Copyright is owned by the Author of the thesis. Permission is given for a copy to be downloaded by an individual for the purpose of research and private study only. The thesis may not be reproduced elsewhere without the permission of the Author.

PARTICLE COATING USING FOAMS AND BUBBLES

A thesis presented in partial fulfilment of the requirements for the degree of

Doctor of Philosophy

in

Chemical and Bioprocess Engineering

at Massey University, Palmerston North, New Zealand

Shakti Singh

2017





ABSTRACT

This thesis investigates powder coating using foams or bubbles. The work initially started on foams. Wettability studies first showed that foams can be used to coat powders. Research then focussed on the fundamental unit of foams, the bubble. An experimental apparatus was designed and built to perform particle-bubble impact studies in air. Bubble solutions comprised of water, hydroxypropyl methylcellulose (HPMC) and sodium dodecyl sulphate (SDS). Four distinct physical behaviours occur when a particle impacts a bubble: (i) particle capture, (ii) particle slide-off, (iii) bubble burst and (iv) bubble self-healing.

The rate processes that occur during particle-bubble impact are; (i), surface area creation by bubble film stretching; (ii), delivery of surface active molecules to the newly created surface; and (iii), stress dissipation as the film is stretched. The ability of the solutions to do (ii) and (iii) are highly complex relying on the thermodynamic equilibrium of the solutions and the local perturbations in the near surface region. Therefore, establishing quantitative boundaries of behaviour is a difficult exercise. It is proposed that, for solutions above the *cac* or *cmc*, (*critical aggregate concentration*, *critical micelle concentration*) where self-healing occurs, the rate of (ii) > rate of (i) and the rate of (iii) > rate of (i). For solutions below the *cac*, where bursting occurs, the opposite is true, the rate of (ii) < rate of (i) and the rate of (iii) < rate of (i). Intermediate behaviours such as slide-off of capture are within the range of self-healing behaviours, but where the energy of the particle is insufficient to penetrate the bubble.

These behaviours are explained by complexation theory. For SDS concentration $\geq cac$ and cmc, small aggregates of SDS and HPMC locally supply surfactant to the surface of the stretching bubble film. This maintains low surface tension stress and self-healing

results. For SDS concentrations < cac, self-healing occurs because the complexation is a HPMC-SDS sea containing SDS islands. The HPMC-SDS sea structure is sufficiently interlinked to simply stretch with the film, while the SDS islands de-aggregate quickly in the near surface region to supply the newly created surface with surfactant. Here the supply rate is faster than the stretching and so the new surface area is populated with SDS molecules. In contrast bursting occurs when the complexation is HPMC-SDS islands in a SDS sea. Here, the rapid film extension is so fast that the islands of HPMC-SDS become isolated and the film loses structural homogeneity. Furthermore, the rate of new surface creation is too fast for diffusion of SDS molecules from the bulk 'sea' to the newly created surface. This results in both an inhomogeneous structure and local increases in surface tension, causing both stress concentration in the film and the Marangoni effect.

Extensional viscosity measurements, conducted in collaboration with Monash University, Australia, produced three behaviours as solutions were thinned: bead-on-string, blob and long-lived filaments. Solutions which produced long lived filaments here correspond to those that self-healed during particle impact (when the impact velocity was sufficient). It is proposed that this long-lived filament behaviour is due to the SDS concentration being > *cmc*, where the SDS micelles act like 'ball-bearings' between the extending HPMC chains.

Coatings were characterised by SEM and gravimetric measurement. Cross-sectional imaging of the soft particle that penetrated self-healing bubbles were found to have a continuous coating layer around the particle. Surface topography of bubble coated particles were compared with classical droplet coated single particles from the literature. Bubble coated particles were found to be smoother than the droplet coated particle.

The knowledge gained here was used to suggest how an industrial-scale particle coater using bubbles may be designed.

I wish you could see it Babuji (Dad)!
With the blessings of my father, Late Mr J.P. Singh and mother, Mrs Durgavati Singh
I dedicate this work to my wife, Renu and son, Advait

ACKNOWLEDGEMENTS

I would like to thank all the people who contributed in some way to make this thesis happen. First and foremost, I would like to express my sincere thanks to my chief supervisor Prof Richard Archer and supervisor Prof Matt Golding, for giving me the opportunity to work on this very challenging and interesting research project. Nothing could have been better than this as my PhD project. Though it took me around one and a half years between getting the offer of a PhD and starting this work, I must say, this was one of the very few good career choices I have made in my life. The calculative supervision and the freedom to utilise creative thinking were just fantastic. Thank you, Prof Richard Archer, for the interest you took in training me when to look out-of-the-box and when to focus, and encouraging me to do mental calculations before performing 'suck-it-and-see' type experiments. You always inspired and supported me for creative thinking, and I thank you for that.

I would like to convey special thanks to Prof Matt Golding for helping me develop understanding around surface and colloid science. Thanks for always being so positive and motivating me during difficult phases of my PhD studies. I liked your 'go for it' attitude.

Special thanks to you, Prof Jim Jones for accepting my request to co-supervise this work as a powder technology and fluid dynamics expert. I greatly benefited from your keen engineering insight, your knack for solving seemingly intractable practical difficulties, and your ability to put complex ideas into simple terms. I always looked forward to those regular weekly/fortnightly catch-ups to share the outputs and seek your opinions.

Special thanks to you, Prof Clive Davies for accepting my request to co-supervise this thesis as a powder technology expert. Special thanks for the interest you took in the

preparation of conference proceedings and presentations. The 'one-step-at-a-time' mantra finally started working for me, I guess, didn't it? ©.

