Before addition	After addition
Strokes [min -1]	30	60
Curing T [C]	25	50

Note:

The low level for the adjustment of the nozzle at 0.5 turns open, corresponds with the application of high pressure (10 - 12 bar), where as 3 turns open represents low pressure (3 - 6 bar).

Cleaning:

After the completion of each experiment the homogeniser had to be dismantled entirely for cleaning purposes. This was done in the following manner:

- unscrew nozzle
- remove spring
- remove plunger
- remove cylinder
- unscrew feed cone
- remove non-return valve

All the parts, especially the non-return valve and cylinder have to be thoroughly cleaned with water to ensure smooth operation and to ensure that no blockages occur in the equipment. From time to time some solvent (monomer, acetone or MEK) was also used to remove build-up from the internal parts.

Analysis:

In addition to the standard analytical tests performed on the product as described in section 4.5 the product properties together with the different levels of the factors applied were entered into a statistical software package, *Statistica*. The data sheets then contained the following:

- measured experimental values for the factors/variables shown in table 4.2 above
- the average particle size of the product for each experimental run
- the opacity of the product measured for each experimental run
- the viscosity of the product measured for each experimental run at a constant shear rate

Multiple linear regression was performed on this data and the results (Anova-table, β-values and correlation coefficients) were used to determine which variable(s) had the most significant influence on the product properties. Additionally certain variables could be eliminated because of its' seemingly insignificant influence if compared to that of the other variables investigated.

4.2.2. BENCH SCALE:

Equipment:

After completion of the laboratory scale batch experiments a batch set-up to be operated on bench scale (10ℓ) was designed, using the principles of operation obtained from the laboratory scale homogeniser and keeping in mind that this equipment should also be compatible with the ultimate continuous process.

A homogeniser was designed consisting of a cylinder with internal parts (spring and plunger) and nozzle geometrically similar to the laboratory scale equipment but on a larger scale to accommodate the higher flow rate applied in the bench scale experiments. Where the laboratory scale homogeniser was operated at approximately 0.1 ℓ per minute, the bench scale homogeniser would have to operate at a minimum of 1 ℓ per minute. Figure 4.6 shows the design of the homogeniser parts.

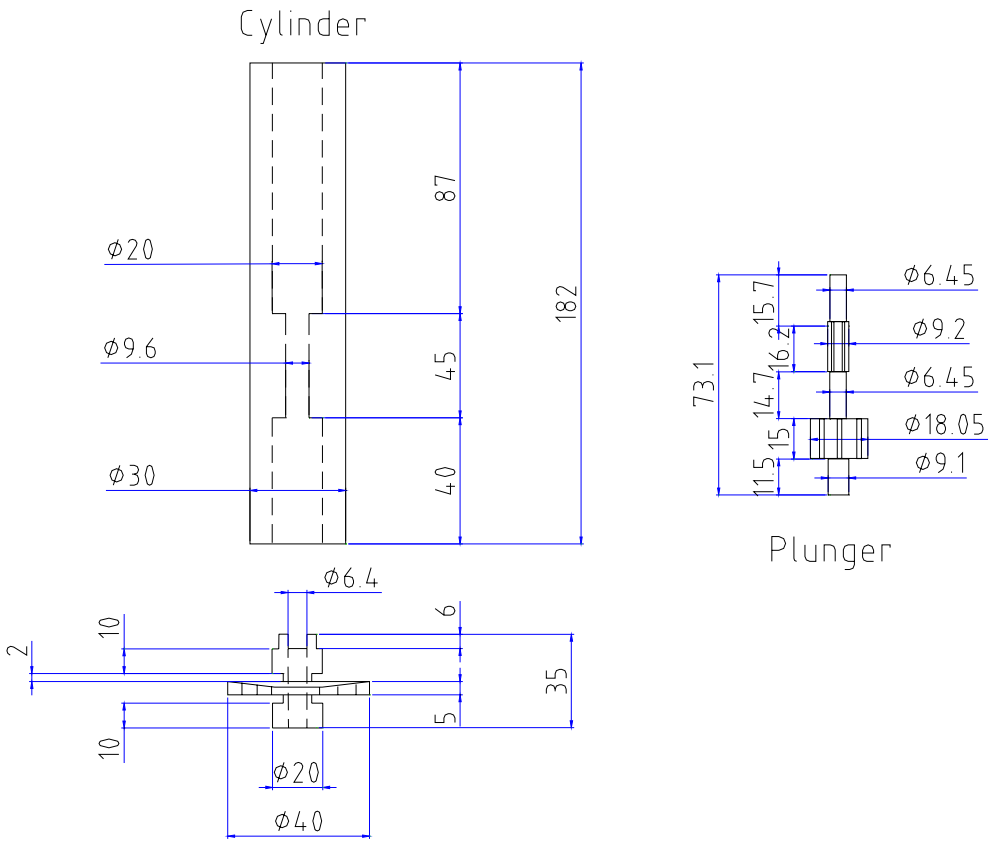


Figure 4.6: One section of the homogeniser for the bench scale set-up

A high-pressure pump was used together with the homogeniser shown above to facilitate the movement of the fluid through the grooves in the plunger. This pump is able to deliver 40 bar pressure at a flow rate between 1 ℓ per minute and 5 ℓ per minute. The pressure delivered by the pump compresses the spring holding the plunger in place and allows the fluid to pass through the grooves in the plunger, much in the same manner as with the laboratory scale equipment. Here the plunger also fits tightly within the walls of the homogeniser so that the only movement of fluid allowed is through the grooves in the plunger.

The head pressure delivered by the pump was found adequate to handle the pressure drop associated with three homogeniser sections (containing three springs and three plungers) in series and therefore the equipment was designed to accommodate three such sections. Each pass through the bench scale homogeniser would then actually equal three passes through the laboratory scale homogeniser. The sections were however designed in such a way that either one, two or three sections could be used at any particular time.

Process description:

The same formulation for the first generation vesiculated beads used in the laboratory scale batch experiments was used in the bench scale batch experiments.

The aqueous phase is charged to a 14 ℓ stainless steel vessel acting as a feed tank to the homogeniser and agitated continuously. This vessel is fitted with a turbine-type impeller (45 ° axial turbine impeller with a 130 mm diameter in a 230 mm diameter tank) similar to that used in the emulsion reactor to exert low shear on the fluid being mixed. The organic phase is prepared separately under a lab stirrer (400 rpm 45 ° axial turbine impeller with a 70 mm diameter in a 220 mm diameter plastic container) and is then added to the aqueous phase at a constant rate in the feed tank. The two phases are mixed under low shear at 130 rpm and this step does therefore <u>not</u> act as an emulsification step, but only to ensure that the fluid is moderately mixed when it is introduced to the homogeniser.

After all the material is charged to the feed tank and adequate mixing is achieved (usually about two minutes after the addition of the organic phase) the pump is activated and fluid is pumped through the homogeniser. Upon exiting the homogeniser the material can either be poured back into the feed tank for a second pass, or the initiator can be added to initiate the cross-linking reaction. Again catalysis is done under a lab stirrer and the product is left overnight to cure without stirring and without applying any heating.

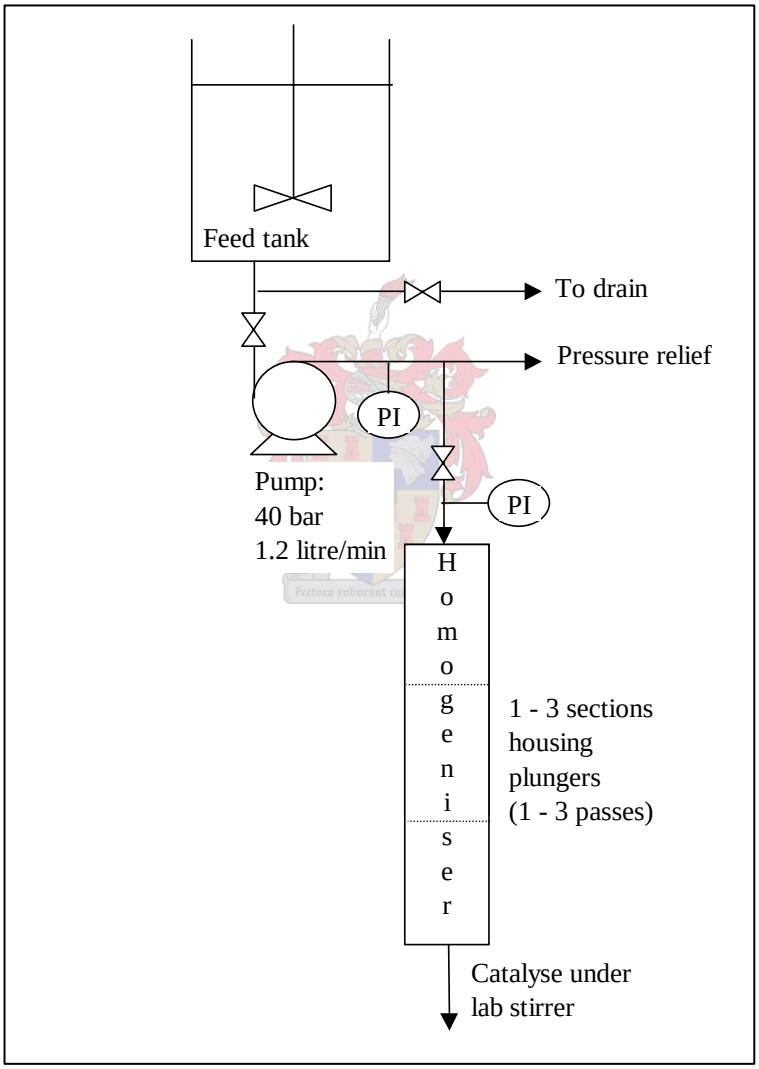


Figure 4.7: Process flow diagram for bench scale batch experiments.

Safety:

Because of the high pressure applied to the process some safety measures were taken. These included two pressure indicators situated in the delivery line of the pump on which the pressure could be monitored. In case of a blockage in the

homogeniser or any other source of increase in pressure the pump could be stopped manually. A strainer was also inserted in this line before the homogeniser to prevent large particles, which would cause a blockage in the homogeniser, from entering it.

Furthermore a pressure relief that would relieve the pressure if it increased in excess of 40 bar (the maximum operating pressure of the pump) was also inserted in the delivery line of the pump

Cleaning:

After the completion of each experimental run the set-up had to be cleaned thoroughly to prevent clocking of the homogeniser and the pipe system. This was relatively easy compared to the cleaning of the laboratory batch set-up, because clean water could be pumped through the system until the residue was removed and the water exiting the product line was clear.

4.3. SEMI-CONTINUOUS EXPERIMENTS:

As mentioned in the introduction to this chapter, semi-continuous experiments were conducted using the same set-up described for the bench scale batch experiments, but with the curing done continuously instead of in a batch fashion under the lab stirrer. The continuous curing was attempted using a loop-reactor.

4.3.1. EQUIPMENT:

The same equipment and set-up used for the bench-scale batch experiments were used for the semi-continuous experiments but with curing done continuously in a loop-reactor. This reactor consisted of 300 m of polyethylene pipe with a diameter of 15 mm. At the minimum flow rate delivered by the high-pressure pump the mentioned diameter produced a fairly low linear velocity (0.1 m/s) inside the pipe. This velocity was chosen because it was considered to produce shear forces insignificant in magnitude to disturb the formation of the beads inside the pipe. The length of the pipe was chosen to correspond with the time required for curing of the beads to be completed and the first 200 m of the pipe was jacketed using polyethylene pipe with a

25 mm diameter. This was done to allow heating of the beads to accelerate the development of the exotherm and therefore reduce the time (and consequently the length of pipe) required for the beads to be cured.

Apart from the loop-reactor some other changes to the batch set-up such as a means of adding the initiator continuously had to be found. It was decided to use a venturi-mixer together with a peristaltic pump to continuously add the initiator into the line of beads exiting the homogeniser. With the increased flow rate affected by the venturi a drop in pressure would also occur. The increase flow rate would ensure relatively good mixing of the initiator and the bead slurry, whilst the drop in pressure in the line would promote easy feeding of the initiator into the line with a slightly higher pressure.

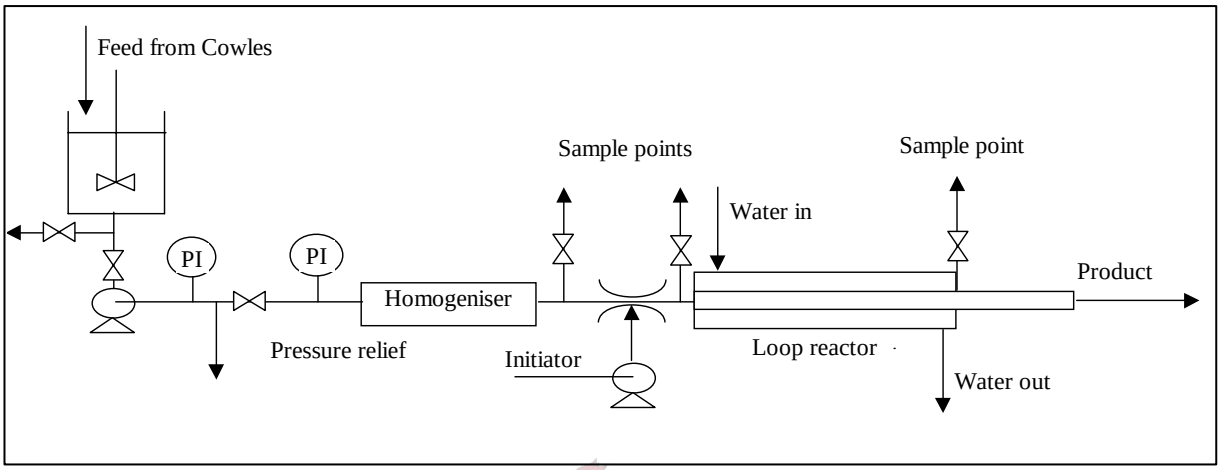
As the project progressed it also became necessary to introduce several static mixers in the loop-reactor to prevent the formation of boundary layers and the separation of the two phases in the pipe before the reaction was completed. These mixers are shown below:

4.3.2. PROCESS DESCRIPTION:

To facilitate continuous feeding to the high-pressure pump and homogeniser a 13 ℓ batch of vesiculated beads was made up in a separate Cowles reactor at low stirring speed (130 rpm for a 120 mm blade in a 220 mm tank). The low speed was used to prevent intensive mixing and emulsification from occurring.

From the feed tank the material was pumped through the homogeniser, as was the case with the batch experiments. Upon leaving the homogeniser the initiator was continuously added through the venturi mixer and the material subsequently pumped through the loop-reactor.

As shown on the process flow diagram (Fig 4.8), provision was also made for several sampling points to monitor product properties at different positions through the process.



.

Figure 4.8: Process flow diagram for continuous experiments using a loop-reactor

4.4. CONTINUOUS EXPERIMENTS:

4.4.1. EQUIPMENT:

A fully continuous set-up was constructed utilising the same equipment as that used in the semi-continuous experiments (high-pressure pump, homogeniser, venturi-mixer and loop-reactor) but with addition of the following:

- a complete continuous feeding section with three feed tanks that hold the organic phase, sterical stabiliser and thickener respectively
- three balances on which the flow rate of the three feed streams can be monitored
- three solenoid valves to control the flow rate of the feed streams

- a 10 ℓ mixing tank (first reactor) in which the feed streams are mixed using a Cowles disperser blade (100 mm in diameter in a 200 mm tank) before being pumped through the homogeniser or flowing through the cascade of reactors
- a second 10 ℓ reactor fitted with a turbine impeller where the initiator can be added
- two balances and dosing pumps for the continuous feed of the initiator system to the second reactor
- cascade of three 10 ℓ reactors offering an alternative to the loop-reactor as a method of continuous curing

All of the reactors are fitted with heating mantles to provide heating if required and with five outlets each. Four of these outlets are situated at different heights on the tank wall to provide a method of varying the residence time of the beads in the tank and the other outlet is situated at the bottom of the tank for draining purposes:

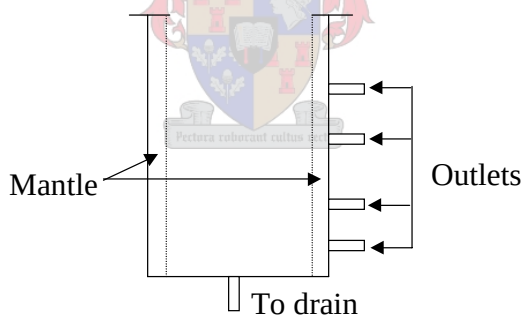


Figure 4.9: 10 ℓ reactor with heating mantle and different outlets.

4.4.2. PROCESS DESCRIPTION:

Feed section:

The feed section of the continuous process consists of three 25 litre plastic containers serving as feed tanks. These were chosen because it was more economic than using stainless steel tanks and it was readily available where as additional time

would be required to make stainless steel tanks. The plastic tanks also have a low mass compared to that of the steel tanks.

The feeding material is kept as follows:

- approximately 23 litres of organic phase (polyester, pigment and monomer) kept under moderate agitation in tank 1 to prevent settling of the pigment
- approximately 19 litres of sterical stabiliser and water in tank 2
- approximately 19 litres of thickener and water in tank 3

The feed tanks are loaded with the required amount of material and the mass weighed off in each container checked with the balance on which it is placed. When charging of the feed material is completed the solenoid valves are activated and feeding at the required flow rate commences.

Emulsification:

Emulsification of the two phases, i.e. organic phase and the aqueous phase used to produce the beads, is achieved either by using the Cowles disperser in the first reactor at a high stirring speed or by pumping the phases through the homogeniser. In the latter the first reactor with the Cowles disperser is used at low stirring speed only as a feed tank to the homogeniser and not as the primary means of emulsification. From here different methods of initiating the reaction and continuous curing can be used to produce the final product.

Cascade of reactors:

When the cascade of reactors is used to facilitate continuous curing the material simply flows under gravitational force from one reactor to the other. The initiators that make up the redox system are added continuously to the second reactor with dosing pumps and are mixed through the bead slurry with the turbine impeller. These initiators are also placed on balances as the feed tanks and the flow rate of material is monitored and recorded to ensure that the correct ratio of initiator to beads is used.

Depending on the residence time required in each tank, an outlet at a particular height in the tank can be used and the curing time can be manipulated in this manner.

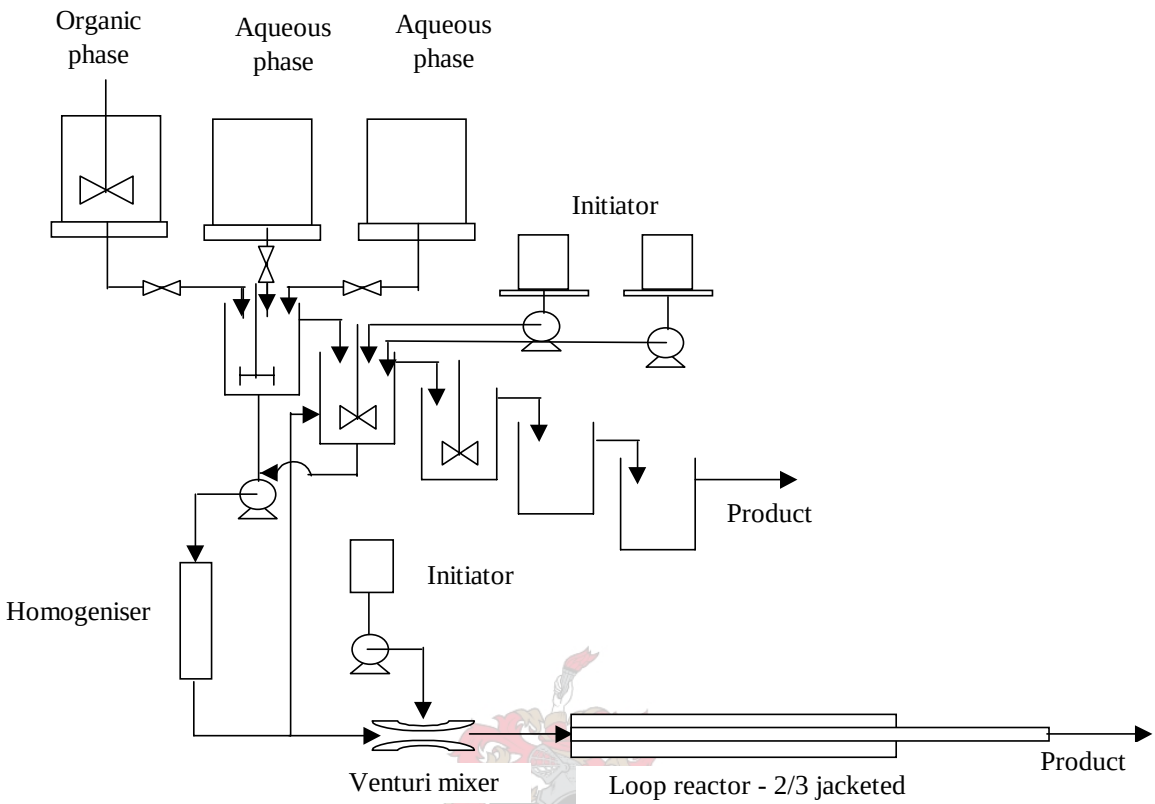


Figure 4.10: Process flow diagram for continuous set-up.

