USE OF MILK PROTEINS AS NANO-PARTICLES IN PREPARATION OF EDIBLE FILMS WITH FUNCTIONAL PROPERTIES

By

SAYED HUSSEIN SAYED ABDELHAMID ABOLILA

B.Sc.Agric. Sc. (Food Sci. & Tech.), Ain Shams University, 2011

A thesis submitted in partial fulfillment
Of
The requirements for the degree of

MASTER OF SCIENCE in

Agricultural Sciences

(Dairy Science and Technology)

Department of Food Science Faculty of Agriculture Ain Shams University

Approval Sheet

USE OF MILK PROTEINS AS NANO-PARTICLES IN PREPARATION OF EDIBLE FILMS WITH FUNCTIONAL PROPERTIES

By

SAYED HUSSEIN SAYED ABDELHAMID ABOLILA

B.Sc.Agric. Sc. (Food Sci. & Tech.), Ain Shams University. 2011

This thesis for the M.Sc. degree has been approved by:
Dr. Ali Ibrahim Ali Mansour Professor of Dairy Science, Faculty of Agriculture, Al-Azhar University
Dr. Yehia Ali El-din Hammad Professor Emeritus of Dairy Science and Technology, Faculty of Agriculture, Ain Shams University
Dr. Rezk Azab Awad Professor of Dairy Science and Technology, Faculty of Agriculture, Ain Shams University
Dr. Ahmed Ismail Metwally Professor of Dairy Science and Technology, Faculty of Agriculture, Ain Shams University
Date of examination 18 / 4 / 2017

USE OF MILK PROTEINS AS NANO-PARTICLES IN PREPARATION OF EDIBLE FILMS WITH FUNCTIONAL PROPERTIES

By

SAYED HUSSEIN SAYED ABDELHAMID ABOLILA

B.Sc.Agric. Sc. (Food Sci. & Tech.), Ain Shams University, 2011

Under the supervision of:

Dr. Ahmed Ismail Metwally

Professor of Dairy Science and Technology, Food Science Department, Faculty of Agriculture, Ain Shams University (Principal supervisor)

Dr. Rezk Azab Awad

Professor of Dairy Science and Technology, Food Science Department, Faculty of Agriculture, Ain Shams University

Dr. Osama Ibrahim El- Batawy

Associate Professor of Dairy Science and Technology, Food Science Department, Faculty of Agriculture, Ain Shams University

ABSTRACT

Sayed H. A. Abo-Lila: Studies on Use of Milk Proteins as Nano-Particles in Preparation of Edible Films with Functional Properties. Unpublished. M.Sc. Thesis, Department of Food Science, Faculty of Agriculture, Ain Shams University, 2017.

The goals of this study were to investigate the characteristics (physiochemical, mechanical and barrier properties) of functional edible films prepared from different types of cow's or buffalo's milk protein using different plasticizer (glycerol or sorbitol). Moreover, our study also carried out to investigate the possibility of using total milk proteinates (TMP) edible film containing some preservatives as a dipping or packaging in Ras cheese during ripening and its effect on the characteristics of cheese quality. The study was conducted in two parts, the first part, eight different types of milk proteins (acid casein, rennet casein, casein co-precipitate and total milk proteinates) were prepared from cow's and buffalo's milk. These proteins were used as polymers to form sixteen edible film samples using different types of plasticizers (glycerol or sorbitol). The result edible films were evaluated physiochemically, mechanically and for their barrier properties. The results indicated that the type of protein polymer and plasticizer used in edible film formation had significant effect on its physiochemical, mechanical and barrier values. Different edible films plasticized by glycerol were higher in moisture content, swelling, water solubility, elasticity, water vapor and gas permeability values, while lower in thickness, tensile strength and elastic modulus values compared with the different edible films plasticized by sorbitol. No significant differences were observed in all physiochemical, mechanical and barrier properties values between different edible films prepared from different cow's proteins and films formed using different buffalo's proteins. It could be concluded that, all types of milk proteins especially total milk proteinates

(TMP) prepared from cow's or buffalo's milk could be used as a suitable polymer for prepare edible film with good physiochemical, mechanical and barrier properties.

