

Influence of plasticizers in pectin films: Microstructural changes



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H I G H L I G H T S

- Pectin microstructural changes were evidenced using plasticizers.
- GLY plasticizer increased the predominant amorphous character of pectin.
- GLY acts as an internal plasticizer.
- PEG was a separate phase in the pectin matrix.
- PEG acts as an external plasticizer.

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This study investigated the effect of two plasticizers, i.e. glycerol (GLY) and polyethylene glycol (PEG), on pectin film structure. The results reveal that glycerol acts as an internal plasticizer. GLY increased the predominant amorphous character of the plasticized films because of decreased intermolecular attraction, resulting in low temperature degradation and allowing the conformational transformation of the galacturonan ring via a boat conformation. Glycerol produced more deformable and weaker films. Also, glycerol led to films with a greater Swelling Index (SI) and Water Vapor Permeability (WVP) value. When PEG was used as the plasticizer, films were also weaker and a lower Young's modulus was obtained compared to the neat pectin film. However, with increasing PEG MW, more compacted films were obtained, resulting in less deformable films. The WAXD spectra and DSC thermograms indicate that PEG existed as a separate phase in the pectin matrix. Moreover, the pectin phase became more compacted and less permeable to water vapor as the PEG MW is increased. These results show that PEG acts as an external plasticizer.

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1. Introduction

Pectin is one of the naturally occurring polysaccharides that has become more and more important over recent years, because this is a material with ecofriendly properties primarily due to the renewability and sustainability of their sources, renewable. The pectin has low cost, because of their abundance in nature. The potential applications of pectin are numerous and involve different fields such as fibers for the textile industry, medical products, cosmetics, bioimplant, delivery of drugs, herbicides, fungicides [1–3]. Pectin is a structural component of the vegetal cell wall, typically isolated from plants of economic importance (citrus, sugar beet, apple, etc.). It is composed of an anionic complex

polysaccharide based on chains of linear regions of (1 → 4)- α -D-galacturonosyl units and their methyl esters, interrupted in places by (1 → 2)- α -L-rhamnopyranosyl units. Fractions of these rhamnopyranosyl residues are branch points for neutral sugar side chains of (1 → 5)- α -L-arabinofuranosyl or (1 → 4)- β -D-galactopyranosyl residues [4,5]. Pectin has a strong hydrophilic character and needs to be cross-linked to prevent dissolution. Its functional groups (-OH, -COOH, -COOCH₃) enable it to interact with several compounds such as glutaraldehyde (GTA), divalent ions (Ca²⁺, Mg²⁺), and diimines, among others [6]. GTA is a common cross-linking agent frequently used in biopolymers because of its excellent reactivity and low cost. However, it has shown some cytotoxicity [7] which can be diminished by washing with ethanol-water solutions. Cross-linking involves the reaction between hydroxyl groups of pectin and aldehyde groups of GTA [8], and the concentration of the cross-linking agent can be used to modulate biopolymer properties [9]. Cross-linked pectin results in a more

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brittle character, which often requires the use of a plasticizer in order to make a sufficiently flexible film. The addition of a suitable plasticizer produces micro-structural changes in the polymer matrix, involving a reduction in the intermolecular forces between polymer chains [10]. Simultaneously plasticized films show an unfavorable increase in gas and vapor permeability and a loss of mechanical properties. Moreover, above a critical concentration of the plasticizer, phase separation or at least plasticizer exclusion from the polymer matrix can occur. Commonly used plasticizers in biopolymers are sorbitol, polyols, and glycerol [10,11]. Also, Polyethylene glycol (PEG) is a biocompatible, nontoxic polymer with good water solubility. It is an efficient plasticizer for bio-polymers, nanocompositivity and is a frequently additive used in pharmaceutical preparations [12].

In this study, we evaluated the effect of two plasticizers, i.e. glycerol (GLY) and polyethylene glycol (PEG), in the structure of pectin films. Several concentrations of GLY and different molecular weights of PEG were used. Micro-structural changes were assessed by wide angle X-ray diffraction (WAXD). The barrier and mechanical properties were also determined in order to evaluate the performance of prepared films.

