

INVESTIGATIONS INTO THE ANTISTALING EFFECT OF WAXY DURUM IN BREAD

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ABSTRACT

Bread staling leads to substantial food wastage and hence economic and environmental burdens in the industrial world. Reduced amylose waxy wheat flour has shown potential as an antistaling additive in bread, although the causal mechanism at the molecular level is not well defined. The waxy durum under investigation in this study represents a novel substrate due to its breeding history, and has shown a strong antistaling effect in bread. Bread made from waxy durum flour was about half as firm initially and 25% less firm than conventional bakers' flour after a week's storage. The aim of this study was to comprehensively analyse the physicochemical and functional properties of this waxy durum flour and starch, to provide insights into its antistaling mechanism.

The swelling and gelatinisation properties of waxy durum were compared to those of a range of normal and waxy cereal starches. It was found that the waxy durum starch exhibited delayed swelling behaviour relative to other waxy cereal starches, most likely due to its higher relative amylose content. Surfactant treatment was found to eliminate diversity of swelling behaviour in normal, but not waxy starches. This suggested that factors other than starch surface proteins and lipids influence the swelling behaviour of waxy starches. As starch retrogradation was identified in the literature as a key factor in bread staling, flour and starch thermal properties were assessed at different water contents. The relationship between starch retrogradation and water content was also found to be different between the waxy and normal wheat starches studied, with retrogradation of waxy starches favoured by a more concentrated system.

Waxy durum starch and flour in isolation were found to exhibit a higher resistance to retrogradation than normal durum, and normal and waxy bread wheat starches. Both waxy flours were found to have a similar crumb softening effect after the first day of bread storage, however only the waxy durum flour produced a significant antistaling effect over longer term storage. It was postulated that the early stage crumb softening effect was related to the impact on rheological behaviour of the dough during the baking process, but that in the longer term the waxy durum reduced amylopectin retrogradation, suggesting that its unique thermal behaviour was the primary factor influencing its antistaling effect with a secondary contribution by minor flour components. The results of this study add to the breadth of current knowledge of the physicochemical and thermal properties of waxy durum starch and flour in particular and waxy starches and flours in general, with particular emphasis on mechanisms of antistaling functionality at the molecular level.

DECLARATION

I certify that this work contains no material which has been accepted for the award of any other degree or diploma in my name, in any university or other tertiary institution and, to the best of my knowledge and belief, contains no material previously published or written by another person, except where due reference has been made in the text. In addition, I certify that no part of this work will, in the future, be used in a submission in my name, for any other degree or diploma in any university or other tertiary institution without the prior approval of the University of Adelaide and where applicable, any partner institution responsible for the joint-award of this degree.

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Laura Blake

May 2015

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ABBREVIATIONS & SYMBOLS

| Abbreviation | Description |
|---------------------|---|
| A ₀ | Avrami equation; initial value of parameter |
| AACC | American Association of Cereal Chemists |
| A _f | Avrami equation; final or limiting value of parameter |
| AGT | Australian Grain Technologies |
| ANOVA | Analysis of variance |
| AP | Amylopectin |
| ATR | Attenuated total reflectance |
| CLD | Chain length distribution |
| DP | Degree of polymerisation (number of glycosyl units) |
| DSC | Differential scanning calorimetry |
| FAME | Fatty acid methyl ester |
| G | Lower temperature amylopectin gelatinisation endotherm |
| GBBSI | Granule Bound Starch Synthase I |
| GC | Gas chromatography |
| GOPOD | Glucose oxidase peroxidase |
| G | Lower temperature amylopectin gelatinisation endotherm |
| G _R | Lower temperature amylopectin retrogradation endotherm |
| HPAEC | High performance anion-exchange chromatography |
| ICPOES | Inductively coupled plasma optical emission spectrometry |
| k | Avrami equation; rate constant |
| LSD | Least significant difference |
| M1 | Higher temperature amylopectin gelatinisation endotherm |
| M1 _R | Higher temperature amylopectin retrogradation endotherm |
| M2 | Amylose-lipid complex melting endotherm |
| mb | Moisture basis (%) |
| MIR & NIR | Mid infrared and near infrared (spectroscopy) |
| MVA | Multivariate data analysis |
| n | Avrami equation; Avrami exponent |
| PAD | Pulsed amperometric detection |
| P content | Phosphorus content |
| PMP | 1-phenyl-3-methyl-5-pyrazolone |
| P-value | Statistical significance |
| RACI | Royal Australian Chemical Institute |
| rpm & rcf | Speed of centrifugation; in revolutions per minute (rpm) and relative centrifugal force (rcf) |
| RVA | Rapid visco analyser or analysis |
| S content | Sulphur content |
| SDS | Sodium dodecyl sulphate |
| SRC | Solvent Retention Capacity |
| t _{0.5} | Avrami equation; half-time (time to reach half the final value) |
| TLC | Thin layer chromatography |
| Tonset | Onset temperature (DSC) |
| Tpeak | Peak temperature (DSC) |
| WAS | Waite Analytical Services |
| wx | Waxy |
| v/v, v/w, w/v & w/w | Solute concentration in solution, specified with respect to weight (w) or volume (v). |

PUBLICATIONS ARISING FROM THIS THESIS

The list of publications associated with this work is provided below. These include journal articles and conference proceedings. The published journal articles are provided at the end of the thesis. Whilst I participated in the writing of the Lafaye et al. (2013) publication, the experimental work was completed by the French exchange students Julie Lafaye and Heiterani Lee, and as such is not included as a chapter in this thesis.

