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Assessment of structure and component mobility within Mozzarella cheese

A thesis presented in partial fulfilment of the requirements for the degree of Doctor of Philosophy (PhD) In Food Technology at Massey University,

Manawatu campus, New Zealand

Jeremy Robert Smith 2013

Abstract

The objective of this study was to identify mechanisms responsible for component mobility relating to structural change within Mozzarella cheese. The use of new techniques alongside well established methods allowed insights to be gained beyond the current understanding of the dynamics within Mozzarella. A number of processing and storage trials were conducted utilising a range of techniques to gain a multi-scale indication of changes in component mobility and structural reorganisation.

Dielectric spectroscopy was explored as a method to characterise both ion and water mobility. Initially a model system was utilised as a means of evaluating the technique prior to being applied to Mozzarella. The model system allowed the composition of the cheese to be systematically controlled, especially the calcium. However, subsequent trials (in real Mozzarella cheese systems) indicated that water movement within the cheese during both maturation and heating confound the dielectric response, indicating the method is not ideally suited to measuring a dynamic Mozzarella system.

Nuclear magnetic resonance was used to probe changes in component mobility within Mozzarella. Initially well-established relaxation methods were used to monitor the decrease in free water within Mozzarella following manufacture. However, after raising the question of the effect of temperature on free water in cheese, relaxation and diffusion measurements were employed as tools to gain an understanding of the dynamics of water movement within the porous cheese structure. This work was extended further by using these techniques to follow a newly manufactured Mozzarella through a storage trial. The relaxation and diffusion measurements were taken at a range of temperatures at each point of the trial. Phosphorus NMR was explored as a novel approach to monitor changes in the arrangement of calcium and phosphorus (as phosphate) within Mozzarella during storage. This in combination with additional techniques characterising structural changes allowed potential mechanisms for the solubilisation of CCP to be discussed.

Collectively these techniques found that Mozzarella undergoes a number of structural changes during storage. Two primary drivers for change were identified from which the other processes cascaded: changing strength in hydrophobic interactions and proteolytic breakdown. Initially the development of the cheese structure was driven primarily by a relaxation in protein matrix (caused by weakening hydrophobic interactions), resulting in the moisture equilibration processes through the associated impact on colloidal calcium phosphate solubility and thus protein-protein interactions. Further structural changes occurred as a result of the proteolytic breakdown of the casein and a possible relaxation in the protein structure. These proteolytic mechanisms dominated maturation behaviour after the moisture equilibration processes were substantially completed (typically >20 days).

This thesis revealed new information relating to the movement of components within Mozzarella, particularly at elevated temperatures. These insights will aid in building a more detailed understanding of the dynamics within Mozzarella. It also highlighted several techniques that show promise as potential tools for assessing the structural changes within Mozzarella cheese.

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Contents

| Αl | bstract | | | ii |
|--------|---------|---------|---|----|
| Αd | cknowl | edgm | ents | iv |
| 1 | Intr | oduct | tion | 1 |
| 2 | Lite | ratur | e Review | 3 |
| | 2.1 | Intro | oduction | 3 |
| | 2.2 | Moz | zzarella | 6 |
| | 2.2. | 1 | Processing steps and subsequent structural changes during Mozzarella manufac | |
| | 2.2. | 2 | Components within Mozzarella | 27 |
| | 2.2. | 3 | Functional Properties of Mozzarella | 34 |
| | 2.3 | Imit | ation Mozzarella & Model Systems | 40 |
| | 2.3. | 1 | Model Systems | 41 |
| | 2.4 | Met | hods for measuring structure & functional properties | 43 |
| | 2.4. | 1 | Physical Properties | 43 |
| | 2.4. | 2 | Microstructural Analysis | 51 |
| | 2.4. | 3 | Component Mobility | 55 |
| 3 | Spe | cific F | Research Objectives and Structure of Thesis | 65 |
| 4 M | | _ | g Dielectric Spectroscopy as a Tool for Studying Composition and Structure of a | 68 |
| | 4.1 | Intro | oduction | 68 |
| | 4.2 | Mat | erials and Methods | 70 |
| | 4.2. | 1 | Materials | 70 |
| | 4.2. | 2 | Confocal Microscopy | 70 |
| | 4.2. | 3 | Texture Profile Analysis | 71 |
| | 4.2. | 4 | Uniaxial compression | 72 |
| | 4.2. | 5 | Dielectric Analysis | 72 |
| | 4.2. | 6 | Model System | 73 |
| | 4.3 | Resi | ults and Discussion | 76 |
| | 4.3. | 1 | Model system development | 76 |