2. Experimental

2.1. Materials

Pectin from Citrus Fruits (CAS 9000-69- degree of methylation, 6.7%, MW = 30–100 kg mol⁻¹) was purchased from Sigma–Aldrich (Denmark). Glutaraldehyde commercialized as 25% Grade II was purchased from Sigma–Aldrich (St. Louis, MO, USA). glycerol, acetone, N,N-dimethylformamide, NaOH, HCl and ethanol were provided by BioPack (Campana, Argentina). PEGs from 200 to 1000 g/mol were purchased from Sigma–Aldrich (St. Louis, MO, USA).

2.2. Film preparations

Neat and plasticized films were obtained from aqueous solutions containing 2% w/v of pectin at 40 °C. Plasticized films were obtained adding different amounts of GLY to the pectin solution in order to obtain concentrations ranging from 0 to 5% w/v or PEG of different molecular weights (from 200 to 1000 Da) at a concentration of 1% w/v. Film forming solutions were cast in Petri dishes (14.5 cm internal diameter) and dried in an oven at 60 °C for 24 h. After that, the films were cross-linked with 50 mL of acetone containing 5% (w/v) glutaraldehyde (Sigma Aldrich) and 1% (w/v) HCl. Finally, the films were washed with ethanol and water. Film preparation was carried out in triplicate. Dried films had similar thickness (approximately 250 µm thick).

2.3. Solubility assays

Samples were dried at 40 °C in an oven-dryer for 24 h and then the initial solids content was measured by weighting. Samples were put in a 50 mL beaker with 30 mL solvent and sealed by Parafilm, and then placed in a thermostat at 25 °C for 48 h. Films were dried for 24 h in a dry oven and then the solid contents were measured. Solubility (%) of film was defined as ratio of the water soluble solids to the initial solids content. Solubility assays were carried out by treating the films with several solvents: acetone (Ac), ethanol (Eth), N,N-dimethylformamide (DMF), and water at 25 °C.

2.4. FTIR analysis

The FTIR spectra were determined by mode using Nicolet

PROTEGE 460 Spectrometer over the range 400 e 4000 cm⁻¹. The number of scans for each sample was 64.

2.5. UV-VIS spectroscopy

UV-VIS spectra of acetone and aqueous extracts of fresh prepared films were recorded on UV-VIS U-2001 Hitachi spectrophotometer over the wavelength range 200–1000 nm.

2.6. Wide angle X-ray diffraction (WAXD)

The X-ray diffraction analyses were carried out in a range of 2θ between 0° and 60° using a Rigaku model D-Max III C device (Tokyo, Japan), a CuKα lamp and a nickel filter. From the diffractograms, the d-spacing (d_{sp}) of each synthesized film was determined by Bragg's equation (Eq. (1)).

$$n\lambda = 2d \sin\theta \quad (1)$$

where n is an integer, λ is the wavelength of the X-rays, d is the interplanar distance or intersegmental distance, and θ is the angle between the incident rays and the plane of scattering. All analyzed samples were conditioned in a humidity- and temperature-controlled chamber for 24 h at 25 °C and 40% relative humidity (R.H.). Diffractograms were fitted using ORIGIN PRO 8 software and the first derivative was used to identify the curve maximum.

2.7. Differential scanning calorimetry (DSC)

The DSC curves were obtained at 10 K/min under a nitrogen atmosphere (Mettler Toledo DSC 831, Giessen Germany). Two scans were performed with each sample, the first from –50 °C to 80 °C in order to remove the thermal history of the samples, and the second from –50 °C to 500 °C.

2.8. Mechanical properties

Tensile tests of the synthesized films were performed at room temperature using a Comten Industries (Series 94 VC) device (Pinellas Park, Tampa FL, USA). Films were cut into strips with a width of 1.1 cm and length of 4.0 cm. To ensure complete relaxation of the polymeric structures and to standardize the experimental procedure, film samples were stored in a humidity- and temperature-controlled chamber for 24 h at 25 °C and 40% R.H. The polymeric strips were then fixed between upper and lower clamps of the tensile tester and the tensile strength was determined at a constant traction speed of 5 mm/min. The mechanical parameter data include the average values from three samples of each film. The film thickness was measured using a Köfer micrometer (precision ± 1 µm) (Germany).

