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Rheological properties of pectin-polycation crosslinked films♣

G. ZSIVANOVITS*, M. MARUDOVA-ZSIVANOVITS[a]
Canning Research Institute, Agricultural Academy, 154 Vassil Aprilov Blvd., 4000, Plovdiv, Bulgaria
[a]*Department of Experimental Physics, University of Plovdiv, 24 Tzar Assen Str., 4000, Plovdiv, Bulgaria*

The effect of chitosan oligomers on pectin films was studied. The films varied in pectin type (charge density and charge density distribution) and in oligomer concentration. The equilibrium degree of swelling was determined in controlled osmotic pressure solutions, until a constant weight was achieved. The rheological properties of swelled films were examined by a Stable Micro Systems penetrometer in tensile mode, with hysteresis and stress relaxation tests. To analyze these curves, the mechanical energy absorption, relative non-elastic deformation and parameters of the Zener model (E_1, E_2 moduli, relaxation time and “stretched exponent” coefficient,□) were calculated. The results show that chitosan oligomers crosslink pectin films. The efficacy of crosslinking depends on the pectin charge density and charge density distribution. The crosslinking leads to a decrease in swelling, and increase in the elasticity and rigidity of the films.

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1. Introduction

When oppositely charged low-valency ions are added to polyelectrolyte solutions, because of the electrostatic interactions, they bond to regions in the chains and crosslink the network [1]. The crosslinked network exhibits the ability to absorb a significant amount of water (swelling), but does not dissolve in water. The properties of these polyelectrolyte systems are expected to change if low valency counterions are replaced by oppositely charged polyions. Their state – hydrogel, coacervate, phase separated – will depend on the interaction between the oppositely charged polyelectrolytes the charge density and charge density distribution; ionic strength; pH; etc. [2]. In this article, we consider the effect of crosslinking of one weak biopolyelectrolyte, pectin, with chitosan oligomers. One motivation for examining the behaviour of pectin is that fractions with different average spacings between charges along the polymer backbone may be obtained. Pectin is one of the major structural polysaccharides of higher plant cells [3]. It consists mostly of galacturonic acid residues and their methyl esters [4]. Naturally, the degree of esterification (DE) of pectin is high in unripe fruits and vegetables, and under the action of methylesterase it decreases during the ripening process [5]. It could be further de-esterified and, based on the type and conditions of the de-esterification, random or block distributions of the carboxyl groups could be achieved. In semi-concentrated solutions, pectin can form gels with divalent counterions such as Ca^{2+} but also with basic biopolyelectrolytes such as chitosan [6-7]. The affinity for crosslinking increases with increasing of charge density along the polymer backbone and increasing of “blockiness” [8]. It has been shown that divalent counterions (Ca^{2+} and Mg^{2+}) crosslink high concentrated pectin networks [9-10]. Irrespective of the counterion, the swelling of the films decreases and their stiffness increases with the ionic strength. The swollen films behave as viscoelastic solids. In addition, the tensile modulus shows a dependence on the pectin type, with the modulus increasing in the order chemically de-esterified < enzyme de-esterified.

The present study aims to examine the rheology and swelling of pectin films, crosslinked with chitosan oligomers and to determine the effect of pectin type on the studied material properties.

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2. Experimental

2.1 Materials

Citrus pectins with random and blockwise charge distributions and various DE were kindly provided by CP Kelco (Table 1). Chitosan oligosaccharide lactate, with a reported degree of deacetylation >90%, was obtained from Sigma. The average degree of polymerization of the chitosan oligomers was determined as 4 [7]. All other chemicals were of analytical grade.

