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INVESTIGATIONS OF THE PHYSICO-CHEMICAL BEHAVIOUR OF STARCH-WATER SYSTEMS

A thesis presented in partial fulfilment

of the requirements for the degree

of Doctor of Philosophy

in Food Technology at

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1981

MASSEY UNIVERSITY

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A B S T R A C T

Starch is a major component of many of the world's food supplies. In order to utilise these supplies effectively the properties of starch must be fully understood. Although starch systems have been investigated quite extensively, there is relatively little information concerning the physico-chemical behaviour of starch under conditions relevant to food processing.

The texture of many fabricated foodstuffs is regulated by adding starch. In many cases the addition of starch causes food systems to behave as viscoelastic pastes. In Australasia, wheat starches are generally used to control texture. However starches from some wheat cultivars do not impart the desired rheological characteristics to foodstuffs and this thesis concerns an investigation into this phenomenon which was investigated in three sections.

In section I, a fundamental study of the rheological properties of wheat starch pastes was performed. Measurements were made of the flow behaviour of pastes under both oscillatory and steady shear conditions. Pastes formed under a range of experimental conditions from various wheat varieties were studied. Both wheat varieties and paste preparation conditions were found to influence rheological behaviour. The results show that differences in the pasting properties of starch pastes may be attributed to two factors, namely the swelling capacity of the starch (the volume which the starch gel particles would occupy when close packed if excess solvent were present) and the size distribution of the granules.

The rheological properties depend on the source of starch since this effects particle swelling capacities and size distributions. Paste preparation conditions influence rheological properties since they alter the volume occupied by gelatinised granules.

The rheological behaviour of starch pastes changes with time when the pastes are stored. The effect of storage on dynamic rigidity was investigated and the results suggested that a crystallisation process is responsible for the increase in dynamic rigidity with time. The results were therefore evaluated using the Avrami equation.

In section II, an investigation was made of the degree of crystallinity, that is the proportion of polymer chains that are in an ordered state, in a number of wheat starch varieties that have different swelling capacities. Measurements of the X-ray crystallinity index, enthalpy change and specific volume were used to investigate crystallinity. The results show that higher swelling capacities are associated with relatively disordered arrangements of polymer chains within granules. The crystallinity results for the various starch fractions with narrow size ranges confirm previous studies showing that small granules tend to be more crystalline. However small granules were found to have higher swelling capacities than large granules. In this instance the increased swelling capacity of small granules as compared to large is probably due to the decreased amount of lipid per unit area at the surface of the small particles.

In section III, Proton (^{1}H) and Carbon-13 (^{13}C) NMR were used to investigate starch pastes made from different wheat varieties that have different pasting properties. ^{1}H spin-lattice (T_1) relaxation times, ^{1}H spin-spin (T_2) relaxation times, polymer hydration coefficients (h) and ^{1}H diffusion coefficients (D) of starch-water systems were determined. Line-widths at half-heights ($\Delta\nu_{1/2}$) of peak intensities at various carbon positions and total ^{13}C liquid signals were also obtained.

In all cases the NMR parameters were not found to be dependent on wheat variety.

The polymer hydration coefficient, that is the amount of water molecules that are in the bound state, was estimated from the ratio of the amplitude of the ^{1}H signal due to unfrozen water at 258K to the amplitude of the ^{1}H signal at 303K. A value of 0.34 gH2O/g dry starch was obtained.

The T_1 and T_2 magnetisation recovery curves for starch pastes were found to be single exponential functions. This suggests a fast molecular exchange of water molecules between different sites in the system. A two-state model based on exchange between bulk and bound water was shown to be adequate in describing the relaxation behaviour of water protons in the system.

Diffusion measurements of water molecules show that there is no restricted or barrier limited diffusion occuring in starch pastes. The diffusion coefficients were interpreted

using various models. The best model was found to be one which takes into account both the obstruction and hydration effects. This gives a shape factor for the suspended gel particles which indicates that water is diffusing through oblate ellipsoids. These are probably amylopectin molecules present in the starch pastes. In an attempt to confirm this possibility, ^{1}H NMR measurements were repeated on a pure amylopectin-water system. The diffusion coefficients of the amylopectin-water system were interpreted using the same model and similar result was obtained for the shape factor of amylopectin molecules.

