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.
CHARACTERISATION OF THE RHEOLOGICAL PROPERTIES OF MOZZARELLA CHEESE

A THESIS PRESENTED IN PARTIAL FULFILMENT OF THE REQUIREMENTS FOR THE DEGREE OF

MASTER OF ENGINEERING

IN

CHEMICAL AND BIOPROCESS ENGINEERING

AT MASSEY UNIVERSITY, MANAWATU, NEW ZEALAND

CHANGJUN ZHU

2013
ABSTRACT

An important usage of Mozzarella cheese is as an ingredient in pizza. For this reason, it is important to understand the functional properties of melting and flow behaviours of mozzarella cheeses. For instance, understanding the influence of temperature and moisture on the rheological properties of mozzarella cheese may help cheese the maker to optimise products.

A modified UW Meltmeter and rotational methods were used to characterise the rheological properties of mozzarella cheese. The temperature impact on the rheology was determined by measurement over the temperature range from 30 to 80 °C. To investigate the moisture content effect on the rheological properties, mozzarella cheese was dried over different salt solutions or by desiccation in a fridge prior to rheological measurement.

Modifications of the UW Meltmeter improved the sample preparation, temperature control during the testing and data analysis. The viscosity data obtained by the UW Meltmeter followed the Arrhenius law with an activation energy of $30.3\pm1.2 \text{ kJ} \cdot \text{mol}^{-1}$. In the rotational method (the shear rate ramp test), the data of viscosity versus shear rate followed the power law model, and the consistency index was fitted to the Arrhenius law and WLF model. The WLF model had a wider temperature range fit than the Arrhenius law. It was found that the viscosity determined from the UW Meltmeter and rotational rheometer was quite different. They are actually measuring different aspects of flow. In this study, the rotational experiment produced results that were more appropriate to explain flow behaviour in cheese in the conditions experienced in pizza baking. The methods to lower the moisture content of mozzarella cheese led to unexpected results where viscosity was not strongly dependent on moisture content. This may have been due to disruption of the structure of the mozzarella cheese during drying.
ACKNOWLEDGEMENTS

It is a great journey through the Master study. There were many challenges for me to study abroad, fortunately I got a lot of helps and supports here from my supervisors, friends, family and some kind people. With these people help and support, I learned a lot and finished my Masters.

Firstly, I would like to thank my supervisor, Professor John Bronlund, for giving me this opportunity to do this study, teaching me how to arrange a project, helping me to address some project problems, and guiding me through my experimental works and thesis writing.

Big thank to my supervisor, Dr. Colin Brown, who help me a lot in experimental works, discussion of any difficulties and especially the revision of my thesis. I appreciate his patience to revise my thesis word for word.

I gratefully acknowledge my Fonterra supervisor, Dr. Phillip Watkinson, for the training of the UW Meltmeter, his advice and discussion, and the help in my milestone reports and thesis.

I would like to thank my Fonterra supervisor, Dr. Graeme Gillies, for the training the rotational rheometer, sharing some helpful knowledge and editing of my thesis.

Thanks to Fonterra for funding this project and providing the equipment. I appreciate all people in the PGP group for some suggestions and discussions. I am also very grateful to the laboratory technicians, John Edwards and Ann-Marie Jackson for the help in lab, the electronics technician, Anthony Wade, and workshop technician, Clive Bardell, for the device developments. Thanks to all the people who helped me.