Table 1. Characteristics of the used pectins

Pectin	Type of de-esterification	Charge distribution	DE, %
P-40	Enzyme	Block	71.2
5A	Chemical	Random	70.6
8F	Enzyme	Block	36.7
5E	Chemical	Random	35.6

2.2 Sample preparation

To prevent initial undesired aggregation between the pectin and the cationic oligomers, they were mixed as dilute solutions in de-ionized water (0.2 g/L pectin). The added chitosan amounts were respectively 22.5, 45, 90, 135, 270, 450 and 625 mg/g. The solutions were then concentrated by a rotor evaporator to approximately 10 mL, and the pH was adjusted to 5–5.5 by 0.1 M NaOH. The films were cast in petri dishes, and dried at 42 °C for 16 h.

2.3 Sample characterization

The solid content of the films was determined by vacuum drying at 60 °C over P_2O_5, until a constant weight was reached.

The swelling test was carried out in concentrated polyethyleneglycol solutions at an osmotic pressure of 2 MPa [11] at room temperature, until a constant weight of the film was reached. The equilibrium swelling degree was determined as the ratio between the weights in the swelled and dry states.

The mechanical properties of the hydrated films were examined by simple extension, by a Stable Micro Systems® Texture Analyzer (TAXT2i). The samples (dry film dimensions 40×4×0.02 mm) were glued to metal holders by a cyanoacrylate adhesive. Two different tests were carried out: 1) Hysteresis test: the sample was loaded and unloaded at a constant deformation rate of 0.02 mm/s. The energy absorption (the ratio between mechanical hysteresis and deformation work) and relative non-elastic deformation were evaluated. 2) Force relaxation test: the sample was extended at a constant deformation rate, and then held at a constant deformation for 30 s. A modified Zener model, which provides a representation of the behaviour of viscoelastic solids (cross-linked polymer), was applied to analyze the force relaxation test [12-13]. It consisted of a Maxwell model and a spring, in a parallel connection. Based on the Zener model, the stress $\sigma(t)$ in the loading section is:

$$\sigma(t) = E_1 at + TaE_2\left[1 - \exp(-t/T)^{\beta}\right] \quad (1)$$

where E_1 is the Young's modulus of the spring, E_2 is the Young's modulus of the spring in the Maxwell element, T is the relaxation time, a is the constant deformation rate, ε is the relative deformation. β is "stretched exponent" coefficient, which considers a spectrum of relaxation times. If the deformation remains constant after time t_1, then the subsequent stress relaxation follows the equation:

$$\sigma(t) = \sigma(t_1)\exp\left(-\frac{t}{T}\right)^{\beta} + E_1\varepsilon(t_1)\left[1 - \exp\left(-\frac{t}{T}\right)^{\beta}\right] \quad (2)$$

Special "Texture exponent" software was used for the data evaluation.

3. Results

3.1 Swelling behaviour

The swelling data were expressed as the hydrated weight of the film related to that of the dry film, suggesting that the films swelled isotropically – Fig. 1.

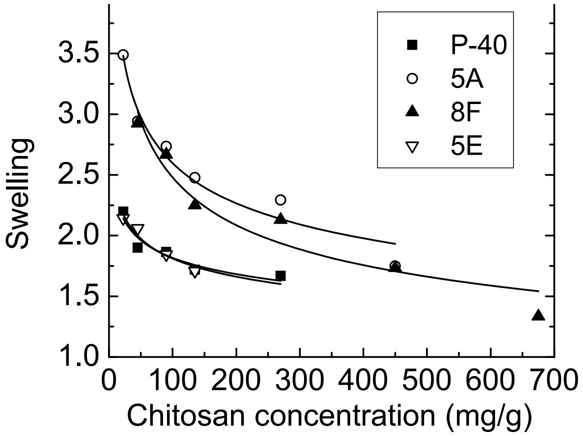

Fig. 1. Swelling behaviour of pectin films, crosslinked with chitosan.

Irrespective of the type of pectin, the swelling decreased with increasing chitosan concentration. The effect is larger for the low DE pectin with a block charge distribution. At a particular chitosan concentration, it is maximum for pectin 5A, followed by 8F and 5E, and it is a minimum for pectin 40.