The ^{13}C liquid signal results confirm that sharp resonances, which correspond to liquid-like behaviour on the NMR time-scale of the polysaccharide chains, are only observed when the starch is gelatinised. The decrease in the line-widths at half heights of the peak resonances at various carbon positions when the pasting temperature is increased is probably due to an increase in mobility of the polymer chains. In the various wheat starch pastes studied, a loss of about one-third of the total ^{13}C liquid signal was observed. This was attributed to the crystallisation of polymeric material, lipid-amylose complexes and remnants of ordered structures in the starch pastes.

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Table of Contents

	Page
Abstract	ii
Acknowledgements	vi
List of Tables	xii
List of Figures	xiv
GENERAL LITERATURE REVIEW	
A.1. Statement	1
A.2. Introduction	1
A.3. The occurrence, composition and structure of starch granules.	1
A.3.1. Occurrence	1
A.3.2. Composition	2
A.3.3 Structure	4
A.4. The gelatinisation process	6
A.5. The structure of pastes	8
SECTION I Rheological properties of starch pastes	
I.1. Introduction	9
I.2. Literature review	9
I.2.1. Empirical measurements	9
I.2.2. Fundamental measurements	12
I.2.2.1. Steady shear conditions	12
I.2.2.2. Oscillatory shear conditions	14
I.3. Scope of the present investigation	15
I.4. Experimental approach	16
I.5. Experimental	17
I.5.1. Materials	17
I.5.1.1. Origin and variety of wheat	17
I.5.1.2. Isolation of wheat starch	17
I.5.1.3. Size fractionation	17
I.5.1.4. Damaged starch	18

Page

I.5.2. Method of paste preparation 19

I.5.3. Measurement of viscoelastic behaviour of wheat starch pastes 20

I.5.3.1. Introduction 20

I.5.3.2. Apparatus 22

I.5.3.3. Experimental procedure 23

I.5.3.4. Treatment of data 23

I.5.4. Measurement of rheological properties of wheat starch pastes under steady shear conditions 24

I.5.4.1. Apparatus 24

I.5.4.2. Experimental Procedure 24

I.5.4.3. Treatment of data 24

I.5.5. Determination of the number of particles per gram of sample and the size distribution of starch granules 25

I.5.6. Determination of the swelling capacity of, and the exudate from, gelatinised granules. 26

I.6. Results 27

I.6.1. Viscoelastic behaviour of wheat starch pastes. 27

I.6.1.1. Linear viscoelastic behaviour 27

I.6.1.2. Frequency dependence of dynamic viscosity and rigidity 28

I.6.1.3. Effect of starch concentration 28

I.6.1.4. Effect of paste preparation condition and starch damage 32

I.6.2. Rheological properties of wheat starch pastes under steady shear conditions 36

I.6.2.1. High shear rate (10-4000 S^{-1}) 36

I.6.2.1.1. Effect of starch concentration 36

I.6.2.1.2. Effect of paste preparation condition 42

I.6.2.2. Low shear rate (0.4 - 10 S^{-1}) 42

I.6.2.2.1. Effect of starch concentration 48

I.6.2.2.2. Effect of paste preparation condition 55

I.6.3. Total number of particles per gram of sample and the size distribution of starch granules 55

Page

I.6.4. Swelling capacity of, and the exudate from, gelatinised granules. 60

I.6.4.1. Swelling capacity 60

I.6.4.1.1. Effect of wheat variety 60

I.6.4.1.2. Effect of paste preparation condition 64

I.6.4.1.3. Effect of fractionation of starch particles according to size 68

I.6.4.2. Exudate 69

I.6.4.2.1. Effect of wheat variety 69

I.6.4.2.2. Effect of paste preparation condition 69

I.6.4.2.3. Effect of fractionation of starch particles according to size 72

I.6.5. Structural features of starch pastes characterised by different dynamic viscosities and rigidities 74

I.6.6. Structural features of starch pastes characterised by different steady shear properties 74

I.6.7. Effect of paste storage on dynamic viscosity and rigidity 79

I.7. Discussion 84

I.7.1. Viscoelastic behaviour under oscillatory shear conditions 84

I.7.2. Rheological properties under steady shear conditions 91

I.7.3. Effect of paste storage on dynamic viscosity and rigidity 95

SECTION II The relationship between the physical structure and the swelling capacity of starch granules

II.1. Introduction and scope of the investigation 100

II.2. Experimental approach 101

II.3. Experimental 102

II.3.1. Materials 102

II.3.2. DSC measurements 102

II.3.3. X-ray measurements 103

II.3.4. Specific volume measurements 104

Page

II.4. Results 104
II.4.1. Enthalpy change during gelatinisation 104
II.4.2. Relative crystallinity 107
II.4.3. Specific volume 108
II.5. Discussion 111