最後，感謝我的父母，朱光載和江泗珠，一直以來對我的教導和支持，感謝他們給我提供這次留學的機會。感謝所以關心我的親朋好友。
Contents

ABSTRACT................................................................................................................................... I
ACKNOWLEDGEMENTS............................................................................................................. II
LIST OF TABLES....................................................................................................................... VIII
LIST OF FIGURES.................................................................................................................... IX
1.  BACKGROUND AND OBJECTIVES ...................................................................................... 1
  1.1.  Background.................................................................................................................... 1
  1.2.  Objective of project ...................................................................................................... 2
2.  LITERATURE REVIEW........................................................................................................... 3
  2.1.  Introduction ................................................................................................................... 3
  2.2.  Melting cheeses ........................................................................................................... 3
    2.2.1.  Cheese composition and structure ................................................................... 3
    2.2.2.  Functional properties of melting cheese ............................................................. 5
    2.2.3.  Mechanism for melting ....................................................................................... 5
    2.2.4.  Factors effecting melting performance ................................................................. 7
      2.2.4.1.  Temperature ................................................................................................. 7
      2.2.4.2.  Moisture ........................................................................................................ 8
      2.2.4.3.  Fat .................................................................................................................. 9
      2.2.4.4.  Calcium ......................................................................................................... 9
  2.3.  Rheology .......................................................................................................................... 10
    2.3.1.  Types of rheological behaviour ........................................................................ 10
      2.3.1.1.  Newtonian fluids ........................................................................................ 10
      2.3.1.2.  Shear thinning flow behaviour .................................................................... 11
      2.3.1.3.  Shear thickening flow behaviour ................................................................. 12
      2.3.1.4.  Plastic flow behaviour (Bingham plastic and viscoplastic) ......................... 12
    2.3.2.  Rheometry methods .............................................................................................. 13
      2.3.2.1.  Capillary viscometers .................................................................................. 14
      2.3.2.2.  Rotational viscometers ............................................................................... 14
      2.3.2.3.  Oscillatory rheometer .................................................................................. 15
2.3.2.4.  Squeezing flow viscometry ................................................................. 15

2.4.  Methods to measure flow during melting ............................................. 16
  
  2.4.1.  UW Meltmeter .......................................................................................... 16
  
  2.4.2.  The Arnott test ......................................................................................... 19
  
  2.4.3.  The Schreiber test ................................................................................... 19
  
2.5.  Mozzarella cheese making ................................................................. 20
  
  2.5.1.  Milk quality ............................................................................................... 20
  
  2.5.2.  2.5.2 Thermal treatment .......................................................................... 20
  
  2.5.3.  Curd formation ......................................................................................... 21
    
    2.5.3.1.  Calcium addition .............................................................................. 21
  
    2.5.3.2.  Acid development ............................................................................. 21
  
    2.5.3.3.  Rennet-Catalyzed coagulation ......................................................... 21
  
  2.5.4.  Cutting ....................................................................................................... 21
  
  2.5.5.  Stretching .................................................................................................. 22
  
  2.5.6.  Molding ..................................................................................................... 22
  
2.6.  Conclusion ................................................................................................. 22

3.  UW MELTMETER METHOD DEVELOPMENT ....................................... 24
  
  3.1.  Introduction .................................................................................................. 24
  
  3.2.  Estimation of key process conditions during pizza baking ................. 24
  
  3.3.  Sample preparation ...................................................................................... 25
    
    3.3.1.  Current cheese sample template .......................................................... 26
      
      3.3.1.1.  Cut quality for the current sample template .................................. 26
      
      3.3.1.2.  Results for sample variation in standard template ...................... 27
    
    3.3.2.  New cheese sample template design .................................................. 27
      
      3.3.2.1.  Cut quality for the new sample template ........................................ 28
      
      3.3.2.2.  Results and comparison with the old template .............................. 28
    
    3.3.3.  Procedures for UW Meltmeter test .................................................... 29
  
  3.4.  Temperature distribution in the UW Meltmeter ................................. 30
    
    3.4.1.  Choice of mozzarella analogue ............................................................. 31
    
    3.4.2.  Temperature of cheese sample during testing ................................. 31
3.4.3. Results ............................................................................................................. 32

3.4.3.1. Halloumi deformation during the test ......................................................... 32

3.5. UW Meltmeter modification ............................................................................. 36

3.5.1. Top plate modification ................................................................................... 36

3.5.2. Testing effects of insulation ........................................................................... 37

3.5.3. Results ............................................................................................................. 37

3.6. Data analysis method ........................................................................................ 38

3.6.1. Biaxial stress growth coefficient calculation ................................................. 38

3.6.2. Regression model for height vs. time ............................................................ 39

3.7. Mozzarella anisotropy and the impact of cheese sampling ......................... 43

3.8. The effect of EPS modification on rheological property ............................ 46

3.9. Conclusion ............................................................................................................. 48