2.9. Swelling index (SI)

An area of 1 cm² of each film was vacuum dried in an oven at 50 °C for 24 h. The dried film was accurately weighed (W_d) and immersed in a flask containing 50 mL of distilled water at 25 °C. After 12 h, swollen samples were withdrawn from the aqueous medium, surface dried to removal of excess surface water by light blotting with tissue paper and weighed (W_w). All experimental trials were carried out in triplicate. The swelling index was determined by the following equation:

$$\%SI = 100 \left(\frac{w_w - w_d}{w_d} \right) \quad (2)$$

2.10. Water vapor permeability

The water vapor permeability (WVP) of the films was determined according to the standard method ASTM E96-80. Film samples were stored for 48 h at 25 °C and 30% R.H. Then, the film was placed in the permeation cell for WVP measurements. The cell had an effective area $A = 9.5 \times 10^{-4}$ (m²) and was located in a humidity- and temperature-controlled chamber at 37 °C and 85% R.H. The cell was weighed at different time intervals. The first 10 measurements were done every 10 min and subsequent measurements were completed every 30 min up to 12 h. All permeation tests were performed in three film samples. The WVP was calculated with the following expression:

$$WVP = \frac{\Delta w}{\Delta t A \Delta P_v} \quad (3)$$

where $\Delta w/\Delta t$ is the water vapor mass or cumulative permeated water per unit time (g s⁻¹), l is the film thickness (m) and Δp_v is the difference between the water vapor pressure on the feed and permeate side of the film (Pa).

3. Results and discussion

3.1. Film solubility

Results of solubility of films in different solvents were reported in [Supplementary material](#). Pectin film was the most resistant to water having 9% of dissolution whereas GLY containing films showed an increase of water solubility as GLY concentration increases (from 9.28 % to 100% for the film 5% GLY after 12 h of immersion). Also when PEG was used as plasticizer, film water solubility decrease as PEG MW increases (from 24.82% to 22.42%). Films presented very low solubility in other solvents assayed.

3.2. FTIR spectra

From the FTIR spectrum of pectin ([Fig. 1](#)), it can be observed that a broad peak at 3450 cm⁻¹ is due to the stretching vibrations of O–H, and bands at 2930–2850 cm⁻¹ are attributed to the C–H stretching vibrations of methyne groups of polymer chains and methyl group of the methyl ester. The bands at 1100 and 1040 cm⁻¹ are assigned to C–O–C stretching vibrations of the saccharide structure. It is further noted that two strong peaks at 1635 and 1429 cm⁻¹ are assigned to asymmetric and symmetric stretching vibrations of carboxyl groups present in pectin. Also, the peaks of 1745 and 1250 cm⁻¹ are attributed to the C=O and C–O component of an ester bond respectively. The pectin spectrum was similar to reported by [\[13–16\]](#) and no great changes appears with plasticizer GLY or PEG are used. However, it was found that area band ratio ester (1745 cm⁻¹) to free carbonyl group (1635 cm⁻¹) = 1,04 in neat pectin film. In films with GLY that ratio was 1,35, and with 1% w/v of PEG 200, PEG 400, PEG 600 and 1000 were 1,27, 1,12, 1,08 and 1,06, respectively. Those results indicate that GLY and some PEG 200 were esterified onto pectin chain during the crosslinking with GLU (esterification catalyzed by acids). Pectin film with PEG 1000 shows similar carbonyl band ratio as neat pectin film, indicating that not any or very low PEG esterification was carried out.

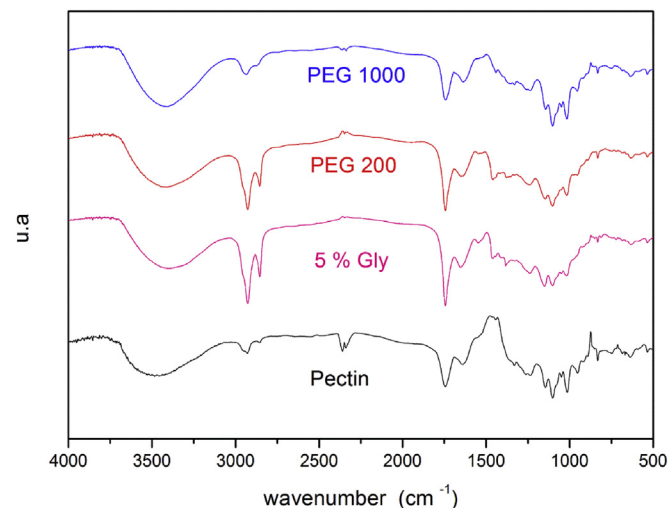


Fig. 1. FTIR spectrum of pure pectin and containing 5% GLY, 1% PEG (MW 200 and 1000).

