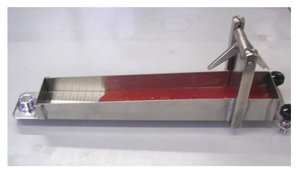

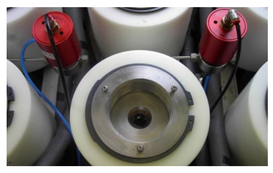



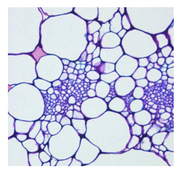


Effect of methoxy-esters distribution pattern on the rheological properties of pectin-calcium gels: Toward understanding pectin structure-function relations

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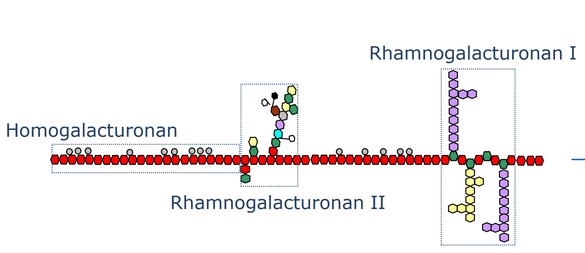
INTRODUCTION



Partially demethoxylated pectin (PDP)

Ca 2+

Junction zone (JZ)

PDP-Ca^{2+} network (gel)

Endogeneous pectin responsible for texture retention of processed fruits / vegetables

Extracted pectin imparts desired texture to food systems

Pectin structural features : DM and PM

(PM as DB_{abs} , indicative for non-methoxylated GalA (NMG) residues present in blocks, thus available for JZ formation)

?

Rheological characteristics

(gel strength) of cured pectin-Ca^{2+} gels

Pectin structure - function relation ?

● *Methyl group* ● *Galacturonic acid (GalA)*

DM: Degree of methoxylation *PM: Pattern of methoxylation* *DB_{abs}: Absolute degree of blockiness*

MATERIALS AND METHODS

STEP I

Citrus pectin (DM ~94%; DB_{abs} < d.l.)

DM = (mole ● / mole ●) x 100

DB_{abs} = (Total NMG released / Total GalA) x 100

Demethoxylation

Plant (Carrot) PME (pH 7.0) | *Fungal (A. aculeatus)* PME (pH 4.5) | *Chemical (NaOH) saponification (pH 11.0)*

P-PDP | **F-PDP** | **C-PDP**

Structural characterization of PDPs: DM and DB_{abs}

DB_{abs} estimation: (1) Endo-PG digestion of PDPs and release of NMG

(2) Chromatographic determination of NMG as mono-, di- and tri-GalA

STEP II

µls $CaCl_2$ solution (30°C)

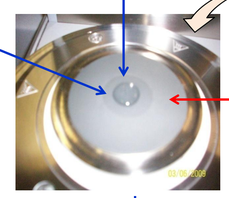
$R = 2[Ca^{2+}] / [COO^-]$

→ $[Ca^{2+}]$ varies with DM

µls PDP solution (2%(w/v); 50°C; pH 6.0)

Δ DM & PM

R = 2.0



Lowering Peltier hood

Peltier controlled Physica MCR 501 rheometer
(on anti-vibration table)

Curing:
50°C for 10 min
50°C - 20°C @ 0.5°C/min
20°C for 5 hours

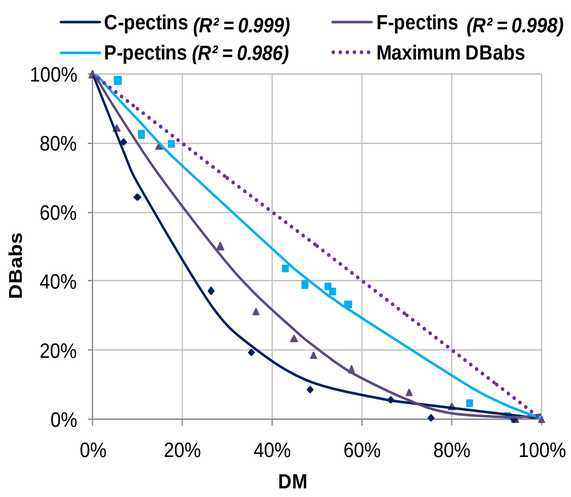
Rheological characterization of PDP-Ca^{2+} gels:
gel strength (G') of cured gels

d.l.: detection limit PG: Polygalacturonase *PME: Pectinmethylesterase* *A.: Aspergillus*