I would like to acknowledge the following specific contributions from:

- Mr Ian Thomas, School of Engineering and Advanced Technology Workshop,
 Massey University, for all your help during my device development.
- Ms Janiene Gilliland, the Riddet Institute, for providing me the laboratory space, especially the 'skinny lab' to set-up my experimental apparatus. This was a perfect working place to perform my rather sensitive experiments.
- Ms Ashley McGrillen for MS Word formatting support during writing and submission of this thesis.
- Assoc. Prof Kevin Pedley, School of Food and Nutrition, for extending his image analysis expertise during device development.
- Prof Paulo Miranda, Federal University of Pernambuco, Brazil for his suggestions to measure bubble film thickness using the FT-IR spectroscope.
- Prof Bryony James, University of Auckland, for her permission to use the ESEM at the University of Auckland, New Zealand.
- Dr Tony Howes, The University of Queensland, for his brief critical discussions around single particle-bubble impact behaviour studies.
- Prof Shane Telfer and Prof Bill Williams, Institute of Fundamental Sciences,
 Massey University, for giving me the opportunity to work as a lab demonstrator
 for Chemistry and Physics classes during these PhD studies. The enthusiasm of
 relatively younger students always inspired me to do good science.
- Dr Luke Fullard, Institute of Fundamental Sciences, for his help during image analysis of particle-bubble impact studies.

- Fourth year engineering project students Mr Jolin, Mr Morgan and Ms Sara for their support. I am happy that my device is in safe hands, Jolin ☺ and pleased to see you have learnt PhD etiquettes pretty quickly☺.
- The Riddet Institute staff including, Mrs Ansley Te Hiwi, Mrs Terri Palmer, Mrs Felicia Stibbards, Mr Chris Hall and Mr. John Henley-King for facilitating this work.
- The Riddet Institute for providing financial support, in the form of the 'Earle Scholarship' and the Riddet travel grant to attend national and international conferences.

I am pleased to have had friendly and helpful colleagues at the Riddet Institute, Institute of Food Nutrition and Human Health, and School of Engineering and Advanced Technology, who created an enjoyable working environment during this study. Special mention goes to Hayley, Amit, Georg, Vikas, Nimmi, Prateek, Natascha, Sandra, Anant and Lakshmi.

Special thanks to Prof Peter Munro for his encouragement and support during these PhD studies. My heartfelt thanks to Mr Stephen Gregory for employing me at Fonterra during my PhD studies. I convey my sense of gratitude to my current manager Dr Steve Taylor for his constant support and encouragement. Thank you so much for always encouraging me to complete my thesis write-up while working at Fonterra. Special thanks to Dr Sheelagh Hewitt, Fonterra, for all your support. I would like to thank my work colleagues here at Fonterra, especially, Graeme, Mita, Sam, Payel, Orianne and Kuldeep for making the work-life enjoyable. Special thanks to Colin for not missing any opportunity to ask, "Have you finished your thesis?" ©

My sense of gratitude to Prof Rajiv Prakash, Indian Institute of Technology, B.H.U., Varanasi, India, for his motivation and encouragement to pursue an industrial research career. Special thanks to my previous managers, Dr Anand Subramony and Dr Krishnamurthy Vyas, during my tenure at Dr Reddy's Laboratories Ltd, Hyderabad, India, for inspiring and enriching my aspiration to pursue a research career. I am thankful to Mr Arvind Misra (IRL, Australia) for encouraging me to move to New Zealand and join this PhD studies. A sense of gratitude to my uncle, Mr Vinay Singh (HCL, India), who has always inspired me since my childhood. Special thanks to my friends Dr Abhishek Kumar Singh (ISM, Dhanbad, India), Dr Rakesh Kumar Mishra (NIIST, Trivandrum, India), Dr Abhinay Mishra (NTU, Singapore), Dr Leela Joshi (USA) and Mrs Deepa Singh (USA) for making my studies fun at different stages of my career.

I express my gratitude to my father, the late Mr Jagdish Prasad Singh, my mother, Mrs Durgavati Singh, for raising me with all love and care, and my brothers, Mr Rajesh Singh and Mr Hemant Singh, and my sisters, Mrs Rekha Singh, Mrs Shashi Singh and Mrs Vandana Singh, for all their sacrifices to make me what I am today. A great family spirit!

This thesis would never have been completed without the unconditional love and support of my wife, Renu. Thank you so much Renu for being such a lovely friend and wife. Thank you my little champ Advait for always bringing a smile to my face during the ups and downs of this PhD. Seeing you growing is pure bliss.

TABLE OF CONTENTS

ABSTRACT	i
ACKNOWLEDGEMENTS	vii
CHAPTER 1 THESIS OVERVIEW	1
1.1 CONTEXT	1
1.2 PROBLEM DEFINITION	1
1.3 PROPOSED SOLUTION	2
1.4 THESIS OBJECTIVE	4
1.4.1 Overall thesis objective	4
1.4.2 Specific thesis objectives	4
1.5 THESIS OUTLINE	6
1.6 POTENTIAL OUTCOMES	7
CHAPTER 2 REVIEW OF LITERATURE	9
2.1 INTRODUCTION	9
2.1 INTRODUCTION	9
2.1 INTRODUCTION	9
2.1 INTRODUCTION	9 13 16
2.1 INTRODUCTION	13 16
2.1 INTRODUCTION	131616
2.1 INTRODUCTION	
2.1 INTRODUCTION 2.2 FILM COATING ON POWDERS 2.3 FOAM 2.3.1 Foam production 2.4 PHYSICAL PROPERTIES OF THE FOAM SYSTEMS 2.4.1 Surface tension 2.4.2 Surface rheology	
2.1 INTRODUCTION	
2.1 INTRODUCTION 2.2 FILM COATING ON POWDERS 2.3 FOAM 2.3.1 Foam production 2.4 PHYSICAL PROPERTIES OF THE FOAM SYSTEMS 2.4.1 Surface tension 2.4.2 Surface rheology 2.5 FOAM DESTABILISATION MECHANISMS 2.5.1 Defoaming and antifoaming	9131616181922

