RHEOLOGICAL MODELS OF PECTIN FILMS

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ABSTRACT

Pectin films were measured by Stable Micro Systems® penetrometer, with relaxation method. Citrus pectins from CP Kelco® were varied in charge distribution and degree of esterification. There was some amidated pectin from PIC Co as well. A controlled hydration by polyethilenglicol (PEG) 20000 solution, with and without different salts and concentrations was taken. The hydration causes swelling. The equilibrium swelling of the films (after 24 hours hydration) was investigated. The force relaxation at constant deformation, achieved by slowly stretching till a small force and after that the deformation were stored for 30 second and force decreasing were measured. The curves were analysed by two rheological models – Maxwell model and Zener model, with a small modification. Results say that the Zener model shows better fitting on relaxation curves, and give some dependences for rheological properties on pectin types and concentrations.

INTRODUCTION

The pectin is the most important mechanical component of the plant cell-wall, because it gives an elastic connection between the cells. The pectin is hydrated by water and salt solution. The hydration environment changes during ripening and storing. In the cell wall there are two different networks: the cellulose (with parallel fibrils) and the pectin. The pectin chains bind the cell-wall components, giving an elastic connection between them (Fig. 1) (Voragen et al, 1995).

Pectins are charged polysaccharides based on uronic acid chains. A fraction of the uronic acid residues are methyl esterified. There are some rhamnose junctions with galactose and arabinose side chains as

well. Based on the amount of esterified molecules, the pectin can be low esterified (LM; up to 50%) or high esterified (HM; higher 50%). It depends on the source and the method for extraction. The charged sections can be with random or block distribution based on the number of charges in a sequence (Guillotin, 2005).

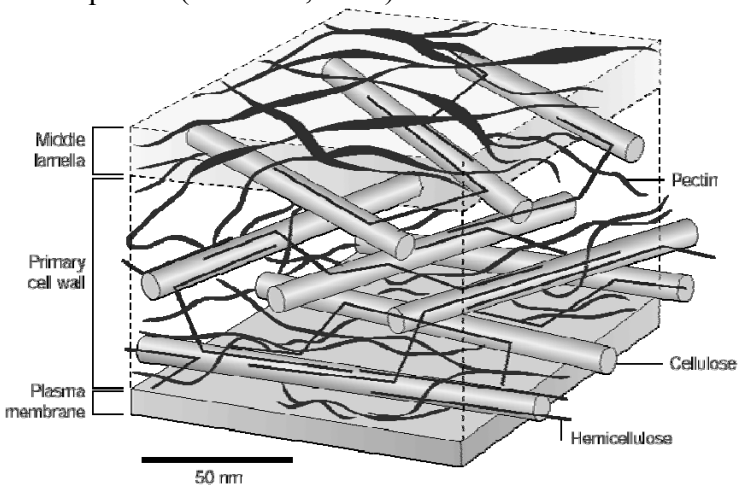


Figure 1 Microstructure of plant cell-wall

The LM pectin forms gel at low concentrations, in the presence of ions with two positive charges, for example Mg^{2+} or Ca^{2+}. In that case the gel has egg-box structure. With more chains make dimmers, or complexes. The junction zones are 14-20 monomers (Ralet et al, 2001). The concentration of ions has high effect for the firmness of the gel, but if the concentration is too high, the result can be ion condensation (Voragen et al, 1995). Low pH or high temperature can give weaker gels. Ions, with one positive charge can't induce gelation.

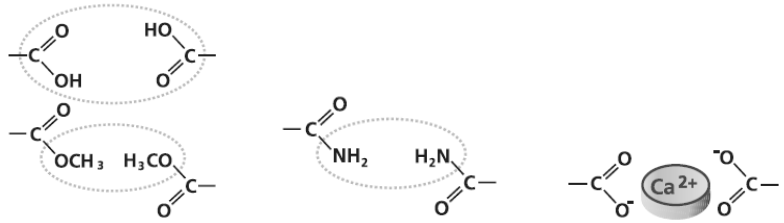


Figure 2 Gelling mechanisms

HM pectins gel, at low pH and high sugar concentration by forming of H bindings (Rolin and De Vries, 1990). Amidated pectin (Am) is deesterified by ammonia from high esterified pectin. That is low esterified, and low amidated pectin. It shows both gelling mechanism together (Fig. 2) (Guillotin, 2005).
The cross-linked and charged pectin network hydrated in equilibrium with an electrolyte solution. The equilibrium solution contains counter-ions. Excess of counter-ions generates an osmotic pressure difference between the network and the solvent. This osmotic pressure difference leads the swelling. It depends on the affinity of polymer for water, on the Donnan effect, and on the network cross-links. The swelling cause a changing of the free energy in the three dimensional polymer networks, during the hydration (Flory, 1953).