Loop-reactor:

With the use of the loop-reactor to continuously cure the beads, the material is either pumped through the homogeniser from the first 10 ℓ reactor or directly from the reactor, through the venturi-mixer where the initiator is added and then through the loop as described in section 4.3.2.

4.5. ANALYTICAL PROCEDURES

After completion of each experimental run the samples were left overnight to allow curing of the beads to take place. In the case of some of the continuous experiments, the samples were tested immediately after exiting the product line.

The following product properties were determined using the analytical procedures described below:

- opacity
- average particle size and particle size distribution
- total solids content
- viscosity
- un-reacted (free) monomer
- degree of vesiculation

4.5.1. OPACITY:

The opacity of a sample is a measure of the dry hiding power it possesses. It is determined from the ratio of the reflectance achieved by a dry film applied to a black surface to the reflectance achieved by the same film applied to a white surface:

$$Opacity = \frac{reflective\ index\ of\ black\ surface}{reflective\ index\ of\ white\ surface} \qquad [4.1]$$

A draw down – thin film (200 μm) on an opacity chart consisting of a white- and black surface – is made and left to dry in the oven at 50 °C for 15 minutes. The reflective indices of the white and black surfaces are then measured respectively using a reflectometer at an angle of 45°, where after the opacity (contrast ratio) is calculated according to equation 4.1. Generally a value of above 0.9 is acceptable, with 1 being the ideal case.

4.5.2. AVERAGE PARTICLE SIZE AND DISTRIBUTION:

After the opacity is determined the sample is prepared for scanning electron microscopy (SEM). This entails cutting out a 1-cm2 portion of film on the white surface of the opacity chart and mounting it to an iron stub. This stub is introduced to the SEM and video images generated of the sample.

The SEM projects an electron beam through a column fitted with scanning coils that deflect the electrons on the sample introduced to the instrument. These penetrate the surface atoms of the sample and collide with their orbital electrons releasing it from the atoms. This leaves the atoms in an ionised state and the electrons with its negative charge on the surface of the atoms. It is these electrons that are detected by the positively charged Secondary electron detector (SED) situated in the microscope and that generate the microscope image. A high concentration of electrons is found on sharp surfaces and these appear brighter than the rounded surfaces represented by a low concentration of free electrons.

To enhance the image generated by the SEM the sample can be plated with gold. This element with its high molecular weight releases secondary electrons that increase the concentration of free electrons on the surface of the sample and therefore creates a brighter image. The sample is plated with gold under vacuum conditions in the presence of argon gas to ensure that foreign molecules, such as hydrogen molecules found in the atmosphere that might influence the quality of the images are displaced.

In this particular study an ABT-60 SEM was used to generate image of the vesiculated bead samples. Video images of the vesiculated beads were generated at different locations and magnifications of the sample and representative images were saved and used in determining the average particle size.

The SEM images were introduced to a computer package, Scion Image, used to determine the average particle size and distribution. This program requires the user to specify the scale being used (obtained from the SEM image) and to physically draw a line across the diameter of each particle displayed on the screen using the mouse (see figure 4.12). It stores all the measurements until the user is satisfied that enough particles (usually 100 particles per image) have been counted to ensure that an accurate particle size, representative of the sample will be achieved. The measurements are then copied into Microsoft Excel where different statistical calculations, including the average particle size, are performed.

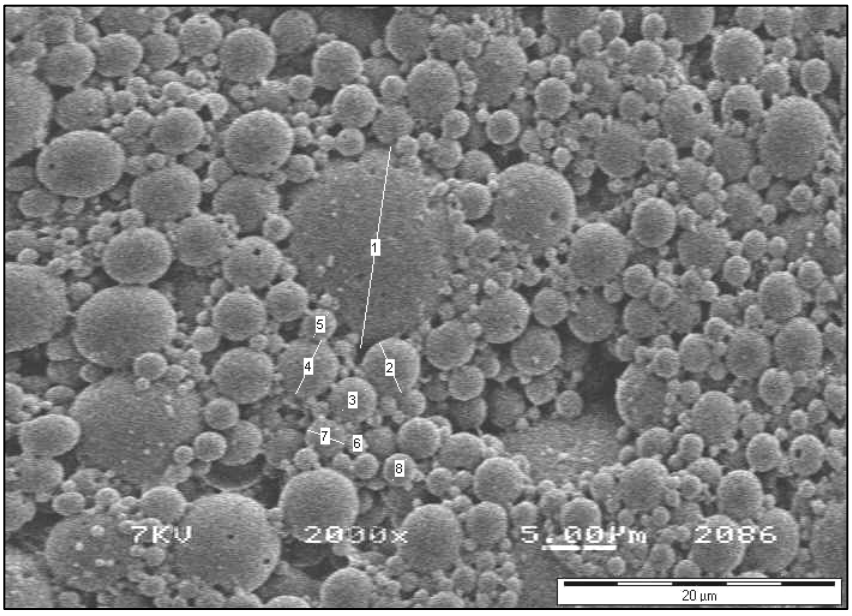


Figure 4.12: SEM image with 8 particles counted.

Statistical calculations:

Number average particle size (arithmetic mean)

$$\overline{x}_n = \sum_{i=1}^{n} \frac{d_i}{n} \qquad [4.2]$$

Volume average particle size

$$\overline{x}_v = \sqrt[3]{\sum_{i=1}^{n} \frac{d^3}{n}} \qquad [4.3]$$

where,

d_i = diameter of the i'th particle measured

n = number of particles measured

4.5.3. TOTAL SOLIDS CONTENT (TSC):

The total solids content is measured as a percentage of the sample introduced to the instrument, a Mettler Toledo HR73 Halogen Moisture Analyser. A sample dish is inserted into the instrument and about 1.5 g of wet sample is introduced. The instrument applies heat up to 180 °C and measures the mass of the sample as it changes with the evaporation of the volatile substances. It reports the weight of the sample that represents the total solids content present in the pan as a percentage of the wet sample as soon as no more evaporation takes place and the mass stabilises.

4.5.4. VISCOSITY:

The viscosity of the sample is measured using a Brookfield rotational viscometer with a LVT range of attachable spindles. These cylindrical spindles are each suitable for a specific viscosity range and can be applied at a range of rotational speeds (0.3 – 60 rpm). The instrument introduces the specific rotational speed chosen by the operator to the spindle and gives the output of the viscosity on the dial as the spindle rotates. Because the beads are a non-Newtonian fluid is also important to note the time the shear rate introduced by the spindle is applied to each sample. The viscosity measurement (in centipoise) is obtained by multiplying the reading on the instrument with a specific parameter suitable for the particular spindle and rotational speed used in the test.

All the vesiculated bead samples were tested using the same spindle (no. 3) at the same rotational speed (30 rpm) and the reading taken after 6 rotations. This was done to ensure that all the samples were subjected to the same shear rate and that the viscosity results obtained in this manner are therefore comparable to each other.

The actual rheological behaviour of the vesiculated beads is complex. For detailed information on the rheological behaviour, the thesis of P.L. Moolman [22] can be consulted.

4.5.5. UNREACTED MONOMER:

This analytical test is used to determine the amount of un-reacted (free) monomer present in the final vesiculated bead product. The apparatus and test procedure is described below.

Apparatus:

A gas chromatograph equipped with pressure controls, flame ionisation detector and a computer software package used to integrate the area under the peaks obtained, is required to determine the amount of free monomer present in the product. The instrument houses a 30 m x 0.32 mm ID fused silica column filled with a chemically bonded low-bleed phase.

Instrument grade helium gas (99.999% pure) is used as the carrier gas with a split velocity of 40 cm/s. The flame ionisation detector is operated using a 45 mℓ/min hydrogen feed and a 450 mℓ/min air feed and an operating temperature of 270 °C.

Operating conditions:

The injector temperature is kept at 220 °C with the following temperature program for the oven:

- constant at 50 °C for 3 minutes
- ramp – 20 °C/min to 120 °C
- ramp – 40 °C/min to 220 °C
- hold at 220 °C for 1 min

Standards and sample preparation:

A calibration mixture (CM) is first prepared with which the relative response factor (RRF) of the monomer, in this case styrene, can be determine. The CM

contains 2 g technical styrene (> 99 % pure) and 2 g Butyloxitol (ISTD) in 100 mℓ analytical grade acetone. 5 mℓ of the CM is diluted to 50 mℓ with the addition of more acetone and this solution is injected three times to the gas chromatograph. From the resulting peaks the RRF of styrene relative to the ISTD is calculated.

3 g of the vesiculated bead sample of which the amount of free monomer is to be determined is added to 4 g of ISTD in a glass centrifuge tube. The tube is tightly capped and sonicated for 3 minutes where after it is centrifuged for approximately 4 minutes. A clear supernatant layer is obtained and the sample is then left for an hour to allow further settling. A sample of 0.5 μℓ of this clear layer is then injected (three times) into the gas chromatograph for testing.

Calculations:

The relative response factor of the monomer is calculated from the results of the calibration mixture injections:

$$RRF = \frac{area_{monomer}}{area_{standard}} \times \frac{concentration_{standard}}{concentration_{monomer}} \qquad [4.4]$$

$area_{monomer}$ = integrated area under the styrene peak on the chromatogram

$area_{standard}$ = integrated area under the ISTD peak on the chromatogram

$concentration_{monomer}$ = concentration of the monomer in the CM

$concentration_{standard}$ = concentration of the ISTD in the CM

The concentration (in ppm) of un-reacted monomer is then calculated with the following equation employing the results obtained from the sample injections:

$$Free\,monomer = \frac{area_{monomer}}{area_{standard}} \times \frac{concentration_{standard} \times average\,RRF_{monomer} \times mass\,of\,standard}{mass\,of\,bead\,sample}$$

[4.5]

$area_{monomer}$ = integrated area under the styrene peak on the chromatogram

$area_{standard}$ = integrated area under the ISTD peak on the chromatogram of

$concentration_{standard}$ = concentration of the ISTD in the diluted sample
mass of standard = mass of ISTD (in g) in the diluted sample
mass of bead sample = mass of beads (in g) diluted with the ISTD

All the concentration values should be expressed as parts per million.

Depending on the minimum detectable area of the integrator a minimum sensitivity of at least 50 ppm monomer and an accuracy of at least 3 % should be achieved.

4.5.6. DEGREE OF VESICULATION:

The degree of vesiculation of the vesiculated beads is calculated as follows:

$$Degree\ of\ vesiculation = \frac{Volume\ occupied\ by\ vesicles\ inside\ the\ beads}{Volume\ of\ beads} \qquad [4.6]$$

To calculate the volume occupied by the vesicles and that of the beads, the diameter of these are required. Currently Plascon is investigating and developing a method by which these diameters can be determined or at least close approximation can be made. This method involves subjecting a dry bead sample to an ultra-microtome instrument by which thin layers of the sample is removed to reveal the vesicles inside the beads. The dry sample is obtained by subjecting the wet vesiculated bead product to a fast rotating centrifuge that cause the beads to settle and allows the separation of the beads and the aqueous solution in which it is suspended. After the aqueous solution is drained off the remaining vesiculated beads are diluted with de-ionised water and again subjected to the centrifuge to ensure that further water-soluble components are removed. This procedure is repeated until the beads are essentially free from any water-soluble components and impurities. It is then placed in an oven to dry overnight.

A small amount of the dry powdered sample is suspended in resin and left in the oven again overnight to allow the resin to cross-link and the beads to set inside the resin. It is this sample with the top layer removed that is introduced to the ultra-microtome.

With the removal of this layer the vesicles inside the beads are revealed. This sample is then covered with gold just as the draw down for the determination of the average particle size described in section 4.5.2 and subjected to the scanning electron microscope. Images of the microtome sample (at different locations on the sample and different magnifications) are stored and used to determine the following:

- average vesicle diameter
- average bead diameter
- average wall thickness

using data analysis similar to that discussed in section 4.5.2.

Since the images are only two-dimensional, the average diameters are used to calculate area instead of volume as required by equation 4.4. The degree of vesiculation is then calculated as follows:

$$Degree\ of\ vesiculation = \frac{Area\ occupied\ by\ vesicles\ inside\ the\ beads}{Area\ occupied\ by\ beads} \qquad [4.7]$$

The image below is a typical SEM image of a sample used to calculate the degree of vesiculation.

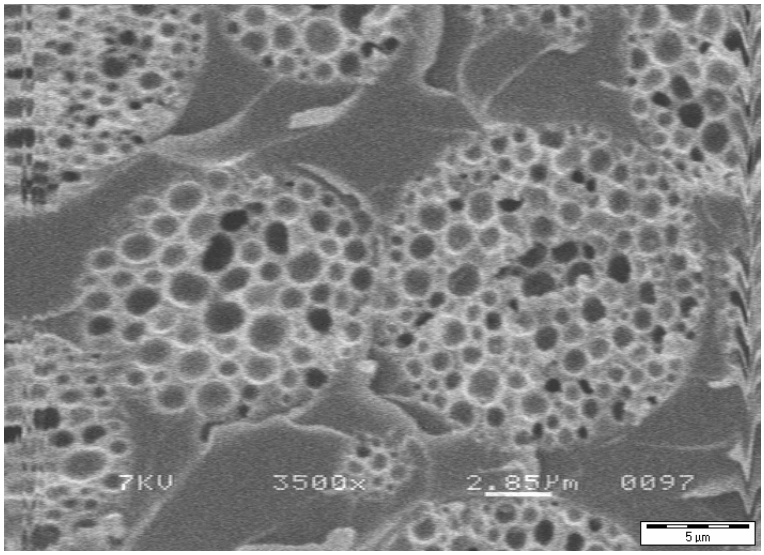


Figure 4.13: SEM image of sample used to calculate degree of vesiculation.

4.5.7. SCRUB RESISTANCE OF PAINT:

The scrub resistance of a thin paint film can be determined using an abrasion scrub tester (Sheen wet abrasion scrub tester 903) equipped with hog bristle brushes. These are wetted with a 0.5 % soap solution and moved up and down mechanically across the film usually applied to a plastic scrub panel. The solution is also sprayed onto the paint film at regular intervals while doing the scrub test to prevent the brushes from drying out.

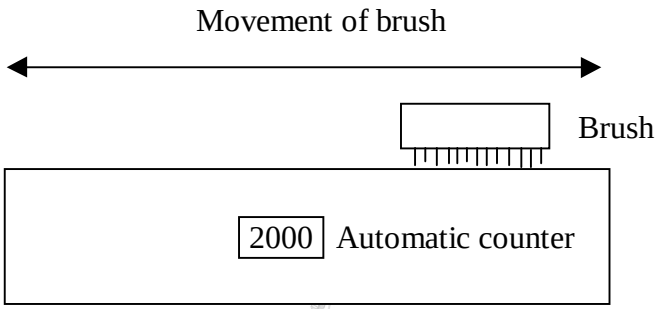


Figure 4.14: Wet abrasion scrub tester.

When a continuous black line of the scrub panel becomes visible through the paint film, the number of cycles that were completed up to this point are recorded and the film labelled to withstand this number of scrubs. It is desirable for a film to withstand in the region of 10 000 scrubs and this is also the maximum number of scrubs tested for. If a film has not failed when this amount of cycles has been reached, the testing is stopped.

CHAPTER 5: RESULTS OF BATCH EXPERIMENTS

5.1. INTRODUCTION

Batch experiments were performed with the pneumatically driven laboratory scale homogeniser shown in chapter 4. These experiments were done to identify the important operating parameters when using the homogeniser set-up to produce vesiculated beads and to investigate the effect of these parameters mainly on the average particle size of the product. Parameters associated with homogeniser operation were identified through literature [21] and each applied at high- and low levels to determine which factors significantly influence the particle size of the product.

After the completion of the laboratory batch experiments and with the important operating parameters identified, a bench scale batch homogeniser was designed. This homogeniser was geometrically similar to the laboratory homogeniser and used in conjunction with a high-pressure pump to achieve emulsification.

The bench scale laboratory experiments were mainly performed to determine if the homogeniser and high-pressure pump set-up could be used to achieve satisfactory product properties if compared to the properties obtained using the Cowles and emulsion reactor processes. With these experiments the range of the product properties were also determined and compared to that achieved with the laboratory scale experiments.

5.2. LABORATORY SCALE EXPERIMENTS:

5.2.1. PLUNGER 1:

A total of seven variables (all the factors, except the plunger geometry, listed above) were used in generating a 2^{k-p} experimental design for the set of experiments done with plunger 1. These factors were applied at the high- and low levels shown in table 4.2. Instead of performing a full factorial of $2^7 = 128$ experiments, a ¼ factorial of $2^5 = 32$ experiments was performed. This reduction in the number of experiments was chosen to save time with the execution of the tedious experiments whilst still accurately determining which of the factors significantly influence the particle size of the product.

After all the experiments with plunger 1 were completed, the values recorded for each factor together with the product properties of each experimental run was entered into a computer software package and multiple linear regression performed. The resulting Anova-table, β-values and correlation coefficients were obtained and conclusions based on these.

Average particle size:

To determine the factors that most significantly influence the average particle size of the homogeniser product, this property was entered as the dependent variable with all the operating parameters entered as independent variables in the software package. The resulting Anova-table is as follows.

Table 5.1: Anova-table.

	Sums of Squares	df	Mean Squares	F	p-level
Regress.	29.421	7	4.203	3.527	0.010
Residual	28.604	24	1.192		
Total	58.025				

The F-value displayed in the table represents the difference in the arithmetic mean between each of the data sets analysed. If this value is larger than unity, it suggests that the variation in the mean between the different data sets can be contributed to the variation in the factors investigated. In this particular case the variation in the average particle size (dependent variable) of the different products can be contributed to the variation in the independent variables. The results obtained with this set of experiments were therefore not influenced by conditions (such as the ambient temperature) that may have varied with the conduction of the experiments from one day to another.

The table below lists the *beta-values* (multiple regression, $R^2 = 0.507$) obtained for the particle size as dependent variable (y). These values satisfy the following equation:

$$y_i = ß_0 + ß_1x_{1i} + ß_2x_{2i} + ... + ß_nx_{ni} + r_i \qquad [5.1]$$

Equation 5.1 is written for the i'th experimental run and n different factors (independent variables). r_i represents the residual error for the i'the experimental run.

Table 5.2: Beta-values for the particle size as dependent variable.

	BETA	St. Err. of BETA
NOZZLE	-0.2706	0.1445
STROKES	-0.5065	0.1447
PASSES	-0.4173	0.1532
ADD_TIME	-0.0986	0.1613
STIRRING	-0.0453	0.1434
WATER	-0.1319	0.1488
CURING_T	-0.1410	0.1444

The significant β-values, representing the factors that have the greatest effect on the particle size, were the following (shown in green in table 5.2):

- Adjustment of the nozzle
- Rate at which the handle works

- Number of passes

These factors are those where the actual β-value exceeds that of the standard error of the β-value. It therefore suggests that the variation in the rate at which the handle works for instance causes a variation in the particle size that is greater than that which can be accounted for by residual error. In contrast to this the factors that have an insignificant effect on the particle size if compared to the effect of the other factors, are those where the β-value is significantly less than that of the standard error of the β-value. These factors for this set of experiments are shown in red and are the following:

- Stirring speed
- Addition time of the pre-dispersion

Opacity:

The same analysis as that done for the particle size was done for the opacity. Here the only factor having a considerable effect on the opacity was found to be the *addition of the water*. See Appendix C1 for the relevant tables.

Viscosity:

For the viscosity the following factors had the greatest effect:

- Adjustment of the nozzle
- Rate at which the handle works
- Number of passes

After completion of the analysis of the first set of experiments performed with plunger 1, it was decided to remove the *stirring speed* and the *addition time of the pre-dispersion* from the list of independent variables investigated for its effect on product properties. These factors were found to have an insignificant influence on the particle size, opacity and viscosity of the product of 32 experimental runs. An average value between the high- and low-level values for these factors was calculated and used in subsequent experiments.

Table 5.3: Stirring speed and addition time of the pre-dispersion used with plungers 2 and 3.

	Stirring speed [rpm]	Addition of pre-dispersion [min]
High	300	4
Low	150	1
Average	225	2.5

5.2.2. PLUNGER 2:

As mentioned above two of the factors previously treated as independent variables were not investigated and applied as such in the experiments that followed. Only five factors were therefore used in the experimentation with the second plunger. These were the following:

- adjustment of the nozzle (creating a specific pressure)
- the rate at which the handle of the homogeniser works (flow rate through the homogeniser)
- the number of passes
- the addition of the water (either together with the stabilisers before addition of the organic phase or just before catalysis after addition of the organic phase) and
- the curing temperature

With the reduction in the number of factors fewer experiments ($2^5 = 32$) than those needed for a full factorial with plunger 1 were required for a full factorial with plunger 2. Therefore a full factorial of experiments was generated for the second plunger in contrast with the ¼ factorial done for the first one.

Average particle size:

The most significant β-values (shown in Appendix C together with all the regression results) for the full factorial of experiments done with plunger 2 was found to be the rate at which the handle works and the number of passes. With this plunger

the adjustment of the nozzle was not shown to be one of the factors having a significant influence on the particle size, as was the case with plunger 1 (see 5.2.1). Its' effect was however not found to be completely insignificant, but just not AS significant as the two factors mentioned above.

It was also found that the curing temperature seemed to have the least significant influence on the particle size of the product. This was not the case with the results obtained from the experiments executed with plunger 1 and therefore this factor was not discarded in future experiments. Further investigation concerning its' influence on product properties was conducted with plunger 3.