2.6.2 Polymer-surfactant interactions at an interface	30
2.7 SPREADING BEHAVIOUR OF A SURFACTANT DROP ON A SURF	ACE . 32
2.8 WETTABILITY ASSESSMENT OF POWDERS	34
2.9 PRIOR ART AND THE KNOWLEDGE GAP	37
CHAPTER 3 HYPOTHESIS TESTING AND CHARACTERISATION OF FO	AM
COATED PARTICLES	45
3.1 INTRODUCTION	45
3.2 EXPERIMENTAL OPTIMISATION	45
3.2.1 Selection of model particle system	45
3.2.2 Optimisation of foaming and coating procedure	48
3.2.3 Materials	49
3.2.4 Methods	50
3.2.4.1 Particle silanisation	50
3.2.4.2 Particle coating using foam	50
3.2.5 Coating structure characterisation	51
3.3 POWDER CHARACTERISATION	51
3.3.1 Wettability assessment	51
3.3.1.1 Visual wettability assessment	52
3.3.1.2 Modified sessile drop technique	52
3.3.1.3 Gel trapping technique	53
3.3.1.4 Micro-level wettability studies by ESEM	55
3.4 RESULTS AND DISCUSSION	56
3.4.1 Wettability studies	56
3.4.1.1 Modified sessile drop technique	56
3.4.1.2 Visual assessment of particle behaviour on water	58
3.4.1.3 Single particle wettability using the gel trapping technique	59
3.4.1.4 Micro level wettability studies using ESEM	61

3.4.2 Coating structure using confocal laser scanning microscope	67
3.5 CONCLUSIONS	68
CHAPTER 4 DEVELOPMENT OF AN EXPERIMENTAL APPARATUS	71
4.1 INTRODUCTION	71
4.2 EXPERIMENTAL APPARATUS	72
4.2.1 Single bubble generation	73
4.2.2 Particle-bubble contacting	77
4.2.3 Mass transfer per particle-bubble impact	81
4.2.4 Video capture	82
4.3 PRELIMINARY STUDIES: BUBBLE GENERATION	85
4.3.1 Experimental rig	85
4.3.2 Experimental protocol	87
4.3.3 Results and discussion	89
4.3.4 Conclusions-Bubble generation	98
4.4 PRELIMINARY STUDIES: PARTICLE-BUBBLE IMPACT	100
4.4.1 Stationary particle suspended over a bubble	101
4.4.2 Bubble gun	102
4.4.3 Falling particle dropped by a particle tweezer	103
4.5 CONCLUSIONS	108
CHAPTER 5 VARIABLE SELECTION AND PHYSICAL CHARACTERIS.	ATION
OF BUBBLE SOLUTIONS AND PARTICLES	111
5.1 INTRODUCTION	111
5.2 KEY VARIABLES AND LEVEL SELECTION	112
5.2.1 Bubble solution	113
5.2.2 Particle type	113
5.2.3 Particle impact speed	114
5.3 EXPERIMENTAL PROTOCOL	

5.3.1 Solution preparation	115
5.3.2 Cleaning and surface modification of glass particles	115
5.3.3 Shear viscosity measurement	116
5.3.4 Contact angle measurements	116
5.3.5 Surface tension measurements	117
5.3.6 Bubble film thickness measurement using FT-IR spectroscopy	117
5.4 RESULTS AND DISCUSSION	118
5.4.1 Shear viscosity measurement	118
5.4.1.1 Influence of concentrations and shear rates on shear viscosity	y118
5.4.1.2 Influence of SDS concentration on the shear viscosity of HP	MC solutions
	119
5.4.2 Surface tension measurements	122
5.4.2.1 Influence of HPMC concentration in SDS solution	122
5.4.2.2 Influence of HPMC concentration in an aqueous solution	123
5.4.2.3 Influence of SDS concentration in HPMC solution	124
5.4.3 Wettability (contact angle) of aqueous HPMC-SDS solutions on	a glass slide
	127
5.4.3.1 Influence of HPMC concentration	127
5.4.3.2 Influence of SDS concentration	128
5.4.4 Bubble film thickness measurement using FT-IR spectroscopy	131
5.5 CONCLUSIONS	133
CHAPTER 6 PARTICLE-BUBBLE IMPACT BEHAVIOUR	135
6.1 INTRODUCTION	135
6.2 PREDICTING PARTICLE-BUBBLE IMPACT BEHAVIOUR	135
6.3 EXPERIMENTAL	
6.4 RESULTS AND DISCUSSION	
6.4.1 Qualitative observation	
o Zamini o oose tanon	1 72

6.4.1.1 Influence of particle to bubble diameter ratio and particle impact spe	
6.4.1.2 Influence of particle shape, surface properties and particle impact sp	
6.4.1.3 Influence of impact angle and impact velocity	155
6.4.2 Qualitative explanation of particle-bubble impact outcomes	160
6.4.2.1 Marangoni effect	160
6.4.2.2 HPMC-SDS complexation	162
6.5 Physical description of particle-bubble impact dynamics	173
6.5.1.1 Relative influence of bubble solution viscosity and surface tension	178
6.5.1.2 Influence of particle surface properties	179
6.5.1.3 Influence of bubble solution surface tension	182
6.6 REGIME MAP OF PARTICLE-BUBBLE IMPACT BEHAVIOUR	182
6.7 CONCLUSIONS	195
CHAPTER 7 EXTENSIONAL FLOWS AND PARTICLE-BUBBLE IMPACT	
BEHAVIOUR	197
7.1 INTRODUCTION	197
7.2 ACOUSTICALLY DRIVEN MICROFLUIDIC RHEOMETER	199
7.2.1 Materials	201
7.2.2 Method	201
7.3 RESULTS AND DISCUSSION	202
7.3.1 Film thinning behaviour vs. particle-bubble impact behaviour	202
7.3.2 Proposed molecular association in the film vs. impact behaviour	208
7.3.3 Extensional viscosity measurements of bubble solutions	211
7.4 CONCLUSIONS	216
CHAPTER 8 BUBBLE COATED SINGLE PARTICLE CHARACTERISATION.	219
8.1 INTRODUCTION	219