RESULTS AND DISCUSSION

❑ Structural characterization of partially demethoxylated pectins (PDPs)

▪ Effect of demethoxylation on DB_{abs}



➢ Each de-esterification method resulted in ≠ relation between DM and DB_{abs} indicating ≠ methoxy-ester distribution pattern.

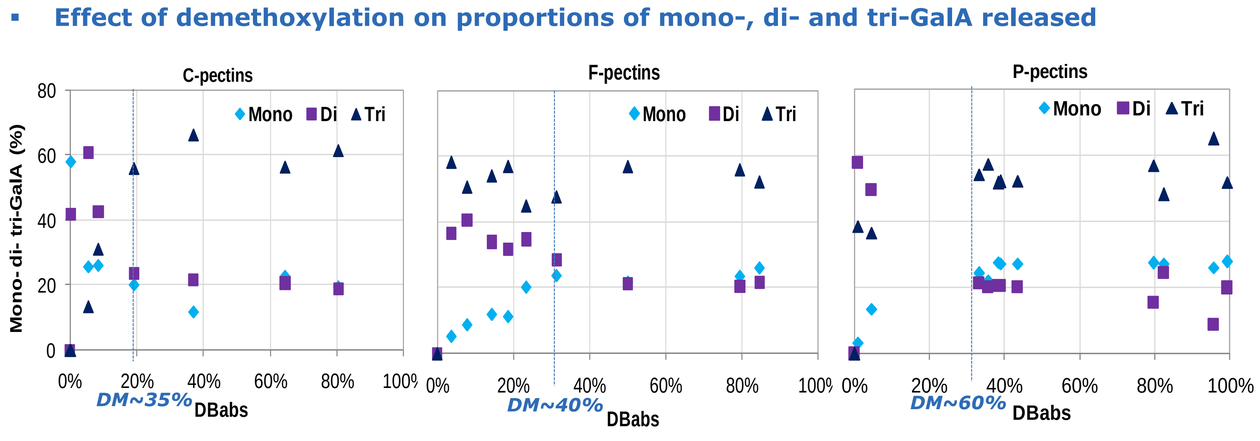
⟶ Occurrence of ≠ number and/or size of NMG blocks at similar DM.

➢ C-pectins (completely random distribution of NMG residues/blocks) revealed an exponential relation (approximated by 3rd order polynomial) between DM and DB_{abs}.

➢ As the distribution pattern of NMG became more blocky, the relation gradually shifted toward linearity.

➢ Actually, a linear relation is theorized between DM and DB_{abs} of ideally (theoretical) blocky pectins, where virtually, all NMG are released by endo-PG as mono-, di- or tri- GalA (implying total NMG released ≈ total NMG residues of pectin), thereby resulting in DB_{abs} ≈ 100%-DM.

▪ Effect of demethoxylation on proportions of mono-, di- and tri-GalA released



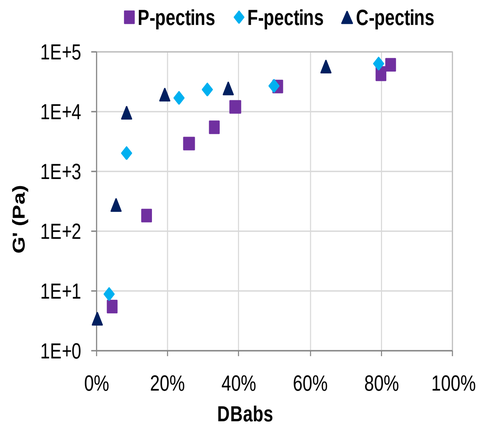
➢ PDPs displayed ≠ proportions of mono-, di- and tri-GalA at early stages of de-esterification.