Opacity:

The regression summary and relevant tables for the opacity as the dependent variable can be seen in Appendix C. From the results obtained the *tempo of movement of the handle* (i.e. the flow rate) seem to have the greatest influence on the opacity of the product. This is an important result, since the movement of the handle is also one of the factors having a significant influence on the particle size (see paragraph above). Contrary to the results obtained with plunger 1, the addition of the water does not have the *most* significant effect on the opacity of the product produced with plunger 2, but its' effect was still investigated in future experiments.

Viscosity:

For the viscosity as the dependent variable none of the independent variables/factors exhibited a significant influence on this product property (see Appendix C2).

Before the experimental design for plunger 3 was generated, another of the variables, the curing temperature, was eliminated because of its' seemingly insignificant influence on the particle size of the product if compared to the other variables.

5.2.3. PLUNGER 3:

For plunger 3 four independent variables were entered into the software package. These included the following:

- adjustment of the nozzle (creating a specific pressure)
- the rate at which the handle of the homogeniser works (flow rate through the homogeniser)
- the number of passes
- the addition of the water (either together with the stabilisers before addition of the organic phase or just before catalysis after addition of the organic phase) and

It was decided to do only a $2^3 = 8$ experiments (1/2 factorial) for this plunger. Here it is important to note that the plunger geometry changed quite dramatically with the addition of an extra section to the plunger (see section 4.2.1). The influence of the plunger design on the product properties could therefore also be determined.

Significant influence:

The factors that most significantly influenced the product properties, as determined with the β-values, are shown in table 5.4.

Table 5.4: Factors that have a significant effect on product properties.

Particle size	Opacity	Viscosity
Adjustment of nozzle	Adjustment of nozzle	Adjustment of nozzle
Number of strokes	Number of strokes	Number of strokes
Number of passes		

Again it was found that the adjustment of the nozzle, the rate at which the handle works and the number of passes significantly effected the particle size of the product. It was also the adjustment of the nozzle and the rate at which the handle works that significantly influenced the opacity and the viscosity of the product.

Insignificant influence:

The addition of the water was found to have an insignificant influence on the both the average particle size and the opacity of the product.

Table 5.5: Factors that have an insignificant effect on product properties.

Particle size	Opacity	Viscosity
Addition of water	Addition of water	-

5.2.4. SUMMARY OF THE EFFECT OF OPERATING PARAMETERS ON PRODUCT PROPERTIES:

After completion of all three sets of experiments the following operating parameters (in the order of increasing effect) were identified as significantly influencing the particle size of the product:

- adjustment of the nozzle (creating a specific pressure)
- number of passes
- rate at which the handle works (flow rate through homogeniser)

By manipulation of these factors the average particle size of the product can therefore be manipulated.

It was found that an increase in any of these factors resulted in a decrease in the particle size.

When the other product properties, i.e. opacity and viscosity, are considered it can be concluded with relative certainty that the *rate of movement of the handle (flow rate)* had a significant influence on these properties. This factor was shown to influence the opacity and the viscosity with two different sets of experiments whilst the effect of pressure (*adjustment of the nozzle*) also seems important for the viscosity of the product produced.

With an increase in the flow rate a decrease in the opacity and the viscosity was observed, whilst an increase in pressure also lead to a decrease in viscosity.

5.2.5. EFFECT OF PLUNGER GEOMETRY ON PRODUCT PROPERTIES:

Average particle size:

The influence of the variation in plunger geometry on the particle size is shown in table 5.6.

Table 5.6: Particle size for different plunger geometry.

	Plunger 1	Plunger 2	Plunger 3
Average particle size	2.5	5.7	1.6
Range	0.6-7	1.7-8.1	0.6-2.7

Note:

Plunger 2 has fewer grooves than plunger 1.

Plunger 3 has an extra section.

Because plunger 2 had fewer grooves than plunger 1, and therefore a lower shear force would be exerted on the particles, a larger average particle size was produced with this plunger. With plunger 3 the shear force was increased with the addition of an extra section on the plunger that actually generates an additional "pass" inside the homogeniser. The particle size consequently decreased as well as the range of particles produced.

It is therefore concluded that increasing the shear force by either increasing the number of grooves on the plunger or the number of sections causes a decrease in the average particle size of the product.

Other properties:

A variation in the opacity and the viscosity of the product was also observed with the variation in the particle size achieved with the variation in plunger geometry. The average values obtained are shown in the table below.

Table 5.7: Average product properties obtained with different plunger geometry.

	Plunger 1	Plunger 2	Plunger 3
Average opacity	0.9	0.9	0.9
Average opacity range	0.88-0.96	0.87-0.95	0.85-0.94
Average viscosity [cPs]	1500	3500	251

It is quite evident that the product produced with plunger 3 exhibited opacity and viscosity values largely different from that obtained with plungers 1 and 2. The low viscosity obtained with plunger 3 can be contributed to the higher shear force applied with this plunger when compared to the others used. It could be that the stabilisation of the long cellulose thickener chains was disrupted and that these chains were effectively broken down with the particles. Furthermore, the low viscosity made it increasingly difficult to draw down a thin film for the determination of the opacity as described in section 4.5.1. The fluid tended to flow all over the opacity chart and the film was disturbed before it could dry and produce the required film thickness. It could therefore be that the opacity measurements were made at locations where the film was thinner if compared to the film produced with a higher viscosity product. The hiding power would therefore seem below standard as observed with the value in table 5.7.

5.2.6. EFFECT OF THICKENER AND COLLOID STABILISER VARIATIONS ON VISCOSITY:

In the paragraph above it was mentioned that the decrease in viscosity observed with the use of plunger 3 could be attributed to the degradation of the cellulose chains of the thickener. Some investigation was therefore done on the effect of variations not only in the HEC (thickener) concentration but also in the PVOH concentration, which also assists in stabilising.

Both the HEC- and PVOH concentration was varied by 10 and 20 % above and below a standard concentration chosen. The concentrations are reported as the mass percentage of the stabilisers in the solution and keeping in mind that 2.5 % and 10 % is the maximum concentrations obtainable for the HEC- and PVOH solutions respectively, the following variations were applied.

Table 5.8: Variation in HEC– and PVOH concentration.

	HEC concentration [mass %]	PVOH concentration [mass %]
Standard	1.00	8
(+10%)	1.1	8.8
(+20%)	1.2	9.6
(-10%)	0.9	7.2
(-20%)	0.80	6.4

Experiments were conducted with the laboratory scale homogeniser with implementation of plunger 3, high pressure (10 bar) and a high flow rate. These parameters were used to produce the maximum shear force attainable so that a worst case scenario could be investigated. The viscosity of the product for each experimental run was measured. From these values a graph was constructed for the runs where the HEC concentration was varied. All other components of the formulation were used at standard levels, including the PVOH at 10 %.

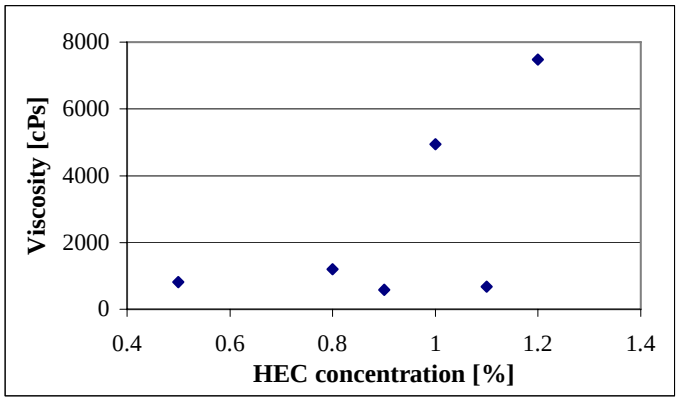


Figure 5.1: The effect of variation in the HEC concentration on viscosity.

From the graph is seen that the viscosity does not show a clear correlation with the HEC concentration, although it is expected that the viscosity should increase with an increase in the thickener concentration. According to the graph above a viscosity

value lower than 1000 cPs and comparable to that achieved with plunger 3 (shown in table 5.7) was obtained at a HEC concentration of approximately 0.5 % (mass). This HEC concentration is five times smaller than the standard concentration (2.5 %) used with the experimentation performed with plunger 3. Essentially it suggests that during the experimental runs performed with plunger 3 the HEC chains were degraded in such a manner that only a fifth of the stabilisation (and thickening) effect was experienced by the particles in the bead slurry.

The graph below shows the values of the viscosity range for varying concentrations of the PVOH solution at a constant concentration of 0.5 % HEC. With a variation in the PVOH concentration the variation in the viscosity is not as large as that found with the variation in the HEC concentration. This seems to indicate that the concentration of the HEC solution has a greater effect on the viscosity that of the PVOH.

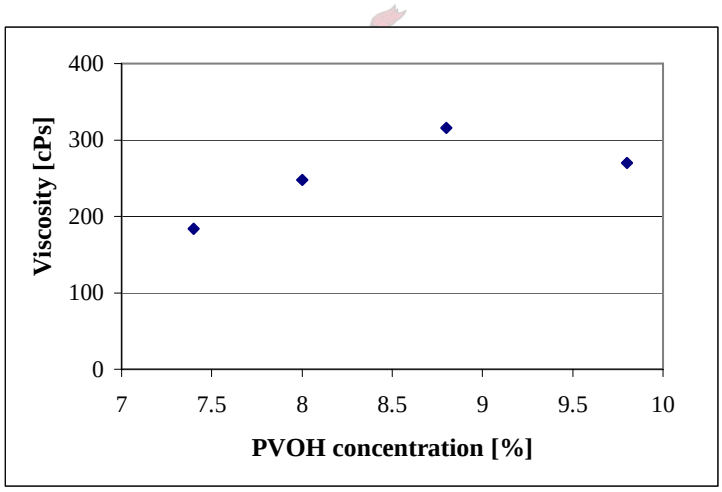


Figure 5.2: The effect of variation in the HEC concentration on viscosity.

Multiple linear regression was performed on the data and revealed that the HEC concentration has the largest influence on the viscosity when compared to the effect of the PVOH solution (see β-values in appendix C). This confirms the conclusion made with the comparison of the two graphs above.

With a change in the concentrations of the two solutions a variation in the percentage solids however also occurs. This was also taken into account and the interactions between the concentration of the HEC and PVOH solutions together with the

percentage solids (with investigation of the correlation coefficients) were investigated. The table below shows the result.

Table 5.9: Correlation coefficients

	% HEC	% PVOH	% SOLIDS	VICOSITY
% HEC	1	0.226	0.735	0.692
% PVOH	0.226	1	0.827	0.269
% SOLIDS	0.735	0.827	1	0.587
VICOSITY	0.692	0.269	0.587	1

The interactions that exist between the HEC concentration, the PVOH concentration and the percentage solids are clearly seen from table 5.9. This was to be expected as the HEC and the PVOH make up part of the total percentage solids. When altering the concentration of the two solutions one should therefore not only be concerned with the effect that these variations have on the viscosity but also remember that the variation in the percentage solids plays a significant part.

5.2.7. REPEATABILITY:

Five experimental runs were performed with the laboratory scale batch homogeniser to determine the repeatability of product properties obtained from vesiculated beads produced with this equipment. For these experiments all the operating conditions were kept constant and the product properties determined. The data on the particle size and distribution are shown in table 5.10 below.

Table 5.10: Particle size data to investigate repeatability.

	Particle size			
	Number average [micron]	Volume average [micron]	Deviation [micron]	Skewness [micron]
Sample 1	1.11	2.55	1.21	2.60
Sample 2	0.98	2.58	1.29	2.81
Sample 3	1.10	2.61	1.32	2.49
Sample 4	1.12	3.07	1.52	3.82
Sample 5	1.14	2.81	1.42	3.05

These results show that the number average particle size and the volume average particle size of the product achieved with this homogeniser is fairly repeatable.

5.2.8. EFFECT OF SURFACTANT ON PRODUCT PROPERTIES:

The effect of adding Tween, a surfactant, to the vesiculated bead formulation was investigated. This surfactant is generally added to improve whiteness of the beads and to increase the opacity of the dry product. For the experiments conducted with the laboratory scale homogeniser the standard vesiculated beads formulation as discussed in section 2.7.1 was used with the addition of 0.58 parts of Tween to the organic phase, before adding it to the aqueous phase.

A set of three experiments was done with Tween added and another set of three experiments without the addition of Tween. For these experiments all the operating parameters were kept constant and the average product properties of the two sets obtained. These are shown in the table below.

Table 5.11: The effect of Tween on product properties.

	Without Tween	With Tween
Average particle size [micron]	1.19	1.09
Viscosity [cPs]	341	1016
Opacity	0.92	0.94

With the addition of Tween a slight decrease in the particle size was observed. This was accompanied by an increase in the opacity and the viscosity of the product. Similar results have been reported with the Cowles process to produce vesiculated beads [18].

The increase in opacity may be ascribed to an increase in the water content of the organic phase due to the influence of the surfactant on the water uptake (see discussion in section 3.4.1). This may produce vesiculated particles containing an increased amount of water and therefore the amount of water left in the aqueous phase surrounding the beads is reduced. An increased viscosity is thus obtained.

5.2.9. EFFECT OF HYDROPHOBICALLY MODIFIED MONOMER ON PRODUCT PROPERTIES:

In section 3.4.1 the use of special additives to enhance product properties was described. This discussion included the addition of LMA, a hydrophobically modified monomer, to increase the water resistance and whiteness of the dry bead product. An investigation of the possibility to produce these beads with the homogeniser and to determine the product properties achievable was therefore performed. With these experiments the LMA was added to the organic phase before addition to the water phase and not at a later stage in the process.

Table 5.12: Product properties obtained with the addition of LMA.

Run no.	LMA [%]	TWEEN [%]	Solids [%]	APS [micron]	Opacity	Viscosity [cPs]
LMA1	5	25	24	6.17	0.88	2760
LMA9	7.5	25	24	-	0.77	3380
LMA2	5	25	28	2.17	0.91	9320

The table above shows the addition of Tween at a level of 25 % of that required by the formulation together with the addition of LMA. This constitutes 0.145 parts of the formulation instead of the 0.58 parts mentioned in section 5.2.8 above. The LMA is added to the organic phase and because this is also a monomer, some of the styrene is replaced by it. 5 % LMA for instance represents the replacement of 5 % of the styrene with LMA.

With the addition of 5 % LMA an average particle size of 6.2 micron was achieved. This is approximately three times larger that the average size obtained with the use of plunger 1 with the standard formulation. Although the opacity showed a decrease when compared to that of the standard formulation, it should be remembered that those larger particles, which would be incorporated in textured- or matt paint, do not require such a high opacity and that this is therefore not a problem.

Increasing the LMA content:

If the results obtained with experiments LMA1 and LMA9 are compared, it seems as thought the increase in the concentration of the LMA in the formulation leads to a decrease in the opacity of the final product. This can be attributed to a decrease in the water present in the organic phase when forming the vesicles and therefore a lower degree of vesiculation will be achieved (see section 3.3.5).

For sample LMA9 the average particle size could not be determined accurately because of excessive agglomeration and the loss in discreteness of the particles. It is probably this clustering that caused the increase in viscosity of the product if compared to viscosity of sample LMA1.

The beads produced with the laboratory scale batch homogeniser were incorporated to paint and the scrub resistance determined. It was found that the paint could withstand more than 10 000 scrubs and the introduction of LMA therefore increased the water resistance.

Increasing the solids content:

The effect of increasing the solids content of the vesiculated bead slurry was also investigated. Sample LMA2 was produced with the same LMA content and operating conditions as that used in the production of sample LMA1. The only difference between the samples was the solids content. From the results it seems as though the increase in solids content, from 24 % for sample LMA1 to 28 % for sample LMA2, caused a sharp decrease in the average particle size. At 24 % solids the product had an average particle size of 6.2 micron, whilst the sample prepared at 28 % solids had an average particle size of 2.2 micron. This reduction in size may be due to increased shearing forces experienced with an increase in solids content. The more particles flow through the small grooves in the plunger, the more these will rub against each other and consequently it will be broken down to smaller particle sizes than when just a few particles flow through the same passage.

With the increased solids content, a dramatic increase in the viscosity of the product is also obtained. This result seemed to suggest that the production of beads with the

addition of LMA at a solids content of 28 % is not viable at present, because of the high viscosity achieved. It was attempted to reduce this viscosity by re-introducing the product to the homogeniser and submitting the particles to shear again. The result is shown below.

Table 5.13: Product properties of beads re-introduced to the homogeniser.

Viscosity [cPs]	Opacity
6560	0.85

Although the viscosity was reduced with about 30 % with the re-introduction to the homogeniser, the viscosity still remained at a very high level. Furthermore a reduction in the opacity also occurred. It therefore seems that re-introduction of the samples to the homogeniser, after curing has been completed, does not enhance product properties in such a way that it is feasible to perform further investigation.

5.2.10. MINIMISING FREE MONOMER (Styrene):

The amount of free monomer in the product produced by the laboratory homogeniser was monitored and attempts made to minimise this undesired component in the final product. Different curing temperatures were applied to the beads by placing the samples in a water bath for different periods of time in an attempt to establish the minimum concentration of free monomer attainable in the product. The results of the free monomer experiments are given below.

Table 5.14: Free monomer results at different curing temperatures.

Run no.	Temperature [C]	Time [hrs]	Free monomer [ppm]
1	21	24	4169
2	50	1.5	5313
3	50	26	1976
4	50	1.5	-
4	70	17.5	6

Note:
Run 4 was left in a water bath for 1.5 hours at 50 C

The free monomer results shown in the table suggest that curing at 50 °C, even for 26 hours, does not reduce the free monomer sufficiently. Run number 4 where the sample was left in the water bath at 50 °C for 1.5 hours and then for a further 17 hours at 70 °C, showed the most promising results, although the long heating time seems a bit unpractical. Further investigation was therefore done to try and reduce the time the sample requires heating in order to reduce the free monomer to acceptable levels. For these experiments the water bath was kept at 70 °C and only the heating time was varied.

Table 5.15: Free monomer results obtained at 70 °C with varying heating periods.

Run no.	Time in waterbath [hr]	Opacity	Free monomer [ppm]
4	0.5	0.94	2600
5	1	0.94	100
1	1.5	0.93	55
2	3.5	0.94	65
3	4.5	0.94	98

It was found that heating at 70 °C for 1 hour drastically reduced the amount of free monomer present in the product. This is a much more practical result than that obtained in the first set of experiments discussed above and also suggests that the heating should be done in a single process step after catalysis and not as post-treatment after curing has been completed.

5.3. BENCH SCALE:

The bench-scale batch experiments were performed using the high-pressure pump and homogeniser set-up shown in section 4.2.2. As mentioned in the introduction to this chapter the main purpose of these experiments was to determine if vesiculated beads with acceptable product properties could be produced using this alternative set-up.

Again a variation in operating parameters was employed and the influence of these on product properties investigated.

5.3.1. EFFECT OF PLUNGER GEOMETRY:

To study the effect of the variation in the plunger geometry and specifically the depth of the grooves in the plunger, two plungers with a variation in the groove depth was used. Plunger 1 was made with a groove depth of 1.7 mm and plunger 2 with grooves of 4.4 mm. These were used to produce vesiculated beads with the standard formulation shown in section 2.7.1 at a constant flow rate of 1.3 ℓ/min. The experimental data and product properties are shown below.

Table 5.16: Effect of plunger geometry on product properties.

Run no	Plunger [no.]	Number of plungers	Passes	Pressure [bar]	Solids [%]	Size [micron]	Opacity	Viscosity [cPs]
CH23.2	2	1	1	16	26.88	1.209	0.9	5700
CH23.4	1	1	1	19	26.85	1.164	0.89	2400

The plunger with the deepest grooves (plunger 2) produced the product with the slightly larger average particle size as was expected from the results obtained with the laboratory scale homogeniser. It is rather surprising that only a 0.045-micron difference exists for a difference of 2.7 mm between the groove depths of the two plungers used. This would seem to suggest that the emulsification induced by the shearing action of the pump dominates the shear exerted by the plungers on the beads and would explain why the average size obtained with the different plungers is fairly constant.

It seems as though the opacity is not effected by the groove depth of the plungers, seeing that this property remained constant with a variation in the depth of the plunger grooves, whilst the viscosity did exhibit some change. This may be attributed to the difference in the homogeniser pressure recorded. Plunger 2 with the deeper grooves created a pressure of 16 bar to which the particles were subjected. This produced a product of 5700 cPs whilst plunger 1 created a pressure of 19 bar and consequently a lower-viscosity product at 2400 cPs. As with the laboratory scale batch experiments where the viscosity was dependent on the adjustment of the nozzle (creating a specific pressure) the viscosity seems to be dependent on the pressure applied to the particles.

5.3.2. EFFECT OF NUMBER OF PLUNGERS/SECTIONS:

In the paragraph above only 1 plunger was used in the homogeniser and it was decided to investigate the effect of increasing the number of plungers on the product properties. For this plungers 1 and 2 with the difference in groove depth was used at a constant flow rate of 1.3 ℓ/min again.

Table 5.17 below shows that the increase in the number of plungers leads to a decrease in the average particle size. This result was obtained for plunger 1 and for plunger 2 with the average particle size reduced with 29 % and 27 % respectively. Again only a slight difference exits between the average sizes obtained with the two plungers

Table 5.17: Effect of the number of plungers on product properties.