8.2 EXPERIMENTAL	219
8.2.1 Materials	219
8.2.2 Methods	220
8.2.2.1 Particle-bubble contact	220
8.2.2.2 Theoretical coating thickness calculations	220
8.2.2.3 Surface structure studies using SEM	220
8.3 RESULTS AND DISCUSSION	221
8.3.1 Weight gain and coating thickness	221
8.3.2 Scanning electron microscopic studies of bubble coated particles	224
8.3.2.1 Surface topography of bubble film coated particles	224
8.4 CONCLUSIONS	228
CHAPTER 9 RECOMMENDATIONS FOR INDUSTRIAL-SCALE COATING	
USING BUBBLES	231
9.1 INTRODUCTION	231
9.2 CONCEPTUAL INDUSTRIAL-SCALE COATER	231
9.2.1 Operating principles	232
9.2.2 Bubble generator	232
9.2.3 Particle disperser	233
9.2.4 Coated particle fluidisation for drying	234
9.3 MICRO-LEVEL PROCESS IDENTIFICATION	236
9.4 CONCLUSIONS AND RECOMMENDATIONS	238
CHAPTER 10 CONCLUSIONS AND SUGGESTIONS FOR FUTURE WORK	241
10.1 GENERAL CONCLUSIONS	241
10.2 SUGGESTED FUTURE WORK	243
BIBLIOGRAPHY	245
APPENDICES	267

10.3 SURFACE CREATION RATES WHEN A PARTICLE IMPACTS A BUBBLE
10.4 MASS TRANSFER FROM BUBBLE TO PARTICLE

LIST OF FIGURES

Figure 1-1: Schematic of film coating of a particle.
Figure 2-1: Cross-section of Wurster coater and phenomena occurring during particle
coating Adapted from Werner et al. (2007)11
Figure 2-2: Possible phenomena taking place during fluidised bed coating. Adapted from
(Nienow, 1995)
Figure 2-3: Foam nomenclature (Denkov, 2004).
Figure 2-4: <i>Microstructure of a foam film.</i>
Figure 2-5: Schematic showing change of surface tension with time of a foaming solution
with different types of surfactants; type III may be ideal for high foamability and stability18
Figure 2-6: Mechanism of foam destabilisation, adapted from Oungbho et al. (1997). 21
Figure 2-7: Coarsening with time, adapted from Saint-Jalmes (2006)
Figure 2-8: Antifoaming mechanism, adapted from Denkov et al. (2004)
Figure 2-9: Schematic presentation of bridging-dewetting mechanism for smooth
spherical particle ($ heta{>}90^\circ$) and for rough non-spherical particle. Adapted from Denkov et
al.(2004)
Figure 2-10: Antifoaming by hydrophobic particle and simultaneous deactivation of
antifoaming activity. Adapted from Kulkarni et al. (1977b)25
Figure 2-11: (a) Monolayer, (b) Newton black film, (c) Common black film, (d) Thick
foam film
Figure 2-12: Polymer-surfactant complex formations at different polymer/surfactant
concentration combinations. Solid black lines represent HPMC chains, blue and yellow
spheres represent to SDS micelle and counter ions, adapted from (Nilsson, 1995; Silva et
al., 2011). The larger blue sphere indicates major hydrophobic association zones 29
Figure 2-13: Schematic of the graph of the surface tension with log concentration of the
surfactant in the polymer aqueous solution; molecular level interaction is also shown in
the inset (adapted and modified from (Jones, 1967))
the inset (adapted and modified from (Jones, 1967))

Figure 2-15: Schematic of the dynamics of surfactant molecules in an aqueous drop over
a hydrophobic surface. Adapted from (Ruckenstein, 2012)
Figure 2-16: Forces involved on a droplet placed on a solid surface34
Figure 2-17: Mechanism of foam generation on interaction with powder. Adapted and
modified from (Prud'homme, 1996)
Figure 3-1 Antifoaming silica after foam processing
Figure 3-2: (a) Image of the planetary mixer and (b) Schematic of the sparging column
used for foaming surfactant/protein solution
Figure 3-3: Schematic of wettability assessment, (a) Sessile drop method, (b) Gel
trapping technique, and (c) ESEM technique
Figure 3-4: Relative protrusion of particle in PDMS elastomer matrix Adapted and
modified from (Cayre and Paunov, 2004); (a) Hydrophilic particle embedded in PDMS
base, (b) Hydrophobic particle embedded in PDMS base55
Figure 3-5: (a) Original image, (b) Processed image for edge detection and contact angle
measurement56
Figure 3-6: Particle wicking phenomenon; the arrows indicate the upper limit of the
glass powder layer
Figure 3-7: (a) Sessile drop on, (a) Silanised particle bed, (b) Surfactant foam coated
silanised particle bed
Figure 3-8: (a) Low and (b) High magnification SEM images of silanised glass particles
trapped in polydimethylsiloxane59
Figure 3-9: (a) Low and (b) High magnification SEM images of surfactant foam coated
silanised glass particles trapped in polydimethylsiloxane
Figure 3-10: ESEM images of surfactant foam coated silanised glass particles at (a) high
and (b) low chamber pressure. 62
Figure 3-11: ESEM images, (a) and (b) of silanised glass particles for contact angle
measurement at different locations
Figure 3-12: ESEM images, (a), (b), (c) and (d) of surfactant foam coated silanised
particles captured at different locations for contact angle measurement63
Figure 3-13: ESEM images, (a), (b), (c) and (d), of high concentration surfactant foam
coated silanised glass particles captured at different locations for contact angle
measurement. 64
Figure 3-14: ESEM images, (a) with little condensation and (b) with moderate
condensation of protein foam coated silanised glass particles65