4. UW MELTMETER RESULTS ................................................................................. 49

4.1. Introduction ......................................................................................................... 49

4.2. Temperature effects on rheological properties ............................................ 49

4.2.1. Method ............................................................................................................ 49

4.2.2. Results ............................................................................................................. 49

4.2.2.1. Melt curves .................................................................................................. 49

4.2.2.2. BSGC as function of temperature ................................................................. 54

4.3. Moisture effect on rheological properties ...................................................... 58

4.3.1. Cheese drying ................................................................................................. 58

4.3.2. Results of cheese drying ................................................................................ 59

4.3.3. Measurement of rheological properties of mozzarella ................................. 61

4.3.4. Rheological results .......................................................................................... 61

4.4. Conclusion ............................................................................................................. 63

5. ROTATIONAL RHEOLOGY METHOD DEVELOPMENT ........................................... 65

5.1. Introduction ......................................................................................................... 65

5.1.1. Rotational rheometer ..................................................................................... 65

5.1.2. Sample preparation ......................................................................................... 68

5.1.3. Procedures for the parallel plate rheometer tests ......................................... 69
LIST OF TABLES

Table 2 - 1 Conventional functional properties of melting cheese (adapted from Fox et al., 2000). 5

Table 3 - 1 Weight of samples cut by two templates ................................................................. 29
Table 3 - 2 The final height of samples .......................................................................................... 33
Table 3 - 3 The base temperature of cheese during testing............................................................. 34
Table 3 - 4 Mean BSGC at 3 BESRs for two fibre direction sample at 30 °C .............................. 44
Table 3 - 5 Mean BSGC at 3 BESRs for two fibre direction sample at 45 °C .............................. 44
Table 3 - 6 Mean BSGC at 3 BESRs for two fibre direction sample at 60 °C .............................. 44

Table 4 - 1 Moisture content and water activity of mozzarella cheese ....................................... 60

Table 6- 1 The consistency index k and behaviour index n at the different temperatures .......... 89
Table 6- 2 The consistency index k regressed from the power law equation with a constant n=0.47
........................................................................................................................................................ 90
Table 6- 3 Viscosity model parameters for mozzarella cheese as function of shear rate and
temperature ....................................................................................................................................... 92
Table 6- 4 WLF model parameters for mozzarella cheese as function of shear rate and temperature
........................................................................................................................................................ 94
LIST OF FIGURES

Figure 2 - 1 Schematic of cheese melting (Rudan & Barbano, 1998). A: Full fat cheese, B: Fat free cheese ...............................................................................................................................................6
Figure 2 - 2 Flow curves of processed cheese at different temperature (Dimitreli & Thomareis, 2004) .......................................................................................................................................................... 8
Figure 2 - 3 The types of rheological behaviours (Bylund, 1995) ................................................................................................................................................................................................. 10
Figure 2 - 4 The strain-rate range for different rheological techniques (Gunasekaran & Ak, 2003) 13
Figure 2 - 5 The basic test configurations of squeezing flow viscometry (Campanella & Peleg, 2002) ........................................................................................................................................ 15
Figure 2 - 6 The UW Meltmeter (Gunasekaran & Ak, 2003) ................................................................................................................................................................................................. 17
Figure 2 - 7 Mozzarella cheese sample height vs. time data obtained from the UW Meltmeter (Wang et al., 1998) ..................................................................................................................................... 18
Figure 2 - 8 BSGC vs. BESR for mozzarella cheese (Wang et al., 1998) ........................................... 18
Figure 2 - 9 The Schreiber test (Gunasekaran & Ak, 2003) ................................................................................................................................................................................................. 19