SECTION III Nuclear Magnetic Resonance studies of wheat starch pastes

III.1. Introduction 115
III.2. Literature review 115
III.3. Scope of the investigation and experimental approach 116
III.4. Theoretical principles of NMR experiment 118
III.4.1. Quantum mechanical description 118
III.4.2. Classical description 119
III.5. Experimental 126
III.5.1. Apparatus 126
III.5.2. Paste preparation 126
III.5.3. Experimental procedure and treatment of data 126
III.6. Results 133
III.6.1. FID signal attenuation upon freezing 133
III.6.2. Self diffusion 135
III.6.3. Spin-lattice and spin-spin relaxation times 142
III.6.4. ^{13}C liquid signal 152
III.7. Discussion 157
III.7.1. Self diffusion 157
III.7.2. Spin-lattice and spin-spin relaxation times 158
III.7.3. ^{13}C liquid signal 159

APPENDICES

Ia Derivation of the simplified equations for the calculations of η' and G' using Oka's quadratic equations. 161

		Page
Ib	A description of the top-drive oscillatory co-axial viscometer	164
Ic	A sample calculation in determining the relative weight-size distribution curve of Gamut wheat starch from Coulter-Counter raw data	168
Id	Extrapolation technique to obtain the swelling capacity of a starch sample	169
Ie	Cumulative mass fraction versus particle size distribution curves for the various wheat starches	170
IIa	One-way analysis of variance, means and 95% Confidence Intervals for the emathalpy changes of various wheat starches	172
IIb	One-way analysis of variance, means and 95% Confidence Intervals for the X-ray relative crystallinity indices of various wheat starches	173
IIIa	A sample calculation showing the percentages of variation in using the simplified form of Equation [III.23] .	174

PUBLICATIONS 175

REFERENCES 176

List of Tables

Table		Page
I.1	Sample calculations of the percentage error in determining η' and G' using Equations [I.3] and [I.4].	22
I.2	Representative measurements of dynamic viscosity η' and rigidity G' as a function of the shear amplitude at an angular frequency of 0.1 rads^{-1} for Aotea wheat starch pastes.	27
I.3	Values of Co, $-m_\infty$, K_1 and correlation coefficient of the least squares fits to Equation [I.17] for various wheat starch pastes.	40
I.4	Percentage by weight of small granules in the various wheat starches.	59
I.5	Total number of granules per gram of sample and number of large granules per gram of sample in the various wheat starches.	60
I.6	Swelling capacities of the various wheat starches at 95.0^{0}C/1h.	64
I.7	Swelling capacities of various wheat starches formed in the Amylograph and of samples containing damaged granules.	67
I.8	Swelling capacities of the various starch fractions with narrow size ranges of Karamu and Raven wheat starches.	69
I.9	Percentages of exudate from gelatinised granules of the various wheat starches.	70
I.10	Percentages of exudate from gelatinised granules of various wheat starches formed in the Amylograph and of samples containing damaged particles.	70
I.11	Percentages of starch exuding from gelatinised granules of the various starch fractions with narrow size ranges of Karamu and Raven wheat starches.	73

Table		Page
I.12	Dynamic viscosities and rigidities at representative frequencies and other characteristics of pastes formed from different wheat starches under a range of conditions.	75
I.13	Apparent viscosities at specified shear rates, yield stresses and other characteristics of pastes formed from different wheat starches under a range of conditions.	77
I.14	Values of regression coefficients and correlation coefficients for the fits of Equations [I.22] and [I.23] at specified frequencies to the results in Table I.12.	89
I.15	Dynamic viscosities and rigidities at a representative frequency and other characteristics of pastes formed from various wheat starches outside the range of experimental conditions in Table I.12.	90
I.16	Values of regression coefficients and correlation coefficients for the fits of Equation [I.25] at specified shear rates.	94
I.17	95% Confidence Intervals of the Avrami exponents from the fits of the dynamic rigidity measurements of Gamenya and Aotea starch pastes to Equation [I.28].	96
II.1	Enthalpy change, relative crystallinity index, specific volume and number fraction of small granules per gram of sample for the various wheat starches.	110
II.2	Enthalpy change, relative crystallinity index and swelling capacity for the various size fractions of Karamu and Raven wheat starches.	110
III.1	The number of 90^0 pulse accumulations required to give satisfactory ^{13}C signals at various starch concentrations.	131
III.2	Values of regression coefficients of the fits of experimental results in Figures III.16 and III.17 to Equation [III.29].	147
III.3	Line-widths at half-height of the peak intensities at various carbon positions of ^{13}C spectra for Gamenya pastes at various starch concentrations.	152

List of Figures

Section I.

