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The MacDiarmid Institute for Advanced Materials and Technology

Microrheological investigations of biopolymer networks

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Abbreviations:

MPT	Multiple Particle Tracking
DWS	Diffusing Wave Spectroscopy
R_{eff}	Ratio of the $[Ca^{2+}]$ quantity over the quantity of the acidic PGA residues which can effectively bind calcium $[COO^-]_{blocks}$
HG	Homogalacturonan
DM	Degree of Methyl-esterification
HM pectin	High-Methoxy pectin
LM pectin	Low-Methoxy pectin
DB	Degree of Blockiness
DB_{abs}	Absolute Degree of Blockiness
RGI	RhamnoGalacturonan I
RGII	RhamnoGalacturonan I
AFM	Atomic Force Microscopy
PME	Pectin Methyl-Esterase
f-PME	Fungal Pectin Methyl-Esterase
p-PME	Plant Pectin Methyl-Esterase
NMR	Nuclear Magnetic Resonance
TEM	Transmission Electron Microscopy
SEM	Scanning Electron Microscopy
PL	Pectin Lyase
PG	PolyGalacturonase
m_{pectin}	Mass of pectin
$m_{uronic\ acid}$	Mass of the charged galacturonic residues

M_W^{GalA}	Molecular weight of the galacturonic residues
C_p	Polymer concentration
L_p	Persistence length
PGA	PolyGalacturonic Acid
R	Ratio [Ca^{2+}] quantity over the total quantity of the acidic PGA
EBSD	Electron Backscattering Diffraction
σ	Stress
G	Shear modulus
γ	Strain
$\dot{\gamma}$	Strain rate
η	Visocosity
ω	Frequency
σ_0	Stress amplitude
γ_0	Strain amplitude
δ	Out of phase angle of the stress
$G^*(\omega)$	Complex viscoelastic modulus
$G'(\omega)$	Elastic modulus
$G''(\omega)$	Viscous modulus
HF	High frequencies
$\hat{G}(s)$	Laplace transform of the shear modulus
MR	Microrheology
k_B	Boltzmann constant
T	Temperature
$\left\langle \hat{\Delta} r^2(\tau) \right\rangle$	Laplace transform of the MSD

a	Brownain particle radius
DLS	Dynamic Light Scattering
PEG	PolyEthylene Glycol
PEO	PolyEthylene Oxyde
$\left\langle \Delta r^2(\tau) \right\rangle$	Mean Square Displacement
τ	Time lag
$g_1(\tau)$	Field autocorrelation function
$g_2(\tau)$	Intensity autocorrelation function
l*	Light mean free path
z_0	Penetration depth
L	DWS sample thickness
$r_\alpha(t)$	Position of the α particle at time t
$D_{rr}(t,\tau)$	Correlated diffusion coefficient
$D_{r\,R}^{\,i}(t,\tau)$	Displacement of the i particle during τ
$D_{r\,R}^{\,j}(t,\tau)$	Displacement of the j particle during τ
R	Distance between 2 particles
$\left\langle \Delta r^2(\tau) \right\rangle_{TPMR}$	MSD for the Two-Point MicroRheology

Abstract

Pectin is a major polysaccharide of the plant cell wall which is known to play a role in many mechanical functionalities, especially when a gel is formed in the presence of calcium. Understanding the gelling abilities of pectin is of great interest to the food industry also, since pectin is a widely used as a gelling agent and thickener. The aim of this study was to apply two complementary microrheological techniques to these systems, multiple particle tracking (MPT) and a light scattering technique called diffusing wave spectroscopy (DWS). While the first one provides fundamental information about the homogeneity of the studied gel, the second gives access to the high frequency behaviour, related to the nature of the basic strands of the network.

Firstly, after verifying the validity of the experimental apparati and analysis approaches in a series of careful control experiments on archetypal systems, a regime where pectin gels exhibit the signatures of semi-flexible networks was identified in experiments carried out on gels made of pectin chains pre-engineered by enzymatic deesterification and subsequently assembled with the release of Ca^{2+}. These results were the first showing that polysaccharides networks could be accommodated within the framework of semi-flexible networks, which have become a paradigm for biological gels, such as the well-known F-actin solutions present in the cell cytoskeleton.

However, in the plant cell wall, where calcium is already present, the assembly mechanism could be controlled in a different manner, and a more biologically relevant system was studied where the action of the plant enzyme pectinmethylesterase was used to liberate ion-binding groups in the presence of Ca^{2+}. Gels formed according to this alternative methodology were found to behave as punctually cross-linked flexible networks, strikingly different from the first results. This would be explained by the presence of short blocks of charged residues.

Finally, experiments on pectins carried out with controlled blocky structures showed that a pectin made of short blocks can exhibit both sorts of network, depending on the polymer and Ca^{2+} concentrations. This lead naturally to the construction of a state diagram for the regimes of assembly, with proposed control parameters being the polymer concentration and the ratio of the amount of Ca^{2+} to the quantity of pectic residues which can effectively bind the calcium into cross-links, christened R_{eff}.

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