Run no	Plunger [no.]	Number of plungers	Passes	Pressure [bar]	Solids [%]	Size [micron]	Opacity	Viscosity [cPs]
CH23.2	2	1	1	16	26.88	1.209	0.9	5700
CH23.1	2	2	1	32	26.45	0.869	0.89	2200
CH23.4	1	1	1	19	26.85	1.164	0.89	2400
CH23.3	1	2	1	31	26.87	0.819	0.89	4060

The increase in the number of plungers does not seem to affect the opacity of the product at all, where as an effect on the viscosity can clearly be seen. Here the increase in pressure observed with the increase in the number of plungers leads to a decrease in the viscosity for plunger 2, but an increase in viscosity for plunger 1. The result obtained with plunger 2 corresponds to previous results obtained and discussed in section 5.3.1 but no explanation for the increase in pressure observed with plunger 1 can be found.

5.3.3. EFFECT OF NUMBER OF PASSES:

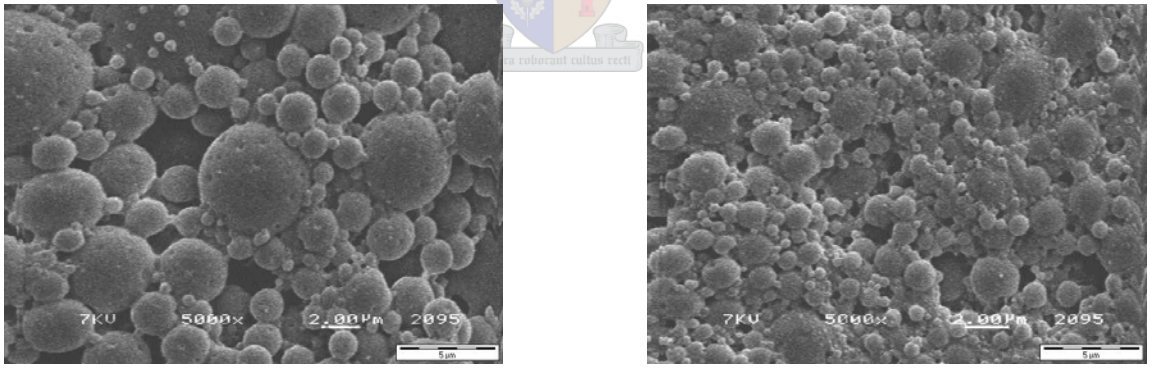
The effect of the number of passes was also investigated. From the results obtained with the laboratory scale homogeniser it was expected that an increase in the number of passes would have a pronounced effect on the average particle size of the product.

Experiments were conducted with plunger 1 with one to three passes and the product properties determined after each pass. To achieve this increase in the number of passes the material, as it exited the homogeniser, was poured back into the feed tank and pumped through the homogeniser again.

Table 5.18: Effect of the number of passes on product properties.

Run no	Plunger [no.]	Number of plungers	Passes	Pressure [bar]	Size [micron]	Opacity	Viscosity [cPs]
CH22.2	1	1	1	15	1.143	0.94	380
CH22.3	1	1	2	16.5	0.638	0.92	360
CH22.4	1	1	3	17	0.527	0.87	220

A decrease in the average particle size was obtained with an increase in the number of passes as was expected. This increase in the shear applied to the particles however adversely effected the opacity of the product. With each pass through the pump and homogeniser the opacity decreased significantly and this can probably be attributed to the loss in discreteness of the beads produced (see figure 5.3). This would seem to suggest that the shear applied by the pump and homogeniser with more than one pass is too large for the beads to form a stable product.



(a) (b)

Figure 5.3: SEM images of vesiculated beads produced with a variation in number of passes. (a) 1 pass, (b) 3 passes.

The question therefore arises whether it would not be preferable to use two plungers and 1 pass rather than one plunger and two passes for instance. With only 1 pass the emulsification achieved with the pump is minimised and the shear forces applied to the particles consequently reduced. This could be a solution to the loss in opacity obtained with the increase in number of passes and shear discussed above.

Experiments were therefore conducted with plunger 1, first by using one plunger and two passes and secondly by using two plungers and one pass. Results are shown in table 5.17.

Table 5.17: 1 plunger and 2 passes vs. 2 plungers and 1 pass.

Run no	Plunger [no.]	Number of plungers	Passes	Pressure [bar]	Solids [%]	Size [micron]	Opacity	Viscosity [cPs]
CH23.5	1	1	2	19	27.05	0.52	0.86	4100
CH23.3	1	2	1	31	26.87	0.819	0.89	4060

If the product properties of the two experimental runs are compared a smaller average particle size is obtained with 2 passes and 1 plunger as opposed to two plungers and 1 pass. This confirms the earlier statement (section 5.3.1) that the emulsification is predominantly achieved by the shearing action of the pump and not by the shear induced by the plungers inside the homogeniser. The reduced shear exerted on the particles with only one pass, also lead to an increase in the opacity if compared to that achieved with the two passes. At 0.89 the opacity achieved with one pass still is below the required level for the manufacturing processes. This may be attributed to a short contact time between the organic- and aqueous phases that would have limited the uptake of water by the polyester globules during the emulsification stage. It was found in the development of the water affinity test as described in chapter 3 that the shorter the contact time between the two phases, the less water is present in the organic phase when analysed.

The addition of Tween as a surfactant was therefore investigated as a possible means of increasing the opacity of the product. The results are shown and discussed in the following section.

It can however be concluded that the number of passes through the pump should be kept at one, with the use of a different number of plungers to manipulate the average particle size.

5.3.4. EMULSIFICATION ACTION OF PUMP:

To investigate the emulsification achieved by the shearing action of the pump and to determine if it produces the dominant shear, the homogeniser set-up was used without any plungers. The pump and cylinders shown in figure 4.4 was therefore the only source of emulsification and seeing that the cylinders contain an orifice of about 9.6 mm its' effect on the beads could essentially be regarded as negligible.

Table 5.18: Properties obtained without the use of plungers.

Size [micron]	Opacity	Viscosity [cPs]
9.40	0.90	920
9.44	0.89	620

As the properties obtained with two different experimental runs and the SEM images shown below show, emulsification and consequently the production of beads was achieved without the use of any plungers and essentially only the use of the pump.

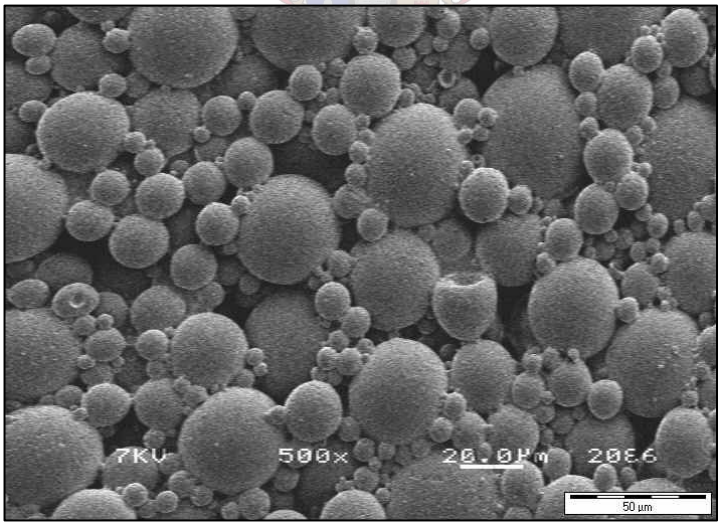


Figure 5.4: Vesiculated beads produced without the use of plungers.

5.3.5. EFFECT OF SURFACTANT:

The effect of Tween on the product properties and especially on the opacity was investigated. This study arose because of the somewhat low values obtained for the opacity with the bench scale experiments discussed above and because the addition of Tween was shown to have a positive effect on the opacity of the product produced with the laboratory scale homogeniser (see section 5.2.8).

Experiments were conducted with plunger 2 and one pass. The results are shown below.

Table 5.19: The effect of Tween on particle size and opacity.

Run no	Tween [%]	Size [micron]	Opacity
KG1	0	1.11	0.92
KG2	0.51	0.958	0.96

With the introduction of the full amount of Tween as required by the formulation (0.51 % mass of the total batch size) an increase in the opacity to a very acceptable level was obtained. This, together with the slight decrease in particle size, corresponds with the results obtained with the laboratory scale homogeniser.

The addition of Tween can therefore be used to increase the opacity of the product to acceptable levels and this will probably occur together with a reduction in the average particle size.

5.3.5. EFFECT OF LMA:

As with the laboratory scale batch experiments the addition of the hydrophobically modified monomer, added to increase water resistance, on the product properties was investigated.

Experiments were conducted with the addition of different amounts of LMA (percentage styrene replaced) with all the operating parameters kept constant.

Table 5.20: The effect of LMA on product properties.

Run no	LMA [%]	Solids [%]	Size [micron]	Opacity	Viscosity [cPs]
CH LMA1.1	5	24	2.16	0.95	2360
CH LMA 4.3	7.5	24	3.23	0.90	3940
CH LMA 3.3	10	24	3.13	0.79	TTTT

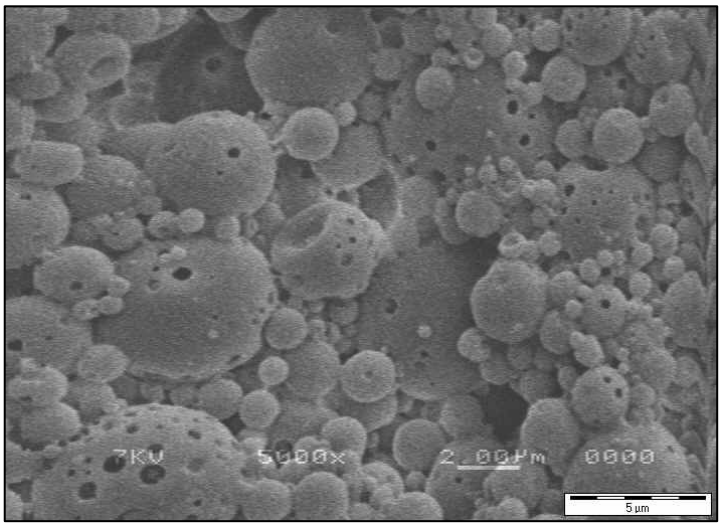
Note: TTTT – too thick to test.

Effect on particle size:

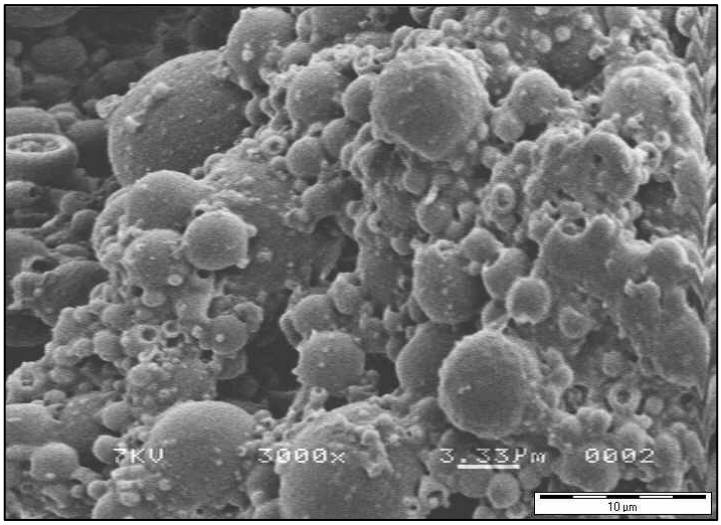
Table 5.20 shows the variation in particle size obtained with the introduction of different amounts of LMA. With the laboratory scale batch experiments it was found that an increase in LMA content caused an increase in the average particle size of the product. For the bench scale experiments an increase in particle size from 2.16 micron to 3.23 micron was achieved with an increase of 5 % to 7.5 % of the styrene replaced. With a subsequent increase of 7.5 % to 10 % of the styrene replaced, the particle size did not change significantly. This seems to suggest that the particle size of the product can be manipulated chemically only up to a certain level, in this case to approximately 3.2 micron. Without the addition of LMA with the same plunger and conditions, the highest particle size obtainable was at 1.2 micron. If this average size is compared to that produced with the addition of LMA, the benefit of using LMA can clearly be seen. It provides the vesiculated beads with a chemical method of increasing particle size.

Effect on opacity and viscosity:

As with the laboratory scale experiments the opacity decreased as the particle size increased, with the opposite tendency observed with the viscosity: the higher the LMA content the higher the viscosity. Both of these tendencies can be explained by the increased agglomeration and loss in discreteness of the particles with an increase in the LMA content.



(a)



(b)

Figure 5.5: SEM images of vesiculated beads produced with a variation in LMA content. (a) 5 % LMA, (b) 10 % LMA.

Again the beads produced with the incorporation of LMA were added to paint and the scrub resistance determined. The paint could withstand a minimum of 10 000 scrubs.

5.4. COMPARISON OF PRODUCT PROPERTIES:

The product properties of the laboratory scale homogeniser experiments and the bench scale homogeniser experiments were compared to that of the Cowles and emulsion reactor process.

Table 5.21: Product properties of homogeniser-, Cowles- and emulsion reactor processes.

	Homogeniser			
	Laboratory-scale	Bench-scale	Cowles	Emulsion reactor
Particle size [micron	0.6-8	0.4-2	2-4	5-10
Opacity	0.92-0.95	0.92-0.96	0.93 minimum	0.93 minimum
Viscosity [cPs]	200-2000	200-4000		

From the table it can be seen that quite a wide range of particles (0.6 – 8 micron) was produced with the laboratory scale homogeniser using different plungers. Unfortunately this wide range of particles could not be duplicated with the bench scale homogeniser, but it seems as though this was due to the high shear exerted by the high-pressure pump. If a different type of pump delivering a lower pressure is used, larger particle sizes could possibly be attained. What is clear however, is the fact that the homogeniser is able to produce smaller particles than the Cowles- or emulsion reactor process with the other properties at acceptable levels.

The opacity values reported in the table are those obtained with the optimisation of operating parameters and are therefore not the full range of values shown in appendix D. It should be remembered that the values shown in the appendix include those obtained with deliberate variation in operating parameters to investigate its effect on product properties and some of these value are thus below standard and not included in the table above.

CHAPTER 6: DEVELOPMENT OF CONTINUOUS PROCESS

6.1. INTRODUCTION:

From the batch process a continuous process incorporating the pump and homogeniser set-up had to be developed. The idea was to first try and produce vesiculated beads with an added section for the continuous curing of the beads. This would be done in a loop reactor of specified length calculated from the delivery flow rate of the pump and the time required for curing to be completed.

The first step in the development of the continuous process was therefore to determine the development of the exotherm of the reaction, as well as the factors that influence the curing process and to identify the parameters that could possibly shorten the time required for its peak to occur. This would also shorten the length of piping required for the loop-reactor and minimise capital cost. With the occurrence of the peak exotherm it was initially believed that the particles have been sufficiently formed to pump it to storage tanks. Consequently the development of the particles after initiation of the reaction would also be determined.

For the process of producing vesiculated beads to be entirely continuous the two components making up the initiator system would therefore also need to be fed continuously. Some investigation as to the mixing intensity of the initiator required to obtain acceptable product properties as well as the time required between the addition of the two components was done to aid in the design of the initiator addition section of the process. In such a process it would be preferable to add the two components of the initiator system at the same position in the process or at least as close as possible to each other.

The results of the semi-continuous process including:

- the continuous initiator system (venturi-mixer and peristaltic pump)
- homogeniser and high-pressure pump

- loop-reactor with heating

is also shown in this chapter.

6.2. EXOTHERM DEVELOPMENT:

Initial investigation done on the development of the exotherm was focussed on determining the time required for the peak exotherm to be reached at normal operating conditions, including curing at room temperature and the amount of cumene hydroperoxide and iron solution (CHP/Fe^{2+}) required by the standard formulation. For these conditions it was found that the peak exotherm for a 500 g batch occurred 70 – 75 minutes after the initiator was added and it reached a temperature of about 40°C.

Table 6.1: Exotherm data for amount of CHP/Fe^{2+} required by the standard formulation.

Peak exotherm at:	
Temperature [C]	Time [min]
39	70
38	75

6.2.1. ALTERNATIVE INITIATING SYSTEM:

The time required (75 minutes) for the peak exotherm to occur when utilising the (CHP)/Fe^{2+} initiating system posed a problem for the continuous processing of the beads where the curing process would probably take place in a loop-type reactor. The piping used inside the reactor would have to be long enough to accommodate a low flow rate such as not to disturb the formation of the beads and for the length of time required by the beads to reach the exotherm. If flow rates in the order of 0.1m/s are considered over a time period of 75 minutes as was found with the experiments discussed above, the loop reactor would have to accommodate piping of 450 m in length. Another redox initiating system combining the present cumene hydroperoxide (CHP)/Fe^{2+} system with EDTA/Sodium formaldehyde sulfoxylate (SFS) was therefore investigated. It was reported in literature [14] that this system would have a

faster dissociation rate than the normal thermal initiator and thus shorten the time and the length of the reactor required for the exotherm to be reached.

Unfortunately the proposed CHP/Fe^{2+} with EDTA/SFS redox initiating system proved to be unsuccessful for the vesiculated beads produced using the homogeniser. Although the exotherm was reached in a much shorter time every sample exhibited excessive viscosity, such that it could not even be stirred. The following was done in an attempt to reduce the viscosity:

- the solids content was varied between 24% and 32% solids
- the amount of catalyst was halved

The above attempts also proved to be unsuccessful. The table in appendix E1 shows the exotherm temperatures and the time that elapsed before it was reached.

6.2.2. MANIPULATING THE CHP/Fe^{2+} INITIATING SYSTEM:

After the completion of the above experiments with the added EDTA/SFS it was decided to double the amount of initiator used in the CHP/Fe^{2+} redox initiating system. It was thought that this might have an effect on the time required for the exotherm to be reached. This was investigated by conducting two experiments, one at 28% solids content and one at 34% solids content, with double the amount of catalyst required by the standard formulation and then measuring the exotherm as well as the time required before it is reached.

Table 6.2: Results of experiments conducted with double the amount of catalyst.

Run no.	% Solids	FeSO4 [g]	CHP [g]	Temperature [C]	Time [min]
28 % solids	-	0.06	0.7	39	70
34 % solids	-	0.08	0.89	38	75
cat13	28	0.13	1.18	43	30
cat14	36	0.17	1.75	42	35

It was found that doubling the amount of catalyst added to the beads caused the time required for the exotherm to be reached, to be halved. Values of 30 – 35 minutes were measured in the case of runs *cat13* and *cat14* compared to the 70 –75 minutes measured with the usual amount of catalyst used. This reduction in the time required before the exotherm is reached would correspond with a consequent reduction of about 50 % of the length of pipe required.

The effect of the increased initiator concentration on the product properties was also investigated. It was found that the increase in initiator adversely effected the opacity of the product and no further investigation concerning a variation in initiator concentration to influence the exotherm was carried out.

Table 6.3: Product properties of beads produced with increased initiator concentration.

Initiator concentration	Particle size [micron]	Opacity	Viscosity [cPs]
Normal	1.10	0.93	2300
Double	1.16	0.89	1500

6.2.3. THE EFFECT OF HEATING ON THE DEVELOPMENT OF THE EXOTHERM:

The effect of increased temperature on the curing of the beads was investigated by performing an experimental run where the beads were left to cure at room temperature and another run where the same sample was left in a water bath at 65 °C to cure at this temperature. The development of the exotherm in each case is shown below.

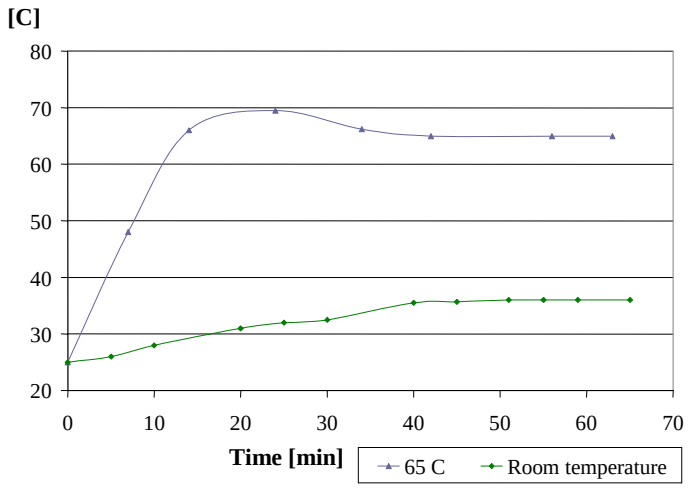


Figure 6.1:Development of the exotherm at room temperature compared to that of 65 °C.

At the elevated temperature the peak exotherm is reached after about 15 – 20 minutes in contrast with the peak exotherm reached after approximately 35 minutes when left to cure at room temperature. This shows that applying heat to the sample after initiation causes a reduction in the time required for the peak exotherm to occur. The product properties of these two samples are shown in table 6.4.

Table 6.4: Product properties of sample cured at room temperature and 65 °C.