➢ From a certain critical DB_{abs} value (~20%, ~30%, and ~30%) corresponding to DM values of ~35%, ~40% and ~60% in C-, F- and P-pectins respectively, all PDPs showed similar proportions of mono-di-tri-GalA, with tri-GalA higher in proportion than the rest. This suggested the occurrence of large NMG blocks in these PDPs

⟶ From critical DB_{abs}, all PDPs show some similarities in distribution of NMG blocks over the entire polymer

❑ Rheological characterisation of PDP-calcium gels (R = 2.0)

▪ Effect of pattern of methoxylation on gel strength (G')



In gel networks, high G' related to high number of cross-link points (junction zones (JZ) for pectin-Ca^{2+} gels) per polymer chain.

➢ In C- and F-PDP gels, a two step increase of G' was observed with increasing DB_{abs}. The initial pronounced increase (DB_{abs} < critical DB_{abs}) was mostly related to increase in number of JZ (mainly increase in umber of NMG blocks per PDP chain) at early de-esterification while the slow increasing step was mostly attributed to an increase in the size of the JZ (mainly increase in size of NMG blocks later during de-esterification).

⟶ PDPs with DB_{abs} < critical DB_{abs} generate gels predominantly characterized by high number of shorter JZ, while PDPs with DB_{abs} ≥ critical DB_{abs} yield networks consisting of few but longer JZ.

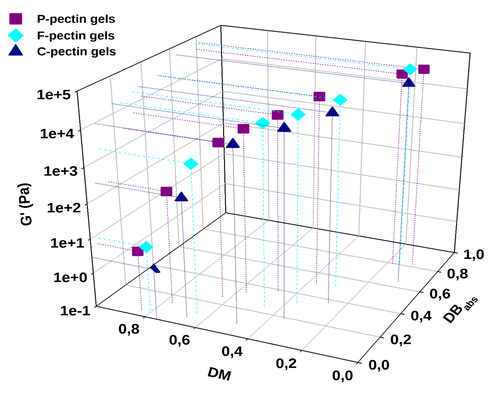
⟶ In C- and F-pectin gels, high G' is either related to high number of JZ or/and longer JZ per pectin chain

➢ P-PDP gels showed a more gradual increase of G' with increasing DB_{abs}. This indicates that the mechanism inducing an increase in G' is rather similar in these gels. In P-pectin gels, increase in G' was related not only to the increase in the number / size of JZ per chains (DB_{abs} < critical Db_{abs}) but also to the number of Ca^{2+} dimerized pectin chains in the network.

⟶ PDPs with DB_{abs} < critical DB_{abs} generate gels predominantly characterized by shorter JZ and few Ca^{2+}dimerized chains, while PDPs with DB_{abs} ≥ critical DB_{abs} yield networks consisting of longer JZ and more Ca^{2+}dimerized chains

⟶ In P-pectin gels, high G' is either related to high number or/and larger size of JZ per pectin chain or/and high number of Ca^{2+} dimerized chains in the network.

▪ Effect of degree and pattern of methoxylation on G'



➢ A combined effect of degree and pattern of methoxylation revealed C-, F- and P-pectin gels having quite comparable strength at rather similar DM.

➢ At similar DM, PDPs carry NMG blocks but while P-PDPs have larger blocks on few chains, many (if not all) F- and C-PDP chains carry shorter and shortest NMG blocks respectively.

⟶ The large size of JZ seems to fully compensate for the presence of few Ca^{2+} dimerized pectin chains in P-pectin gel networks, so that the net effect of all parameters (number & size of JZ per chain and number of dimerized chains) becomes rather comparable at similar DM.

CONCLUSION

➢ Increase in the number of NMG blocks per PDP chain, thus increase in the number of junction zones per chain in corresponding Ca^{2+} gels, results in an increase of gel strength.

➢ Increase in the size of NMG blocks per PDP chain, thus increase in the size of junction zones in corresponding Ca^{2+} gels, equally results in an increase of gel strength.

➢ Increase in the number of demethoxylated chains, thus increase in the number of dimerized chains in the corresponding Ca^{2+} gel also results in an increase of gel strength.

⟶ In concentrated pectin-Ca^{2+} gels saturated with Ca^{2+}, DM (rather than PM) plays a major role in controlling gel strength.

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