3.2 Mechanical behaviour

The mechanical properties of pectin films were studied at deformations less than 5%. Over the timescales examined, the materials behaved as viscoelastic solids. The dependences of elastic moduli E_1 and E_2 on the chitosan concentration are presented in Fig. 2 and Fig. 3.

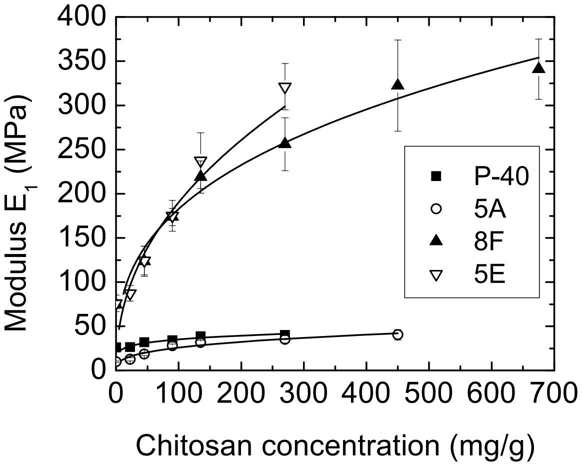

Fig. 2. Elastic modulus E_1 of pectin films.

The following observations can be made: 1) Both elastic moduli increased with increasing chitosan concentration; 2) The effect of the polycationic concentration is larger in the case of low DE pectins; 3) The values of the elastic moduli for high DE pectins show a tendency to reach a plateau at the highest counterion concentrations; 4) The charge density distribution does not affect the values of the elastic modulus E_1.

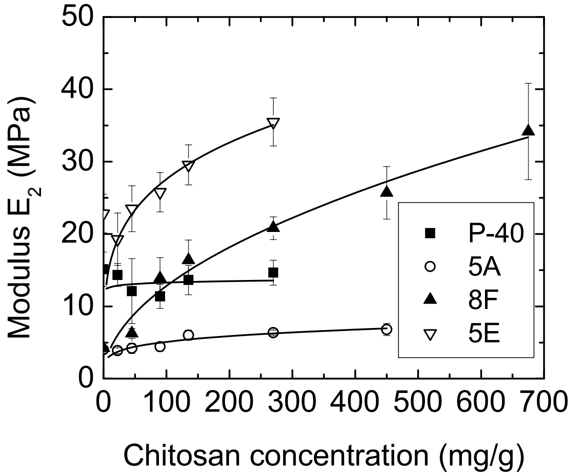

Fig. 3. Elastic modulus E_2 of pectin films.

The pectin films were examined in the elastic deformation zone, but they do not show ideal elasticity and possess small non-elastic deformations – Fig.4. The non-elastic deformation decreased with increasing chitosan concentration. The smallest value is observed for the pectin 8F and the largest one for pectin 5A.

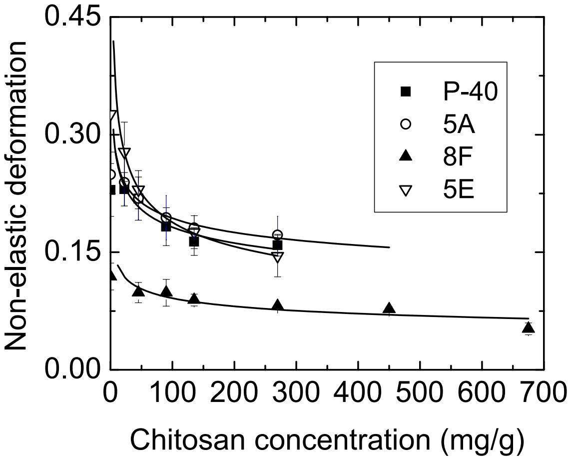

Fig. 4. Relative non-elastic deformation of pectin films.

A similar tendency is observed in the dependence of the absorbed energy constant on the chitosan concentration – Fig. 5. The smallest values are for pectin 5E. The adsorbed energy is larger for high DE pectins.