| | 4.3.2 | Observations during Manufacture | . 77 |
|----|-----------|--|------|
| | 4.3.3 | Confocal Imaging | . 78 |
| | 4.3.4 | Texture Profile Analysis | . 80 |
| | 4.3.5 | Dielectric Spectroscopy | . 82 |
| | 4.3.6 | Critical calcium level | . 91 |
| | 4.3.7 | Effect of Processing | . 93 |
| | 4.3.8 | General discussion | 100 |
| | 4.4 C | onclusion | 104 |
| 5 | The as | sessment of water mobility in Mozzarella cheese during the initial stages of storage | 106 |
| | 5.1 Ir | stroduction | 106 |
| | 5.2 N | laterial and Methods | 108 |
| | 5.2.1 | Material | 108 |
| | 5.2.2 | Confocal Microscopy | 108 |
| | 5.2.3 | Scanning Electron Microscopy | 108 |
| | 5.2.4 | NMR Spectroscopy | 109 |
| | 5.2.5 | Expressible Serum | 110 |
| | 5.2.6 | Dielectric Spectroscopy | 110 |
| | 5.2.7 | Composition | 110 |
| | 5.3 R | esults and Discussion | 111 |
| | 5.3.1 | Composition | 111 |
| | 5.3.2 | Confocal Microscopy | 111 |
| | 5.3.3 | Scanning Electron Microscopy | 112 |
| | 5.3.4 | NMR Spectroscopy | 114 |
| | 5.3.5 | Expressible Serum | 117 |
| | 5.3.6 | Dielectric Spectroscopy | 118 |
| | 5.3.7 | General discussion | 126 |
| | 5.4 C | onclusions | 129 |
| 6 | An inv | estigation into the mechanisms driving structural change in Mozzarella and Cheddar | |
| ch | neese dur | ng maturation | 131 |
| | 6.1 Ir | troduction | 131 |

| 6 | .2 | Materials and Methods | 132 |
|---|-------|---|-----|
| | 6.2.1 | 1 Material | 132 |
| | 6.2.2 | 2 Confocal Microscopy | 133 |
| | 6.2.3 | 3 Urea-polyacrylamide gel electrophoresis | 133 |
| | 6.2.4 | 4 NMR Spectroscopy | 134 |
| | 6.2.5 | 5 Uniaxial Compression | 134 |
| | 6.2.6 | 6 Meltability | 134 |
| | 6.2.7 | 7 Scanning Electron Microscopy | 135 |
| | 6.2.8 | 8 Analysis of key processing steps for Mozzarella | 135 |
| 6 | .3 | Results and Discussion | 136 |
| | 6.3.1 | 1 Composition | 136 |
| | 6.3.2 | 2 Confocal Microscopy | 137 |
| | 6.3.3 | 3 Scanning Electron Microscopy | 143 |
| | 6.3.4 | 4 Urea PAGE | 146 |
| | 6.3.5 | 5 NMR | 148 |
| | 6.3.6 | 6 Uniaxial Compression | 150 |
| | 6.3.7 | 7 Melt | 153 |
| | 6.3.8 | 8 Structural differences during manufacturing | 154 |
| | 6.3.9 | 9 General Discussion | 156 |
| 6 | .4 | Conclusion | 159 |
| 7 | | nvestigation into the effect of maturation on the dielectric and rheological proper | |
| | | lla cheese during end-use heating | |
| | | Introduction | |
| 7 | .2 | Materials and Methods | |
| | 7.2.1 | | |
| | 7.2.2 | 5 , | |
| | 7.2.3 | · · · · · · | |
| 7 | .3 | Results and Discussion | |
| | 7.3.1 | | |
| | 7.3.2 | · | |
| | 7.3.3 | 3 General Discussion | 185 |

| | 7.4 | Conclusion | . 189 |
|-----------|-------|---|-------|
| 8 Ch | | essment of the changes in the structure and component mobility of Mozzarella and cheese during heating | . 190 |
| | 8.1 | Introduction | . 190 |
| | 8.2 | Material & Methods | . 192 |
| | 8.2. | 1 Materials | . 192 |
| | 8.2.2 | 2 Rheology | . 193 |
| | 8.2. | 3 Magnetic resonance | . 193 |
| | 8.3 | Results & Discussion | . 196 |
| | 8.3. | 1 Rheology | . 196 |
| | 8.3.2 | 2 Magnetic resonance | . 201 |
| | 8.3. | 3 General discussion | . 222 |
| | 8.4 | Conclusion | . 227 |
| 9 life | | ping water migration and heat induced changes in Mozzarella cheese during early she magnetic resonance techniques | |
| | 9.1 | Introduction | . 228 |
| | 9.2 | Material & Methods | . 229 |
| | 9.2. | 1 Material | . 229 |
| | 9.2.2 | 2 Magnetic Resonance | . 230 |
| | 9.3 | Results & Discussion | . 232 |
| | 9.3. | 1 Relaxation | . 233 |
| | 9.3. | 2 Diffusion | . 240 |
| | 9.3. | 3 DT2 | . 248 |
| | 9.3.4 | 4 General discussion | . 251 |
| | 9.4 | Conclusion | . 254 |
| 10 M | | evestigation into the role of calcium in the structure and component mobility of | . 256 |
| | 10.1 | Introduction | . 256 |
| | 10.2 | Materials and Methods | . 258 |
| | 10.2 | 2.1 Materials | . 258 |
| | 10.2 | 2.2. Cheese manufacture | 258 |

