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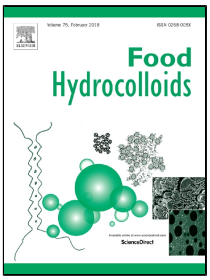

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Highlights

- Edible films from pectin and PEG were prepared.
- Film formation was supported by hydrogen bonding between components.
- Thermal and mechanical properties were affected by concentration and molecular weight of PEG.
- The increasing PEG concentration caused an increase in water vapor permeability.
- Films showed potential to be used in food packaging industry.

Edible blend films of pectin and poly(ethylene glycol): Preparation and physico-chemical evaluation

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Abstract

The aim of this study was the development of novel polysaccharide based films intended to be used as edible food packaging material. The films were prepared by solution casting method using highly methoxylated pectin (PEC) and poly(ethylene glycol) (PEG) of various molecular weights (400, 600 and 1000 $gmol^{-1}$) in different ratios (5:1, 3:1 and 1:1). The film formation was supported by hydrogen bonding between PEC and PEG, which was evidenced by means of ATR-FTIR and NMR analysis. TGA revealed that generally PEG behaves like a pro-degrading agent for pectin, except in the case of PEC/PEG film with a ratio of 1:1. Furthermore, DSC thermograms indicated that PEG1000 exists as a separate phase in the pectin matrix while the fomulations with PEG400 and PEG600 showed mainly amorphous morphology. The addition of PEG enhanced the plasticization of PEC films, as evidenced by progressive decreasing of the glass transition temperature values (T_g). The tensile test measurements showed that increasing concentration of PEG produced weaker and more flexibile films. Due to the increased molecular mobility, the pectin phase became more permeable to water vapor as the PEG concentration increased. The obtained results showed that the combination of both polymers resulted in interesting bio–inspired edible films with the potential to compete with commercially used synthetic package materials.

Keywords: Pectin; Poly(ethylene glycol); Plasticization; Edible films; Hydrogen bonding

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1. Introduction

The food package must be designed to fulfill a number of important functions including containment and protection of food, maintaining food sensory quality and safety, extending shelf-life and retaining the beneficial effects of food products (Nanou et al, 2014). The use of synthetic materials is ubiquitous in food industry wherein they provide mechanical, chemical and microbial protection from the environment and allow product display. Petrochemical plastics, such as low- and high-density poly(ethylenes) (LDPE and HDPE), poly(propylene) (PP), poly(styrene) (PS) poly(ethylene terephthalate) (PET) and poly(amide) (PA) are well known as they play an important role in our daily lives (Marsh & Bugusu, 2007). Nevertheless, these plastic materials are responsible of the environmental problems related to their waste management, due to the huge volumes of plastic waste materials produced. Indeed, they do not readily degrade either in landfill or in composting facilities due to their biologically inert nature. In order to work towards a sustainable development, research is increasingly focusing its attention on eco-friendly packaging materials based on biodegradable polymers coming from renewable and available sources, as appealing eco-sustainable and cost-competitive bioplastics (Lambert, Sinclair & Boxall, 2014). Depending on their origin, biodegradable polymers can be synthetic or natural. Poly(vinyl alcohol) and polyesters are the most interesting among the former (Guimarães et al, 2015), whereas polysaccharides, proteins and polyesters produced by microorganisms, such as poly(lactic acid) (PLA) (Mahmood et al, 2016), poly(hydroxyalkanoates) (PHA), all of them referred to as biopolymers, belong to the latter (Angelini et al, 2014, Ortega-Toro et al, 2016). Polysaccharides such as cellulose, pectin, starch, chitosan, alginate, (Fabra et al, 2014, Cavallaro et al, 2011, Biddeci et al, 2016) are arousing huge scientific interest as renewable and available biopolymers potentially exploitable as novel eco-friendly food packaging material (Razzaq et al, 2016).

Among them, pectin is one of the most abundant polysaccharide extracted from cell walls of most plants and fruits, such as apple, orange, lemon, and mango. It is an anionic polysaccharide formed by linear chain of poly-α-(1-4)-D-galacturonic acid with varying degrees of methyl esterification (Khotimchenko et al, 2008). The esterification degree (DE) determines the solubility of pectin, its gelling and film forming properties and therefore its industrial applicability. Actually, due to the simple and cytocompatible gelling mechanism, pectin has been exploited for different biomedical applications including drug delivery, gene delivery, wound healing and tissue engineering (Munarin, Tanzi & Petrini, 2012). As a matter of fact, the gelling properties of this polysaccharide can be specifically tuned, playing a key role in several applications. As an example, due to its ability to form a gel in acidic conditions, pectin has been widely used in food and beverage industries, as a thickening and gelling agent and as colloidal stabilizer in food products such as jams, yogurt drinks, fruity milk drinks, and ice cream (Laurent & Boulenguer, 2003). Being biodegradable, biocompatible and edible biopolymer, pectin represents a suitable polymer for the development of bio-based films for food packaging. Despite these advantages, pectin films are far from being appealing from the application point of view, because of their poor chemo-physical properties and unsuitable mechanical performances.