Figure		Page
I.1	Sinusoidally varying stress and strain for periodic deformation of a linear viscoelastic system.	20
I.2	Amplifier circuit diagram for the oscillatory coaxial viscometer.	167
I.3	Plots of the log of the dynamic viscosity and rigidity as a function of the log of the angular frequency for pastes containing different concentrations of Aotea wheat starch.	29
I.4	Plots of the dynamic viscosity of Gamenya and Aotea pastes as a function of the starch concentration at several frequencies.	30
I.5	Plots of the dynamic rigidity of Gamenya and Aotea pastes as a function of the starch concentration at several frequencies.	31
I.6	Plots of the log of the dynamic viscosity and rigidity as a function of the log of the angular frequency for pastes made from Gamenya wheat starch (3.75%) under different temperature/time treatments.	33
I.7	Plots of the log of the dynamic viscosity and rigidity as a function of the log of the angular frequency for pastes made from Aotea wheat starch (6.00%) at several damaged levels.	34
I.8	Plots of the log of the dynamic viscosity and rigidity as a function of the log of the angular frequency for pastes formed from Aotea wheat starch (6.50%).	35
I.9	Plots of the log of the apparent viscosity as a function of the log of the shear rate for various starch pastes.	37

Figure		Page
I.10	Plots of the log of the apparent viscosity as a function of the log of the shear rate for pastes containing different concentrations of Gamut wheat starch.	38
I.11	Plots of the pseudo-plasticity constant of Raven starch pastes as a function of the starch concentration.	39
I.12	Plots of the apparent viscosity at a shear rate of $120s^{-1}$ of Raven and Karamu starch pastes as a function of the starch concentration.	41
I.13	Plots of the log of the apparent viscosity as a function of the log of the shear rate for Gamut starch pastes (7.00%) prepared by varying pasting temperature, at a constant heating time of 1h.	43
I.14	Plots of the pseudo-plasticity constant of Gamut starch pastes as a function of the pasting temperature for several starch concentrations.	44
I.15	Plots of the apparent viscosity at a shear rate of $120s^{-1}$ of Gamut starch pastes as a function of the pasting temperature.	44
I.16	Plots of the log of the apparent viscosity as a function of the log of the shear rate for Hilgendorf starch pastes (5.77%) prepared by varying pasting time, at a constant pasting temperature of $95.0^{0}C$.	45
I.17	Plots of the pseudoplasticity constant of Hilgendorf starch pastes as a function of the pasting time for several starch concentrations.	46
I.18	Plots of the apparent viscosity at a shear rate of $120s^{-1}$ of Hilgendorf starch pastes as a function of the pasting time.	46
I.19	Plots of the log of the shear stress as a function of the log of the shear rate for various starch pastes.	47
I.20	Plots of the log of the shear stress as a function of the log of the shear rate for given concentrations of Gamut starch pastes.	49

Figure		Page
I.21	Plots of the yield stress of pastes prepared from Raven and Karamu wheat starches against the starch concentration.	50
I.22	Plots of the log of the shear stress as a function of the log of the shear rate for Gamut starch pastes (7.0%) prepared by varying pasting temperature, at a constant heating time of 1h.	51
I.23	Plots of the yield stress of pastes prepared from Gamut wheat starch as a function of the pasting temperature.	52
I.24	Plots of the log of the shear stress as a function of the log of the shear rate for Hilgendorf starch pastes (5.00%) prepared by varying pasting time, at a constant pasting temperature of 95.0^{0}C.	53
I.25	Plots of the yield stress of pastes prepared from Hilgendorf wheat starch as a function of the pasting time.	54
I.26 a-f	Relative weight versus particle size distribution curves for the various wheat starches.	56
I.27 a-f	Relative number versus particle size distribution curves for the various wheat starches.	61
I.28	Plot of the swelling capacity of Gamut wheat starch as a function of the pasting temperature, at a constant pasting time of 1h.	65
I.29	Plot of the swelling capacity of Hilgendorf wheat starch as a function of the pasting time, at a constant pasting temperature of 95.0^{0}C.	66
I.30	Plot of the percentage of exudate from gelatinised granules of a Gamut wheat starch as a function of the pasting temperature, at a constant heating time of 1h.	71
I.31	Plot of the percentage of exudate from gelatinised granules of Hilgendorf wheat starch as a function of the pasting time, at a constant pasting temperature of 95.0^{0}C.	71

