PROPERTIES OF RECOMBINED MILK PROTEIN COMPOSITE GELS: EFFECTS OF PROTEIN SOURCE, PROTEIN CONCENTRATION AND PROCESSING TIME

A THESIS PRESENTED IN PARTIAL FULFILMENT OF THE REQUIREMENTS
FOR THE DEGREE OF
MASTER OF TECHNOLOGY
IN
FOOD TECHNOLOGY
AT MASSEY UNIVERSITY, PALMERSTON NORTH,
NEW ZEALAND

ROBYN ROSEMARY FINDLAY

2002

ABSTRACT

Increased knowledge of the interactions involved in the manufacture of Milk Protein Composite Gels (MPCGs) is essential for the further development of dairy-based analogue and recombined products and the advancement of novel product development. This study investigated MPCG manufacture using four protein sources (Rennet Casein, skim milk cheese (SMC), milk protein concentrate (MPC 85), calcium-depleted milk protein concentrate (IX MPC 85)), three protein to water (P/W) ratios (0.4, 0.5, 0.6) and four processing times (0, 4, 8, 16 minutes). The properties of the products were investigated using confocal and transmission electron microscopy, as well as rheological and functional tests.

Protein source was found to have the greatest impact on product characteristics, followed by P/W ratio with processing time having little, and often inconsistent, effects. Increased protein concentration resulted in a higher viscosity during manufacture, a decrease in fat droplet size, an increase in gel firmness, and a decrease in meltability. Increased processing time resulted in a decrease in fat droplet size, few significant changes in firmness (both small- and large-strain), and an increase in meltability.

Fracture property analysis showed that SMC produced softer, more elastic gels than Rennet Casein. The whey-containing samples produced softer, more brittle gels with little difference between them. Small-strain analysis showed that all samples were weak gels but the results did not follow the same trend as the fracture properties. The samples increased in firmness in the following order: SMC < Rennet Casein < IX MPC 85 < MPC 85.

Microstructure analysis showed the presence of whey protein aggregates in the MPC 85 and IX MPC 85 samples. These samples also demonstrated aggregation of the lipid droplets, which was attributed to the presence of whey proteins. Reduced levels of calcium resulted in lower levels of emulsification (larger lipid droplets) due to lower in-process viscosities.

Correlations between large- and small-strain testing showed that the correlation coefficient was dependent on the protein source being used and that although the level of correlation was not high, there was a general positive trend. The small-strain and UW Meltmeter tests did not agree on the order of increasing meltability except for the SMC samples, which were significantly more meltable than the other protein sources. The two tests were poorly correlated ($R^2 = 0.446$).

ACKNOWLEDGEMENTS

I would like to thank the Fonterra Research Centre (FRC) for providing this project and allowing me to write a Masters Thesis on work I have done as part of the Composite Gels group. I would like to thank my supervisors Prof. Harjinder Singh, Dr. Sheelagh Hewitt and Dr. Michael Whitton for their guidance and wisdom.

I would like to thank the following staff members at FRC for their input into this work. Mike Donkin for his suggestion and support for conducting a Masters degree through FRC. Gerhard Hoppe for allowing me to finish it. Dr. David Reid for his unrivalled enthusiasm, unwavering support and un-paid, after hours thesis editing. Andrew Saunders for all his assistance in planning and editing this work. Dr. Philip Watkinson for all his knowledge of fracture properties and meltabilty testing. Robbie Buwalda for all his assistance in the pilot plant and his knowledge of both equipment and processing techniques. Robyn Hirst for her expertise in microscopy techniques and results analysis. Dr. Siew Kim Lee for her assistance with the small-strain rheology equipment. Warren Fitzsimons for his assistance in sample production and processing advice early in the project.

I would also like to thank several Massey University staff members: Dr. Yacine Hemar for his expertise in small-strain rheology, Rod Bennet for his assistance in writing up, and Dr. Rogerio Pereira for his understanding of the equipment and manufacturing procedures.

I would also like to thank my colleagues for their support, encouragement and knowing when not to ask how it is going; Joanna Shepherd, Sophia Stathopolous, Janiene Gilliland, Arron Harford, Robert Hacking, Liz White, Satyendra Ram and Donald Love.

Thanks go to Emma Bermingham for her tales of PhD woes and also to Dave Thomas and Kane Champan for their encouragement.

Paul, thank you for your endless faith and your support over the last four and a half years that has helped to get me here today.