Furthermore, there are numerous drawbacks related to the film-forming process by means of casting method. Like most of the polysaccharides, pectin is glassy at room temperature, so its shrinkage following the evaporation of water or rapid drying, causes defects such as cracks or curling in the films (Obara & McGinity, 1995). These films are often brittle and stiff due to extensive interactions between polymer molecules, so the addition of the corresponding plasticizers is required (Gennadios, Hanna & Kurth, 1997). Plasticizers decrease intermolecular forces between polymer chains, increasing their flexibility and extendibility. They act by interposing between macromolecular polymeric chains, reducing cohesion within the film and enhancing the free volume inside the film structure (Banker, 1966; Wojciechowska, 2012; Avolio et al, 2015). With respect to the specific system, the selection of a plasticizer is based on the compatibility and permanence of the plasticizer, the amount necessary for plasticization, and the desired physical properties of the films. The food-grade plasticizers most commonly used in blend with pectin, are poly(ethylene glycol) (PEG), glycerol, propylene glycol, and sorbitol (Aydinli & Tutas, 2000). Poly(ethylene glycol) is commercially available over a wide range of molecular weights from 300 $gmol^{-1}$ to 10000 $gmol^{-1}$, and due to excellent biocompatibility and non-toxicity, it is often blended or compounded with other polymers (Zhang et al, 2002). With reference to the other reported polysaccharide based films, it was shown that PEG of lower molecular weights exhibits better plasticizing effect. The increasing molecular weight of PEG caused the decrease in its polarity and solubility, as well as in its ability to interact with polymer chains (Turhan, Sahbaz & Guner, 2001). Also, the PEGs of higher molecular weights are solids, so they might crystallize and cause phase separation.

In this study, we evaluated the plasticizing effect of poly(ethylene glycol) on the properties of pectin based films. The films were prepared by blending apple pectin (PEC) and poly(ethylene glycol) (PEG) of various molecular weights (400, 600 and 1000 $gmol^{-1}$) in different ratios (5:1, 3:1 and 1:1).The investigation of structural (FTIR, NMR), bulk (DSC, TGA) and macroscopic properties (tensile tests and WVP) of PEC/PEG films have been discussed in order to set up new, eco-sustainable materials for edible food packaging application.

2. Materials and methods

2.1 Raw materials

Pectin from apples with a 70–75% esterification degree, DE, was purchased from the Sigma-Aldrich Company (USA). Poly(ethylene glycol) of different molecular weights (400, 600 and 1000 $gmol^{-1}$) were all supplied by Merck (Germany).

2.2 Film preparation

Neat and plasticized films were obtained from aqueous solutions containing 2% w/v of pectin at 50 °C in the presence of few drops of 0.1 M HCl (solutions were adjusted to pH 3). The previously calculated amount of PEG (with specified molecular weight of 400, 600 and 1000 $gmol^{-1}$) was added to the single pectin solution in order to obtain mixtures with different

PEC/PEG weight ratios (5:1, 3:1 and 1:1), as shown in Table 1. The PEC/PEG solutions were cast into circular shape Teflon molds (11 cm in diameter) and dried in an oven at 50 °C for 48 h.

2.3 ATR-FTIR analysis

Attenuated Total Reflection Fourier Transform Infrared (ATR-FTIR) spectroscopy was carried out on the surface of PEC/PEG films using a Perkin Elmer Spectrum 100 spectrometer, equipped with a Universal ATR diamond crystal sampling accessory. All the samples were analysed at 25 °C. Spectra were collected as an average of 16 scans in the range 4000–480 cm^{-1}, with a resolution of 4 cm^{-1}. Prior to measurements, the samples were kept for 24 h at 60 °C under vacuum.

2.4 NMR analysis

Nuclear magnetic resonance (^{13}C NMR) spectroscopy was used for addressing the chemical composition and structure of PEC/PEG films. Cross-polarization (CP) carbon spectra were recorded on a Bruker Avance II 400 spectrometer operating at a static field of 9.4 T, equipped with a 4 mm MAS probe and using a ^{1}H $\pi/2$ pulse width of 3.0 μs, a contact time of 2 ms and a repetition time of 4 s. Finely cut samples were packed into 4 mm zirconia rotors sealed with Kel-F caps and spun at a spinning speed of 10 kHz.

Table 1. Composition of the PEC/PEG films

Sample	Blending ratio	Sample ID*
PEC/PEG 400	5:1	P5/400
	3:1	P3/400
	1:1	P1/400
PEC/PEG 600	5:1	P5/600
	3:1	P3/600
	1:1	P1/600
PEC/PEG 1000	5:1	P5/1000
	3:1	P3/1000
	1:1	P1/1000

**The samples are designated to point out the PEC/PEG ratio (5, 3, and 1) as well as the molecular weight of PEG used in the specific formulation (400, 600, and 1000 $gmol^{-1}$).*

2.5 Mechanical analysis

Mechanical properties were performed using Instron dynamometer model 1185, equipped with a 1 kN load cell, according to the ASTM D638 (2010) standard test method at 23 ± 2 °C and 45 ± 5% relative humidity (RH). Dumbbell-shaped films (4 mm wide, 26.73 mm long and 0.05 mm thick) were used and tested at a crosshead speed of 2 mm min^{-1}. Prior to measurements, all the films were conditioned at 25 °C and 50% RH for 48 h.

149 2.6 Thermal analysis
150 Differential Scanning Calorimetry (DSC) was performed using a TA DSC-Q2000 instrument
151 equipped with a TA Instruments DSC cooling system under a nitrogen purge gas flow of 30 mL
152 min^{-1}. Indium was used to calibrate the calorimeter. Approximately 6 mg of the samples were
153 sealed in aluminum pans and analyzed. In order to estimate the influence of the residual water on
154 the thermal properties of the pectin films, two different DSC measurements were performed. In
155 the first one, all the samples were placed in hermetic aluminum pans, in order to preserve their
156 water content. The heating run ranged from -80 to +100 °C, with heating rate of 20 °C min^{-1}.
157 In the second test, all the specimens were equilibrated at -80 °C and heated up to 100 °C at 20
158 °C/min. Then an isotherm step was performed at 100 °C for 30 min in order to remove the free
159 and bound water. Afterwards, the samples were cooled up to -80 °C at 10 °C/min, thermally
160 stabilized for 1 min at then re-heated up to 200 °C at 20 °C/min. For each sample, data analysis
161 was averaged on a set of three measurements.
162 Thermogravimetric analysis (TGA) was performed by means of a Mettler-Toledo TG-SDTA 851,
163 under nominal nitrogen flow of 30 $mLmin^{-1}$, in the temperature range from 25 to 800 °C and at
164 the heating rate of 20 °C min^{-1}. The measurements were performed on samples of about 5 mg,
165 placed in ceramic crucibles and for each sample, thermogravimetric tests were performed in
166 triplicate. The obtained values of thermogravimetrical and DSC parameters were repeatable
167 within ±3%.
168
169 2.7 Scanning electron microscopy
170 Morphological analysis of the film surfaces was performed using a Jeol JSM 5800 Scanning
171 Electron Microscope with an acceleration voltage of 20 kV. The surfaces of the PEC/PEG films
172 were coated with platinum under vacuum using a Polaron CS502 sputter coater before the
173 analysis.