- Blake, L.H., Jenner, C.F., Gidley, M.J & Cozzolino, D. 2015. Effect of surfactant treatment on swelling behaviour of normal and waxy cereal starches. *Carbohydrate Polymers* **125**, 265-271.
- Blake, L., Jenner, C.F., Barber, A.R., Gibson, R.A., O'Neill, B.K. & Nguyen, Q.D. 2015. Effect of waxy flour blends on dough rheology and bread quality. *International Journal of Food Science & Technology* **50**, 926-933.
- Lafaye, J. Lee, H. Blake, L. & Jenner, C. 2013. Waxy durum acts as a unique form of crumb softener in bread. *Journal of Cereal Science* **58**, 393-399
- Blake, L., Jenner, C. F., Barber, A. & O'Neill, B. Waxy durum: novel starch with antistaling effects. Cereals 2013. Proceedings of the 63rd Australian Cereal Chemistry Conference in association with International Association for Cereal Science and Technology, 25th-28th August 2013, Freemantle, WA, Australia.
- Blake, L., Jenner, C. F., Barber, A. & O'Neill, B. Waxy durum slows staling in bread: mechanism of action. Cereals 2012. Proceedings of the 62nd Australian Cereal Chemistry Conference, 26th-29th August 2012, Gold Coast, QLD, Australia.
- Blake, L., Jenner, C. F., Barber, A. & O'Neill, B. Waxy durum flour as an antistaling agent in baked goods. AIFST 2012. Proceedings of the 45th Annual AIFST Convention, 15th- 17th July 2012, Adelaide, SA, Australia.
- Blake, L., Jenner, C. F., Barber, A. & O'Neill, B. Antistaling effects of waxy durum addition in sponge cakes. Cereals 2011. Proceedings of the 61st Australian Cereal Chemistry Conference, 4th-9th September 2011, Coolangatta- Tweed Heads, N.S.W. Australia.

STRUCTURE OF THIS THESIS

This thesis is presented as a combination of papers that have been published, as well as chapters that have not yet been submitted for publication. The published papers have been formatted to be consistent with the other results chapters and the acknowledgements sections removed. However, these chapters were prepared as standalone for publication. Therefore, this style of presentation results in some areas of repetition, particularly in the introductions and methods sections. The final journal publications as they appear in print are provided at the end of the thesis for reference. A single reference list (formatted in the style for *International Journal of Food Science & Technology*) is provided at the end of the thesis.

Chapter 1 provides an overview of the literature and the objectives of this research. Each chapter also includes a brief introduction of the literature and concepts relative to that piece of work. Chapter 2 details the material and methods used throughout the thesis. The published articles also contain materials and methods sections. However, Chapter 2 contains the most detailed description of experimental methodology, as published work was abridged due to space and word limitations. The other results chapters, not yet published, also include a short section entitled experimental methodology, which details which methods were used in that chapter and a brief discussion of the experimental design.

Chapter 3 comprises a paper published in *Carbohydrate Polymers*, entitled ‘Effect of surfactant treatment on swelling behaviour of normal and waxy cereal starches’. It describes the effect of a common surfactant treatment on the swelling behaviour of four normal and waxy cereals; durum, bread wheat, barley and maize. In this chapter, the behaviour of the waxy durum material is compared to these other starches. Unpublished results from this study that were peripheral to the aims of the paper, but were of importance to the broader aims of this thesis are included in Appendix A.

Chapter 4 describes the thermal properties of the waxy durum in a concentrated system. This chapter follows on from Appendix A of Chapter 3, which details the thermal behaviour of waxy durum starch in a dilute system. These results have not yet been submitted for publication. The waxy durum starch was found to contain a relatively high amylose content (8.8%), compared to both literature values for waxy wheat starches and the previous harvest of this cultivar. Chapter 5 investigates potential causes of this high amylose content, and its impact on the physicochemical behaviour of the waxy durum starch.

Chapter 6 comprises a paper published in the *International Journal of Food Science & Technology*. It primarily describes the dough rheological behaviour of waxy flour blends and

the correlations to baking performance. Chapter 7 outlines the bread staling experiments, including combined texture analysis and differential scanning calorimetry analyses. These results have not yet been submitted for publication. Chapter 8 provides a synthesis of the findings contained in this thesis and includes recommendations for future work.