The base deformations of rheology are the elastic and viscous deformations, but the biological materials contain bound water and show these properties together. Based on the superposition principle of rheology the pectin, like other biological materials has properties of viscoelastic solid (Fig. 3) (Sitkei, 1981).

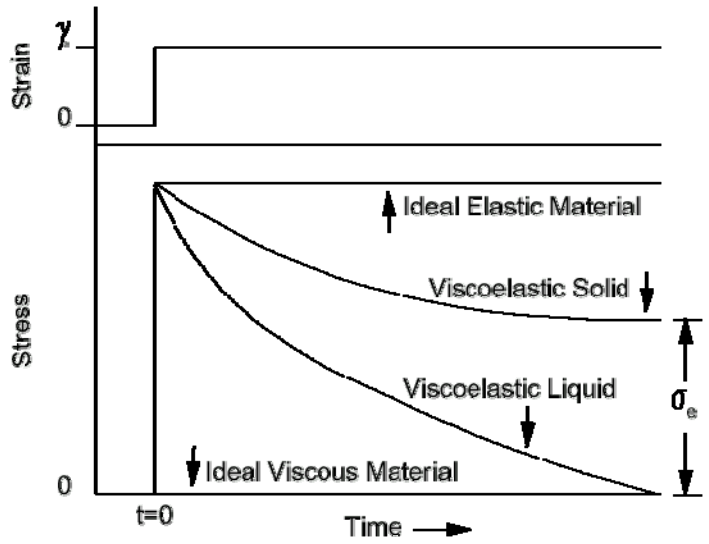


Figure 3 Material types in rheology

To study viscoelastic properties relaxation method (deformation holding in time, during extension) was used. To analyse relaxation curves two rheological models were used: Maxwell and Zener model. In the Maxwell model there is a serial connection between elastic, and viscous element. In the Zener model there is a parallel connection between elastic, and Maxwell element. (Sitkei, 1981). To follow non-exponential properties of the relaxation section the Zener model was extended with a β constant, based on literature suggestions (Dobreva et al, 1997).

MATERIALS AND METHODS

Used pectin types showed in table 1.

Table 1 Used pectin types

Pectin type	Method for deesterification	Esterification degree	Charge distribution
812634-40	Enzyme	71.2 (HM)	Random
0001-8-F	Enzyme	36.7 (LM)	Block
98246-5-A	Acidic	70.6 (HM)	Random
98246-5-E	Acidic	35.6 (LM)	Block
amidated pectin LA-410		29.0/20 (amid) (LM/LAm)	

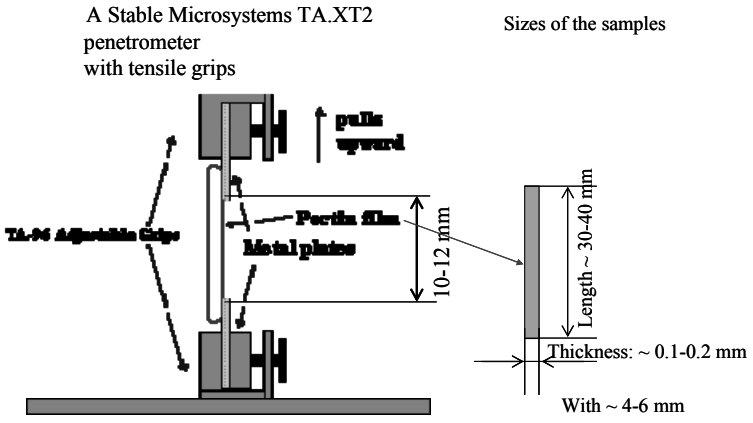
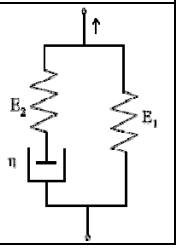
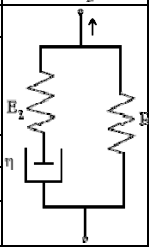