174 2.8 Water vapor permeability (WVP)
175 WVP tests were conducted according to ASTM E96 standard method. The samples with exposed
176 area of 6.54 cm^2 were sealed over a circular opening of permeation cells (BYK-Gardner) filled
177 with distilled water. These cells were kept in oven at 25 °C under 50% RH. After the system
178 reached steady state conditions, the weight change of the cell was measured every 2 h. Each film
179 was tested three times to confirm repeatability of measurements. The standard deviation was
180 ±10%.
181 The weight losses of films were plotted with respect to time, and the linear least-square method
182 was used for the calculation of the parameters given by Equation 1 (Gennadios, Hanna & Kurth,
183 1997):
184
185 $$WVP = \frac{L \cdot WVTR}{A \cdot \Delta p} \quad (1)$$
186

where WVTR is the water vapor transmission rate of films (g s^{-1}), L is average thickness of the film (mm), A is the permeation area (mm^2), Δp is the difference in water vapor pressure between the two exposed sides of the film (Pa).

3. Results and discussion

The film preparation showed to be successful for all the investigated PEC/PEG ratios. The solution casting method applied hereby has proven to be an effective procedure to obtain visually uniform films with homogeneous and smooth surfaces without pores or cracks. The light-yellow coloration, originated from the pectin component, could be observed for all of the investigated samples (Fig.1).

Fig.1. Visual appearance of the P3/400 film.

3.1 ATR-FTIR spectroscopy

Infrared Spectroscopy represents a valid tool to assess the physical or chemical interactions between components in polymeric blend systems. ATR-FTIR spectra related to P1/400 and P5/400, P1/600 and P5/600, and P1/1000 and P5/1000 films and neat pectin in the range from 2000 to 800 cm^{-1} are shown in Figure 2.

Fig.2. ATR-FTIR spectra of a) P1/400 and P5/400, b) P1/600 and P5/600, c) P1/1000 and P5/1000 films.

In particular, the strong absorption bands occurring at 1737 and 1605 cm^{-1} are attributed to the ester carbonyl (-$COOCH_3$) groups and asymmetrical stretching vibration of carboxylate ion (COO^-). The intensity of –$COOCH_3$ band is higher if compared to the one of carboxylated group, which is characteristic of a highly methoxylated pectin (Gnanasambandan & Proctor, 2000).
The so called "fingerprint" peaks observed at 1145, 1097 and 1012 cm^{-1} were assigned to the symmetric stretching vibrations of C-O-C, C-OH and C-C bonds from the ring structure of the pectin (Assifaoui et al, 2010).
After the addition of PEG 400, the peaks assigned to the ester and carboxylate stretching vibrations of neat pectin were shifted to higher frequencies (Table 2). In the case of the carboxylate band, the shifts were more pronounced for the samples with lower content of PEG. The addition of PEG1000 caused prominent shifts of the peak attributed to the stretching vibration of carboxylate group, but only a slight shift of the peak deriving from the stretching of C=O group (Table 2).

Table 2. The vibrational modes of carbonyl region

Samples/Band frequency (cm^{-1})	COO^- (asym)	$COOCH_3$
Neat pectin	1605	1737
P1/400	1630	1747
P5/400	1615	1743
P1/600	1627	1745
P5/600	1610	1740
P1/1000	1639	1736
P5/1000	1628	1739

The appearance of new peaks associated with possible chemical interactions between pectin and PEG were not evidenced. All the shifts observed in the corresponding PEC/PEG spectra may be attributed to the interactions between pectin and PEG via formation of hydrogen bonds (Wang, Waterhouse &Sun-Waterhouse, 2013).

3.2 NMR analysis

The ^{13}C NMR spectroscopy was used to gather more information about interactions between pectin and PEG. There were no significant differences between spectra of PEC/PEG films with various film compositions except for the relative intensity of pectin and PEG signals, hence, only spectra of the neat pectin, P1/400, P1/1000 and PEG 1000 are shown in Figure 3a.

The main signals of pectin repeating unit (D-galacturonic acid) are observed at ≈ 100 ppm (C-1), 170 ppm (C-6, carboxyl) and overlapped in the region 70 – 90 ppm (C-2 and C-3 at 70 ppm, C-5 at ≈ 72 ppm, C-4 at ≈ 80 ppm). A strong CH_3O signal is observed at 53 ppm, due to the high degree of esterification of the pectin under investigation. No change in the ratio between the area of methoxy peak and the other pectin signals was found, showing that the degree of esterification did not change during the preparation of the materials.

The spectra of the films containing PEG differed only slightly from that of the neat pectin. The signals of the PEG were clearly observed at 70.6 ppm (main chain CH_2-O) and at 61.3 and 72 ppm (terminal CH_2-O and CH_2-OH) (Synytsya, Copíková & Brus, 2003). Carbon signals in PEG were noticeably narrower than in pectin, pointing out a fast segmental motion. Also a slight change in the shape of the complex C-1 and C-4 peak was observed, underlining an effect of PEG on chain conformation of pectin. Interesting differences can be evidenced in the shape of the peaks in the carboxyl region of PEG containing materials. The downfield shoulder present in pectin spectrum, assigned to free carboxyl/carboxylate groups (Zhu et al, 2014), is not observed in P1/400 and P1/1000 samples, while the main peak is slightly shifted upfield (see inset of Figure 3). This finding suggests a protonation of COO^- groups of pristine pectin following the treatment in acidic solutions and a possible involvement of these groups in hydrogen bonding with PEG. A significant conversion of the carboxylic groups of pectin to esters by reaction with PEG can be ruled out, as in this case a new signal for the esterified CH_2O- of PEG should be present in the range 62 – 65 ppm.