Figure 3 - 1 Mozzarella cheese melting during pizza baking .......................................................................................................................... 24
Figure 3 - 2 Cork borer and wire cutter ................................................................................................................................................................................................. 25
Figure 3 - 3 Existing cheese sample template ................................................................................................................................................................................................. 26
Figure 3 - 4 The shape of sample cut by the current original template ................................................................................................................................................................................................. 27
Figure 3 - 5 New cheese sample template ................................................................................................................................................................................................. 28
Figure 3 - 6 The shape of a sample cut by new template. ................................................................................................................................................................................................. 28
Figure 3 - 7 UW Meltmeter ................................................................................................................................................................................................. 29
Figure 3 - 8 The modified top plate ................................................................................................................................................................................................. 32
Figure 3 - 9 The mechanism of heat transfer during UW Meltmeter test. A: during the pre-heating; B: mechanical testing ................................................................................................................................................................................................. 32
Figure 3 - 10 The temperature of cheese base. A: three samples tested at 40 °C; B: three samples tested at 70 °C ................................................................................................................................................................................................. 33
Figure 3 - 11 Temperatures of cheese centre, cheese top and plate top. A: three samples tested at 40 °C; B: three samples tested at 70 °C ................................................................................................................................................................................................. 35
Figure 3 - 12 The modified top plate attached with EPS ................................................................................................................................................................................................. 37
Figure 3 - 13 The temperatures of cheese centre, cheese top and upper surface of top plate. A: three samples tested at 40 °C; B: three samples tested at 70 °C ................................................................................................................................................................................................. 38
Figure 3 - 14 The raw data record at the beginning of the UW Meltmeter test ................................................................................................................................................................................................. 39
Figure 3 - 15 Compare between experimental data and predicted data by double exponential decay model at 60 °C ................................................................................................................................................................................................. 40
Figure 3 - 16 The regression of sample height vs. time at 30 °C by two models and its residuals. A: raw data and the MMF model; B: raw data and the double exponential decay model; C: the residuals for the MMF model; D: the residuals for the double exponential decay model. ................................................................................................................................................................................................. 42
Figure 3 - 17 The regression of sample height vs. time at 45 °C by two models and its residuals. A: raw data and the MMF model; B: raw data and the double exponential decay model; C: the residuals for the MMF model; D: the residuals for the double exponential decay model. ................................................................................................................................................................................................. 42
Figure 3 - 18 The regression of sample height vs. time at 60 °C by two models and its residuals. A: raw data and the MMF model; B: raw data and the double exponential decay model; C: the residuals for the MMF model; D: the residuals for the double exponential decay model. ..........43

Figure 3 - 19 The fibre direction of samples. N: normal direction; P: parallel direction ..........44

Figure 3 - 20 Biaxial stress growth coefficient vs. biaxial extensional strain rate of mozzarella samples at different temperature ................................................................................................... 45

Figure 3 - 21 Height of mozzarella samples vs. time .............................................................. 46

Figure 3 - 22 Biaxial stress growth coefficient vs. biaxial extensional strain rate of mozzarella samples ................................................................................................................... 46

Figure 4 - 1 The height of triplicate cheese samples VS time at 30 and 80 °C ......................50

Figure 4 - 2 The height of mozzarella cheese samples VS time at varied temperature ..........50

Figure 4 - 3 The solid fat content as function of temperature in Emmental cheese (from Lopez et al. 2006) .............................................................................................................................................51

Figure 4 - 4 The BSGC VS BESR plots for Mozzarella cheese samples at varied temperature ....52

Figure 4 - 5 The comparison between the BSGC VS BESR plots for mozzarella cheese samples at 40 °C and 60 °C from the present study and literature (Wang et al., 1998) .................52

Figure 4 - 6 The comparison between the BSGC VS BESR plots for mozzarella cheese samples at 40 °C and 60 °C from the present study and the corrected literature data (Wang et al., 1998) ......53

Figure 4 - 7 Biaxial elongational viscosity vs. temperature for Cheddar from a UW Meltmeter (Muthukumarappan et al., 1999a) .................................................................................................. 54

Figure 4 - 8 Arrhenius plots of viscous flow for mozzarella samples with different stretching conditions (Ma et al., 2013) ............................................................................................................ 56

Figure 4 - 9 Effect of temperature on the elongational viscosity of process American cheese at 0.015 s⁻¹ biaxial strain rate (Campanella et al., 1987) ............................................................................................................. 57

Figure 4 - 10 Effect of temperature on the elongational viscosity of mozzarella cheese at 0.001 s⁻¹ BESR ................................................................................................................................................ 57

Figure 4 - 11 Relationship between moisture content and water activity of mozzarella cheese, and water sorption isotherms for imitation cheese at 5 °C (Duggan et al., 2008) ......................... 60