Figure 3-15: Rhodamine-B stained sodium caseinate foam coated glass ballotini: (a) 3-
D view showing upper surface, (b) a single z-slice of surfactant coated glass particle at
the equator67
Figure 4-1: Conceptual key-processes of particle coating using foams or bubbles 71
Figure 4-2: (a) Co-flowing capillary nozzle, (b) T-junction nozzle
Figure 4-3: Hamilton needle connected with T-junction
Figure 4-4: <i>Micro-syringe pump to supply bubble liquid and air at the T-junction.</i> 76
$\textbf{Figure 4-5:} \textit{ Bubble nozzle fixed on a Vernier calliper in a polycarbonate chamber.} \dots 77$
Figure 4-6: Particle tweezer connected to a suction pump through PVC tube on a z-
moving stage79
Figure 4-7: Particle-bubble impact chamber and the particle tweezer's base table, fixed
on the anti-vibration plate80
Figure 4-8: <i>Impact chamber with particle tweezer and bubble nozzle alignment strings.</i>
Figure 4-9: <i>High speed camera on an x, y and z moving stage with a macro-lens.</i> 83
Figure 4-10: Schematic diagram of experimental apparatus for single particle-bubble
impact study. (A); camera with macro-lens, (B); X,Y,Z moving stage, (C); computer, (D)
and (E); syringe pumps connected to T-junction, (F); vacuum pump with a 2-way
$stopcock\ (M),\ (G);\ particle\ handler\ fixed\ with\ z-moving\ stage\ stationed\ on\ the\ table\ (N),$
$(H);\ particle\ attached\ with\ particle\ handler,\ (I);\ rectangular\ polycarbonate\ chamber\ (J)$
$bubble\ stationed\ on\ the\ nozzle,\ (K);\ bubble\ nozzle\ fitted\ with\ movable\ scale,\ (L);\ LED\ to$
illuminate bubble
Figure 4-11: (a) Hamilton needles, (b) T-junctions.
$\textbf{Figure 4-12:} \ \textit{Experimental set-up to explore mechanism of bubble formation in air.} \ \dots 87$
Figure 4-13: Liquid slug and air pocket formation at a T-junction; (a), initial formation
and wetting; (b), sequential liquid slugs and air pockets; and (c), liquid slug movement
into the nozzle. Eight to ten air and liquid slugs were measured and averaged at each
experimental condition. 90
Figure 4-14: Observation of bubble formation at a T -junction; (a) $-$ (e) progression of a
liquid slug followed by an air pocket to expand into a bubble with some drainage (see
(d)) down the outside of the nozzle91
Figure 4-15: Bubble generation behaviour for trial with HPMC-3% (w/v) in a 2.2 mm T-
junction topped by a needle with internal diameter 1.6 mm, (a) bubble chaining
phenomenon. (b) bubble slide-off phenomenon. and (c) bubble burst phenomenon 92

Figure 4-16: Liquid slug length (H _L) (mm) as a function of air/solution ratio for trials
with HPMC-3% (w/v) in a 2.2 mm and 1.1mm T-junction at low flow rates (0.2 mL/min
liquid flow rate)94
Figure 4-17: Liquid slug length (H _L) (mm) as a function of air to liquid ratio for trials
with HPMC-3% (w/v) in a 2.2 mm and 1.1 mm T-junction at high flow rates (0.04 mL/ml
liquid flow rate)94
Figure 4-18: Air slug length (H _A) (mm) as a function of air to liquid ratio for trials with
HPMC-3% (w/v) in a 2.2mm and 1.1 mm T-junction at low flow rates (0.2 mL/min liquid
flow rate)95
Figure 4-19: Air slug length (H_A) (mm) as a function of air to liquid ratio for trials with
HPMC-3% (w/v) in a 2.2 mm and 1.1 mm T-junction at high flow rates 0.04 mL/min liquid to the contract of th
flow rate)95
Figure 4-20: Terminal bubble diameter (d _B) (mm) observed before slide-off or burst as a
function of air/solution ratio for trials with HPMC-3% (w/v) in a 2.2 mm and 1.1 mm T-
junction at low flow rate ratios97
Figure 4-21: Terminal bubble diameter (d _B) (mm) observed before slide-off or burst as a
function of air/solution ratio for trials with HPMC-3% (w/v) in a 2.2 mm and 1.1mm T-
junction at high flow rate ratios97
Figure 4-22: Terminal bubble diameter observed before slide-off or bursting as a
function of needle internal diameter for trials with HPMC-3% (w/v) in a 2.2 mm T-
junction98
Figure 4-23: Selected image sequence from left to right of (a) a dry glass particle of 2
mm diameter (b) a bubble film coated wet glass particle, with a (HPMC-5% (w/v)
aqueous bubble) ($\mu = 0.014 \ Pa.s, \ \sigma = 45.59 \ mN/m$)
Figure 4-24: Selected image sequence of impact between a moving SDS-water; $\mu = 0.001$
Pa.s, $\sigma = 34.2$ mN/m, bubble generated by a bubble gun and a 1mm glass particle hung
by a copper wire
Figure 4-25: Selected image sequence of particle-bubble interaction between (a) a 0.25%
(w/v) SDS-water bubble of 7.0 ± 0.5 mm diameter and a spherical glass particle of 1 mm,
(b) a 0.26% (w/v) HPMC-water bubble of 7.0±0.5 mm diameter and a spherical glass
particle of 1 mm. Time difference between two images is 0.5 ms
Figure 4-26: Selected image sequence of particle-bubble interaction behaviours with (a)
a SDS-water bubble (b) HPMC-water bubble, particle position was fixed and bubble