Fig.3. a) ^{13}C NMR spectra of the neat pectin and the PEC/PEG film. The carboxyl region is highlighted in the figure inset. Spinning sidebands are marked by a dot. b) Hydrogen bonding between PEG and PEC chains.

According to the FTIR and NMR analyses, the PEC/PEG film formation was supported by hydrogen bonding between PEC and PEG and could be established between carboxyl, methylester and hydroxyl groups of pectin and oxygen atoms of the PEG. However, the methylester substitution pose more steric hindrance, so the interactions between methylester groups and oxygen atom from PEG could be considered as negligible (Embuscado, 2014). Therefore, the most probable interactions are between COOH groups from the pectin and ether-hydroxyl groups of PEG (Fig.3b). The pKa value for the pectin with DE of 72.9% has been found to be 3.5 (Michel, Thibault & Doublier, 1984). So, in order to avoid the ionization of –COOH groups and electrostatic repulsion within the pectin chains, all the samples were synthesized under the pH value of 3 as above mentioned in the experimental section.

3.3 Mechanical analysis

Mechanical parameters such as tensile strength (TS) and Young's modulus of elasticity (E) are reliable indicators for the cracks formation in polymeric films used for packaging (Robertson, 2009). Table 3 summarizes the values of TS and E modulus for the PEC/PEG films, as well as the values of TS and E parameter for commercial synthetic package materials adopted from literature. The thickness of the PEC/PEG films was aproximately 50 μm. The neat pectin film was very fragile and it was impossible to determine its tensile strength and E modulus.

Table 3. Tensile strength (TS) and Young's modulus of elasticity (E) for the PEC/PEG films

Sample	TS, MPa	E, GPa	Reference
P5/400	31±5	0.29±0.04	This work
P3/400	21±3	0.17±0.02	
P1/400	13±2	0.10±0.01	
P5/600	36±5	0.39±0.06	
P3/600	29±4	0.34±0.05	
P1/600	20±3	0.22±0.03	
P5/1000	48±7	0.45±0.07	
P3/1000	28±4	0.31±0.05	
P1/1000	12±2	0.07±0.01	
LDPE	7-17	0.14-0.30	Mark, 2007
HDPE	20-40	0.7-1.4	
PP	30-40	1-2	
PS	30-60	2.4-3.2	

As expected, the mechanical properties of the films changed considerably with the use of PEG plasticizers. The mechanical property parameters provided by the tensile test measurements are

shown in Table 3. Increasing concentration of PEG produced weaker (TS decreased) and more flexibile films (E modulus decreased). These results can be explained as a consequence of the reduced intermolecular forces between pectin chains after the PEG was added. With exception of P1/1000 film, the increase in molecular weight of PEG led to more rigid behavior (E increased) resulting from the denser chain packing within films (Pasini Cabello et al, 2015). The similar trend was observed for poly(lactide)/PEG blends reported by Li et al (2015). The lowest TS values obtained for the P1/1000 film indicated that the addition of PEG 1000 above 33 wt % probably caused the disruption of the PEC phase continuity and an extensive separation of PEG phase. Compared to the other pectin based films reported in literature, the tensile strength values obtained for the PEC/PEG films were significantly higher (12-48 MPa). This could be caused by the differences in the way of preparation, pectin type and final thickness of the films (Wang, Waterhouse &Sun-Waterhouse, 2013; Synytsya, Copíková & Brus, 2003; Zhu et al, 2014). For comparison, the relevant mechanical parameters of the commercially used synthetic package material are also presented in Table 3.

3.4 Thermal analysis

TGA and DSC analyses were performed to get insight on the properties of the PEC/PEG film at molecular level. Figure 4 shows the TGA and DTG curves of the neat pectin powder and the PEC/PEG films.

Fig.4. The TGA (a, b) and DTG (c, d) curves of neat pectin powder and PEC/PEG films.

The TGA/DTG curve of the neat pectin showed two weight loss steps. The first step, in the temperature range from 50 to 100 °C was assigned to the vaporization of water, and the second one, in the temperature range from 200 to 320 °C (reaching maximum at 240 °C), was attributed to the decomposition of the pectin chain (Fig.4) (Tripathi, Mehrotra & Dutta, 2010). Thermal degradation of pure PEG is a one-step process taking place in a temperature range from 310 to 390 °C, depending on its molecular weight (Cavallaro, Lazzara & Milioto, 2013; Yanshan et al, 2014). The degradation process of the PEC/PEG films exhibited three degradation stages: a) elimination of water from 50 to 100 °C; b) degradation of the pectin chains around 240 °C and c) decomposition of the PEG molecule from 300 to 400 °C. Based on the shape of weight loss curves (Fig.4 a,b) and DTG curves (Fig.4 c,d) it could be concluded that degradation of PEC/PEG films was affected by the concentration and molecular weight of PEG.

The onset temperatures were determinated based on DTG curves (Table 4). As shown in Figure 4 c, d the onset degradation temperatures of the PEC/PEG films were slightly anticipated compared to the neat pectin (225 °C) and this trend was more pronounced for higher PEG contents in the films. Contrary, sample P5/1000 delayed onset degradation temperature in comparison to the neat pectin.