Cured at:	Average size [micron]	Opacity	Viscosity [cPs]
room temperature	1.101	0.93	2300
65C for 1 hour	1.075	0.94	1420

The properties measured for the two samples compare well and suggest that curing at elevated temperature for 1 hour does not adversely effect the properties shown in the table. Furthermore it seems as though the increased temperature enhances the discreteness of the particles, as shown by the SEM images below. This might explain the slightly higher opacity measured for the sample cured at elevated temperature.

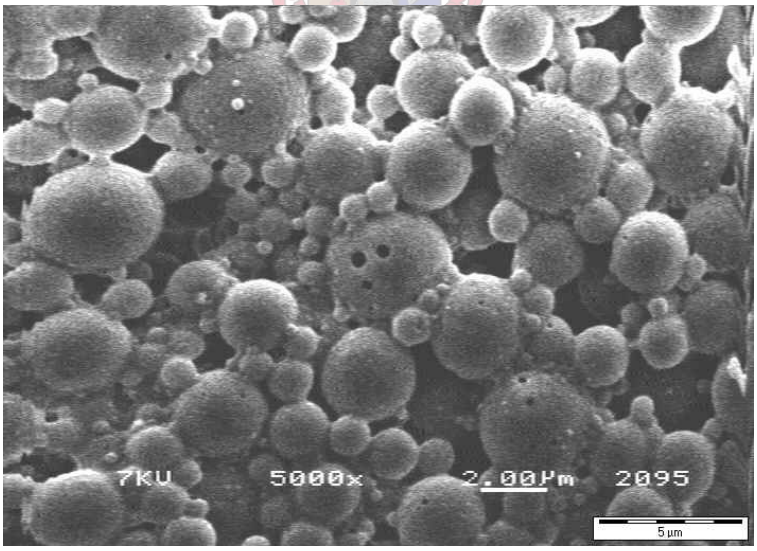


Figure 6.2: SEM image of sample cured at room temperature.

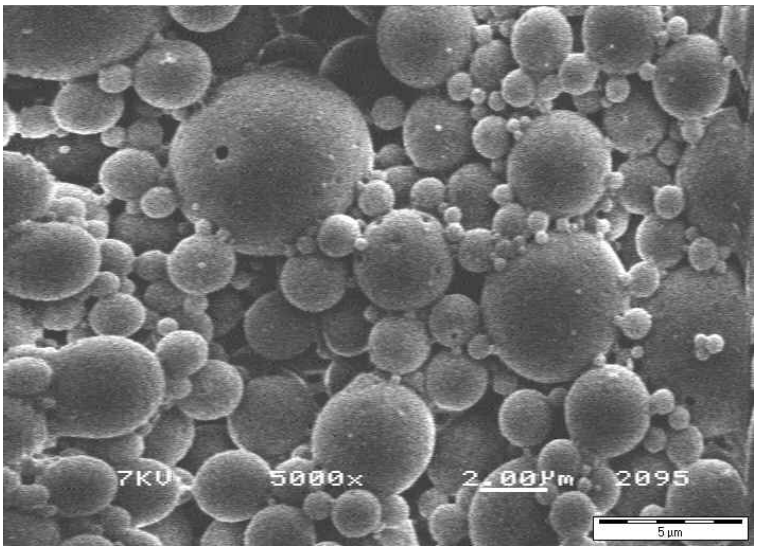


Figure 6.3: SEM image of sample cured at 65 ℃.

The same operating conditions as those used to prepare the samples discussed above were used to produce vesiculated beads that were left to cure in a water bath at 70 ° C for 15 minutes. This was done to investigate the effect of a shorter time spent at the elevated temperature on product properties.

Just as the results discussed above the table below shows that curing at 70 °C for only 15 minutes did not adversely effect the measured properties and in fact caused an improvement in the opacity of the product.

Table 6.5: Curing at different lengths of time at elevated temperature.

Cured at:	Average size [micron]	Opacity	Viscosity [cPs]
room temperature	1.101	0.93	2300
65C for 1 hour	1.075	0.94	1420
70C for 15 min	0.8	0.95	2640

The increase in opacity may again be attributed to the improved discreteness of the particles obtained by heating for 15 minutes.

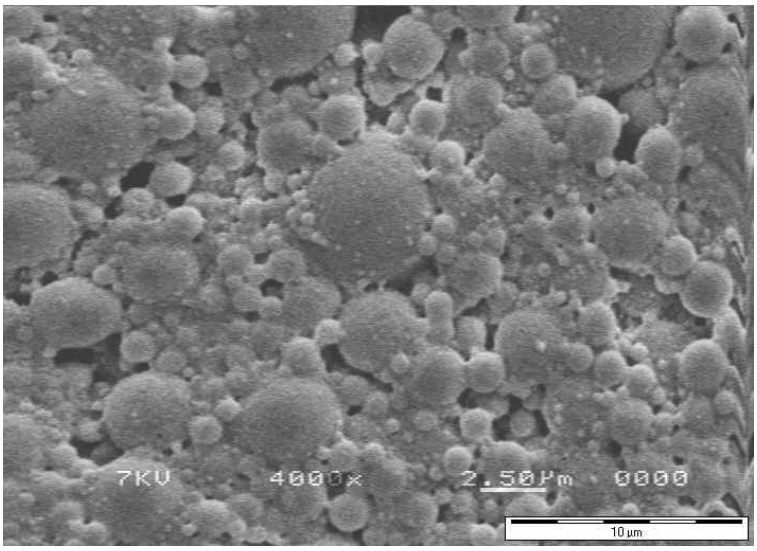


Figure 6.4: Sample cured at room temperature.

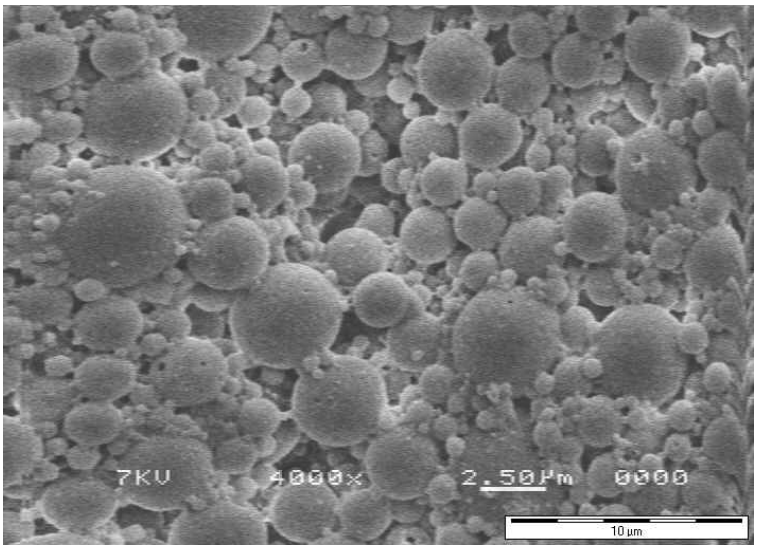


Figure 6.5: Sample cured at 67 ℃ for15 minutes.

From the exotherm data it can be seen that the temperature of the sample left in the water bath for 15 minutes still increased after it was removed from the heat source. This increase continued until about 68 °C was reached after approximately 18 minutes. It is however difficult to conclude when exactly the peak exotherm of this sample was reached because a large temperature difference existed between the water bath and the surrounding atmosphere and the heat loss to the atmosphere should be taken into account.

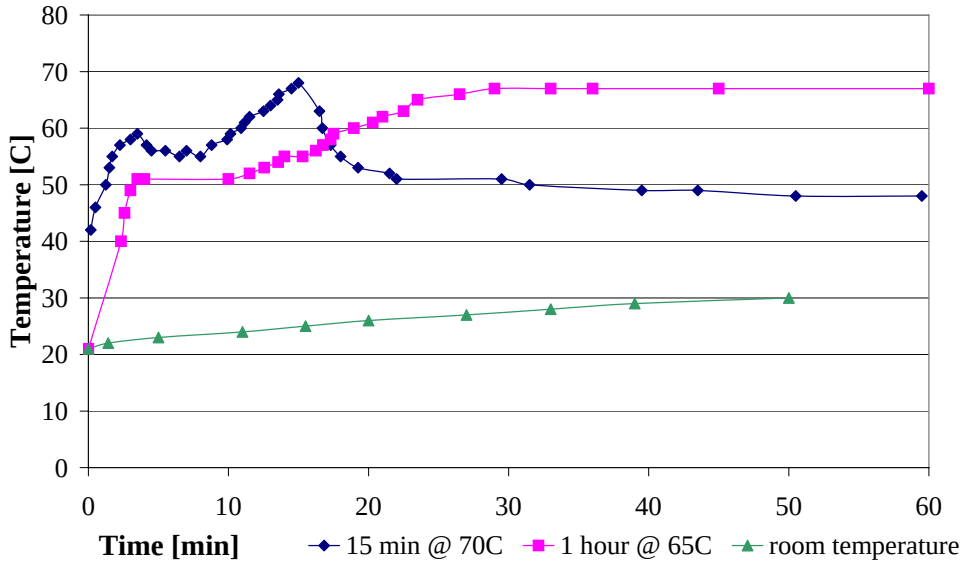


Figure 6.6: Exotherm development for samples at 65 °C for 1 hour and at 70 °C for 15 minutes compared to curing at room temperature.

LMA modified formulation:

The effect of applying elevated temperatures when the LMA modified beads are cured was also investigated. With these experiments the curing temperature was varied between 77 °C and 35 °C and the samples were left in a water bath for 15 minutes at 77 °C, 55 °C and 35 °C respectively. The development of the exotherm as well as the product properties was measured in each case. These are shown in table 6.6 below.

The experimental run where the product was left to cure at 77 °C for 15 minutes exhibited the highest opacity value whilst the other properties listed together with the discreteness of the particles (see SEM images of figures 6.7 and 6.8), were all within acceptable limits. It therefore seems as though curing at temperatures above 55 °C is desirable for the formation of discrete particles.

Table 6.6: Product properties of samples prepared with 7.5 % LMA and cured in a water bath at different temperatures for 15 minutes.

Run no	Curing at:	Average size [micron]	Opacity	Viscosity [cPs]
CH LMA 4.1	35C for 15 min	2.92	0.92	1400
CH LMA 4.2	55C for 15 min	2.21	0.93	940
CH LMA1.2	77C for 15 min	2.25	0.96	920

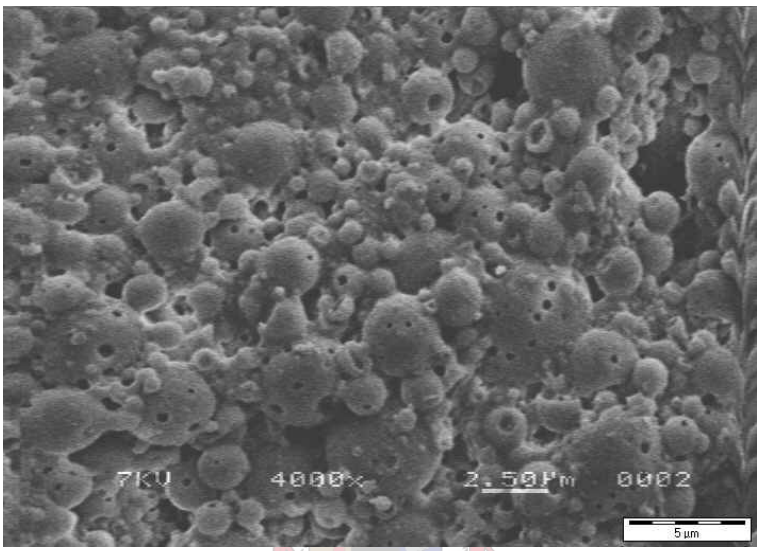


Figure 6.7: SEM image of sample cured at 35 ℃ with LMA formulation.

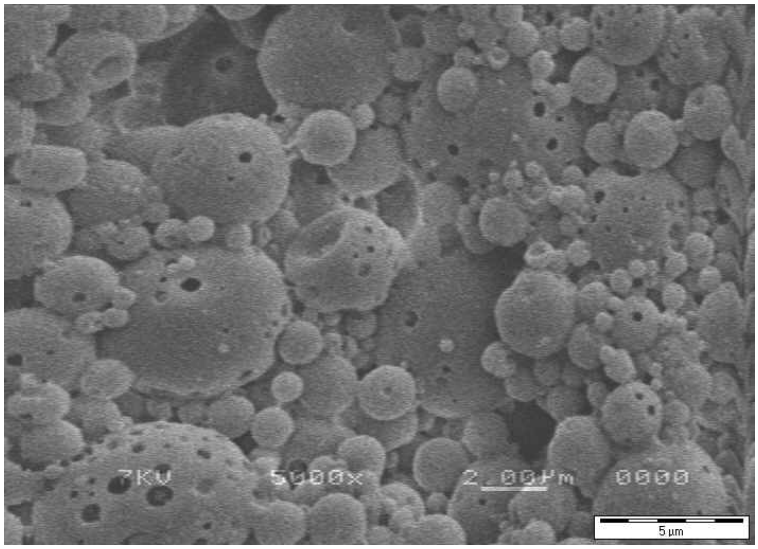


Figure 6.8: SEM image of sample cured at 77 ℃ with LMA formulation.

The opacity value at 0.96 obtained for the sample cured at 77 °C with the LMA modified formulation also corresponds with the opacity obtained without the addition

of LMA as presented in table 6.5. This seems to suggest that the addition of LMA does not adversely effect the opacity of the product when the sample is cured at elevated temperature. With some of the batch experiments it was found that the addition of LMA caused loss in discreteness of the particles and consequently a reduction in opacity (see section 5.3.5). It could be that with the application of heat the diffusion processes are limited because the reaction is forced to completion in a relatively short period of time. Enough time is therefore not available for the particles to agglomerate since they are essentially cured shortly after they are formed.

It can therefore be concluded that curing at elevated temperature not only shortens the time elapsed before the peak exotherm is reached but also enhances the discreteness of the particles. This leads to increased opacity both for the standard formulation and for the LMA modified formulation.

Peak exotherm and particle development:

As mentioned above it would be difficult to determine when exactly the peak exotherm is reached if the temperature of the sample cured at 77 °C is simply measured and recorded both inside and outside of the water bath. A large temperature difference again existed between that of the water bath and the atmosphere and the losses to the latter would have to be taken into account. Therefore it was decided to draw different samples from the product at different time intervals. The reaction was stopped right after each sample was taken and the samples subjected to scanning electron microscopy to obtain a visual indication of the development of the particles as time progresses. This would give more conclusive information as to when the peak exotherm is reached and the particles have consequently been formed.

The figure below shows the development of the particles as time progressed after the addition of the initiator. It should be remembered that this sample was heated for only 15 minutes and that it was left to cure further at room temperature.

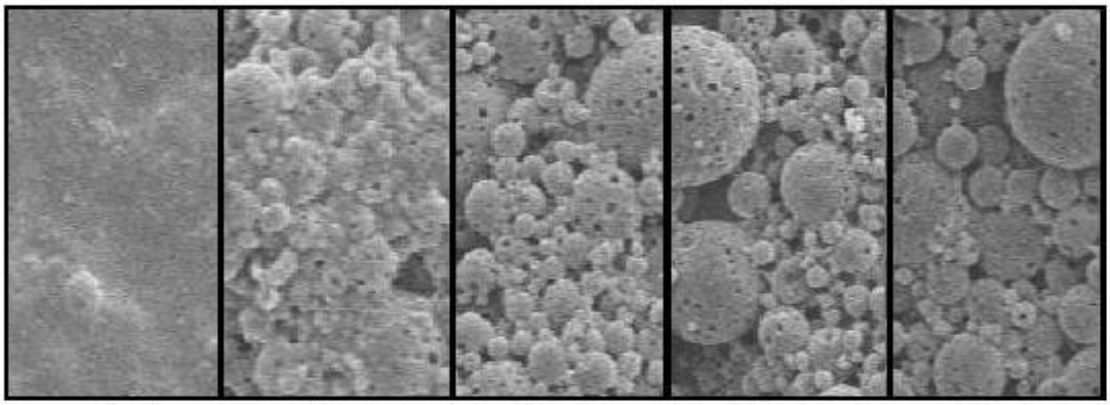


Figure 6.9: Particle development with time after initiation of the reaction.

From the figure it can be seen that the particles have been formed after approximately 20 – 25 minutes after the initiator was added. This would suggest that if heating in the loop-reactor for the continuous curing is applied at about 70 °C for 15 minutes the beads should be sufficiently cured after 25 minutes to be pumped to storage tanks. At a flow rate of 0.1 m/s a pipe length of at least 150 meters would therefore be needed.

6.3. ADDITION OF THE INITIATOR:

For the continuous process the addition of the initiator would also have to be continuous and in such a manner that the initiator is thoroughly mixed throughout the fluid flowing in the loop-reactor. Some investigation of the importance of the mixing intensity of the initiator as well as the time required between the addition of the two components making up the initiator system was done. The effect of these parameters on the development of the exotherm and some product properties was determined with different experimental runs with the laboratory scale batch homogeniser.

6.3.1. EFFECT OF MIXING INTENSITY:

To study the effect of the mixing intensity on the product properties two experimental runs were performed and different stirring speeds applied with the laboratory stirrer during initiation of the reaction. For this experiment a 2-minute interval was allowed

between the addition of the two components of the initiating system as prescribed by the standard formulation.

The development of the exotherm of each run is shown in the graph below and it seems as though no difference exists between its' development with a variation of 433 rpm to 235 rpm (85 % variation) in stirring speed.

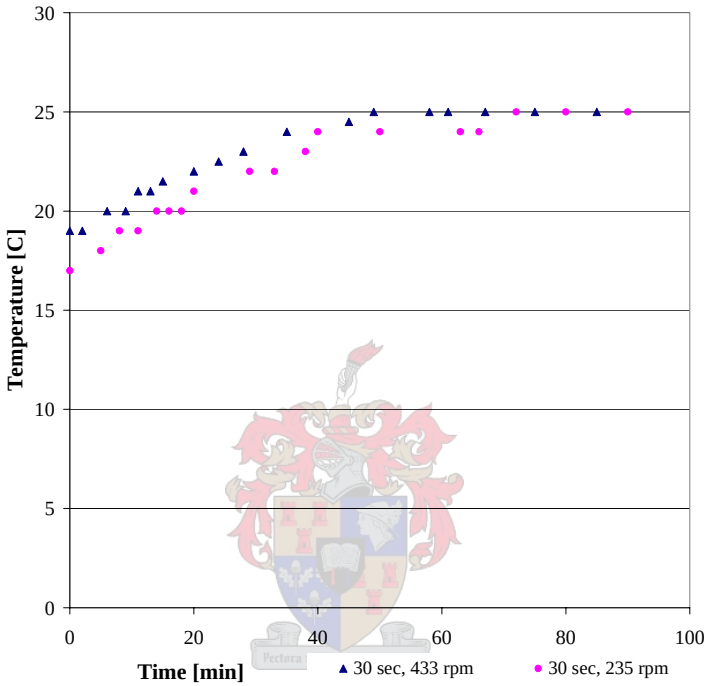


Figure 6.10:Dependence of exotherm on mixing intensity.

The other product properties were also measured and are shown in the table below.

Table 6.7: Effect of mixing intensity on product properties.

Stirring speed [rpm]	Average size [micron]	Opacity	Viscosity [cPs]
235	1.1	0.92	2600
433	1.03	0.91	2100

It can clearly be seen that the variation in stirring speed and therefore in the mixing intensity applied with the addition of the initiator does not significantly influence product properties.

6.3.2. EFFECT OF TIME:

The time allowed between the addition of the components making up the initiator system, namely $FeSO_4$-solution and cumene hydroperoxide was also varied and the effect on the product properties established. With the continuous addition of the initiator in the continuous process it would be preferable to feed the initiator at one point in the loop-reactor instead of 2 minutes apart as required by the standard formulation. This would also easily accommodate any changes in flow rate that would influence the distance required between the two feeding positions.

Two experimental runs were therefore preformed at the same operating conditions but with the time between the addition of the $FeSO_4$-solution and cumene hydroperoxide at 30 seconds and 2 minutes respectively.

The product properties obtained with the two runs are shown below. It seems as though the variation in addition time of the initiator does not affect the product properties since these are quite similar.

Table 6.8: Effect of addition time between initiators on product properties.

Addition time [min]	Average size [micron]	Opacity	Viscosity [cPs]
0.5	1.1	0.92	2600
2	0.91	0.93	2800

The development of the exotherm of the two runs discussed above was also monitored and evidently does not show any dependence of the exotherm on the addition time of the initiators.

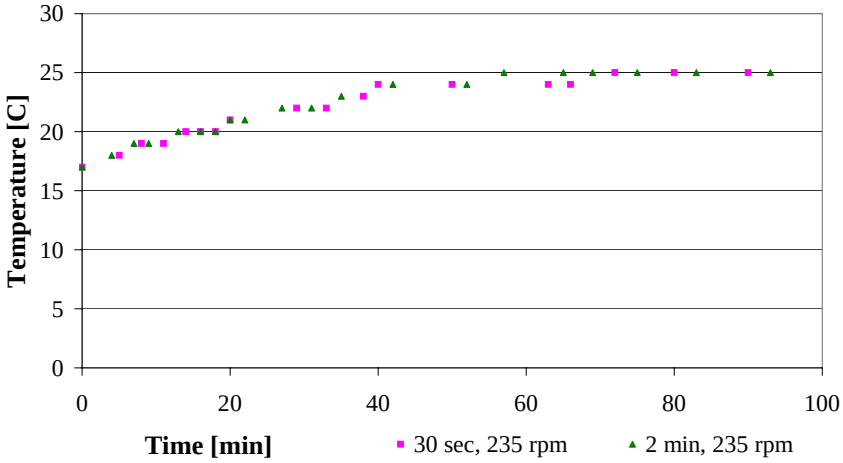


Figure 6.11: Development of the exotherm for samples with different addition time of the initiator.