inflated and (c) SDS-water bubble was inflated beneath a hydrophilic particle hung by
the particle tweezer
Figure 4-27: Selected images showing bubble bursting pattern when a glass particle of
1 mm diameter impacts with a bubble of (a) SDS-water, 0.25% (w/v), (b) HPMC-water,
0.015% (w/v), (c) HPMC-water, 0.065% (w/v), (d) HPMC-water, 0.520% (w/v).The
number above each image is time after first impact between a particle and a bubble. 107
Figure 5-1: Schematic of bubble scanning sung FT-IR spectroscopy for bubble film
thickness measurements
Figure 5-2: Influence of polymer concentration and shear rate on viscosity of HPMC
aqueous solution (n=1)
Figure 5-3: Comparison of the shear viscosity of 0.065 to 1.0% (w/v) HPMC aqueous
solution each at five levels of SDS concentration from 0-9 mM L^{-1} at 15 s^{-1} shear rate
(n=1)
Figure 5-4: Surface tension of aqueous solution of SDS and HPMC-SDS $(n=3, S.E)$. 123
Figure 5-5: Influence of HPMC concentration on the equilibrium surface tension of
aqueous solution, (n=3, S.E.).
$\textbf{Figure 5-6:} \ \textit{Top: Surface tension graph of HPMC-SDS aqueous solution at 0.065-1.0\%}$
(w/v) concentration of HPMC with six levels of SDS surfactant: 0 mM L^{-1} , 0.56 mM L^{-1}
$1.12~\text{mM}~\text{L}^{-1}$, $2.25~\text{mM}~\text{L}^{-1}$, $4.5~\text{mM}~\text{L}^{-1}$ and $9~\text{mM}~\text{L}^{-1}$, at each HPMC concentrations (n=3)
S.E.). Bottom: Schematic of surface tension isotherm showing T1 (cac of surfactant) and
T2 (cmc of surfactant) in polymer-surfactant (neutral-anionic) solutions
Figure 5-7: Influence of HPMC concentrations on the contact angle with hydrophilic and
hydrophobic glass slides, $(n=3, S.E.)$.
Figure 5-8: Contact angles of hydrophilic glass slide with aqueous HPMC and HPMC-
SDS solutions ($n = 3$, $S.E.$).
Figure 5-9: Contact angles of hydrophobic glass slide with aqueous HPMC and HPMC
SDS solutions ($n = 3$, S.E.).
Figure 5-10: Film thicknesses of aqueous bubbles of 0.065% (w/v), 0.26% (w/v), 0.52%
(w/v) and 1.0% (w/v) HPMC with three levels; 0 mM L^{-1} , 2.25 mM L^{-1} , and 9 mM L^{-1} of
SDS using FT-IR spectroscopy, $(n=5, S.E.)$. 132
Figure 6-1: (a)-(f) Envisaged particle-bubble impact behaviour
Figure 6-2: Impact behaviour diagram showing how the combinations of bubble
formulation, particle properties and impact velocity determine the impact behaviour
Qualifications of surface tension are ~40 mN/m when SDS was combined with HPMC.