The glass transition temperature was detected for all the samples, except for the P1/1000 film where the T_g was covered by wide endothermic peak related to the melting of the PEG1000 (Fig.5, Table 5). The non isothermal DSC run showed the T_g value of neat pectin at 51 °C. Except for the P5/1000 and P3/1000, the T_g values of all considered PEC/PEG films were below the T_g

value of neat pectin. In addition, the T_g values of the films were lower when the PEG content was up to 33 wt% (P5 and P3) while for the further increase of the PEG in system T_g values shifted to higher temperatures (P1).

As mentioned before, the addition of PEG produced micro-structural changes in the polymer matrix by involving a reduction in the intermolecular forces between polymer chains, so it was expected for T_g values to be decreased (Martucci, Accareddu & Ruseckaite, 2012). The strong melting peak observed for all P/1000 films confirmed the formation of two phase systems. The P3/400, P5/400, P3/600 and P5/600 thermograms did not show melting peaks, indicating a good miscibility of the components and mainly amorphous morphology (Fig.5).

Table 4. The onset and degradation temperatures obtained by TGA

Sample	Onset, ^oC	Pectin degradation, ^oC	PEG degradation, ^oC
Neat pectin	225	240	-
P5/400	223	237	372
P3/400	222	237	321
P1/400	216	237	312
P5/600	223	238	370
P3/600	221	238	351
P1/600	216	238	366
P5/1000	228	243	382
P3/1000	223	241	388
P1/1000	220	238	388

The increasing PEG1000 concentration caused the shifting of enthalpy (ΔH_m) and melting point (T_m) values from 1.21 J/g and 28.65 °C (P5/1000) to 24.75 J/g and 30.91 °C (P1/1000), respectively, indicating that blending of these components was affected by both concentration and molecular weight of PEG. Hence, the highest T_g values of the PEC/PEG films were obtained in presence of PEG1000, wherein the plasticizing effect was partly suppressed due to limited miscibility of the components over the investigated concentration ranges.

Fig.5. DSC scans of non-dried PEC/PEG films of various compositions.

When the free unbound water was removed by first heating run and the T_g value was determined during the second heating run (dried films), the T_g of the PEC/PEG films was significantly shifted to higher values, confirming the strong influence of residual water on the chains mobility. The T_g of the neat pectin powder was found to be at 133 °C. An increase in PEG concentration caused the decrease in T_g values due to enhanced chain mobility (See Table 5). During the cooling process, crystallization peak of PEG could be seen for all the PEC/PEG films, while the melting peak of PEG was observed in the second heating run. Nevertheless, with a decrease of PEG concentration in pectin matrix, the enthalpy of melting (which correlates with crystallinity of

PEG in films) decreased from 19.65 J/g to 2.12 J/g (PEG400), 26.45 J/g to 1.47 J/g (PEG600) and 29.70 J/g to 2.29 J/g (PEG1000), respectively. This dependence confirmed some miscibility between pectin and PEG even if phase separation of PEG 1000 occurred. The melting temperature also decreased with decreasing concentration of PEG in films, ranging between 4.4 °C and 3.9 °C (PEG400), 17.6 °C and 11.9 °C (PEG600) and 36.4 °C and 32.4 °C (PEG1000). The trend related to the decrease in T_m values of PEG with an increasing pectin concentration may be attributed to the crystal size reduction, more pronounced crystalline defects or changes of PEG's crystals structure (Alfonso & Russell,1986).

Table 5. T_g values of the PEC/PEG films obtained by nonisothermal and isothermal DSC scan

Sample	Tg, ºC	
	Non-dried samples	Dried samples
Neat pectin	50	133
P5/400	44	98
P3/400	42	95
P1/400	50	93
P5/600	47	113
P3/600	44	109
P1/600	46	94
P5/1000	54	127
P3/1000	51	118
P1/1000	covered by wide endothermic peak	110

3.5 SEM analysis

The SEM micrographs of the neat pectin and the PEC/PEG films with component ratio 5:1 and 3:1 were homogeneous with a flat surface without cavities (images not presented). At the highest PEG concentration (blending ratio 1:1), there were no significant differences regarding the surface morphology of P/400 and P/600 samples (images not presented), while the addition of PEG 1000 caused prominently rougher and denser structure (Fig.6.). The numerous inhomogeneous domains located on the P1/1000 film surface could be the consequence of the poor miscibility of the components over the given concentration range, followed by an extensive separation of PEG 1000 phase.

Fig.6. SEM micrographs of the P1/400 (a, a1) and P1/1000 (b, b1) films at various magnifications.

3.6 Water vapor permeability

Generally, the addition of a plasticizer modifies the properties of the film by reducing the intermolecular interactions between the polymer chains, thus increasing the WVP of the film.

Table 6. The WVP parameters of the PEC/PEG films

Sample	WVP x10^{12}, $gm^{-1}s^{-1}Pa^{-1}$	Reference
P5/400	292	
P3/400	271	
P1/400	470	
P5/600	293	
P3/600	410	
P1/600	485	This work
P5/1000	302	
P3/1000	298	
P1/1000	473	
LDPE	0.067-0.087	
HDPE	0.017-0.038	Sung et al, 2013
PP	0.023-0.046	
PS	0.11-0.46	

Based on the data given by Table 6, an increase of PEG amount in the films formulations led to an increase in water vapor permeability, mainly due to the increased molecular mobility of pectin chains. Another proposed reason could be the clustering of plasticizer molecules at high concentrations, resulting in a discontinuous structure in film matrix (Cerqueira et al, 2012). The WVP values varied from $2.7x10^{-10}$ to $4.85x10^{-10}$ $gm^{-1}s^{-1}Pa^{-1}$ and no significant influence with respect to the molecular weight of PEG was found. The obtained values of water vapor permeability were higher by several orders of magnitude than those reported for the films made from PS, LDPE and HDPE, as shown in Table 6.