In the second part, eight Ras cheese samples were manufactured and dipped or packaged by different types of edible coating solutions or films prepared from buffalo's total milk protein (TMP), some of which containing different preservatives. Control Ras cheese were neither dipped nor packaged with any film or wax, while one of other cheese treatment was coated by paraffin wax. The other treatments were either dipped or packaged whether with TMP containing or not preservatives, namely 0.1% of mixture of nisin+natamycin (1:1) or potassium sorbate+natamycin at the same level and ratio.

The obtained results revealed that, the coating of Ras cheese with TMP edible film led relatively to reduce the rate of cheese moisture loss and hence the salt in water phase remained in the ranges those encouraged the growth of lactic acid bacteria to develop more acidity and hence enhanced the ripening rate as explained from the determined ripening indices (Soluble nitrogen and Total volatile fatty acids). That has indeed reflected in the relative cheese weight stability during ripening. The presence of preservatives in the film kept cheese under microbiological control according to the yeast and moulds count. Organoleptically, the cheese coated with TMP persevered with potassium sorbate+natamycin whether by dipping or packaging gained the highest sensory scores.

The forgoing results led to conclude that, Ras cheese could be hold its weight during ripening period besides improve its marketing quality when coated with edible film based on milk protein especially persevered with 0.1 % of mixture of potassium sorbate+natamycin (1:1).

Key words: milk protein, edible film, functional properties, dipping Ras cheese, packaging Ras cheese

ACKNOWLEDGMENT

My endless thanks are to Allah for conciliation and providing patience. I would like to express my deep sincere gratitude to *Prof. Dr. Ahmed I. Metwally* Professor of Dairy science and Technology, Food Science Dept., Faculty of Agriculture, Ain Shams University, *Prof. Dr. Rezk A. Awad* Professor of Dairy Science and Technology, Food Science Dept., Faculty of Agriculture, Ain Shams University and *Dr. Osama I. El-Batawy* Associate Professor of Dairy Microbiology and Technology, Food Science Dept., Faculty of Agriculture, Ain Shams University for their kindness constrictive criticism, their efforts, helpfulness continuous supervision, providing the necessary advice and help throughout this work.

I sincerely thank and appreciate *Prof. Dr. Yehia. A. Heikal* Professor of Food Science and Technology, Food Science Dept., Faculty of Agriculture, Ain Shams University for his efforts, helping, kindness and generous advice during my work in this research.

The author would like to express his deep thanks to *Prof. Dr.*Stefan junge, Dipl.- Eng. Katharina Kaiser and Mrs. Sandra solga
(Institute of packaging engineering, (Beuth university of applied sciences, Berlin-Germany) as well as Mrs. Jana Brugger and Mr.

Bernd Lallinger, (Brugger Feinmechanik GmbH, Munich-Germany) for the facilities and guidance provided by gas-permeability tests of the casein films.

Last, and by no means least, my heartfelt thanks to my colleagues and all staff in Food Science Department, Faculty of Agriculture, Ain Shams University.

LIST OF CONTENTS

No.		Page
	LIST OF TABLES	VI
	LIST OF FIGURES	V III
	LIST OF ABBREVIATIONS	X
I	Introduction	1
П	Review of Literature	4
1.	Definition and Functionality of edible films and	4
	coating	
2.	Classification of edible films and coatings	6
2.1.	Polysaccharide edible films and coating	6
2.1.1.	Cellulose and derivatives edible films and coating	7
2.1. 2 .	Chitin and chitosan edible films and coating	8
2.1. 3 .	Starch edible films and coating	9
2.1.4.	Alginate edible films and coating	12
2.1.5	Carrageenan edible films and coating	13
2.1.6	Pectin edible films and coating	14
2.1.7	Agar edible films and coating	16
2.2	Lipid and wax edible films and coating	17
2.3	Protein edible films and coating	18
2.3.1	Gelatin edible films and coating	18
2.3.2	Corn zein edible films and coating	19
2.3.3	Soy protein edible films and coating	21
2.3.4	Wheat gluten edible films and coating	22
2.3.5	Milk protein edible films and coating	23
3.	Application of edible film and coating in food	37
	and dairy industry	
III	Materials and Methods	57
1	Materials	57
1 1	Raw Milk	57