3.3. UV–Visible spectra

In order to determine if GLY or PEG might react with GLU, we performed UV–Vis. spectroscopic analysis in acetone and aqueous extracts of fresh pectin films. We prepared a reference solution of glycerol and glutaraldehyde in acetone reproducing crosslinking solution used. It was proved that absorption wavelength of reference solution at 340 nm was not found in the film extracts in acetone as well as in water. These results proved that the reaction between glycerol and glutaraldehyde did not occur in crosslinked films.

3.4. WAXD and DSC analysis

The structures of pectin films were investigated by WAXD analysis. Please see [Supplementary material](#) for WAXD diffractograms. The WAXD films patterns showed broad peaks in the 2θ range of 5–60°. The top of the broad peaks on each X-ray pattern was attributed to inter-segmental interference and is representative of the average inter-segmental distance, i.e. the mean inter-chain distance (d-spacing) [\[17,18\]](#). The d-spacing data obtained from Equation (1) are listed in [Table 1](#). It has been reported well defined peaks at 12.7°, 16.72°, 18.42°, 25.32° and 40.14° of 2θ related to pure pectin crystallinity [\[3,19\]](#). In this study, pectin film showed a broad peak at 16° of 2θ confirming the presence of some crystalline order. Other researcher have informed diffractogram of the pristine film pectin showing two distinct “humps” at 13° and 22° of 2θ [\[3,20,21\]](#). However such samples were not crosslinked. Also, the effect of the plasticizer glycerol was observed in the WAXD curves. All curves showed an amorphous structure. However, as the glycerol content in pectin films increased, the curve intensities diminished. Glycerol addition diminished the WAXD band intensity due the increased amorphous character (higher disorder) [\[22–24\]](#). Intermolecular hydrogen bonds of pectin were substituted by glycerol-pectin hydrogen bonds and covalent ester formation, thereby reducing the pectin intermolecular attraction, but no changes in the d-spacing values were observed. These results are in accordance with the hypothesis of [\[25\]](#) suggesting that the plasticizer “solvates” polar sites on the polymer chain, thus reducing intermolecular attraction.

DSC thermograms of the pectin-based films can be seen in [Supplementary material](#). The thermal behavior of pectin samples

Table 1
Parameters of XRD patterns.

Film	2 θ [grade]	d _{sp} (Å)	Rel. Intensity (counts/s)
Pectin	16.0	5.56	419.51
0.3% GLY	16.0	5.56	379.37
0.5% GLY	16.0	5.56	374.56
1.0% GLY	16.0	5.56	369.42
3.0% GLY	16.0	5.56	356.72
5.0% GLY	16.0	5.56	346.51
PEG 200	17.1	5.2	319.33
PEG 300	17.2	5.17	340.31
PEG 400	17.6	5.03	364.67
PEG 600	18.3	4.86	383.55
PEG 1000	18.7	4.83	399.47

has been previously described by [26–28]. These researchers mentioned that pectin thermal behavior depends on the chemical composition and on state transitions, occurring during processing, as well as on the interdependence of both factors. Some pectin samples showed an exothermic degradation peak between 180 and 270 °C. Also, an endothermic pre-peak appeared before the degradation peak, corresponding to a conformational change that might be the transformation from the more stable ⁴C₁ chair conformation of the galacturonan ring via a boat conformation ^{1,4}B to the inverse ¹C₄ chair conformation. This conformational change has a higher free energy G according to [29–33]. These thermal events are present in the DSC thermograms. The pure pectin thermogram shows only an exothermic degradation peak at 236 °C, and there is no endothermic pre-peak. Otherwise, as glycerol addition increased, the degradation peak appeared at lower temperatures for 0.5% and 1% (234 °C and 227 °C, respectively). The film with 5% glycerol showed a degradation peak at 236 °C. However, all glycerol-containing films showed endothermic peaks, i.e. at 205 °C for 0.5% and 1% and at 209 °C for 5%. Such events confirm the predominant amorphous character of plasticized films since weaker intermolecular attraction results in low temperature degradation; this allows the conformational transformation of the galacturonan ring via the boat conformation. From the above results (WAXD and DSC or only DSC), it appears that the GLY plasticizer had a protective effect that retarded pectin degradation.

