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Hierarchical Structure Function Models of Biopolymer Networks

Thesis submitted to the Institute of Fundamental Sciences, Massey University,
New Zealand in partial fulfilment of the requirements for the degree of

Doctor of Philosophy in Physics

Palmerston North, October 2011

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Abstract

This project aimed to bridge the structure-function divide in polysaccharide networks so that the rheological properties of multi-chain assemblies might be predicted from the fine structures of the constituent polymers and their mode of assembly. The polysaccharide pectin is an important constituent of the plant cell wall and when cured into a gel the mechanical properties of its networks have recently come into the focus of research via extensive microrheological studies, in which interesting connections between the gel's mechanical response, gelation conditions and the pectin fine structure were discovered. This tunability makes it therefore a promising model system for further experiments and computer-aided investigations, and accordingly it is the focus of this thesis.

Firstly, a small angle X-ray scattering study of different microrheologically well-characterized ionotropic pectin gels was undertaken to gain insights into the structures of the assembled elementary network strands. The SAXS results paired with molecular modelling confirm that gels which are semiflexible from a microrheological point-of-view contain large bundles of aggregated dimers compared to the more flexible networks, where predominantly single chain sections and dimers are found to contribute. These later gels can be formed among other ways using a biomimetic methodology exploiting plant enzymes.

Secondly, after learning that networks could be experimentally manifest where single chains form the majority of links between nodes, in contrast to the better known hierarchical structures of polysaccharide gels, a computational approach was pursued to investigate the behaviour of biopolymer networks comprised of single polysaccharide chains using the experimentally measured force extension relation for pectin. This exhibits interesting force-induced conformational transitions that have been investigated in their own right. A 2-dimensional model was initially chosen for practical purposes. The study supports the hypothesis that conformational transitions could have biological significance as stress-switches in signalling processes, but that they are unlikely to affect the bulk rheological properties of tissue.

Finally, the model was further expanded into 3-dimensions to test quantitatively its predictions of the shear moduli of such systems. To this end a comparison with rheological prestress experiments on enzymatically induced pectin gels was undertaken. The model was found to successfully describe the observed nonlinear rheology for completely percolated, strong gels, based only on the polymer concentration and an experimentally accessible single chain force-extension relationship; for the first time providing a true bottom-up example to the properties of soft materials.

Acknowledgements

Thanks first to Bill Williams for being such an enthusiastic and supportive supervisor and to my co-supervisor Leif Lundin for invaluable guidance, regardless of being located in Melbourne. Thanks for introducing me to this interdisciplinary field, giving me the possibility to attend conferences and the great flexibility when it came down to balance the lab and tide times. Discussions - not just about pectin - with Padmesh Anjukandi, Yacine Hemar and Romaric Vincent have been fun and stimulating. I also want to acknowledge the helpful collaborators at CSIRO, especially Stephen Homer for the help with the prestress experiment, as well as Sofia Øiseth, Andrew Leis, Sandra Crameri and Alex Hyatt for providing the TEM images, the SAXS/WAXS beamline team at the Australian Synchrotron, in particular Nigel Kirby, and Kate Nairn for support during the running of the SAXS experiments. Many thanks to Aurelie Cucheval for help with the sample preparations and the microrheological analysis, and also for all the (long) coffee breaks. Cheers to all the members of the biopolymer group, especially Stephen Keen, Lisa Kent, Brad Mansel and Davide Mercadante. It was great to have 'obnoxious' discussions in the office and the odd beer after hours. I am grateful for all my friends: thanks to the NZ-crew, it made life overseas very enjoyable, and cheers as well to the guys in Austria for the continuous 'online-support'. Zu guter Letzt möchte ich meinen Eltern und Geschwistern meinen herzlichen Dank aussprechen - eure Unterstützung war auch am anderen Ende der Welt grandios. En Anne, dank je wel voor de inspiratie en alle moois dingen die we samen doen.

This research is supported by the Commonwealth Scientific and Industrial Research Organisation (CSIRO), Australia.

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List of Publications

- [P1] E. Schuster, L. Lundin and M.A.K. Williams, *Insights into the potential functionality of single-chain force-induced conformational transitions in polymer networks: Implications for polysaccharide signaling in the plant cell wall*, Physical Review E **82**, 051927 (2010).
- [P2] E. Schuster, A. Cucheval, L. Lundin and M.A.K. Williams, *Using SAXS to reveal the degree of bundling in the polysaccharide junction-zones of micro-rheologically-distinct pectin gels*, Biomacromolecules **12**, 2583 (2011).
- [P3] E. Schuster, L. Lundin and M.A.K. Williams, *Biomimetic Polysaccharide Gels Allow Quantitative Bottom-Up Prediction of Network Mechanics*, submitted.

List of Abbreviations

AE	Affine entropic regime
AFM	Atomic force microscopy
AM	Affine mechanical regime
AN	Affine network model
CE	Capillary electrophoresis
CEWLC	Clickable extensible wormlike chain
CG	Conjugate gradient
DFT	Density-functional theory
DM	Degree of methylesterification
DN	Discrete Network Model
DP	Degree of polymerisation
DWS	Diffusing wave spectroscopy
EANC	Elastically-active network chain
EWLC	Extensible wormlike chain
FE	Force-extension
GWLC	Glassy wormlike chain
HG	Homogalacturonan
HWLC	Helical wormlike chain
MR	Microrheology
MSD	Mean-square displacement
NA	Non-affine regime
OZ	Ornstein-Zernike equation
PGA	Polygalacturonic acid
PME	Pectinmethylesterase

pPME	plant PME
SANS	Small angle neutron scattering
SAXS	Small angle X-ray scattering
SEC	Subelastic chain model
TEM	Transmission electron microscopy
WLC	Wormlike chain