No.		Page
1.2	Rennet	57
1.3	Glycerol and sorbitol	57
1.4	Nisin, natamicin and potassium sorbate	57
1.5	Salt	57
1.6	Yoghurt Starter cultures	57
2	Methods	58
2.1	Preparation of different type of milk proteins	58
2.1.1	Preparation of Acid casein	58
2.1.2	Preparation of Rennet casein	58
2.1.3	Preparation of Casein co-precipitate	58
2.1.4	Preparation of Total milk proteins	58
2.2	Preparation of edible films from various milk	
	proteins using different plasticizer	59
2.3	Preparation of coating solution from buffalo's total	
	milk protein (TMP) containing different	
	preservatives	60
2.4	Manufacture of Ras cheese dipped or packaged by	
	buffalo's TMP edible films containing different	
	preservatives.	61
3	Analytic Methods	65
3.1	Analyses of different milk protein preparations	65
3.2	Edible films testes	65
3.2.1	Moisture Content (MC)	65
3.2.2	Film thickness	65
3.2.3	Film Swelling	66
3.2.4	Film water solubility	66
3.2.5	Tensile testing	66
3.2.6	Water vapor permeability	67
3.2.7	Oxygen permeability	68
3.3	Ras cheese analysis	71

No.		Page
3.3.1	Cheese yield	71
3.3.2	Physiochemical Analysis	71
3.3.2.1	Cheese moisture loss	71
3.3.2.2	Dry matter	71
3.3.2.3	Fat and protein contents	71
3.3.2.4	Salt in water phase content	72
3.3.2.5	Acidity and pH values	72
3.3.3	Ripening parameters	72
3.3.3.1	soluble nitrogen (SN)	72
3.3.3.2	Total volatile fatty acids (TVFA) determination	72
3.3.4	Microbiological Analyses	72
3.3.4.1	Lactic acid bacterial count	72
3.3.4.2	Salmonella spp. Detection	73
3.3.4.3	Staphylococci count	73
3.3.4.4	Coliform bacterial count	73
3.3.4.5	Yeast and molds count (M/Y)	73
3.3.5	Sensory evaluation	73
3.3.6	Statistical Analysis	73
IV	Results and Discussion	74
Part I	Preparation and properties of edible films using	
	different types of cow's and buffalo's milk	
	proteins.	74
1	physicochemical properties of different types milk	74
	protein used for edible film preparation	
2	properties of edible films using different types of	
	cow's and buffalo's milk proteins	76
2.1	Physiochemical properties	76
2.2	Mechanical Properties	84
2.2.3	Barrier properties	92

No.		Page
Part II	Evaluation of edible film based on milk protein	
	for Ras cheese coating.	111
1	Physio-chemical properties	114
2	Microbiological examination	128
3	Sensory properties	134
V.	Summary and Conclusion	138
VI.	References	149
VII.	Arabic Summary	

LIST OF TABLES

No.		Page
1	physicochemical properties of different types of milk	
	proteins used for edible film preparation.	75
2	Physiochemical properties of various edible film formed	
	from different type of cow's and buffalo's milk protein	
	using different plasticizer (glycerol and sorbitol).	78
3	Mechanical (Tensile strength, Elongation and Young's	
	modulus) properties of various edible film formed from	
	different type of cow's and buffalo's milk protein using	
	different plasticizer glycerol and sorbitol).	85
4	Barrier properties (Water vapor permeability) of various	
	edible films formed from different type of cow's and	
	buffalo's milk protein using different plasticizer (glycerol	
	and sorbitol).	93
5	Average oxygen permeation values for cow's and buffalo's	
	protein films plasticized with 3 % glycerol.	103
6	Average air permeation values for cow's and buffalo's	
	protein films plasticized with 3 % glycerol.	104
7	Average oxygen permeation values for cow's and buffalo's	
	protein films fortified with 3 % sorbitol.	105
8	Solubility and diffusion of oxygen gas through milk	
	protein films.	108
9	Solubility and diffusion of air gas through milk protein	
	films.	109
10	Cheese yield (%) of Ras cheese samples, dipped and	
	packaged with (TMP) based on edible film containing	
	different preservatives during ripening.	113
11	Cheese moisture loss (%) of Ras cheese samples, dipped	
	and packaged with (TMP) based on edible film containing	
	different preservatives during ripening.	115