The WAXD curves using PEG as the plasticizer are also determined. The intensity bands were also diminished when higher MWs of PEG were used. Moreover, the peaks were augmented to higher 2 θ angles when higher MWs of PEG were used. As a result, the d-spacing decreased (Table 1). PEG has only two hydrogen bonds per molecule that is able to interact with a polysaccharide [34] and pectin was less esterified as PEG MW used increases. Therefore, the degree of esterification of the pectin decreases with increasing molecular weight of PEG. These remarks lead to the PEG behaves differently than the GLY. The WAXD results obtained in the present study suggest that using PEG, Hydrogen bonding between plasticizer and pectin would appear more likely in amorphous region acting as external plasticizer. These changes in the mobility of chain segments of pectin in amorphous regions probably affect the entire film structure, causing the spacing within crystalline section to be slightly stretched. As higher MW of PEG were used, the pectin structure became more compacted (smaller d-spacing) in order to accommodate weakly H-bonded PEG molecules and less PEG esterified pectin. Similar results have been reported by other authors [35,36]. They demonstrated that as the PEG MW increased, its polarity and solubility decreased, reducing its ability to interact with the polymer. In contrast, glycerol seemed to act as an internal plasticizer because of its small size, more ester formation ability and strong H-bonding capacity (three H-bonds per molecule), which led to breakdown of the intermolecular

connectivity between pectin chains.

The DSC curves of pectin using PEG as a plasticizer are shown in [Supplementary material](#). Endothermic PEG melting events were present in the pectin-based films (–4 °C, 15 °C and 35 °C, for PEG MW 400, 600, and 1000 Da, respectively). The melting points of PEG MW 400, 600 and 1000 Da are 3 °C, 22 °C and 37 °C, respectively. PEG 200 and 300 did not showed melting events in the measured range. Enthalpy of melting (ΔH_m) of PEG MW 400, 600 and 1000 Da were calculated and resulted = 0.593 J/g, 2.822 J/g and 3.5512 J/g, respectively. Recently it has been reported [12,37] the PEG (MW = 20000) crystallinity in pectin films by studying melting process and it was found that interactions between PEG 20000 and pectin reduce the crystallinity fraction of the PEG. In this study, it can be observed that the crystalline fraction of PEG is greater as the molecular weight of PEG increases. The thermograms reveal that the exothermic degradation of pectin occurred at 235 °C. Finally, the final degradation peaks of PEG were found at 317 °C, 331 °C, 351 °C, and 376 °C, for 400, 600 and 1000 Da PEG, respectively. Grassie et al. [38] reported that PEG degradation starts at the C–C bond at the α position to the C–O bond or at the C–O bond itself. The slightly higher threshold of degradation temperature seen as the PEG MW increased was due to longer and therefore less volatile chain fragment formation during the degradation process. The results from the thermal analysis of pectin using PEG as a plasticizer confirm the WAXD spectra, indicating that as MW increase, PEG becomes a separate phase in the pectin matrix. Moreover, the pectin phase became more compacted as the PEG MW increased. These results prove that PEG acted as an external plasticizer. Similar findings have been reported in alginate/PEG blends by [39].

3.5. Tensile tests

The bulk properties of a polymer are most often of end-use interest. These are the properties that dictate how the polymer actually behaves on a macroscopic scale. The ultimate tensile strength (σ_{ult}), tensile elongation or yield strength (% ϵ_y), and Young's modulus or tensile modulus of elasticity (E) are the most important and widely measured properties of materials used in structural applications, i.e. low elastic moduli are advantageous to prevent the initiation and propagation of cracks in polymeric films used for packaging.