The SEM images also show no apparent difference between the discreteness and the shape of the beads formed.

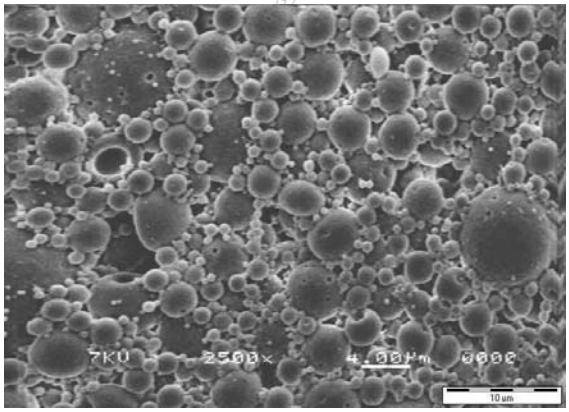


Figure 6.12: SEM image of sample with 2 minutes between addition of components of initiator system.

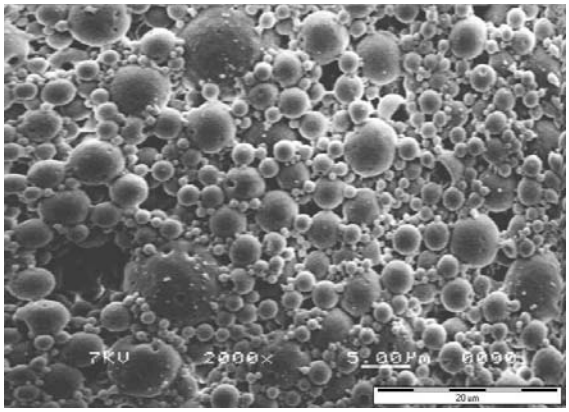


Figure 6.12: SEM image of sample with 30 seconds between addition of components of initiator system.

From the results discussed above it can be concluded that the addition of the components of the initiator system does not have to be 2 minutes apart as required by the standard formulation. *In the continuous process these components can therefore be added as soon as 30 seconds after each other without adversely affecting product properties.*

6.4. RESULTS OF SEMI-CONTINUOUS EXPERIMENTS:

Semi-continuous experiments were conducted with the set-up including the loop-reactor for continuous curing shown in chapter 4. These experiments were done to determine whether it is possible to produce vesiculated beads that are cured when it leaves the loop-reactor and what properties (discreteness and shape of the particles, particle size, opacity and viscosity) can be obtained with such a set-up.

For all the semi-continuous experiments the formulation with added Tween (but without LMA) at a 24 % solids content was used except where mentioned otherwise.

6.4.1. EFFECT OF HEATING TEMPERATURE ON PRODUCT PROPERTIES:

The first experimental run performed with the loop-reactor set-up produced a vesiculated bead product with agglomerated, non-discreet particles and a fairly low opacity at 0.79. This product was not cured at the time it exited the reactor since the temperature still increased with a further 5 °C. At this point it was thought that the formation of the agglomerated particles could be attributed to the incomplete development of the reaction and the temperature of the water bath supplying the heat to the reactor was consequently increased in an attempt to force the reaction to completion. For the first two experimental runs the loop-reactor consisted of a total of 200 m of pipe with the first half equipped with a heating section. This heating section supplied heated the beads for 15 minutes as was found adequate for the experiments discussed in section 6.3 above at the flow rate employed.

The table below gives a comparison of some of the product properties obtained with an increase in the jacket temperature from 42 °C to 53 °C. It was found that the increase in curing temperature caused an increase in the opacity of the product although this property still did not reach an acceptable value and the product was also not cured when it left the reactor. However an increase in the temperature of the product was observed when compared to that of run KG3 and only a further rise of 2 °C in its temperature occurred after it exited the reactor.

Table 6.9: Effect of increased temperature of the water in the jacket of the loop-reactor on particle discreetness, opacity and the exotherm.

Run no.	H2O T [C]	Product T [C]	Exotherm reached?	Opacity	Discreet	Agglomerates?
KG3	42	28	no	0.79	no	yes
KG4	53	38	no	0.87	no	yes

Although the product produced with the loop-reactor did not display acceptable properties, the beads produced were in fact round particles with a distribution and average particles size comparable to that obtained with the bench scale batch experiments. The agglomeration can clearly be seen on the SEM image below.

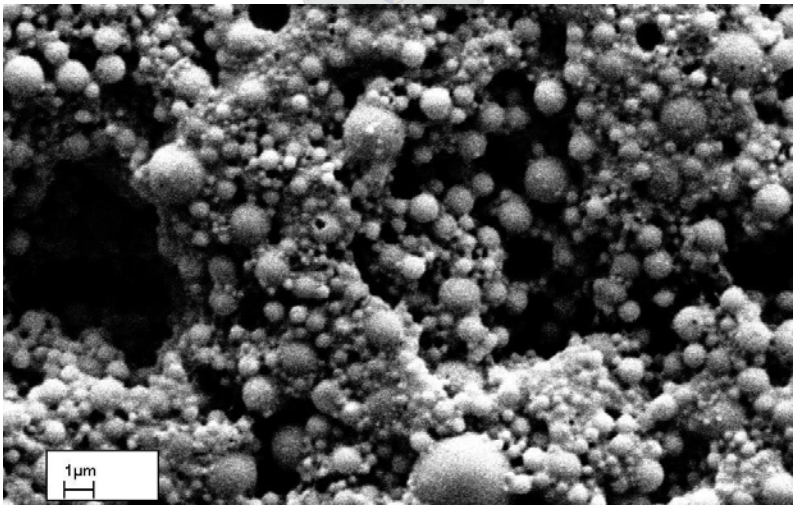


Figure 6.13: SEM image of run KG 4 produced with the loop-reactor.

For run KG 4 two additional samples were drawn from the process at a position after the initiator was added, but before entering the loop-reactor. The one sample was left to cure in a water bath at 55 °C, whilst the other was stirred for 2 minutes and then

introduced to the same water bath. This was done to determine whether the agglomeration and poor product properties were caused by the loop-reactor in itself or with the addition of the initiator even before entering the reactor. The results of these two runs are shown below.

Table 6.10: Samples cured in water bath and not through loop-reactor.

Run no.	Opacity	Discreet	Agglomerates?
KG4a (water bath)	0.85	no	yes
KG4b (stirred)	0.86	no	yes

Since the properties obtained with the samples cured in the water bath are comparable to that obtained with the loop-reactor (table 6.9) it seems as though the loop-reactor was not the cause of the non-discreet and agglomerated particles being produced. Instead it could have been that the initiator was added at too low a concentration and that this inhibited the development of the reaction.

6.4.2. EFFECT OF INITIATOR FLOW RATE AND CONCENTRATION ON PRODUCT PROPERTIES:

As mentioned above the possibility existed that the concentration or the flow rate of the initiator was at too low levels and that this adversely effected the product properties. Some experimentation was therefore performed with a variation in the flow rate and the concentration of the initiator respectively.

Table 6.11: Effect of increased flow rate and concentration of the initiator on product properties.

	Initiator			
Run no.	Addition [ml/min]	Conc . [g/ml]	Opacity	Discreet
KG4a	7	0.008	0.85	no
KG5a	14	0.01	0.91	yes
KG6a	14	0.04	0.89	no

If the result of runs KG 4 and KG 5 are compared it can be seen that the increased flow rate of the initiator lead to an increase in the opacity and it also enhanced the discreteness of the particles produced. In contrast to this the run (KG 6) conducted with the same increased flow rate at 14 mℓ/min with an increased concentration

produced particles with a lower opacity and a loss in discreteness of the particles, similar to the initial experiments where an increase in initiator concentration reduced the opacity.

It therefore seems as though the initiator concentration should be kept at approximately 0.008 g/mℓ at a flow rate of 14 mℓ/min.

6.4.3. EFFECT OF INCREASED LENGTH OF THE REACTOR ON PRODUCT PROPERTIES:

The result obtained with run KG 4 discussed in section 6.4.1 seemed to suggest that this product was closer to reaching the peak exotherm when it left the reactor than that of run KG 3. The length of the reactor was therefore increased to allow more time for the reaction to be completed inside the reactor. An extra 100 meters was added to the reactor (now 300 meters in length), constituting a further 15 minutes of residence time available for curing inside the pipe, with heating still being applied to the first 100 meters.

KG 6 was performed with this increased length of the loop-reactor and with an increase in initiator concentration from 0.008 g/mℓ, used up to this point, to 0.04 g/mℓ as shown in section 6.4.2. Again a sample (KG6a) was drawn after addition of the initiator and left in a water bath to cure to investigate the effect of the loop on product properties.

Table 6.12: Properties of experimental run with increased length of the reactor.

Run no.	H2O T [C]	Product T [C]	Exotherm reached?	Size [micron]	Opacity	Discreet	Agglomerates?
KG6a	-	-	-	0.72	0.89	no	no
KG6	50	28	no	0.78	0.81	no	yes

If the properties of samples KG6 and KG6a are compared it again seems as though the low opacity values achieved are not only limited to the product produced through the loop but it also occurs with the product cured in the water bath. As discussed in the section above the reason for the low opacity in this particular run can be attributed

to the high concentration of initiator used. Unfortunately it does seem as though the loop-reactor is responsible for the formation of the agglomerates in the product. It could be that the stabilisation system of the HEC and PVOH is broken down with the continued movement through the reactor and the shear forces exerted on the particles by the reactor walls. This theory is supported by the low viscosity of the product at approximately 200 cPs.

Although the loop-reactor experienced an increase in length and more time was therefore allowed for the beads to cure, it still was not entirely cured when it left the loop-reactor. A further increase of 2°C occurred after the product exited the process, suggesting that the peak exotherm had not been reached inside the reactor.

6.4.4. EFFECT OF AN INCREASED HEATING SECTION ON PRODUCT PROPERTIES:

In an attempt to force the exothermic reaction to completion inside the 300 meter loop-reactor, a further 100 meters of jacketed heating was added to it. This extra section was added after the existing 100 meters of heating so that the first 200 meters of the reactor would be jacketed and only the last 100 meters are without any heating.

Some other changes were also made to the experimental set-up. This entailed two extra sample points being added. The one sample point was added before the initiator is added, right after the homogeniser, and the other sample point was situated after the 200 meters of heating in the reactor. These points were added to control product properties and monitor the product's development throughout the process.

Table 6.13 show the properties of the different samples taken throughout the process. It not only reveals a variation in the opacity of the product at different sample points, but also shows quite a variation in viscosity and the presence of agglomerates.

Table 6.13: Properties obtained with an increased heating section at different sample positions in the process.

Run no.	Viscosity [cPs]	Opacity	Discreet	Agglomerates?
KG10a (catalise under lab stirrer)	280	0.93	no	no
KG10b (cure in water bath)	1400	0.91	no	no
KG10c (after 100m heating)	1080	0.89	yes	yes
KG10	200	0.91	no	yes

Opacity:

Although the opacity values reported in the table are at acceptable values for the product and those cured in the water bath, these values might be misleading without the luminosities of the white- and black surfaces being reported respectively. These were both at rather low levels (see table below) and therefore produced a seemingly good opacity.

Table 6.14: Luminosity values of the white- and black surfaces.

	Luminosity of	
Sample no.	White surface	Black surface
KG10c	81.8	92
KG10	84.1	91.5

Viscosity:

In section 6.4.3 above it was mentioned that the movement of the particles through the loop-reactor could break down the stabilisation system of the vesiculated beads and that this might be the cause of the low-viscosity product. Therefore the viscosity values of the samples taken throughout the process are reported above and can it clearly be seen that the viscosity reduces as the particles move through the reactor.

Agglomerates:

Again agglomerates were only present in the samples drawn from the loop-reactor.

From the above discussion it can be concluded that *the movement of particles through the loop-reactor causes a reduction in the viscosity of the product as well as the formation of agglomerates.*

6.4.5. EFFECT OF INCREASED STABILSER CONCENTRATION ON PRODUCT PROPERTIES:

The reduction in viscosity of the product as it flows through the loop-reactor may be attributed to the degradation of the stabilisation system and therefore the concentration of the stabilisers (HEC and PVOH) was increased in an attempt to overcome this problem. The first experiment, run KG 11, was performed with 30 % more HEC while the second run, KG 12, was performed with an increase of 30 % in both stabilisers at a constant solids content. The product properties of all the samples taken through out the process are shown below.

Table 6.15: Product properties of runs performed with an increase in stabiliser concentration.

Run no.	Viscosity [cPs]	Opacity	Discreet	Agglomerates?
KG11a (catalise under lab stirrer)	-	0.88	no	no
KG11b (cure in H2O-bath)	-	0.85	no	no
KG11c (after 200m heating)	250	0.88	no	no
KG11	200	0.88	no	no
KG12a (catalise under lab stirrer)	3200	0.94	no	no
KG12b (cure in H2O-bath)	3400	0.91	no	no
KG12c (after 200m heating)	180	0.88	no	no
KG12	250	0.88	no	no

Notes
KG11 - 30% more HEC
KG12 - 30% more HEC and PVOH

It can be seen that the increase in stabiliser concentration prevented the formation of agglomerates in the product, but the other properties, such as the opacity, discreteness of the particles and the viscosity still remained at very low and unacceptable values. Even with the increase in concentration of the stabilising system it seems as though the shear forces exerted on the particles are still disrupting the formation of discrete particles and other acceptable product properties.

What is encouraging to note from the results shown above is the high opacity values obtained with runs KG 12 a and KG 12 b. These results suggest that with an increase in the viscosity of the product a subsequent increase in the opacity does occur.

6.4.6. EFFECT OF STATIC MIXERS IN THE LOOP-REACTOR:

Since the increase in stabiliser concentration did not yield the desired results of acceptable viscosity and opacity levels it was decided to introduce static mixers to the loop-reactor at regular intervals. It was postulated that these would increase the mixing intensity inside the reactor and prevent the heavy stabiliser chains from separating from the other components in the formulation with the formation of boundary layers as the fluid flows inside the reactor. For this experimental run the standard formulation (standard levels of stabilisers and no Tween), an increased jacket temperature of 60 °C and increased solids content at 28 % was used. All of these adjustments were made to aid the prevention of settling in the pipe.

Table 6.16: Effect of static mixers added to the loop-reactor on product properties.

Run no.	Viscosity [cPs]	Opacity	Discreet	Agglomerates?
KG13a (catalise under lab stirrer)	1840	0.93	yes	no
KG13b (cure in water bath)	1360	0.92	yes	no
KG13c (cure at room temp.)	500	0.88	yes	no
KG13d (after 200m heating)	520	0.93	yes	no
KG13	720	0.94	yes	no

With the introduction of the static mixers and the increased solids content acceptable opacity and viscosity values were obtained for the product produced after curing in the loop reactor. This product also contained discreet particles and no agglomerates were formed as shown by the SEM image below.

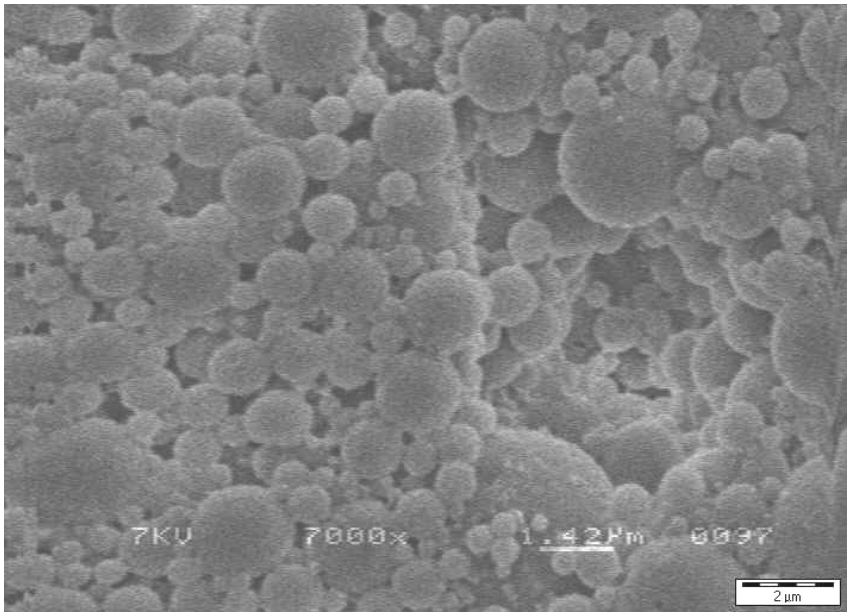


Figure 6.14: SEM image of sample cured in loop reactor.

This result proves that vesiculated particles with acceptable properties can be produced with the homogeniser and loop-reactor set-up at the operating conditions used in this particular experimental run. These can be used in the construction of the fully continuous set-up.

CHAPTER 7: CONCLUSIONS AND RECOMMENDATIONS

7.1. INTRODUCTION:

Initially this study was focussed on producing vesiculated beads with the homogeniser suitable for introduction into gloss paint. For this particular application vesiculated beads in the order of 1 micron and with other properties similar to that obtained with the Cowles process would be required. Soon it however became apparent that the homogeniser could be incorporated in a continuous process for the production of vesiculated beads.

The homogeniser process started off as a laboratory scale batch process from where it developed, first into a bench-scale batch process and then into a semi-continuous bench-scale process that utilised newly designed equipment. This equipment included a homogeniser designed from the laboratory scale batch model, a high-pressure pump, continuous initiator feed through a venturi mixer and a loop reactor for continuous curing of the beads. The main aim of all the experiments performed with the above-mentioned equipment was to investigate and ultimately determine the process conditions that favour the production of vesiculated beads with acceptable product properties. These are discussed in the sections that follow.

7.2. CONCLUSIONS:

7.2.1. IMPORTANT OPERATING PARAMETERS:

Laboratory-scale batch experiments:

During the execution of the laboratory-scale batch experiments the important operating parameters and its' effect on product properties were determined.

- It was found that the *pressure, number of passes and the flow rate* significantly influenced the particle size of the product and that an increase in any of these parameters resulted in a decrease in the average particle size.
- The opacity and viscosity of the product were also significantly effected by changes in the flow rate through the homogeniser and again an increase in the flow rate caused a decrease in both of the properties mentioned above. Further it seemed as though the pressure also had a meaningful influence on the viscosity.
- By changing the *plungers* inside the homogeniser a notable effect on the average particle size was observed. With an increase in the number of grooves on the plunger or with an increase in the number of sections an increase in the shear exerted on the particles occurred and this lead to a consequent reduction in particle size.

Bench-scale batch experiments:

- The important operating parameters for the bench-scale batch experiments seemed to be the number of passes through the homogeniser and the number of plungers. It can be concluded that the number of passes through the homogeniser should be kept at one, with the use of a different number of plungers to manipulate the average particle size. With an increase in the number of passes, the shear exerted on the particles by the pump becomes too large and the particles tend to loose discreteness and opacity.
- During the bench-scale batch experiments the effect of the *curing temperature* on product properties was also investigated. It was found that curing at elevated temperature (50 – 70 °C) enhances the discreteness of the particles and consequently improved values for the opacity was achieved.

7.2.2. IMPORTANT CHEMICAL VARIATIONS:

The following conclusions can be made for both the laboratory-scale and bench-scale set-ups:

- It was found that the viscosity of the product generally increases as the concentration of the components of the stabiliser system, i.e. *hydroxy ethyl cellulose and partially hydrolysed polyvinyl acetate*, is increased. With a variation in the concentration of these components a subsequent variation in the solids content is experienced and this has a further effect on the viscosity.
- With the addition of *Tween*, a surfactant, to the process an increase in the opacity as well as the viscosity is experienced. Furthermore a slight decrease in the average particle size occurs.
- A hydrophobic monomer, *laurel methacrylate*, was also added to the formulation in an attempt to increase the water resistance of the final product. It was found that this additional monomer caused an increase in the average particle size and the viscosity of the product. Unfortunately a loss in discreteness of the particles and therefore a decrease in the opacity of the samples cured at room temperature occurred. This problem was however overcome with the application of heat during the curing process as discussed in section 7.2.1.

7.2.3. CONTINUOUS PROCESS:

- It is possible to produce vesiculated beads with the standard formulation at 28 % total solids content with the semi-continuous process. This process utilises a homogeniser, high-pressure pump, continuous addition of the initiator through a venturi-mixer and a loop reactor to facilitate continuous curing of the beads. The beads produced with this process exhibited acceptable product properties when compared to that of the Cowles process.
- Unfortunately the beads were not entirely cured when leaving the process and the temperature still increased with about 1 °C after exiting the loop reactor.

- Contrary to current beliefs in the paint industry this study shows that the concept of continuous curing can be applied to the vesiculated beads systems. With further refinement/development of the continuous process presented here it could very well be the future of the vesiculated beads industry.