No.		Page
12	Dry matter (%) of Ras cheese samples, dipped and packaged with buffalo's total milk proteinates (TMP)	
	based on edible film containing different preservatives	
	during ripening.	117
13	Fat and Protein contents (%) of Ras cheese samples, dipped and packaged with TMP based on edible film	
	containing different preservatives during ripening.	118
14	Salt in water phase value (SWP) (%) of Ras cheese	
	samples, dipped and packaged with TMP based on edible	
	film containing different preservatives during ripening.	
		120
15	Changes in titratable acidity (%) and pH value of Ras	
	cheese samples, dipped and packaged with (TMP) based	
	on edible film containing different preservatives during	
	ripening.	123
16	Change in Soluble nitrogen / Total nitrogen content	
	(SN/TN) (%) of Ras cheese samples, dipped and	
	packaged with (TMP) based on edible film containing	
	different preservatives during ripening.	126
17	Change in total volatile fatty acids content (TVFA) (%)	
	of Ras cheese samples, dipped and packaged with (TMP)	
	based on edible film containing different preservatives	
	during ripening.	128
18	Lactic acid bacterial count (log CFU/g) of Ras cheese	
	samples, dipped and packaged with (TMP) based on	
	edible film containing different preservatives during	
	ripening.	130
19	Yeast and molds count (log CFU/g) of Ras cheese	
	samples, dipped and packaged with (TMP) based on	
	edible film containing different preservatives during	
	ripening.	133
	· •	

No.		Page
20	Sensory scores of Ras cheese samples, dipped and	
	packaged with TMP based on edible film containing	
	different preservatives during ripening.	136

LIST OF FIGURES

No.		Page
1	Flow diagram for preparing different type of cow's	
	and buffalo's milk proteins.	60
2	Flow diagram for preparing of various edible films	
	using different type of cow's and buffalo's milk	
	protein.	63
3	Flow diagram of manufacture the different Ras	
	cheese samples dipped or packaged by buffalo's	
	TMP edible films containing different preservatives	64
4	Universal testing machine (Zwick / Roell,	
	Germany) for mechanical properties measurement.	67
5	Brugger apparatus for gas permeability	68
	measurement.	
6	An example for the course of permeability values	
	during the penetration test.	70
7	The development of pressure difference between the	
	two cells and the achievement of steady state gas	
	permeation.	70
8	Moisture content (%) of various edible films made	
	from different type of cow's and buffalo's milk	
	using different plasticizers.	79
9	True thickness (mm) of various edible films made	
	from different type of cow's and buffalo's milk	
	using different plasticizers.	80
10	Swelling (%) of various edible films made from	
	different type of cow's and buffalo's milk using	
	different plasticizers.	81
11	Water solubility of various edible films made from	
	different type of cow's and buffalo's milk using	

No.		Page
	different plasticizers.	83
12	The force (N) and the extension (mm) at the yield	
	point of the force- strain- curve of various edible	
	films made from different type of cow's and	
	buffalo's milk using different plasticizers.	87
13	Elongation at break (%) of various edible films	
	made from different type of cow's and buffalo's	
	milk using different plasticizers.	90
14	Tensile strength (MPa) of various edible films made	
	from different type of cow's and buffalo's milk	
	using different plasticizers.	91
15	Elastic modulus (MPa) of various edible films made	
	from different type of cow's and buffalo's milk	
	using different plasticizers.	91
16	Water vapor permeability of various edible films	
	made from different type of cow's and buffalo's	
	milk using different plasticizers.	94
17	Oxygen penetration curves for films obtained from	
	cow's acid casein + 3% glycerol. A) time -	
	penetration value curve. B) pressure - time curve.	95
18	Oxygen penetration curves for films obtained from	
	cow's rennet casein + 3% glycerol. A) time -	
	penetration value curve. B) pressure - time curve.	96
19	Oxygen penetration curves for films obtained from	
	cow's casein co-precipitate + 3% glycerol. A) time-	
	penetration value curve. B) pressure - time curve.	97
20	Oxygen penetration curves for films obtained from	
	cow's total milk proteinates + 3% glycerol. A) time -	0.0
	penetration value curve. B) pressure - time curve.	98
21	Oxygen penetration curves for films obtained from	
	buffalo's acid casein + 3% glycerol. A) time -	