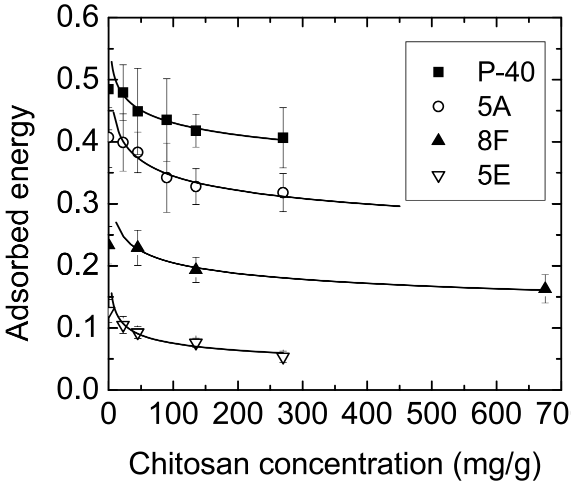

Fig. 5. Adsorbed energy of pectin films.

Irrespective of the pectin type and chitosan concentration, the value of “stretched exponent” coefficient was calculated as 0.7, which indicated a relatively broad spectrum of relaxation times.

4. Discussion

One of the aims of this research is to identify the aspects of pectin/chitosan interaction. The swelling behaviour of the crosslinked films is typical of polyelectrolytes, where the swelling is governed by the Donnan equilibrium. The ionic contribution to the osmotic pressure for 1:1 electrolytes is [14]:

$$\pi \approx \left[c^2 / A(c + 4Ac_s)\right]RT \qquad (3)$$

where c and c_s are the molar concentration of the polymer segments and salt, and A is the number of monomers between the effective charges. The reasons for suppressing the swelling with increasing chitosan concentration could be summarized as: 1) the number A decreases with increasing ionic strength, because of counterion condensation [15]; 2) the effect of crosslinking. The density of the crosslinks is proportional to the polycation concentration, and the resistance of the pectin network to osmotic pressure increases.

The network of block high DE pectin was more stable, due to the ability for creating junction zones, and therefore it swelled less. Another reason for the reduced swelling could be the comparatively low charge and in that case crosslinking would dominate in comparison with the polyelectrolyte effect. It is unexpected that low DE block pectin (8F) swelled more than a random one (5E). This could be due to the repulsive interactions between the charges in the macromolecule.

The speculation about the crosslinking effect of the chitosan could be further confirmed from the results of the mechanical examination. The tendencies observed for the effect of chitosan concentration on the mechanical parameters are relevant to its crosslinking effect. Common features of polyelectrolyte binding are the electrostatic interactions. Based on the theory of rubber elasticity [16], the following expression relates the elastic modulus E to the chain molecular weight between crosslinks, M_c

$$E \sim cRT / M_c \qquad (4)$$

where c is the concentration of the polymer in the network, and R and T have their usual meanings. An increased chitosan concentration leads to an increase in the crosslink density, and the films become more elastic – the elastic moduli increase and the non-elastic deformations decrease.

As far as, at a constant concentration of the crosslinking agent, the elastic moduli are proportional to the network density (i.e. the DE of pectin), the influence of the chitosan on the high DE pectins is much smaller. The block distribution of the charge facilities the ionic interactions and therefore the efficacy of the crosslinking agent is improved.

An increase in the modulus E_2, and the changes in the adsorption energy suggested that the chitosan not only makes the pectin film more rigid, but also causes changes in its structure, for example films may becomes more frangible.

5. Conclusions

It was shown that the chitosan oligomers can act as crosslinking agents for pectin films. Their efficacy is better for low DE pectins with a block distribution of the charge. The crosslinking leads to a decrease in swelling, and an increase in the elasticity and rigidity of the films.

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*Corresponding author: zsivig@yahoo.co.uk