7.2.4. MECHANISM FOR PARTICLE FORMATION:

Factors that influence water affinity:

- It was found that the amount of water present in the organic phase and therefore responsible for the formation of the vesicles might be linked to the *final liquid acid value* of the polyester being used. A linear correlation exists between the water content of the organic phase and the final liquid acid value of the polyester for the range of the latter specified.
- With an increase in the amount of *DETA* an increase in the water taken up by the polyester occurs. A saturation point however exists at about 60 % (mass) for the water content.
- An increase in the amount of *Tween* added leads to an increase in the water affinity of the polyester, again until about 60 % (mass) of water is entrapped. If more Tween is added after this point, a decrease in the water uptake occurs.
- The presence of the *partially hydrolysed polyvinyl acetate* is critical to achieve water uptake in the organic phase because without this stabiliser practically no water is entrapped within the organic phase. This indicates that it is actually the affinity of the polyester for the water phase that causes the formation of vesicles, and not its' affinity for pure water.
- The addition of *laurel methacrylate* causes a decrease in the amount of water taken up by the polyester

Level of components used in formulation:

- The optimum level of the *DETA* and the *Tween* required to achieve the maximum water content of the organic phase should be determined for each

batch of polyester manufactured. It seems as though the optimum level lies at different values for each batch and therefore it should be determined experimentally for each batch.

- It should be noted that the optimum amounts of DETA or Tween used to achieved a maximum water content does not necessarily represent the optimum level of these components required to produce acceptable values for other product properties, such as opacity.

Linking product properties to water affinity:

- No simple correlation exists between the amount of water entrapped within the organic phase and the opacity although a water content of between 50 – 60 % (mass) seems desirable to achieve an acceptable opacity.
- The degree of vesiculation and especially the size of the vesicles play an important role in the opacity achieved. Therefore two different products can have the same water content in the organic phase but might display different opacity values.

Pectora roborant cultus recti

7.3. RECOMMENDATIONS AND FUTURE WORK:

The following recommendations can be made upon completion of this study:

- The fully continuous set-up for the continuous processing of vesiculated beads is currently under construction and should be used for the further development of a process for the continuous production of the beads. It is recommended that these experiments be performed at a lower flow velocity through the loop reactor than that used in this study. This will ensure a longer residence time for the beads inside the reactor and the reaction might therefore be completed when the beads exit the process. The heating section can also be lengthened in an attempt to force the reaction to completion.
- An in-depth study concerning the water taken up by the polyester and other product properties, such as viscosity, should be conducted. It is recommended that the test methods described in this study should be used to determine the water content of the organic phase for different polyester batches and these batches used to produce vesiculated beads using a standard process. By determining the product properties and comparing the different results meaningful conclusions could be drawn.
- Further development of the method of determining the degree of vesiculation could be done until an easy and reliable method is obtained. This will lead to a better understanding of the relationship between the degree of vesiculation, average size and shape of the vesicles and the wall thickness of the beads and the product properties such as viscosity and opacity.

REFERENCES:

1. Scholz, W.**;** *Surface coatings Volume 1, Raw materials and their Usage,* Third edition, Chapter 31; Chapman & Hall, London, **1993.**

2. Ritchie, P.; Stewart, D.M.D.; *Surface coatings Volume 1, Raw materials and their Usage,* Third edition, Chapter 23; Chapman & Hall, London, **1993.**

3. Roskill reports on metals and minerals; *Titanium minerals and pigments*; http://www.roskill.co.uk; **2002.**

4. *Paint components*; www.icipaints.com/dulux; **2002**.

5. Gaulius, R.J.; *Surface coatings Volume 1, Raw materials and their Usage,* Third edition, Chapter 22; Chapman & Hall, London, **1993.**

6. Gillian, J.; Kershaw, R.W.; *Vesiculated cross-linked polyester resin granules,* Application number 70\8592; Dulux Australia ltd., **1969**.

7. http://www.coatingworld.com, December **2002.**

8. http://www.paintinfo.org, December **2002.**

9. Farrall, A. W.; *Engineering for Diary and Food Products,* Chapter 12; John Wiley and Sons Inc.

10. McKetta, J.J.; *Encyclopaedia of Chemical Processing and Design,* Vol. 18; Marcel Dekker Inc., **1983**, p76 – 81.

11. Penboss, I.A.; *Surface coatings Volume 1, Raw materials and their Usage,* Third edition, Chapter 18; Chapman & Hall, London, **1993.**

12. McKetta, J.J.; *Encyclopaedia of Chemical Processing and Design*, Vol. 39; Marcel Dekker Inc., **1992**, p323 – 327.

13. Gunning, R.H.; Henshaw, B.C.; Lubbock, F.J.; *Polyester granules and process*, Application number 73/8448; Dulux Australia ltd., **1972**.

14. Tioxide group ltd.; *Bead polymerization process;* Application number GB2075523; **1981**.

15. Goldsbrough, K.; Hodge, J.C.W.; *Production of vesiculated polymer beads*, Application number 82/7714; Tioxide group plc, **1982**.

16. Karickhoff, M.; *Vesiculated beads*, Application number 517/491; The Sherwin Company, Ohio, **1983**.

17. Engelbrecht, J.; Internal report: *Vesiculated beads: Various aspects of manufacture*; Plascon Research Centre, Stellenbosch, **2002**.

18. Terblanche, J.C.; *The development of vesiculated beads;* MSc.Eng thesis, Department of Chemical Engineering, University of Stellenbosch, April **2003.**

19. Kirk-Othmer; *Chemical Encyclopaedia of chemical technology*, Volume 8, Third edition; **1978**, p921-p923.

20. *Homogenizers*, Ormerod Engineers Ltd.; Rochdale, England.

21. Gous, K.; *Homogenization of vesiculated beads;* B.Eng Final year project, Department of Chemical Engineering, University of Stellenbosch, **2000**.

22. Moolman, P.L.; *Rheology of coating systems;* MSc.Eng thesis, Department of Chemical Engineering, University of Stellenbosch, April **2003.**

APPENDIX A: PROPERTIES OF DIFFERENT POLYESTER BATCHES

APPENDIX A1: POLYESTER MANUFACTURED BY COMPANY A

Details	Specification	DV 2721	DV 4696	DV 5008
Batch time [hrs]	24	-		
Processing temperature [C]	220	-		
Final acid value [mg KOH/g]	24 - 28	-		
Total TBC [ppm]	177	-		
Final Liquid Properties				
Acid value [mg KOH/g]	16 - 19	19.0	17.9	18.7
Volatile content [%]	32 - 34	27.8		
Viscosity [Gardner Holdt]	T - 8 - U	W - 9 - X		
Viscosity [cPs] (LVF, #3, 60 rpm)	900 - 1100	1625		
Stability @ 120 C	4 hrs min	-		
Relative density	1.09 - 1.13	1.134		
Curing characteristics @ 25 C				
Time to gel [min]	40 - 55	96.8		
Cure time (gel to peak) [min]	50 - 65	111.3		
Peak exotherm [C]	178 - 185	186		
GPC Analysis				
Number average		1662		
Weight average		3331		
Polydispersity		2.004		

Pectora roborant cultus recti

APPENDIX A2: POLYESTER MANUFACTURED BY COMPANY B

Details	Specification	A	B	C
Batch time [hrs]	24	14.5	11	20.5
Processing temperature [C]	220	220	220	210
Final acid value [mg KOH/g]	24 - 28	23.6	25.5	25.6
Total TBC [ppm]	177	183	177	183
Final Liquid Properties				
Acid value [mg KOH/g]	16 - 19	16.0	18.3	16.5
Volatile content [%]	32 - 34	30.1	29.9	31.7
Viscosity [Gardner Holdt]	T - 8 - U	T - 8 - U	T - 3 -U	T - 6 - U
Viscosity [cPs] (LVF, #3, 60 rpm)	900 - 1100	810	804	780
Stability @ 120 C	4 hrs min	18 min	26 min	16 min
Relative density	1.09 - 1.13	1.124	1.123	1.124
Curing characteristics @ 25 C				
Time to gel [min]	40 - 55	45	54	63
Cure time (gel to peak) [min]	50 - 65	56.3	63	77
Peak exotherm [C]	178 - 185	186	198.9	192
GPC Analysis				
Number average		1549	1673	1523
Weight average		4332	3732	3541
Polydispersity		2.79	2.23	2.32

Pectora roborant cultus recti

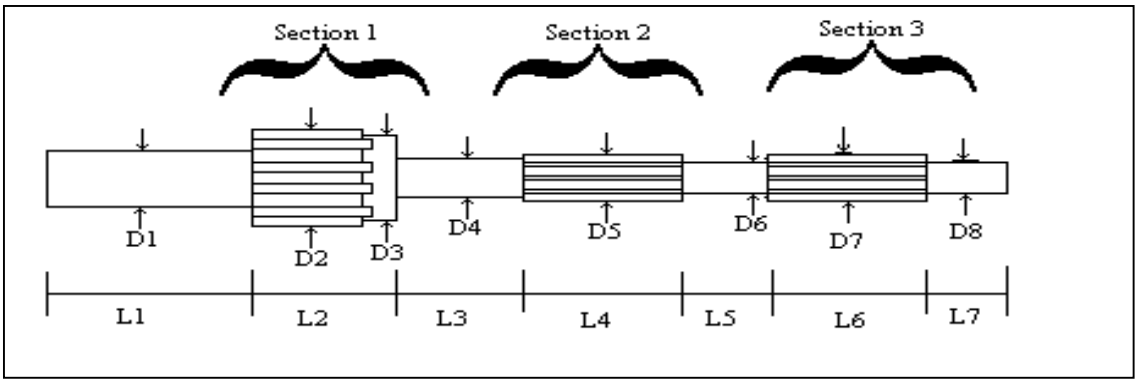
APPENDIX A2: POLYESTER MANUFACTURED BY COMPANY B

Details	D	I
Batch time [hrs]	26.5	11
Processing temperature [C]	210	220
Final acid value [mg KOH/g]	27.2	31.5
Total TBC [ppm]	177	177
Final Liquid Properties		
Acid value [mg KOH/g]	17.9	20.1
Volatile content [%]	31.6	31.4
Viscosity [Gardner Holdt]	-	T - 1 - U
Viscosity [cPs] (LVF, #3, 60 rpm)	720	660
Stability @ 120 C	20 min	23 min
Relative density	1.122	1.127
Curing characteristics @ 25 C		
Time to gel [min]	67	44.5
Cure time (gel to peak) [min]	81	51.3
Peak exotherm [C]	189.5	202
GPC Analysis		
Number average	1377	-
Weight average	2768	-
Polydispersity	2.01	-

Pectora roborant cultus recti

APPENDIX B: PLUNGER DIMENSIONS

APPENDIX B1: PLUNGER DIMENSIONS FOR LABORATORY SCALE HOMOGENISER

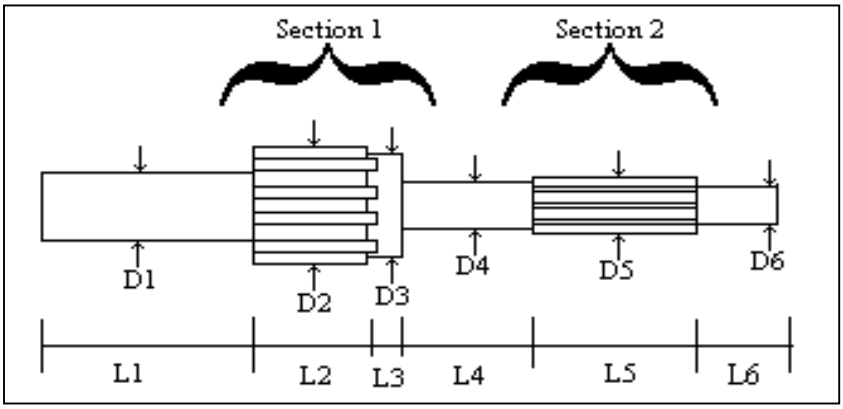


Plunger no.	Plunger Dimensions (mm)							
	D1	D2	D3	D4	D5	D6	D7	D8
1	4.70	7.70	7.30	3.30	4.70	3.30	-	-
	L1	L2	L3	L4	L5	L6	L7	
	7.6	7.5	6.6	8.4	8.2	-	-	
2	D1	D2	D3	D4	D5	D6	D7	D8
	4.80	7.70	7.20	3.00	4.70	3.30	-	
	L1	L2	L3	L4	L5	L6	L7	
	7.8	7.6	6.8	8.2	8.3	-	-	
3	D1	D2	D3	D4	D5	D6	D7	D8
	4.70	7.70	7.20	3.20	4.70	3.30	4.7	3.3
	L1	L2	L3	L4	L5	L6	L7	
	7.7	7.7	4.1	5.5	4.1	5.5	4	

All groove dimensions as below:

Groove dimensions [mm]			
Section 1		Section 2	
Length	Depth	Length	Depth
5.5	0.2	8.5	0.2

APPENDIX B2: PLUNGER DIMENSIONS FOR BENCH SCALE HOMOGENISER



	1	2
D1	9.1	9.2
D2	18.05	18.05
D3	14.6	14.6
D4	6.45	6.45
D5	9.2	9.2
D6	6.45	6.45
L1	11.45	11.45
L2	8.7	8.6
L3	6.3	6.6
L4	14.7	14.7
L5	16.2	16.35
L6	15.7	15.5
Groove depth	1.7	4.43

All measurements in mm

APPENDIX C: REGRESSION RESULTS

APPENDIX C1: REGRESSION RESULTS - Plunger 1

1. Opacity

ANOVA-table

	Sums of Squares	df	Mean Squares	F	p-level
Regress.	0.0032	7	0.0004518	0.8223	0.5785
Residual	0.0132	24	0.0005495		
Total	0.0164				

	BETA	St. Err. of BETA
NOZZLE	-0.171	0.185
STROKES	0.165	0.185
PASSES	0.101	0.196
ADD_TIME	0.137	0.206
STIRRING	0.054	0.183
WATER	0.334	0.190
CURING_T	0.120	0.185

Correlation coefficients

	NOZZLE	STROKES	PASSES	ADD_TIME	STIRRING	H2O
NOZZLE	1	-0.0350	0.0000	-0.1109	-0.0050	0.0000
STROKES	-0.0350	1	-0.0058	0.1162	0.0139	0.0175
PASSES	0.0000	-0.0058	1	-0.3364	0.0100	0.0000
ADD_TIME	-0.1109	0.1162	-0.3364	1	0.0269	-0.2470
STIRRING	-0.0050	0.0139	0.0100	0.0269	1	-0.0067
WATER	0	0.0175	0.0000	-0.2470	-0.0067	1
CURING_T	-0.009	-0.0445	0.0089	-0.1099	-0.0112	0.0089
OPACITY	-0.194	0.1881	0.0553001	0.0475	0.0584	0.3042

	CURING_T	OPACITY
NOZZLE	-0.0089	-0.1936
STROKES	-0.0445	0.1881
PASSES	0.0089	0.0553
ADD_TIME	-0.1099	0.0475
STIRRING	-0.0112	0.0584
WATER	0.0089	0.3042
CURING_T	1	0.1019
OPACITY	0.1019	1

2. Viscosity

ANOVA-table

	Sums of Squares	df	Mean Squares	F	p-level
Regress.	58594684.04	7	8370669.1	1.6273278	0.17569569
Residual	123451503.5	24	5143812.6		
Total	182046187.5				

	BETA	St. Err. of BETA
NOZZLE	-0.4439	0.1694
STROKES	-0.1855	0.1697
PASSES	-0.3178	0.1797
ADD_TIME	-0.0227	0.1892
STIRRING	-0.0340	0.1682
WATER	0.0024	0.1745
CURING_T	-0.0011	0.1694

Correlation coefficients

	NOZZLE	STROKES	PASSES	ADD_TIME	STIRRING	WATER
NOZZLE	1	-0.0350	0.0000	-0.1109	-0.0050	0
STROKES	-0.0350	1	-0.0058	0.1162	0.0139	0.0175
PASSES	0.0000	-0.0058	1	-0.3364	0.0100	0.0000
ADD_TIME	-0.1109	0.1162	-0.3364	1	0.0269	-0.2470
STIRRING	-0.0050	0.0139	0.0100	0.0269	1	-0.0067
WATER	0	0.0175	0.0000	-0.2470	-0.0067	1
CURING_T	-0.0089	-0.0445	0.0089	-0.1099	-0.0112	0.0089
VICOSITY	-0.4347	-0.1711	-0.3095	0.1105	-0.0382	0.0050

	CURING_T	VICOSITY
NOZZLE	-0.0089	-0.4347
STROKES	-0.0445	-0.1711
PASSES	0.0089	-0.3095
ADD_TIME	-0.1099	0.1105
STIRRING	-0.0112	-0.0382
WATER	0.0089	0.0050
CURING_T	1	0.0112
VICOSITY	0.0112	1

APPENDIX C2: REGRESSION RESULTS - Plunger 2

1. Particle size

ANOVA-table

	Sums of Squares	df	Mean Squares	F	p-level
Regress.	45.880	5	9.176	5.189	0.002
Residual	45.980	26	1.768		
Total	91.86				

	BETA	St. Err. of BETA
NOZZLE	-0.1484	0.1636
STROKES	-0.4932	0.1621
PASSES	-0.4190	0.1630
WATER	0.1206	0.1648
CURING_T	-0.0346	0.1653

Correlation coefficients

	NOZZLE	STROKES	PASSES	WATER	CURING_T	SIZE
NOZZLE	1	-0.0105	-0.1160	0.0331	0.0969	-0.0939
STROKES	-0.0105	1	-0.0023	-0.0673	0.0260	-0.4997
PASSES	-0.1160	-0.0023	1	-0.0385	0.0296	-0.4063
WATER	0.0331	-0.0673	-0.0385	1	0.1783	0.1588
CURING_T	0.0969	0.0260	0.0296	0.1783	1	-0.0527
SIZE	-0.0939	-0.4997	-0.4063	0.1588	-0.0527	1

2. Opacity

ANOVA-table

	Sums of Squares	df	Mean Squares	F	p-level
Regress.	0.0041	5	0.0008	2.5358	0.0536
Residual	0.0084	26	0.0003		
Total	0.0125				

	BETA	St. Err. of BETA
NOZZLE	-0.1363	0.1765
STROKES	0.4915	0.1733
PASSES	0.0999	0.1743
WATER	-0.1552	0.1746
CURING_T	-0.0189	0.1765

Correlation coefficients

	NOZZLE	STROKES	PASSES	WATER	CURING_T	OPACITY
NOZZLE	1	-0.0161	-0.1048	-0.0383	0.1598	-0.1517
STROKES	-0.0161	1	0.0423	-0.0589	0.0194	0.5067
PASSES	-0.1048	0.0423	1	-0.0383	0.0300	0.1403
WATER	-0.0383	-0.0589	-0.038	1	0.1068	-0.1848
CURING_T	0.1598	0.0194	0.030	0.1068	1	-0.0447
OPACITY	-0.1517	0.5067	0.140	-0.1848	-0.0447	1

2. Viscosity

	BETA	St. Err. of BETA
NOZZLE	-0.1358	0.2566
STROKES	0.0530	0.2452
PASSES	-0.0899	0.2458
WATER	-0.0050	0.2489
CURING_T	-0.0701	0.2611

Pectora roborant cultus recti

APPENDIX C3: REGRESSION RESULTS - Plunger 3

1. Particle size

ANOVA-table

	Sums of Squares	df	Mean Squares	F	p-level
Regress.	3.158	4	0.789	5.644	0.093
Residual	0.420	3	0.140		
Total	3.577				

	BETA	St. Err. of BETA
NOZZLE	-0.285	0.198
STROKES	-0.681	0.199
PASSES	-0.547	0.198
WATER	-0.004	0.199

Correlation coefficients

	NOZZLE	STROKES	PASSES	WATER	SIZE
NOZZLE	1	0.034	-4.2E-17	5.9E-17	-0.308
STROKES	0.034	1	0.034	-0.102	-0.709
PASSES	-4.2E-17	0.034	1	-1.5856E-17	-0.570
WATER	5.9E-17	-0.102	-1.6E-17	1	0.065
SIZE	-0.308	-0.709	-0.570	0.065	1

2. Opacity

ANOVA-table

	Sums of Squares	df	Mean Squares	F	p-level
Regress.	0.009	4	0.002	1.063	0.50
Residual	0.006	3	0.002		
Total	0.015				

	BETA	St. Err. of BETA
NOZZLE	-0.614	0.372
STROKES	0.462	0.374
PASSES	0.103	0.372
WATER	-0.015	0.373

Correlation coefficients

	NOZZLE	STROKES	PASSES	WATER	OPACITY
NOZZLE	1	0.034	-4.2E-17	5.9E-17	-0.598
STROKES	0.034	1	0.034	-0.102	0.446
PASSES	-4.2E-17	0.034	1	-1.5856E-17	0.119
WATER	5.9E-17	-0.102	-1.6E-17	1	-0.063
OPACITY	-0.598	0.446	0.119	-0.063	1

3. Viscosity

ANOVA TABLE

	Sums of Squares	df	Mean Squares	F	p-level
Regress.	176160	4	44040	1.183	0.464
Residual	111668	3	37223		
Total	287828				

	BETA	St. Err. of BETA
NOZZLE	-0.460	0.360
STROKES	0.568	0.362
PASSES	0.168	0.360
WATER	-0.194	0.362

Correlation coefficients

	NOZZLE	STROKES	PASSES	WATER	VICOSITY
NOZZLE	1	0.0340	-4.2293E-17	5.9482E-17	-0.4409
STROKES	0.0340	1	0.0340	-0.1021	0.5781
PASSES	-4.2293E-17	0.0340	1	-1.5856E-17	0.1878
WATER	5.9482E-17	-0.1021	-1.5856E-17	1	-0.2524
VICOSITY	-0.4409	0.5781	0.1878	-0.2524	1