In Table 2, the mechanical property parameters provided by the tensile test measurements are shown. Pectin film presents an E value of 3270 MPa whereas Cavallaro et al. informed E = 2370 MPa [12,40]. Such difference can be addressed to crosslinking of pectin film made in this study and/or different sample storage prior to mechanical properties measurements. As was expected, the mechanical properties of the pectin films changed considerably with the use of GLY or PEG plasticizers. Increasing the amount of glycerol produced weaker and more deformable films (σ_{ult} decreased and ϵ_y increased). Additionally, an increase in the amount of glycerol led to an increase in the flexibility of the pectin films (E modulus decreased). These results can be explained as a consequence of microstructural changes due the increased amorphous character with an increasing amount of GLY (WAXD analysis). The addition of 1% of PEG with increasing MW led to weaker pectin-PEG films (smooth decline in σ_{ult} values) exhibiting more rigid behavior (ϵ_y decreased and E increased). As it was reported by Cavallaro et al. [12] similar behavior was found (a decrease of ϵ_y and σ_{ult}) when PEG 20000 was added to pectin (PEG/Pectin ratio of 1 and 4). However in such study a slight improvement of E was observed respect to neat pectin film. WAXD analysis showed that pectin films with smaller d-spacing, i.e. films with more dense chain packing, were obtained as the PEG MW increased, resulting in higher values of Young's modulus.

Table 2
Mechanical Properties of Pectin-GLY-PEG films.

Film	ϵ_y (%)	σ_{ult} (MPa)	E (MPa)
Pectin	4.83 ± 0.561	69.33 ± 1.38	3270 ± 8.76
0.3% GLY	11.09 ± 0.51	56.05 ± 1.21	505 ± 5.14
0.5% GLY	11.09 ± 0.70	22.07 ± 1.49	199 ± 2.52
1.0% GLY	30.75 ± 0.48	19.07 ± 2.01	62.0 ± 0.37
3.0% GLY	54.00 ± 1.42	14.71 ± 1.21	27.2 ± 0.47
5.0% GLY	71.64 ± 0.95	4.48 ± 1.31	6.1 ± 0.08
PEG 200	40.36 ± 0.82	33.39 ± 0.95	82 ± 0.28
PEG 300	30.00 ± 1.03	32.03 ± 1.36	106 ± 0.11
PEG 400	20.82 ± 0.76	35.65 ± 1.23	171 ± 0.15
PEG 600	15.00 ± 0.94	31.23 ± 1.42	208 ± 0.96
PEG 1000	13.18 ± 0.67	28.40 ± 1.28	215 ± 0.34

3.6. Swelling index and water vapor permeability

It is well-known that, due to the hydrophilic nature of hydrocolloids, the swelling index is an important property to be determined. In Fig. 2, the impact of glycerol and PEG on the swelling index can be observed. From these results, it seems clear that the addition of glycerol (a highly hygroscopic molecule) produced films with greater water uptake than films without it. Films containing 5% glycerol showed a five-fold greater swelling index. This behavior agrees with the WAXD results since glycerol leads to the breakdown of molecular interconnectivity between pectin chains, allowing the absorption of large numbers of water molecules.

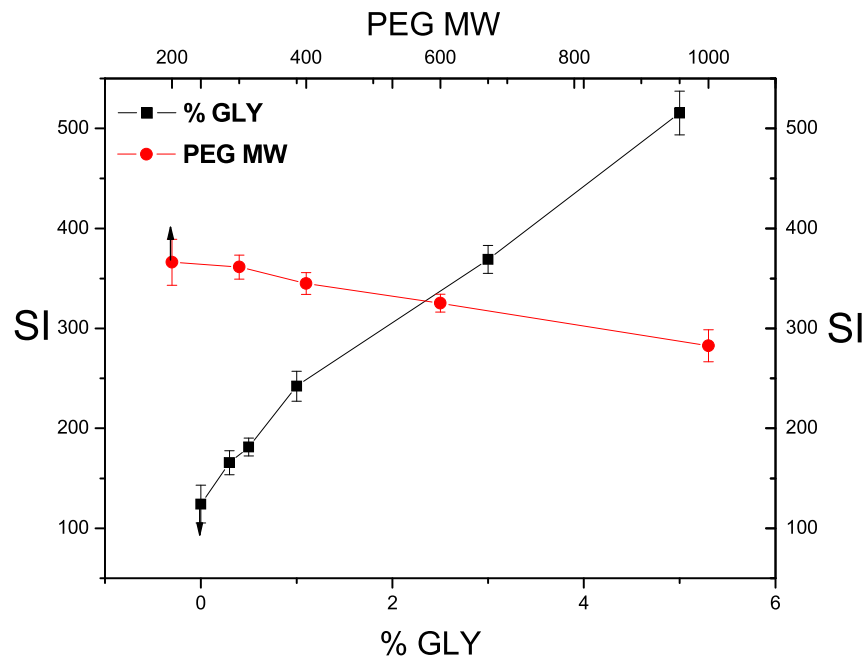


Fig. 2. Swelling index of Pectin films containing GLY at different concentrations and 1% PEG of different molecular weights. Error bars means SD.

