Making dense covalent arabinoxylan gels with high swelling properties: A strategy based on water extraction through osmotic compression (1)

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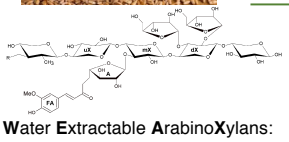
Context and objectives

Enzymatic oxidation of feruloylated arabinoxylan solutions produce covalent macroporous hydrogels with a huge water holding capacity which make them powerful encapsulation matrix(2). Even if their covalent network is stable, WEAX gels remain mechanically brittle because of their low polymer content that is required for the oxidative gelation process.

In this study, we propose a **strategy for producing more concentrated and less fragile hydrogels**. It is based on the **extraction of water from 1% (w/v) WEAX enzymatic gels using osmotic compression**. This approach aims to reinforce the mechanical resistance of the gels before swelling, while preserving their covalent network and swelling capacity.

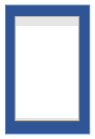
Material and methods



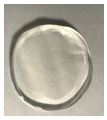
Water **E**xtractable **A**rabino**X**ylans: WEAX (purity:64%)

Gelation — *Enzymatic oxidation* — 1 % WEAX Gels (w/v)

+2h, 20°C

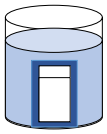


Dialysis cassette
WEAX + citrate buffer 0.1 M, pH4 + **laccase (3 U.mg^{-1} FA)**



Osmotic compression — *Polymer concentration* — 12/22 % WEAX Gels (w/v)

+3 j, 4°C



PEG 10/20 % (w/v) + citrate buffer 0.1 M, pH4

Methods- characterization

Cylindrical sampling

20 mm

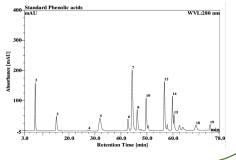
$V_{1\%}$: 1.27 +/- 0.09 cm^3
$V_{10\%}$:0.16 +/- 0.02 cm^3
$V_{20\%}$:0.14 +/- 0,03 cm^3

Rheology

Swelling

H_2O+ 0.02% azide, 20 h, 20°C:

Biochemical analysis



Results

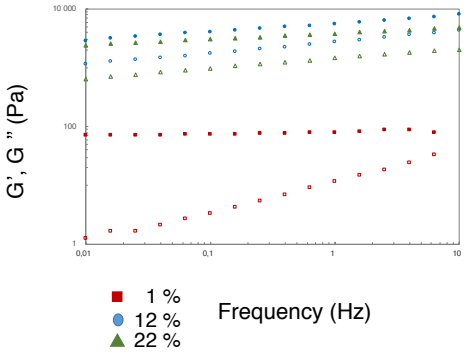
WEAX content % (w/v)	di-FA µg. mg^{-1} AX	Tri-FA µg. mg^{-1} AX
1	0.26 +/- 0.02	0.02 +/- 0.00
12	0.60 +/- 0.04	0.05 +/- 0.01
22	0.66 +/ 0.02	0.06 +/- 0.00

two-times more covalent connectivity

WEAX content % (w/v)	G' Pa	G" Pa
1	79 +/- 5	12 +/- 1
12	4521 +/- 1022	2199 +/- 768
22	4194 +/- 1684	2340 +/- 1156

two-order of magnitude higher

Mechanical spectra



Results

Swelling capacity

WEAX swollen gel content % (w/v)	q g H2O.g^{-1} WEAX	G' Pa
0.8 +/- 0.0	126 +/- 3	72 +/- 1
1.1 +/- 0.0	93 +/- 4	132 +/- 35
1.3 +/ 0.2	78 +/- 10	164 +/- 18

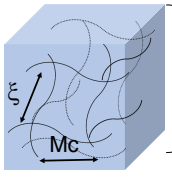
- 30%

X2

q: swelling ratio

0.7 % (w/v) **alginate gels: q= 16-72 g H_2O.g^{-1}** alginate(3)

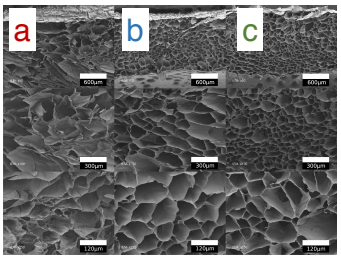
1 % (w/v) **chitosan gels: q= 14-18 g H_2O.g^{-1}** chitosan(4)



ρ_c crosslink density
ξ : mesh size
Mc: average molecular weight between two crosslinks

Microscopic observations of WEAX cryogels at swelling equilibrium

(a): 1 % WEAX
(b): 12 % WEAX
(c): 22 % WEAX



scale bars are 600, 300 and 120 µm, from the top to the bottom

Theoretical calculation of structural properties

WEAX gel content before swelling % (w:v)	Flory-Rehner modified by Peppas and Merrill: Mc g.mol^{-1} .10^3	ξ nm	ρ_c mol.cm^{-3}. 10^{-6}
1 +/- 0	188 +/- 1	308 +/- 3	8.9 +/- 0.0
12 +/- 4	171 +/- 4	265 +/- 7	9.8 +/- 0.2
22 +/-3	151 +/- 20	236 +/- 22	11.1 +/- 1.1

Conclusions:

- ✓ osmotic compression is very efficient to reach polymer content up to 20 % (w/v)
- ✓ gels keep an homogeneous structure of mesh size above 200 nm
- ✓ two times more covalent crosslinks
- ✓ increase by two-order magnitude of the viscoelastic properties
- ✓ highly water holding capacity maintained
- ✓ huge swelling volume factor as they swell 10-20 times their initial volume
- ✓ mechanically reinforced even at swelling equilibrium

✗ The structure and properties of the 12 and 22% (w/v) WEAX compressed gels are not strongly different neither in both the unswollen and swollen state

References
(1)Assor-Antoine et al., *Applied Polymer Materials*, In press.
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