Figure		Page
I.32	The development of dynamic rigidity at various ageing temperatures as a function of time for Gamenya starch pastes.	80
I.33	The development of dynamic rigidity at various ageing temperatures as a function of time for Aotea starch pastes.	81
I.34	The development of dynamic viscosity at various ageing temperatures as a function of time for Gamenya starch pastes.	82
I.35	The development of dynamic viscosity at various ageing temperatures as a function of time for Aotea starch pastes.	83
I.36	Plots of the log of the dynamic rigidity at a frequency of 0.05 rads $^{-1}$ versus log (C-Cs) for pastes made from Gamenya and Aotea wheat starches.	86
I.37	Plots of the log of the dynamic viscosity at a frequency of 0.05 rads $^{-1}$ versus log (C-Cs) for pastes made from Gamenya and Aotea wheat starches.	86
I.38	Plots of the log of the apparent viscosity at a shear rate of 120s $^{-1}$ of Raven and Karamu starch pastes versus log (C-Cs).	92
I.39	The fits of dynamic rigidity measurements for Gamenya starch pastes to Equation [I.28] at various ageing temperatures.	98
I.40	The fits of dynamic rigidity measurements for Aotea starch pastes to Equation [I.28] at various ageing temperatures.	99
Section II.		
II.1	Typical DSC thermograms of starch samples.	105
II.2	Plots of the average enthalpy change as a function of the water:starch ratio for Raven and Karamu wheat starches.	106
II.3	Typical X-ray normalised diffractometer traces of starch samples.	109

Figure		Page
II.4	Plot of the X-ray correlation crystallinity index as a function of the swelling capacity of various wheat starches.	112
Section III.		
III.1	Free Induction Decay (FID)	121
III.2	Pulse field-gradient method.	123
III.3	The evolution of M_z as a function of time.	123
III.4	The relationship between the ^1H relaxation times and the correlation time of water molecules.	124
III.5	Plots of ln (Ao-A) against time for two concentrations of Gamenya starch pastes.	128
III.6	Plots of ln A against time for two concentrations of Gamenya starch pastes.	129
III.7	Plots of ln A/Ao against I^2 for two concentrations of Gamenya starch pastes.	129
III.8	Typical FT ^{13}C NMR spectra.	132
III.9	Plots of the relative ^1H signal amplitude of pastes at 258K against the starch concentration for Aotea and Gamenya wheat varieties.	134
III.10	Plot of the relative ^1H signal amplitude at 258K against the amylopectin concentration for the amylopectin-water system.	134
III.11	Plots of the diffusion coefficient of water in pastes against the starch concentration for Aotea and Gamenya wheat varieties.	136
III.12	Plot of the diffusion coefficient of water in the amylopectin-water system against the amylopectin concentration.	136
III.13	Plot of the D/Do as a function of the volume fraction of polymer (Ø) for Gamenya starch pastes.	140
III.14	Plot of D/Do as a function of the weight fraction of polymer (W) for Gamenya starch pastes.	141

Figure		Page
III.15	Plot of D/Do as a function of the weight fraction of polymer (W) for the amylopectin-water system.	141
III.16	Plots of T_1 and T_2 of ^1H in pastes made from Aotea and Gamenya wheat varieties as a function of the starch concentration.	143
III.17	Plots of T_1 and T_2 of ^1H in the amylopectin-water system as a function of the polymer concentration.	144
III.18	Plots of $\frac{1}{T_{1obs}}$ of ^1H in pastes made from Aotea and Gamenya wheat starches as a function of (hc/1-hc).	148
III.19	Plots of $1/T_{2obs}$ of ^1H in pastes made from Aotea and Gamenya wheat starches as a function of (hc/1-hc).	149
III.20	Plot of $1/T_{1obs}$ of ^1H in the amylopectin-water system as a function of (hc/1-hc)	150
III.21	Plot of $1/T_{2obs}$ of ^1H in the amylopectin-water system as a function of (hc/1-hc).	151
III.22	Plots of the ^{13}C liquid signal per unit mass of starch as a function of the starch concentration for various pastes.	153
III.23	Plots of the total ^{13}C liquid signal for Karamu and Raven starch pastes (7.00%) as a function of the pasting temperature, at a constant heating time of 1h.	155
III.24	Plot of the line width at half-weight of the various carbons of the ^{13}C spectra of Karamu starch pastes as a function of the pasting temperature.	156
Plate 1	The top-drive oscillatory co-axial viscometer	166