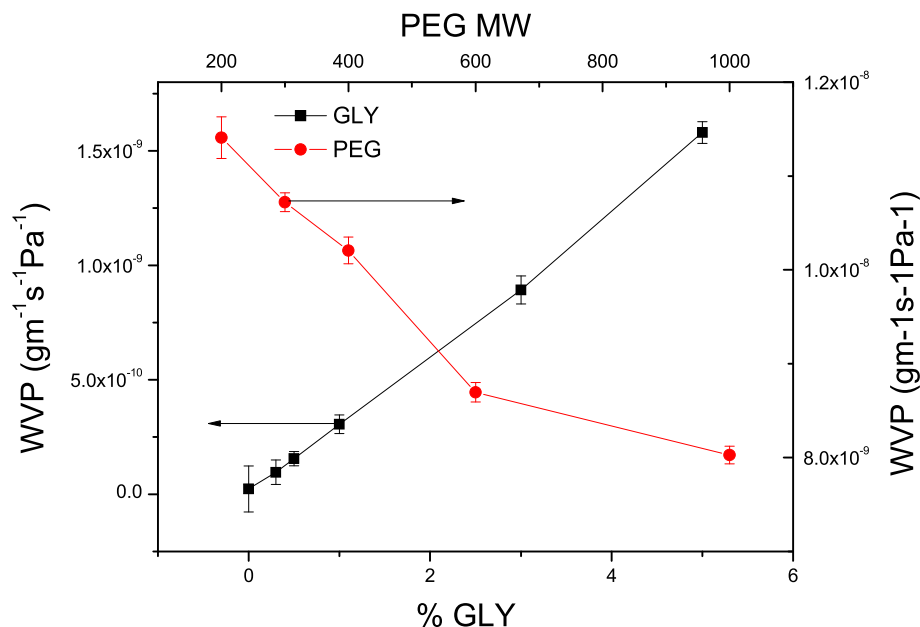


Fig. 3. WVP of Pectin films containing GLY at different concentrations and 1% PEG of different molecular weights. Error bars means SD.

However, less hygroscopic films can be obtained when high molecular weight PEG was used as the plasticizer. The microstructural changes observed in the pectin films in the WAXD studies revealed that PEG produced a more compacted material. As a result, water uptake was hindered in these films.

In Fig. 3, the WVP values for all films are plotted. In agreement with the swelling index results, the WVP results showed the same tendencies for glycerol and PEG, since the WVP increased with increasing amounts of GLY and decreased with the PEG molecular weight. Glycerol acts as internal plasticizer that improves the permeability of water vapor molecules through the film. In contrast, PEG reduces water vapor transport due to the more compact structure obtained with increased PEG MW.

4. Conclusions

Microstructural changes were studied in pectin films when glycerol and PEG were used plasticizers. Glycerol ester was partially formed during the crosslinking process of pectin. Using glycerol as a plasticizer increased the predominant amorphous character of the plasticized films because of decreased intermolecular attraction, resulting in low temperature degradation and allowing the conformational transformation of the galacturonan ring via a boat conformation. These microstructural changes had an impact on the mechanical and barrier properties. Glycerol produced weaker and more deformable films. Also, the addition of glycerol led to films with greater swelling index and WVP values than those in pure pectin films. These results show that glycerol acts as an internal plasticizer. In contrast, as the PEG MW increased a lesser amount of ester groups are produced, hence, a more compacted and less deformable films were obtained. The WAXD spectra and DSC thermograms showed that PEG was a separate phase in the pectin matrix. These results show that PEG acts as an external plasticizer. By increasing the PEG MW, films with lower WVP values were obtained. These results are indicative that films with different structural and functional properties can be obtained from pectin selecting an internal or external plasticizer. Thus, biopolymeric films with interesting and tunable barrier and mechanical properties useful for specific purposes can be developed.

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Appendix A. Supplementary data

Supplementary data related to this article can be found at <http://dx.doi.org/10.1016/j.matchemphys.2015.06.019>.

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