Conclusions

Pectin/poly(ethylene glycol) films were prepared successfully by solution casting method using highly methoxylated pectin (PEC) and poly(ethylene glycol) (PEG) of various molecular weights (400, 600 and 1000 $gmol^{-1}$) in different ratios (5:1, 3:1 and 1:1). The film formation was supported by the formation of hydrogen bonds, most probably established between carboxyl groups from pectin and oxygen atoms from PEG. The increasing PEG concentration produced weaker and more flexible films, while increase in molecular weight of PEG contributed to the films rigidity. It was found that thermal stability of the PEC/PEG films was affected by the concentration and molar mass of PEG. In general, the onset degradation temperatures of the PEC/PEG films were slightly reduced compared to the neat pectin (225 ^oC) and this trend was more pronounced at higher PEG concentrations. The highest T_g values of the PEC/PEG films were obtained in presence of PEG1000 indicating the most suppressed plasticizing effect of PEG 1000, probably due to the limited miscibility of the components. The two phase morphology of P/1000 samples was additionally confirmed by SEM analysis. The WVP was increased by the increase in PEG concentration, while it was not affected by its molecular weight. Finally, the presented study revealed satisfactory performances of the investigated system to be used for

edible food packaging application. Still, in order to keep the eco-friendly approach and potential to compete with commercially available food package materials, additional efforts should be directed toward a further improvement of PEC/PEG films.

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Figure captions

Fig.1. Visual appearance of the P3/400 film.

Fig.2. ATR-FTIR spectra of a) P1/400 and P5/400, b) P1/600 and P5/600, c) P1/1000 and P5/1000 films.

Fig.3. a) ^{13}C NMR spectra of the neat pectin and the PEC/PEG film. The carboxyl region is highlighted in the figure inset. Spinning sidebands are marked by a dot. b) Hydrogen bonding between PEG and PEC chains.

Fig.4. The TGA (a, b) and DTG (c, d) curves of neat pectin powder and PEC/PEG films.

Fig.5. DSC scans of non-dried PEC/PEG films of various compositions.

Fig.6. SEM micrographs of the P1/400 (a, a1) and P1/1000 (b, b1) films at various magnifications.