Figure 4 - 12 The height VS time for triplicate cheese samples of the highest and lowest moisture content ............................................................................................................................................. 61

Figure 4 - 13 The height VS time for the different moisture content mozzarella cheese ..........62

Figure 4 - 14 BSGC vs. BESR for the different moisture content mozzarella cheese at 50 °C....62

Figure 4 - 15 BSGC of mozzarella cheese as function of moisture content at BESR of 0.001 s⁻¹... 63

Figure 5 - 1 Parallel-plate measuring system ........................................................................66

Figure 5 - 2 Cheese slicer (A) and 20 mm cork borer (B) ....................................................... 69

Figure 5 - 3 Typical creep curve showing with the various elements of the Burgers model (Steffe, 1996) .............................................................................................................................................. 70

Figure 5 - 4 The shear viscosity VS. shear rate in the high stress creep tests ....................... 71

Figure 5 - 5 Shear strain recorded as function of time at different temperatures. A: 40°C; B: 50°C; C: 60°C; D: 70°C .......................................................................................................................... 73

Figure 5 - 6 The creep and recovery curves for mozzarella cheese at different temperatures....75
Figure 5 - 7 The creep and recovery curves of mozzarella cheese ripened for 36 days (Olivares et al., 2009) ......................................................................................................................................... 75
Figure 5 - 8 Time effect on viscosity of mozzarella cheese for different temperature. A: 30 °C; B: 40, 50 and 60 °C........................................................................................................................................ 77
Figure 5 - 9 Shear viscosity VS shear rate plots for mozzarella cheese samples at varied temperature using the rotational viscometer ........................................................................................................ 79
Figure 5 - 10 The complex modulus and loss tangent as a function of temperature in the temperature sweep test using oscillatory method ................................................................................ 80
Figure 5 - 11 Complex viscosity as a function of temperature in temperature sweep test using oscillatory method .................................................................................................................................. 81

Figure 6 - 1 Comparison of the shear viscosity between the samples with two fibre directions ... 84
Figure 6 - 2 The shear viscosity of mozzarella as function of shear rate at different temperatures .................................................................................................................................................. 86
Figure 6 - 3 Comparison of rheological properties of mozzarella cheese obtained from different methods (Muliawan & Hatzikiriakos, 2007) ...................................................................................................................... 87
Figure 6 - 4 Schematic of the form transformation of cheese with varied temperature ............... 89
Figure 6 - 5 The Arrhenius relationship between the consistency index and temperature .......... 91
Figure 6 - 6 Comparison between the experimental data and model predictions for shear viscosity vs. shear rate .......................................................................................................................................................... 93
Figure 6 - 7 The WLF relationship between the consistency index and temperature .......... 94
Figure 6 - 8 Comparison between the experimental data and predicted curve of shear viscosity vs. shear rate using the WLF model .................................................................................................... 95
Figure 6 - 9 Viscosity as function of shear rate for different moisture content cheeses at 50 °C ... 97
Figure 6 - 10 Viscosity as function of shear rate for different moisture content cheeses at 60 °C .97
Figure 6 - 11 Viscosity as function of shear rate for different moisture content cheeses at 70 °C .98
Figure 6 - 12 Relationship between shear viscosity and moisture content of mozzarella at 50 °C .98
Figure 6 - 13 Relationship between shear viscosity and moisture content of mozzarella at 60 °C .99
Figure 6 - 14 Relationship between shear viscosity and moisture content of mozzarella at 70 °C 99
Figure 6 - 15 Shear stress change during the testing ..................................................................... 101
Figure 6 - 16 Moisture loss during fridge drying over time ........................................................... 102
Figure 6 - 17 Viscosity as function of shear rate for different moisture content cheeses at 50 °C103
Figure 6 - 18 Relationship between shear viscosity and moisture content of mozzarella ..........104
Figure 6 - 19 Comparison between the data obtained from UW Meltmeter and rotational tests .......................................................................................................................................................... 105

Figure 9 - 1 Procedure of characterisation of cheese ................................................................. 118
Figure 9 - 2 Cheese slicer (A) and 20 mm cork borer (B) ................................................................. 119