| 10. | 2.3 | Composition | 262 |
|------|--------|--|-----|
| 10. | 2.4 | Uniaxial compression | 262 |
| 10. | 2.5 | Meltability | 262 |
| 10. | 2.6 | Pizza baking evaluation | 262 |
| 10. | 2.7 | Confocal microscopy | 263 |
| 10. | 2.8 | Scanning electron microscopy | 263 |
| 10. | 2.9 | Urea PAGE | 263 |
| 10. | 2.10 | Magnetic resonance | 264 |
| 10. | 2.11 | Soluble calcium | 265 |
| 10. | 2.12 | Dielectric spectroscopy | 265 |
| 10. | 2.13 | Statistical analysis | 266 |
| 10.3 | Resi | ults and Discussion | 266 |
| 10. | 3.1 | Observations during processing | 266 |
| 10. | 3.2 | Composition | 266 |
| 10. | 3.3 | pH | 267 |
| 10. | 3.4 | Compression | 268 |
| 10. | 3.5 | Melt | 270 |
| 10. | 3.6 | Pizza baking performance | 272 |
| 10. | 3.7 | Confocal microscopy | 273 |
| 10. | 3.8 | Scanning electron microscopy | 277 |
| 10. | 3.9 | Urea PAGE | 278 |
| 10. | 3.10 | Magnetic resonance | 281 |
| 10. | 3.11 | Soluble calcium | 290 |
| 10. | 3.12 | Phosphorus NMR | 293 |
| 10. | 3.13 | Dielectric spectroscopy | 296 |
| 10. | 3.14 | Statistical analysis | 302 |
| 10.4 | Gen | eral discussion | 303 |
| 10.5 | Con | clusion | 308 |
| 11 (| Conclu | ıding Discussion and Future work | 310 |
| 11.1 | Eval | uation of techniques used to characterise component mobility | 310 |
| 11 2 | Con | stituents and their role in structure | 311 |

| 11.2.1 | Protein | 311 |
|----------|---------------------------------------|-----|
| 11.2.2 | Fat | 312 |
| 11.2.3 | Aqueous phase | 312 |
| 11.3 Th | e development of structure | 312 |
| 11.3.1 | Cooker | 312 |
| 11.3.2 | Stretching | 313 |
| 11.4 Str | ructural evolution during storage | 314 |
| 11.4.1 | Equilibrium processes | 314 |
| 11.4.2 | Proteolysis | 315 |
| 11.4.3 | Effect of structural change | 316 |
| 11.5 Str | uctural transformation during heating | 318 |
| 11.5.1 | Cold structure | 318 |
| 11.5.2 | 20-35°C | 318 |
| 11.5.3 | 35-55°C | 319 |
| 11.5.4 | 55°C and above | 319 |
| 11.6 Fu | ture work | 322 |
| 12 Refer | rences | 324 |

| Symbol / Abbreviation | Meaning |
|-------------------------|---|
| ε* | Complex permittivity |
| ϵ_0 | Permittivity of free space |
| ε' | Dielectric constant |
| ε" | Dielectric loss factor |
| G' | Storage modulus |
| G" | Loss modulus |
| Tanδ | Loss tangent |
| η* | Complex viscosity |
| ω_0 | Larmor frequency |
| γ | Gyromagnetic ratio |
| B ₀ | Magnetic field |
| I | Proton intensity |
| A | Proton intensity of casein associated water |
| В | Proton intensity proportional to free water |
| Т | time |
| T ₁ | Longitudinal (spin-lattice) relaxation |
| T ₂ | Transverse (spin-spin) relaxation |
| NMR | Nuclear Magnetic Resonance |
| MRM | Magnetic resonance microscopy |
| D_0 | Free diffusion |
| A | Tortuosity |
| Т | Time |
| $(\frac{S}{V_p})$ | Surface to volume ratio |
| Θ | Time constant (Pade fitting parameter) |
| D(t) | Diffusion as a function of time |
| MAS ³¹ P NMR | Magic angle spinning phosphorous (31) |
| | nuclear magnetic resonance |
| CLSM | Confocal laser scanning microscope |
| TPA | Texture profile analysis |
| SEM | Scanning electron microscopy |
| Δ | Observation times |
| Δ | Pulse duration |