Figure 1

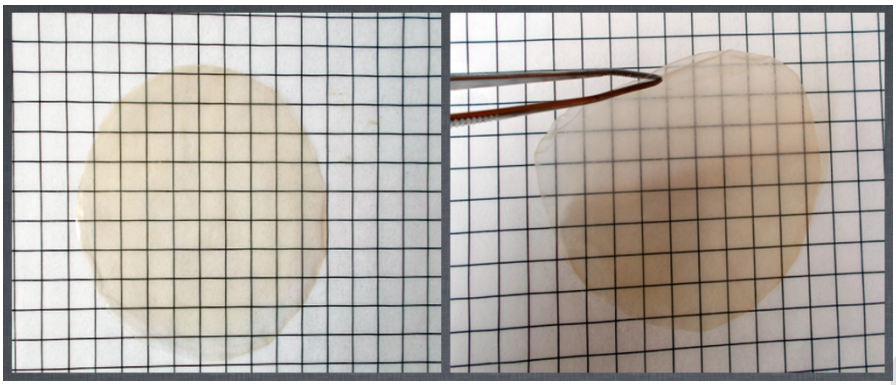


Figure 2

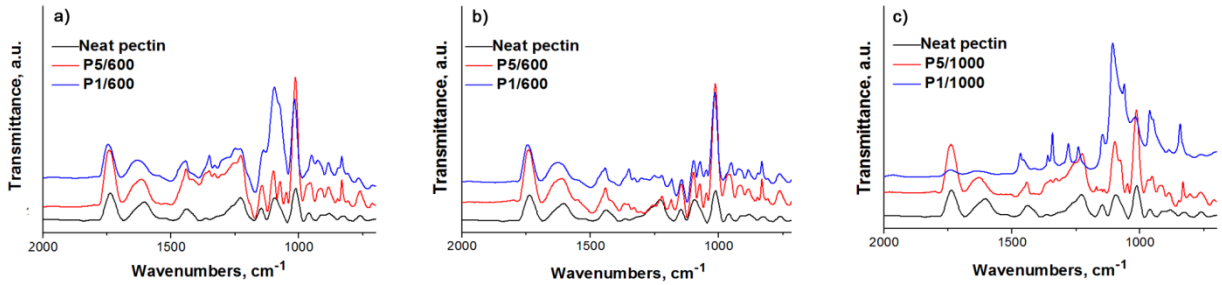


Figure 3

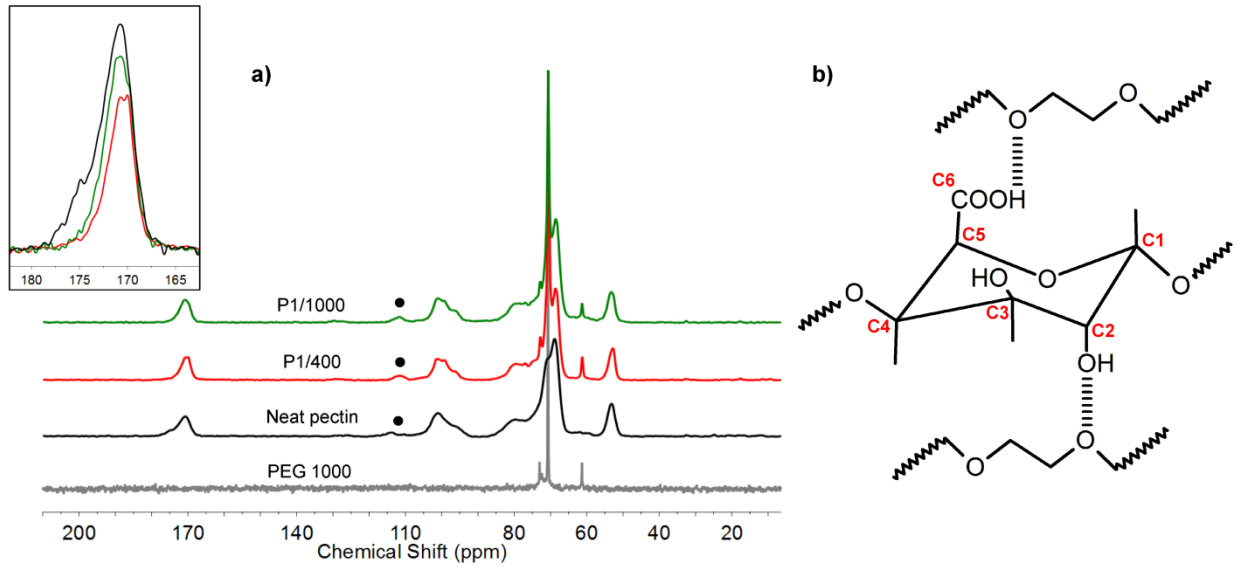


Figure 4

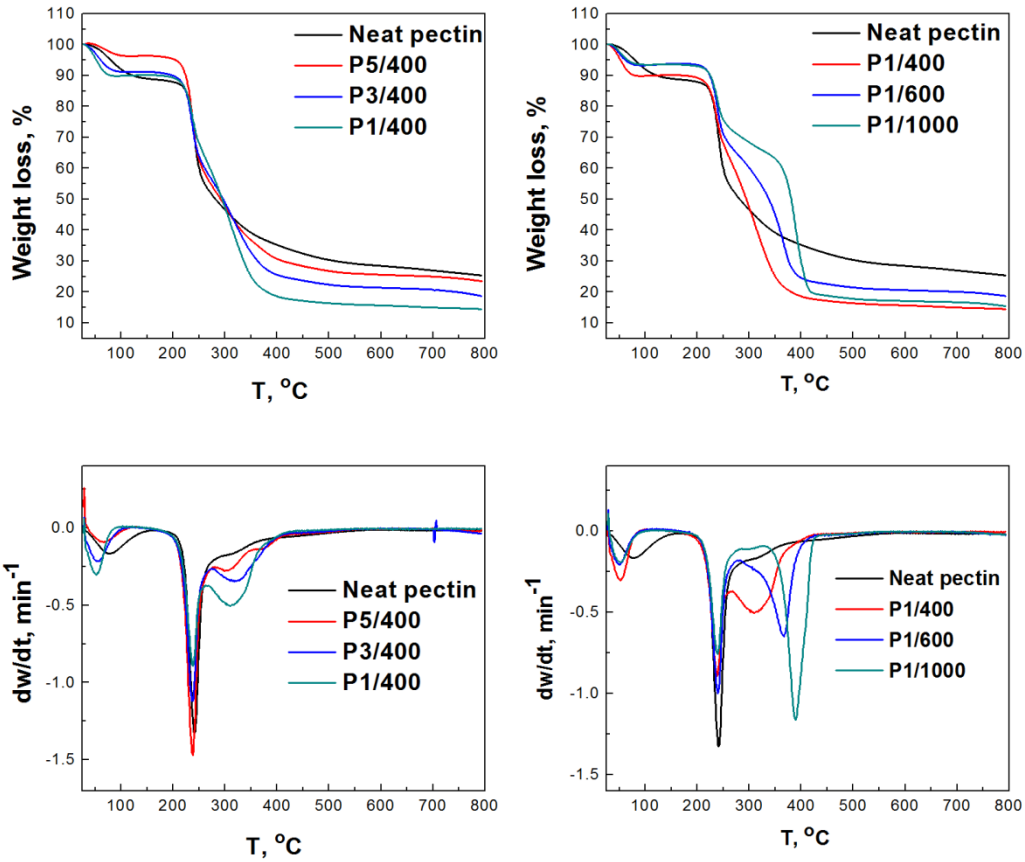
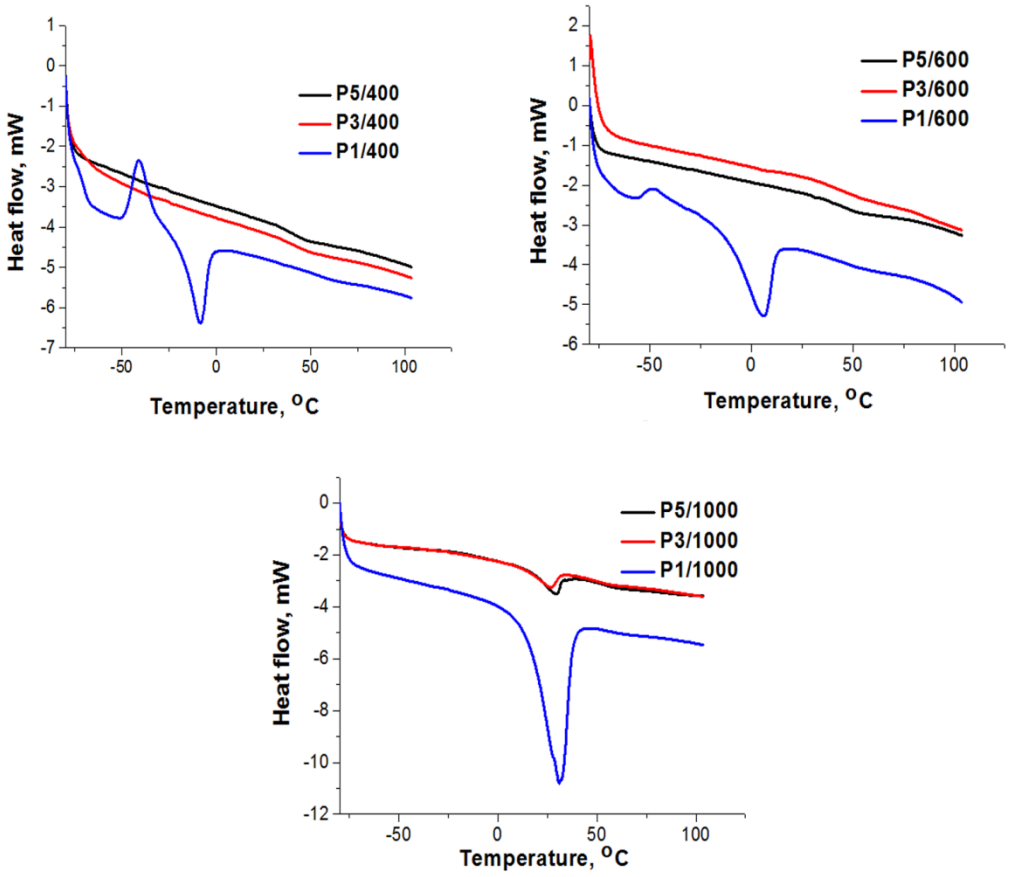


