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PHD THESIS

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# Structure and Dynamics of Biopolymer Networks

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*A thesis presented in partial fulfillment of the  
requirements for the degree of*

*Doctor of Philosophy  
in  
Physics*

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# Abstract

The aim of this work was to further understand the structural and dynamical properties of pectin-based biopolymer networks. This is pertinent to furthering our understanding of the plant cell wall and has further implications for the food and pharmaceutical industries where biopolymer networks play a fundamental role in thickening and stabilizing food products and controlling the rate of drug release.

Firstly, microrheological studies on an acid-induced pectin network revealed previously unseen slow motions of the network at times longer than one second. This "slow mode" is reminiscent of so-called alpha processes that are predicted with mode coupling theory in colloidal glasses. Such slow motions present in the networks are a signature of an out-of-equilibrium system and lead to further work on studying slow relaxation processes in pectin networks.

Secondly, structural and rheological measurements were performed on the acid-formed pectin networks. It was found using small-angle x-ray scattering that the network was composed of flexible cylindrical entities with a radius of 7 Å. At larger length scales these entities were arranged in a clustered confirmation that upon heating increased in density, indicating the importance of kinetic trapping for the initial network formation.

Finally, multi-speckle dynamic light scattering experiments were performed on three different ionotropic pectin gels formed with calcium to study the dependence of the slow dynamics on the junction length (and binding energy) between pectin chains. It was found that increasing the junction length slows the dynamics until a point where the internal stress becomes so large that the dynamics increase again. Spatially resolved photon correlation spectroscopy measurements revealed previously unmeasured millimetre sized heterogeneity in the networks. Angle-resolved multi-speckle photon correlation spectroscopy showed conclusively that the dynamics are driven by internal stresses and further more allowed the temporal heterogeneity to be measured.

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- [1] R R Vincent, B W Mansel, A Kramer, K Kroy, and M A K Williams. Microrheological behaviour and nonlinear rheology of networks assembled from polysaccharides from the plant cell wall. *New Journal of Physics* **15(3)** March 2013. ISSN 1367-2630. doi: 10.1088/1367-2630/15/3/035002.
- [2] B W Mansel, C-Y Chu, A Leis, Y Hemar, H-L Chen, M A K Williams. Zooming In: Structural Investigations of Rheologically Characterized Hydrogen-Bonded Polysaccharide Networks, submitted to *Biomacromolecules*
- [3] B W Mansel, M A K Williams, Internal Stress drives slow glassy dynamics and quake-like behaviour in ionotropic pectin gels, submitted to *Soft Matter*
- [4] Y F lim, R G Lentle, P W M Janssen, M A K Williams B W Mansel, P Chambers. Determination of Villous Rigidity in the Distal Ileum of the Possum (*Trichosurus vulpecula*). *PLoS ONE* **19(6)** June 2014. ISSN 1932-6203 doi: 10.1371/journal.pone.0100140.
- [5] Y F Lim, M A K Williams, R G Lentle, P W M Janssen, B W Mansel, S A J Keen, P Chambers. An exploration of the microrheological environment around the distal ileal villi and proximal colonic mucosa of the possum (*Trichosurus vulpecula*). *Journal of The Royal Society Interface* **81(10)** Feb 2013. ISSN 1742-5689. doi: 10.1098/rsif.2012.1008.