~56 mN/m when only HPMC was used, and in-between when SDS and HPMC were used
<i>together.</i> 145
Figure 6-3 Selected image sequence (top to bottom) illustrating particle-bubble impact
behaviour, (a) HPMC-0.065% (w/v)-0 mM L^{-1} SDS (b) HPMC-0.26% (w/v)-0 mM L^{-1}
SDS (c) $HPMC-1.0\%$ (w/v)-0 mM L^{-1} SDS (d) $HPMC-0.065\%$ (w/v)-2.25 mM L^{-1} SDS
(e) $HPMC-0.26\%$ (w/v)-2.25 mM L^{-1} SDS (f) $HPMC-1.0\%$ (w/v)-2.25 mM L^{-1} SDS (g)
$HPMC-0.065\% (\text{w/v})-9 mM L^{-1} SDS (h) HPMC-0.260\% (\text{w/v})-9 mM L^{-1} SDS (h) HPMC-0.260\% (\text{w/v})-9 mM L^{-1} SDS (h) HPMC-0.260\% (\text{w/v})-9 mM L^{-1} SDS (h) HPMC-0.260\% (\text{w/v})-9 mM L^{-1} SDS (h) HPMC-0.260\% (\text{w/v})-9 mM L^{-1} SDS (h) HPMC-0.260\% (\text{w/v})-9 mM L^{-1} SDS (h) HPMC-0.260\% (\text{w/v})-9 mM L^{-1} SDS (h) HPMC-0.260\% (\text{w/v})-9 mM L^{-1} SDS (h) HPMC-0.260\% (\text{w/v})-9 mM L^{-1} SDS (h) HPMC-0.260\% (\text{w/v})-9 mM L^{-1} SDS (h) HPMC-0.260\% (\text{w/v})-9 mM L^{-1} SDS (h) HPMC-0.260\% (\text{w/v})-9 mM L^{-1} SDS (h) HPMC-0.260\% (\text{w/v})-9 mM L^{-1} SDS (h) HPMC-0.260\% (\text{w/v})-9 mM L^{-1} SDS (h) HPMC-0.260\% (\text{w/v})-9 mM L^{-1} SDS (h) HPMC-0.260\% (\text{w/v})-9 mM L^{-1} SDS (h) HPMC-0.260\% (w/v)-9 mM L^{-1} SDS (h) HPMC-0$
0.260% (w/v)-9 mM L^{-1} SDS and (i) HPMC-1.0% (w/v)-9 mM L^{-1} SDS. All bubbles
$(\emptyset6.5\pm1.0 \text{ mm})$ are impacted by a 1 mm glass particle at 9.0 m s ⁻¹ . The number in the
time column is the time after first impact in ms
Figure 6-4: Self-healing phenomenon with varying particle types; (a) smooth spherical
hydrophilic glass particle of 1 mm diameter and impact velocity 1.2 m/s, (b) smooth
spherical hydrophobic glass particle of 1 mm diameter and impact velocity 1.2 m/s, (c)
smooth spherical hydrophobic glass particle of 2 mm diameter and impact velocity 1.2
m/s, (d) rough cylindrical hydrophilic glass particle of 1.5 mm diameter and impact
velocity 1.2 m/s, (e) rough cylindrical hydrophilic glass particle of 1.5 mm diameter and
impact velocity 2.1 m/s, (f) smooth spherical hydrophilic glass particle of 3 mm diameter
and impact velocity 2.1 m/s, (g) smooth spherical polyethylene particle of 0.8 mm
diameter and impact velocity 2.1 m/s. The bubble formulation was HPMC-0.260% (w/v)- $$
9 mM L^{-1} SDS, bubble of 6.5 ± 1.0 mm for all particle and impact velocities. The number
above each image is the time after first impact in ms
Figure 6-5: Schematic showing impact angle between a particle and a bubble 155
Figure 6-6: Particle-bubble impact behaviour at higher impact angle; (a) 1 mm
hydrophilic or hydrophobic particle impacted with an impact velocity of 0.9 m/s at a
central angle more than 15° with a HPMC-0.26% (w/v) bubble, (b) 1 mm hydrophilic or
$hydrophobic\ particle\ impacted\ with\ an\ impact\ velocity\ of\ 0.9\ m/s\ at\ a\ central\ angle\ more$
than 15° with a HPMC-1.0% (w/v)-9 mM L ⁻¹ SDS bubble, (c) 1 mm hydrophilic or
hydrophobic particle impacted with an impact velocity of 3.3 m/s at a central angle more
than 15° with a HPMC-1.0% (w/v)-9 mM L^{-1} SDS bubble. The number above each image
is the time after first impact in ms. The small imperfection seen in this image is due to a
small bubble attached to the inner wall of the larger bubble157
Figure 6-7: Surface tension curves of HPMC-SDS concentrations combinations showing
cac and cmc of SDS and corresponding impact behaviour from a bubble obtained from
respective solutions. The cac of SDS for a solution of HPMC-1.0% (w/v) is measured to

be 1.12 mM L^{-1} . For the other HPMC concentrations of 0.52% (w/v), 0.26% (w/v) and
0.065% (w/v), the cac is measured to be 2.25 mM L^{-1} . The cmc of a pure SDS solution is
8.3 mM L^{-1} , but for the binary solutions the cmc is 4.5 mM L^{-1}
Figure 6-8: (A) HPMC, SDS and HPMC-SDS adsorption at interface and in bulk in a
bubble film at (a) no SDS in HPMC bubble solution (the sketch shows a HPMC molecule
$with \ hydrophilic \ (blue) \ and \ hydrophobic \ (brown) \ parts), \ (b) \ SDS \ concentration, \ c < cac,$
(c) c=cac and (d) c>cac, cmc. (B) Corresponding impact outcomes, (a) Bubble burst,
Particle capture, (b) Particle slide-off, (c) Bubble self-healing and (d) Bubble self-
healing. The schematics of interfacial adsorption of HPMC, SDS and HPMC-SDS are
inspired by Dong et al.(2009)
Figure 6-9: (a) Schematic of molecular behaviour of (a) a static film (a1) stretching film
with replenishment (a2) stretching film which bursts because there is inadequate
replenishment and corresponding images (b) of particle-bubble impact behaviour
(c <cac)< td=""></cac)<>
Figure 6-10: (a) Schematic of molecular behaviour of (a) a static film (a1) stretching film
with replenishment (a2) stretching film which self-heals because there is adequate
replenishment and corresponding images (b) of particle-bubble impact behaviour
(c≥cac)
Figure 6-11: Mechanisms for the two relaxation times for a surfactant solution above
critical micelle concentration (cmc). Adapted and reproduced from (Dhara & Shah, 2001b)
Figure 6-12: Schematic illustrations of the increase in the number density of SDS
aggregates/micelles with HPMC and corresponding explanation for particle-bubble
impact behaviour
Figure 6-13: Sequential images (from left to right) of the impact a particle of diameter I
mm glass onto \varnothing 7 mm bubble with formulation of HPMC-1.0% (w/v)-9 mM L ⁻¹ SDS.
Impact velocity is 2.1 m/s and time between two images is 0.5 ms. The particle bounced
back on colliding with the bubble nozzle at 2.5 ms
Figure 6-14: <i>Measurements of particle and bubble position for a</i> \emptyset 7 mm <i>single bubble</i>
with formulation of HPMC-1.0% (w/v)-9 mM L^{-1} SDS being impacted by a particle of $\varnothing 1$
mm glass at an impact velocity 2.1 m/s
Figure 6-15: <i>Measurements of particle and bubble velocity for a</i> \varnothing 7 mm <i>single bubble</i>
with formulation of HPMC-1.0% (w/v)-9 mM L^{-1} SDS being impacted by a particle of \varnothing 1