Figure 5



743 Figure 6
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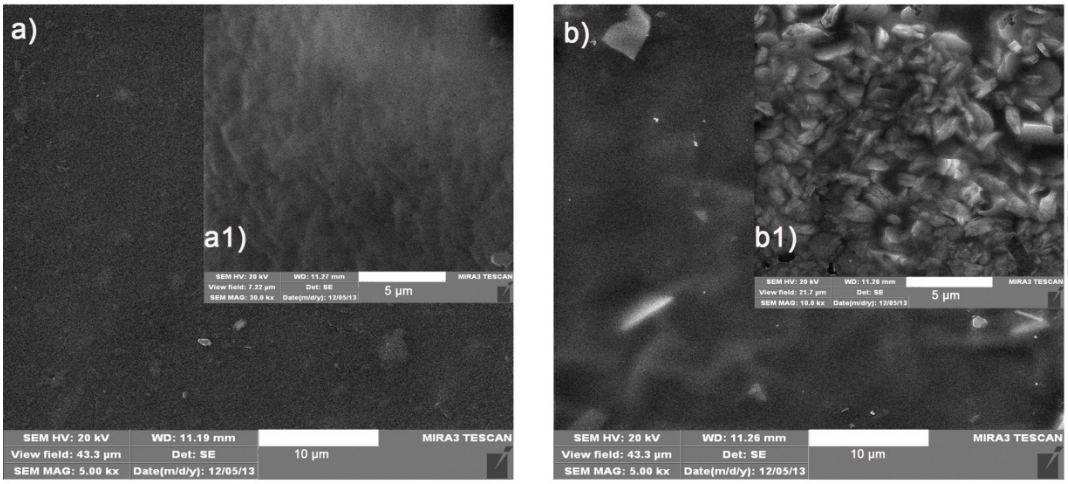

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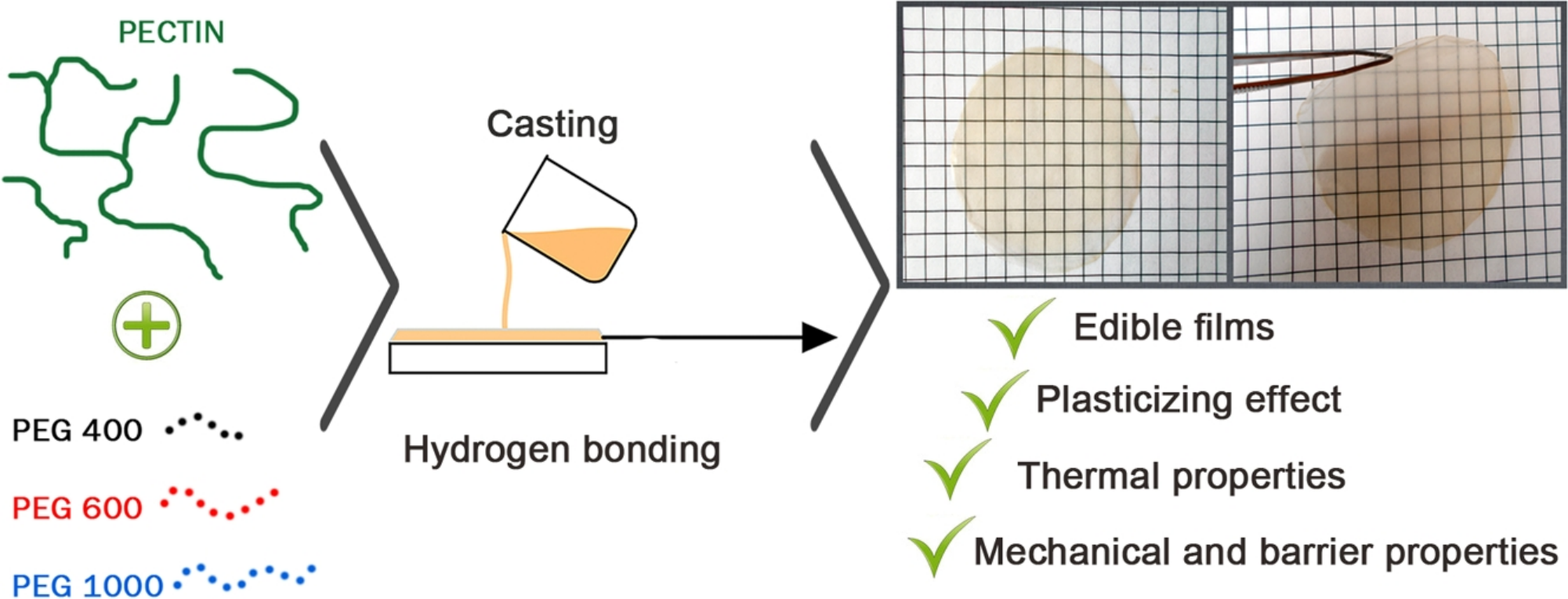
PECTIN
PEG 400
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Mechanical and barrier properties