TABLE OF CONTENTS

LIST OF FIGURES

LIST OF TABLES

LIST OF EQUATIONS

NOMENCLATURE

ℓ	Length (mm)	(Rheology)
$\delta\ell$	Change in length (mm)	(Rheology)
ε	Strain (-)	(Rheology, normal)
σ	Stress (Pa)	(Rheology, normal)
γ	Shear strain (-)	(Rheology, tangential)
τ	Shear stress (Pa)	(Rheology, tangential)
H	Sample height at any time (mm)	(Compression testing)
H_o	Initial sample height (mm)	(Compression testing)
Δh_t	Displacement of crosshead at time *t* (mm)	(Compression testing)
v	Speed of compression (mm s^{-1})	(Compression testing)
F_t	Force during lubricated compression at time *t* (N)	(Compression testing)
r_o	Initial radius of sample (m)	(Compression testing)
σ_{max}	Maximum stress (Pa)	(Compression testing)
σ_∞	Infinite stress (Pa)	(Compression testing)
$\dot{\varepsilon}_o$	Initial strain rate (s^{-1})	(Compression testing)
ε_{max}	Maximum strain (-)	(Compression testing)
ε_c	Cauchy strain (-)	(Compression testing)
ε_H	Hencky strain (-)	(Compression testing)

σ_o	Maximum stress (Pa)	(Oscillatory rheology)
γ_o	Maximum strain (-)	(Oscillatory rheology)
$\sigma_{el.}$	Elastic material reaction stress (Pa)	(Oscillatory rheology)
$\sigma_{v.}$	Viscous material reaction stress (Pa)	(Oscillatory rheology)
$\dot{\gamma}$	Strain rate/Shear rate (s^{-1})	(Oscillatory rheology)
G'	Storage modulus (Pa)	(Oscillatory rheology)
G"	Loss modulus (Pa)	(Oscillatory rheology)
G*	Complex modulus (Pa)	(Oscillatory rheology)
G^*_{min}	Minimum complex modulus (Pa)	(Oscillatory rheology)
δ	Phase angle (°)	(Oscillatory rheology)
tan δ	Loss tangent	(Oscillatory rheology)
ω	Oscillation frequency (Hz)	(Oscillatory rheology)
η^*	Apparent viscosity	(Oscillatory rheology)

ABBREVIATIONS

AMF	Anhydrous milk fat
Ca	Calcium
C/P ratio	Calcium to protein ratio
CSA	Calcium sequestering agent
DSP	Disodium phosphate
EMC	Enzyme modified cheese
FRC	Fonterra Research Centre Limited
FTRC	Food Technology Research Centre
HPLC	High-performance liquid chromatography
IX MPC	Ion-exchanged MPC (calcium depleted)
MPC	Milk protein concentrate
MPCG	Milk protein composite gel
Na	Sodium
NaCl	Sodium chloride
NCN	Non-casein nitrogen
NPN	Non-protein nitrogen
NZDRI	New Zealand Dairy Research Institute
P/W ratio	Protein to water ratio
SALP	Sodium aluminium phosphate
SMC	Skim milk cheese

SMP	Skim milk powder
TEM	Transmission electron microscopy
TMP	Total milk protein
TN	Total nitrogen
TPA	Texture profile analysis
TSC	Trisodium citrate
TSP	Trisodium phosphate
WPC	Whey protein concentrate
WPI	Whey protein isolate

A copy of the Nomenclature and Abbreviations is given in a fold-out format at the back of this thesis.

1.0 INTRODUCTION

Milk protein composite gels (MPCGs) can be formed directly from milk, by recombining milk protein powders or via roux[1] formation with fat and milk protein powders. The two latter methods of forming milk protein gels are extremely versatile and products can be made to resemble a soft mousse-like product through to a hard cheese-like product through manipulation of the composition and processing methods (Saunders *et al.*, 1996c). These adaptable gels can be manufactured from a large range of stable intermediate protein products, such as Rennet Casein, milk protein concentrates (MPCs), calcium-depleted milk protein concentrates (IX MPCs[2]), skim milk powder, skim milk cheese (SMC) powder, sodium caseinate and calcium caseinate. These protein products influence the final flavour and texture of the product. The water content, amount and type of lipid, flavour and processing conditions can also be varied to produce a range of end products. Other ingredients may be used to influence texture and flavour, such as calcium chelating agents, salts, hydrocolloids, starches, enzyme modified cheese (EMC) and commercial flavour compounds.

Although milk protein gel products have been produced both commercially and for research purposes, the work has generally focused on emulating an existing product or investigating processed cheese. There has been little systematic work done to understand the chemical and physical interactions that affect the characteristics of the final product.

Composition, pH, shear, temperature, time, salt, emulsifiers, protein source, lipid, mixer design, mixing speed, cooling rate, order of addition, rate of addition, pH, acid type and level and the interactions between each of these affect the characteristics of the final product.

Increased knowledge of the mechanisms and outcomes of these interactions is essential for the further development of dairy-based analogue products and the advancement of novel product development (Saunders *et al.*, 1996c; Thompson and Hewitt, 2000). The work described in this thesis focuses on the effects of protein source, protein concentration and processing time on the product characteristics of recombined milk protein gels.

[1] Mixture of fat and protein powder
[2] IX MPCs are MPCs that are calcium depleted by ion exchange (IX)