mm glass at an impact velocity 2.1 m/s. Velocities are obtained from the smoothed
position curves shown in Figure 6-14
Figure 6-16: Experimental deceleration rates for all runs at an impact velocity of 0.9
<i>m/s</i>
Figure 6-17: Deceleration values for all experiments plotted against the surface tension
and viscosity
Figure 6-18: The position of 1 mm diameter (a) hydrophilic and (b) hydrophobic glass
particles gently place on bubbles of HPMC-0.260% (w/v)-9 mM L^{1} SDS after 30 seconds.
Figure 6-19: Particle penetration length into the bubble film at 1.5 ms for a HPMC-
0.520% (w/v)- 0.56 mM L^{-1} SDS bubble with 1 mm hydrophilic and hydrophobic particles
impacting with different velocities ranging between 0.9 m/s to 2.7 m/s (n=5, S.E.) 181
Figure 6-20: Particle penetration length of a 1 mm hydrophilic spherical glass particle
into bubble films 1.5 ms after impact, obtained from HPMC-0.520% (w/v) with varying
concentrations of SDS from 0-9 mM L^{-1} SDS. The particle impact velocity was 0.9 m/s,
(n=5, S.E.)
Figure 6-21: (a) Fourier number versus Capillary number, (b) Schmidt versus Capillary
number. Both are for an impact velocity of 0.9 m/s of a Ø1 mm diameter particle
impacting a ~ 26.5 mm bubble
Figure 7-1: Acoustic driven microfluidic device for extensional viscosity measurement
(Image supplied by Amarin McDonnell)200
Figure 7-2: Thinning behaviour verses particle-bubble impact behaviour of HPMC
solution at different SDS levels. 204
Figure 7-3: Filament thinning behaviour of bubble solution, (a) HPMC-1.0% (w/v)-0
mM L ⁻¹ SDS, (b) HPMC-1.0% (w/v)-1.12 mM L ⁻¹ SDS, (c) HPMC-1.0% (w/v)-2.25 mM
L^{-1} SDS, (d) HPMC-1.0% (w/v)-9 mM L^{-1} SDS. The number over each image shows the
time from the start of the thinning
Figure 7-4: Schematics of HPMC-SDS molecular interactions in solutions, (a) without
SDS, (b) with low to intermediate concentration of SDS tested (0.55-1.12 mM L^{-1}), and
(d) with concentration slightly greater than the critical micelle concentration of SDS
tested (9 mM L^{-1}) and corresponding thinning behaviour between two plates of
extensional viscometer
Figure 7-5: Particle-bubble impact behaviour and corresponding thinning, and
molecular structure of the bubble film

Figure 7-6: Extensional viscosity as a function of SDS concentration for HPMC
solutions
Figure 7-7: Extensional viscosities of HPMC-water solutions at different strains with
different level of SDS concentrations: (a) 0.065% (w/v), (b) 0.26% (w/v), (c) 0.52% (w/v)
and (d) 1.0% (w/v)
Figure 7-8: Particle-bubble impact behaviour, visual extensional flow behaviour,
schematic graphical extensional flow behaviour and schematic molecular-level
association at SDS concentrations, <cac, and="" at="" cac="">cac</cac,>
Figure 8-1: Total weight of uncoated and coated 1,2 and 3 mm diameter particles with
$HPMC-1.0\%$ (w/v)-9 mM L^{-1} SDS bubbles
Figure 8-2: Number of droplet-particle impacts vs. amount of coating deposited in a
droplet based particle coating system. This graph is reproduced from (Ström et al., 2005).
Figure 8-3: Coating thickness per particle-bubble contact for 1, 2 and 3 mm diameter
particles
Figure 8-4: (a) Uncoated glass particle, (b) HPMC-SDS bubble film coated glass particle
and (c) Hydroxypropyl cellulose (HPC) droplet coated glass particle. The SEM image of
the HPC droplet coated glass particle was reprinted from (Ström et al., 2005) 225
Figure 8-5: Backscattered electron mode SEM images of transversal cross-section of
HPMC coated Cellulose Acetate Phthalate particle
Figure 8-6: Edge morphology of (a) HPMC-SDS, (b) NaCAS, (c) NaCAS-SDS and (d)
NaCAS-PEG-SDS bubble coated 1 mm diameter glass particle
Figure 8-7: Uncoated and HPMC bubble film coated porous glass particle
Figure 9-1: Conceptual industrial-scale powder coater using bubbles
Figure 9-2: Conceptual micro-scale phenomena occurring in conceptual rotating drum-
hased industrial-scale particle coater

LIST OF TABLES

Table 2.1: Particle coating attributes. 1	3
Table 2.2: Summary of the research questions to be investigated in this thesis	2
Table 3.1 Comparative contact angle values of silanised and surfactant foam coate	d
silanised glass powders or particles using different techniques6	7
Table 4.1 Viscosities and surface tensions of HPMC (PC603) solutions at 20°C, wit	h
standard error (n=3)	7
Table 4.2: Experimental plan, air:liquid ratios and two T-junctions. 8	8
Table 4.3 Experimental plan, polymer concentrations. 8	9
Table 4.4 Experimental plan, nozzles. 8	9
Table 5.1 Variables involved in bubble particle impact experiments. 11	2
Table 6.1: Range of experimental condition responsible for particle capture (C), particle	le
slide-off (L), bubble burst (B) and self-healing bubbles (S)	9
Table 6.2 : Conditions for self-healing to occur. Bubble size was 6.5 ± 1.0 mm. For the	e
statement HPMC $< 1.0\%$ (w/v), this means the three solutions at concentrations of 0.065	5,
0.26 & 0.52% (w/v)	1
Table 6.3: Counts of bubble burst (B), particle capture (C), particle slide-off (L) and	d
bubble self-healing (S) for particle-bubble impact behaviours using 1 mm spherical	ıl
hydrophilic glass particles. Drainage time of a bubble was controlled between 2 and	5
seconds to keep the bubbles reproducible	9
Table 6.4: Relevant dimensionless numbers for a particle impacting a bubble an	d
forming a stretched film tube. This work was done by Prof Jim R. Jones	4