Figure 4 Instrument settings

Table 2 Equations for used models

	Equation for loading section	
Maxwell model		
	$\sigma(t) = f_1 \varepsilon$	
f_1=	Tensile (elasticity) modulus	
f_0=		
f_2=		
Zener model		
	$\sigma(t) = E_1 aT + Taf_1\left(1 - e^{-t/T}\right)$	
f_1=	Part of elasticity modulus (E_2)	
f_0=		
f_2=	T	

	Equation for relaxation section	
Maxwell model		
	$\sigma(t) = f_1 e^{-t/f_2} + f_0$	
f_1=	Slope	
f_0=	Y intercept	
f_2=	Relaxation time	
Zener model		
	$\sigma(t) = \sigma(t_1) e^{-t/f_2} + f_1 \varepsilon(t_1)\left(1 - e^{-t/f_2}\right)^{f_0}$	
f_1=	Part of elasticity modulus (E_1)	
f_0=	Non-exponanciality (β)	
f_2=	Relaxation time	

Pectins were varied in method for deesterification, in esterefication degree and in charge distribution. For hydration polyethylene glycol 20000 Da solutions were used. The osmotic pressure of solutions were 5 MPa, and $CaCl_2$, $MgCl_2$, KCl salts were used in different concentration (0, 10, 30, 50 mol/m^3) to model the ionic environment in the cell-wall.

To study rheological properties a Stablemicro-systems table penetrometer was used, in tensile mode, with deformation holding in time

while tension settings (Fig. 4). Loading forces were varied from 0.1 N till rupture point in 0.1 N steps. The loading speed was constant, 0.02 mm/s. The samples were glued to metal plates, in tensile grips. The relaxation curves were analysed by linear (Maxwell model) and non-linear (Zener model) regression (Table 2). The results from model were analyzed with mathematical way for errors, and for information contain of the constants.

RESULTS AND DISCUSSION

1. Mathematical way for errors: table 2 shows the equations, for the regressions. From those regressions there are results for fitting errors, and parameter errors. The figure 5 compare the fittings and parameter errors. Directions 1-3 for loading section (r^2, fitting error parameter error), 4-8 for relaxation section (r^2, fitting error, errors of 3 parameters). Events for more optimal results were counted The results shows, just one parameter error was more often higher for the Zener model, like for Maxwell model. That parameter error is coming from viscoelastic properties of pectin (Fig. 5).

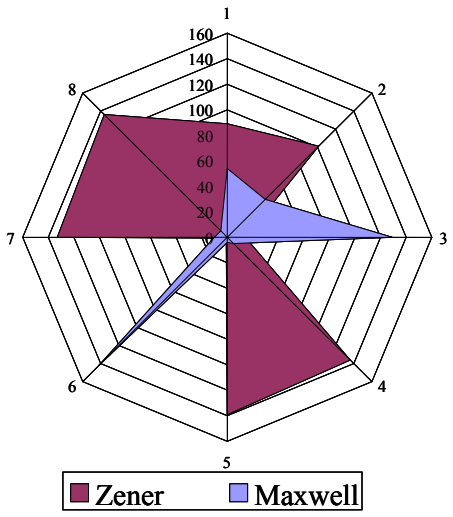


Figure 5 Error comparison
bigger area means better fitting, and smaller errors

2. Results from the model: For elasticity of pectin Maxwell model shows just the tensile modulus, like linear slope of the loading section. There is no connection between loading and relaxation section by parameters. But with Zener model for fitting curve to loading section has to use E_1 parameter and the relaxation time from relaxation section. Those give non-linear character for loading section, and β non-exponentiality for relaxation section. The tensile modulus shows just the differences among pectin types, like LM, HM, and Am (Kroon-Battenburg et al, 1986). Elasticity modules from Zener model (E_1, E_2) even show the effect of ion-condensation (Yoo SH et al, 2003) for K^+ and network collapse (Peleg, 1997) for Ca^{2+}, and Mg^{2+} with bigger ion concentrations. Non-exponentiality shows different constant values for pectin types.

CONCLUSIONS

- The Zener model had better fitting for the relaxation curves than the Maxwell model.
- The Zener model gave more parameters for elasticity.
- These parameters are more informative like from the Maxwell model.

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