APPENDIX C3: EFFECT OF HEC AND PVOH CONCENTRATIONS ON VISCOSITY

	BETA	St. Err. of BETA
% HEC	0.665	0.221
% PVOH	0.118	0.221

Correlation coefficients

	%_HEC	%_PVOH	VICOSITY
%_HEC	1	0.23	0.69
%_PVOH	0.23	1	0.27
VICOSITY	0.69	0.27	1

Correlation coefficients

	% HEC	% PVOH	% SOLIDS	VICOSITY
% HEC	1	0.226	0.735	0.692
% PVOH	0.226	1	0.827	0.269
% SOLIDS	0.735	0.827	1	0.587
VICOSITY	0.692	0.269	0.587	1

Pectora roborant cultus recti

APPENDIX D: EXPERIMENTAL DATA FOR BATCH EXPERIMENTS

APPENDIX D1: EXPERIMENTAL DATA FOR LAB SCALE EXPERIMENTS WITH *PLUNGER 1*

Run no	Nozzle	Strokes [min-1]	Passes	Add time [min]	Stirring [rpm]	Water	Curing T [C]	Ambient T [C]	Pressure [bar]	Vicosity [cPs]	Particle size [micron]	Opacity
K101	Open	26	2	1	153	Beginning	50	21	6	7700	6.94	0.94
K105	Open	26	5	1	153	End	50	21	6	3380	3.4	0.91
K103	Open	70	2	1	155	End	24	24	9	760	2.18	0.94
K107	Open	76	5	1	155	Beginning	24	24	6.5	380	2.04	0.92
K120	Closed	60	2	1:05	304	Beginning	24	24	12	840	3	0.94
K127	Open	80	2	4	304	Beginning	24	24	10.5	300	2.89	0.94
K102	Closed	32	2	1	148	End	23	23	11	600	3.44	0.92
K109	Open	32	2	4	150	End	23	23	6.5	4980	2.44	0.93
K116	Closed	76	5	3:53	148	Beginning	23	23	11.5	260	1.35	0.89
K126	Closed	34	2	4	306	Beginning	23	23	12	220	2.4	0.9
K131	Open	76	5	3:57	308	End	23	23	6.5	440	2.3	0.93
K117	Open	32	2	1	296	Beginning	23	23	6.5	8360	6.95	0.9
K121	Open	30	5	0:56	297	End	25	25	7.5	1480	2.87	0.94
K128	Closed	70	2	4:10	297	End	52	25	10.5	300	1.37	0.87
K119	Open	80	2	1	296	End	52	25	7	8820	1.32	0.95
K111	Open	68	2	4	150	Beginning	52	26	6	1340	2.68	0.94
K108	Closed	64	5	0:57	150	End	52	26	10	660	2.35	0.96
K110	Closed	28	2	3:56	150	Beginning	51	22	11	240	2.9	0.88
K104	Closed	74	2	1	150	Beginning	51	22	11.5	180	1.3	0.94
K114	Closed	30	5	3:58	150	End	53	23	10.5	460	2.5	0.92
K132	Closed	70	5	4	298	Beginning	53	23	11	420	1.37	0.94
K112	Closed	72	2	3:30	147	End	23	23	10	1340	2.03	0.94
K124	Closed	74	5	1	301	End	23	23	10	400	1.4	0.96
K122	Closed	28	5	1:05	303	Beginning	51	23	10	360	1.6	0.93
K125	Open	28	2	3:40	298	End	53	23	6.5	240	3.2	0.95

APPENDIX D1: Continue.....

Run no	Nozzle	Strokes [min-1]	Passes	Add time [min]	Stirring [rpm]	Water	Curing T [C]	Ambient T [C]	Pressure [bar]	Vicosity [cPs]	Particle size [micron]	Opacity
K115	Open	76	5	3:30	155	End	53	23	6.5	300	1.16	0.96
K106	Closed	30	5	1	155	Beginning	23	23	9.5	1100	2.3	0.91
K130	Closed	30	5	3:50	303	End	23	23	9.5	440	2.3	0.93
K129	Open	32	5	3:52	303	Beginning	50	26	5.5	600	2.1	0.93
K123	Open	64	5	1:02	303	Beginning	50	26	8	260	0.6	0.91
K118	Closed	30	2	1	302	End	50	26	10	300	3.1	0.96
K113	Open	30	5	3:30	148	Beginning	26	26	7	1960	2	0.94

1. Experiments were done in random order.
2. Run no: 123, 1 = plunger 1, 23 = standard run no (see experimental design).
3. *Closed* nozzle refers to having the nozzle half a turn open, whilst *open* nozzle refers to three turns open.
4. Water added at the *end* refers to water being added at stage 2 no 7, whilst water added at the *beginning* refers to addition at stage 2, together with no 4 - 6 (see formulation).
5. Elevated *curing temperatures* (50 C and higher) were achieved by putting the samples in a waterbath at a constant temperature.
6. All the stirring in each experiment was done at the same *stirring speed* .

APPENDIX D2: EXPERIMENTAL DATA FOR LAB SCALE EXPERIMENTS WITH PLUNGER 2

Run no	Nozzle	Strokes [min-1]	Passes	Water	Curing T [C]	Ambient T [C]	Pressure [bar]	Vicosity [cPs]	Particle size [micron]	Opacity
8	Closed	72	5	Beginning	23.5	23.5	10.5	11040	2.4	0.93
13	Open	28	5	End	20	20	6	2420	3.3	0.93
27	Open	68	2	End	52	20	6.5	920	2.9	0.91
11	Open	72	2	End	23.5	23.5	6.5	10360	5.9	0.92
24	Closed	70	5	Beginning	51	20	10	180	1.7	0.93
23	Open	70	5	Beginning	51	20	3.5	200	1.8	0.92
22	Closed	32	5	Beginning	51	19	9.5	6840	4.7	0.94
7	Open	76	5	Beginning	21	21	6.5	440	2.7	0.94
1	Open	28	2	Beginning	23.5	23.5	6	12600	7.6	0.90
14	Closed	32	5	End	20	20	11	100	2.2	0.87
25	Open	31	2	End	51	19	4	n/a	3.7	0.91
21	Open	29	5	Beginning	23	23	6.5	208	2.2	0.93
16	Closed	64	5	End	20	20	11.5	160	1.9	0.94
32	Closed	66	5	End	51	21	9	6180	2.8	0.93
12	Closed	68	2	End	19	19	9	340	2.5	0.94
28	Closed	68	2	End	51	23	11.5	2780	4.7	0.94
9	Open	40	2	End	21	21	6	6500	8.1	0.93
5	Open	34	5	Beginning	21	21	5	240	5.1	0.93
3	Open	68	2	Beginning	20	20	7	1620	2.8	0.94
2	Closed	28	2	Beginning	20	20	9.5	200	4.4	0.90
18	Closed	30	2	Beginning	50	21	10	460	3.3	0.94
6	Closed	40	5	Beginning	21	21	6.5	n/a	4.2	0.91
30	Closed	30	5	End	50	20.5	9	n/a	3.9	0.90
10	Closed	29	2	End	23	23	11.5	136	6.9	0.88
20	Closed	68	2	Beginning	52	23	11.5	148	2.3	0.91
26	Closed	29	2	End	52	23	12	1580	5.9	0.92

APPENDIX D2: Continue.....

Run no	Nozzle	Strokes [min-1]	Passes	Water	Curing T [C]	Ambient T [C]	Pressure [bar]	Vicosity [cPs]	Particle size [micron]	Opacity
15	Open	66	5	End	21	21	4.5	11360	2.7	0.94
4	Closed	80	2	Beginning	19	19	11	n/a	2.6	0.94
31	Open	80	5	End	50	23	5	n/a	2.9	0.95
29	Open	34	5	End	51	20.5	4.5	10240	4.4	0.89
19	Open	86	2	Beginning	51	23	5	n/a		0.94
17	Open	40	2	Beginning	51	23	5.5	n/a	6.1	0.9

APPENDIX D3: EXPERIMENTAL DATA FOR LAB SCALE EXPERIMENTS WITH PLUNGER 3

Run no	Nozzle	Strokes [min-1]	Passes	Water	Curing T [C]	Pressure [bar]	Vicosity [cPs]	Particle size [micron]	Opacity
2	Closed	42	5	Beginning	21	10.5	144	1.1	0.91
3	Closed	78	2	Beginning	21	11.5	236	1.3	0.90
7	Open	78	2	End	21	5	368	1.5	0.94
5	Closed	30	2	End	21	10.5	152	2.7	0.86
8	Closed	78	5	End	21	11.5	140	0.65	0.86
6	Open	30	5	End	21	5	155	1.9	0.91
4	Open	78	5	Beginning	21	5	710	1.4	0.92
1	Open	36	2	Beginning	21	6	108	2.6	0.85

APPENDIX D4: EXPERIMENTAL DATA FOR LAB SCALE EXPERIMENTS

(LMA MODIFIED FORMULATION)

Run no	LMA [%]	TWEEN [%]	Curing [C]	Solids [%]	APS [micron]	Opacity	Viscosity [cPs]
LMA1	5	25	Room	22.77	6.17	0.88	2760
LMA2	5	25	Room	27.34	2.17	0.91	9320
LMA3	5	25	77 for 15 min	27	1.79	0.91	4160
LMA6	5	25	50 for 15 min (cumene)	24	13.88	0.92	5100
LMA7	10	25	50 for 15 min	24	30.20	0.80	4820
LMA8	7.5	25	50 for 15 min	24	15.83	0.80	2700
LMA9	7.5	25	Room	24	-	0.77	3380
LMA9-post hom.	7.5	25	Room	24	27.28	0.72	2380

APPENDIX D5: EXPERIMENTAL DATA FOR BENCH SCALE BATCH EXPERIMENTS

Run no	Polyester [batch no]	Change in formulation	TWEEN [%]	Solids [%]	Flow rate [l/min]	Plungers [no.]	Sections	Passes	Pressure [bar]	Solids [%]	Size [micron]	Opacity	Viscosity [cPs]
CH2.1	2721	-	-	28	1.48	2	1	1	16	10.89	indiscreet particles	0.95	160
CH2.2	2721	-	-	28	1.48	2	1	2	16	24.09	0.972	0.94	5480
CH3	2721	-	-	28	1.48	2	1	3	16	26.39	1.379	0.93	900
CH4.1	2721	-	-	28	1.48	none	3	1	0	26.36	9.401	0.9	920
CH4.2	2721	-	-	28	1.48	1	2	1	32	26.5	0.985	0.93	1280
CH1	4696	-	-	28	1.48	1	2	1	30	26.5	0.716	0.91	1800
CH5.1	4696	-	-	28	1.48	none	3	1	0	27.04	9.722	0.9	8720
CH5.2	4696	-	-	28	1.48	2	2	1	16	26.78	1.859	0.84	5600
CH5.3	4696	-	-	28	1.48	2	3	1	30	26.66	0.981	0.8	4500
CH5.4	4696	-	-	28	1.48	3	2	1	13	26.43	2.188	0.87	5580
CH5.5	4696	-	-	28	1.48	3	3	1	31	26.54	1.861	0.83	5820
CH6.1	4696	-	-	28	1.43	none	3	1	0	28.65	9.437	0.89	620
CH6.2	4696	-	-	28	1.43	none	3	2	0	29.35	5.824	0.9	1200
CH11.1	4696	-	-	28	1.36	none	3	1	0	25.79	1.941	0.8	1140
CH11.2	4696	-	-	28	1.36	none	3	2	0	27.11	1.712	0.76	3760
CH12.1	4696	-	-	28	1.36	none	3	1	0	27.08	2.871	0.93	5380
CH12.2	4696	-	-	28	2.31	none	3	1	4	26.3	0.871	0.88	1700
CH13	4696	(-20% styrene)	18.45	28	1.36	none	3	1	0	-	-	0.95	550
CH14	4696	(-20% styrene)	15.43	28	1.36	none	3	1	0	-	-	0.9	340
CH15.1	5008	-	-	28	1.32	none	3	1	0	27.38	2.143	0.87	2850
CH15.2	5008	-	-	28	3.81	none	3	1	2.5	27.38	-	0.86	1680
CH21.1	5008	(-20% styrene)	20	24	1.32	3	3	1	32	19.73	-	0.9	160
CH21.2	5008	(-20% styrene)	20	24	1.32	3	3	1	16.5	21	1.98	0.93	280
CH21.3	5008	(-20% styrene)	20	24	1.32	3	3	1	32	21	0.76	0.89	120
CH21.4	5008	(-20% styrene)	20	24	1.32	3	3	1	16	21.6	-	0.91	140

APPENDIX D5: Continue....

Run no	Polyester [batch no]	TWEEN [%]	Solids [%]	Flow rate [l/min]	Plungers [no.]	Sections	Passes	Pressure [bar]	Solids [%]	Size [micron]	Opacity	Viscosity [cPs]
CH22.1	5008	20	24	1.33	3	1	1	14	22.59	0.787	0.94	320
CH22.2	5008	20	24	1.34	3	3	1	15	22.97	1.143	0.94	380
CH22.3	5008	20	24	1.35	3	3	2	16.5	23.4	0.638	0.92	360
CH22.4	5008	20	24	1.28	3	3	3	17	22.14	0.527	0.87	220
CH23.1	5008	20	28	1.304	4	3	1	32	26.45	0.869	0.89	2200
CH23.2	5008	20	28	1.304	4	3	1	16	26.88	1.209	0.9	5700
CH23.3	5008	20	28	1.304	3	3	1	31	26.87	0.819	0.89	4060
CH23.4	5008	20	28	1.304	3	3	1	19	26.85	1.164	0.89	2400
CH23.4 A	5008	20	28	1.304	3	3	1	19	26.75	0.89	0.85	4800
CH23.4B	5008	20	28	1.304	3	3	1	19	26.84	1.059	0.89	3840
CH23.5	5008	20	28	1.304	3	3	2	19	27.05	0.52	0.86	4100
CH23.6	5008	20	28	1.304	3	3	3	19	26.67	0.441	0.86	2120
CH24.1	5008	50	28	1.21	4	3	1	32	26.75	1.091	0.95	1820
CH24.2A	5008	50	28	1.21	4	3	1	16	26.43	1.101	0.93	2300
CH24.2B	5008	50	28	1.21	4	3	1	16	26.59	1.158	0.89	1500
CH24.2C	5008	50	28	1.21	4	3	1	16	26.95	1.075	0.94	1420
CH24.2D	5008	50	28	1.21	4	3	1	16	27.16	0.829	0.88	1100
CH24.3	5008	50	28	1.21	4	3	2	16	26.88	-	0.95	2160
CH26.1	5008	50	28	1.21	4	3	1	28	26.14	0.88	0.95	2640
CH26.2	5008	50	28	1.21	4	3	1	28	26.2	0.88	0.92	3120
CH26.3	5008	50	28	1.21	4	3	1	28	26	0.82	0.92	-
CH27.1	5008	50	28	1.21	4	3	1	32	25.95	0.797	0.95	3320

APPENDIX D6: EXPERIMENTAL DATA FOR BENCH SCALE BATCH EXPERIMENTS

(LMA MODIFIED FORMULATION)

Run no	LMA [%]	TWEEN [%]	Curing [C]	Solids [%]	Size [micron]	Opacity	Viscosity [cPs]
CH LMA1.1	5	25	Room	24	2.16	0.95	2360
CH LMA1.2	5	25	77C for 15 min	24	2.25	0.96	920
CH LMA 2	5	25	78C for 15 min	24	2.39	0.95	3400
CH LMA 3.1	10	25	50C for 10 min	24	3.15	0.85	4400
CH LMA 3.2	10	25	50C for 15 min	24	3.22	0.82	4460
CH LMA 3.3	10	25	Room	24	3.13	0.79	TTTT
CH LMA 4.1	7.5	25	35C for 15 min	24	2.92	0.92	1400
CH LMA 4.2	7.5	25	55C for 15 min	24	3.04	0.93	940
CH LMA 4.3	7.5	25	Room	24	3.23	0.9	3940
CH LMA 5.1	7.5	25	42C for 15 min	24	3.39	0.9	-
CH LMA 5.2	7.5	25	50C for 15 min	24	3.03	0.9	-
CH LMA 5.3	7.5	25	Room	24	2.75	0.92	-

<u>APPENDIX E:</u> EXPERIMENTAL DATA OF SEMI-CONTINUOUS EXPERIMENTS

		$FeSO_4$		Cured in H2O bath	Cured in loop reactor		Exotherm					
Run no	Tween	Addition [ml/min]	Conc . [g/ml]	H2O Temp	H2O T	Product T	reached?	APS	TSC	Viscosity	Opacity	Discreet
KG3.3 - 5 litre	100%	7	0.008	-	42	28	no	0.82	20.18	2220	0.82	no
KG3.3 - 2 litre	100%	7	0.008	-	42	28	no	1.12	23.28	2460	0.79	no
KG4a	100%	7	0.008	50	-	-	-	0.72	23.54	-	0.85	no
KG4b (stirred)	100%	7	0.008	50	-	-	-	0.94	23.65	-	0.86	no
KG4	100%	7	0.008	50	53	38	yes	1.06	23.12	-	0.87	no
KG5a	100%	14	0.01	55	-	-	-	0.88	22.95	-	0.91	yes
KG5b (stirred)	100%	14	0.01	55	-	-	-	0.92	23.65	-	0.89	yes
KG6a	100%	14	0.04	50	-	-	-	0.72	23.41	-	0.89	no
KG6b	100%	14	0.04	50	-	-	-	1.08	23.25	-	0.92	no
KG6	100%	14	0.04	-	50	28	yes	0.78	23.53	-	0.81	no
KG7a	50%	14	0.04	50	-	-	-	0.8	22.65	-	0.8	no
KG7b (stirred)	50%	14	0.04	51	-	-	-	0.85	23.56	-	0.82	no
KG7	50%	14	0.04	-	51	34	yes	0.79	21.47	260	0.86	no
KG8a	100%	14	0.008	50	-	-	-	0.98	24.05	-	0.88	-
KG8	100%	14	0.008	-	55	36	yes	1.21	23.3	-	0.87	-
KG9a (catalise under lab stirrer)	100%	14	0.008	50	-	-	-	1.35	23.45	-	0.96	yes
KG9b	100%	14	0.008	50	-	-	-	1.4	23.6	-	0.96	yes
KG9c (stirred)	100%	14	0.008	50	-	-	-	1.12	23.33	-	0.97	yes
KG9	100%	14	0.008	-	55	36	no	1.3	21.78	200	0.96	yes
KG10a(catalise under lab stirrer)	100%	14	0.008	55	-	-	-	0.69	24.53	280	0.93	no
KG10b	100%	14	0.008	55	-	-	-	0.78	24.51	1400	0.91	no
KG10c (after 100m heating)	100%	14	0.008	-	53	40	no	0.9	22.54	1080	0.89	yes
KG10	100%	14	0.008	-	53	26.5	no	1.03	22.08	200	0.91	no
*KG11a(catalise under lab stirrer)	100%	14	0.008	55	-	-	-	0.79	23.65	-	0.88	no
KG11b(cure in H2O-bath)	100%	14	0.008	55	-	-	-	0.95	23.87	-	0.85	no
KG11c(after 200m heating)	100%	14	0.008	-	48	26	-	0.86	23.23	250	0.88	no
KG11	100%	14	0.008	-	48	30	no	1.05	23.45	200	0.88	no
*KG12a(catalise under lab stirrer)	100%	14	0.008	55	-	-	-	1.12	22.77	3200	0.94	no
KG12b(cure in H2O-bath)	100%	14	0.008	55	-	-	-	0.97	22.65	3400	0.91	no
KG12c(after 200m heating)	100%	14	0.008	-	56	38	-	0.86	21.05	180	0.88	no
KG12	100%	14	0.008	-	56	34	no	0.97	20.83	250	0.88	no

		$FeSO_4$		Cured in H2O bath	Cured in loop reactor		Exotherm					
Run no	Tween	Addition [ml/min]	Conc . [g/ml]	H2O Temp	H2O T	Product T	reached?	APS	TSC	Viscosity	Opacity	Discreet
KG13a	100%	14	0.008	55	-	-	-	1.14	28.43	1840	0.93	yes
KG13b(heated)	100%	14	0.008	55	-	-	-	1.07	27.47	1360	0.92	yes
KG13c(room T)	100%	14	0.008	-	-	-	-	1.1	27.85	500	0.88	yes
KG13d(after 200m heating)	100%	14	0.008	-	60	38	-	0.88	27.65	520	0.93	yes
KG13	100%	14	0.008	-	60	36	no	0.89	27.43	720	0.94	yes

Notes

KG11 - 30% more HEC

KG12 - 30% more HEC and PVOH

LUMINOSITY VALUES OF LOOP PRODUCT:

	Luminosity of:	
Run no.	Black surface	White surface
KG3	74.8	90.3
KG4	79.3	81.5
KG6	72.4	89.4
KG7	77.2	89.9
KG8	80.7	92.5
KG9	87.1	91
KG10	84.6	92.5
KG11	82.4	93.2
KG12	80.4	91.4
KG13	86.5	92.0