

Thermoplastic Films Based on Polyelectrolyte Complexes of Arabino Glucurono-Xylan and Polyethylenimine

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This work investigates film formation using polyelectrolyte complexes (PECs) of xylan and polyethylenimine (PEI). Different xylan/PEI mass ratios (from 50/50 to 90/10) and pH values (5.0 and 7.0) are analyzed and both parameters have an effect on complex size and film properties. Furthermore, the mass ratio corresponding to the neutralization charge depends on pH. When xylan/PEI mass ratios are near the neutralization charge ratio, a coacervation process is observed. In this case, separation between the coacervate and the supernatant dilute phase is possible. In the supernatant, both concentrations, xylan and PEI, depend on pH. The complex suspensions are used to obtain films by PECs casting/evaporation process. For films obtained from the whole suspension, by increasing the xylan content the stress at break is improved (up to 23 MPa for 85/15, at pH 7.0) and the strain at break is decreased (to 2.5%). When only coacervate is used to prepare films, the tensile strength is higher, reaching a value of 37 MPa for 85/15 mass ratio. Dynamic mechanical thermal analysis shows that the glass transition temperature (T_g) of the films is affected by composition. The thermoplastic behavior of a 50/50 xylan/PEI film is confirmed using a hot-compression molding.

plasticizers^[6,7] or using it in combination with chitosan, which is another natural polyelectrolyte.^[8–10] Despite its advantages, xylan has low solubility which is a limitation due to the high amount of water that needs to be evaporated to obtain films. In the case of chitosan, which also shows limited solubility, acid medium is needed to dissolve it. It could be favorable to use a cationic polyelectrolyte with high solubility that combined with xylan forms film. An interesting property of xylan was proved by Börjesson et al.^[11] They could obtain films from etherified xylan powder and, using a hot-melt compression-molding technique, they demonstrated that thermoplastic capacity can be attained by chemical modification of arabinoxylan from wheat bran.

Polyethylenimine (PEI) is a synthetic, cationic and branched polyelectrolyte, which is obtained by the polymerization of aziridine. It is widely used in many applications, especially in the paper industry

to flocculate negatively charged fibers^[12] and in water treatment for metal ions removal.^[13] Particularly, Wang's group developed two novel sensors (a humidity sensor^[14] and a formaldehyde sensor^[15]) by coating quartz crystal microbalance with bacterial cellulose (BC) membranes and PEI/BC membranes, respectively. Both sensors showed high sensitivity with good linearity and exhibited a good reversible behavior, indicating that PEI/BC membrane materials could act as a promising candidate for the production of high performance, low cost sensors. Li et al.^[16] prepared polyelectrolyte complex films with excellent oxygen barrier properties, using PEI/PAA (poly(acrylic acid)), while Baig et al.^[17] obtained PSS (poly(styrene sulfonate))/PEI membranes, demonstrating the great versatility of PEI combined with anionic polyelectrolytes. Linear PEI has also been used to investigate new drug delivery systems.^[18] Although PEI has many uses, it is not possible to obtain films using solely this polyelectrolyte.

Polyelectrolyte complexes (PECs) are formed by the association of oppositely charged polyelectrolytes; stable colloids, flocculants, or metastable coacervates can be obtained.^[19,20] Under certain conditions a dispersion of specific PECs can undergo a phase separation resulting in the formation of a dense phase (complex coacervate) and a supernatant diluted phase. This supernatant coexisting phase will also contain a low concentration of both polymers.^[21] Haile et al.^[22] prepared thin films using a polyelectrolyte complex coacervate composed of PEI and polyacrylic acid. These authors formed a coacervate by controlling

1. Introduction

According to the biorefinery concept, it is possible to separate biomass resources into their basic components and convert them into value-added products, biofuels, and chemical products.^[1] Particularly, the production of biobased food packaging films mostly originated from polysaccharides is being extensively explored.^[2,3] Biodegradable films made from renewable sources can potentially replace synthetic packaging films and consequently reduce the environmental problems associated with their improper disposal.^[4,5]

Xylan, the major hemicellulose present in hardwoods and gramineous plants, is an anionic biodegradable polyelectrolyte. This polymer has a great potential to be used in the production of new value-added materials. Actually, some studies have investigated the film forming capacity of xylan by the addition of

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the ionic strength of the aqueous solution to obtain a material of high barrier to oxygen. These films have applications such as supported membranes for separations, cell growth substrates, anti-corrosion coatings, biocompatible coatings, and drug release media, among others.^[23] The utilization of the coacervate allows the elimination of a considerable amount of water.

Ström et al.^[24] studied in detail the coacervation phenomenon between pine xylan and PEI. They observed a phase separation and the formation of a flocculated precipitate, whose characteristics depended on the polyelectrolyte mass ratio used. To the best of our knowledge, the combination of xylan and PEI in the field of films and coatings has not been explored yet. The study of the interaction between these polyelectrolytes can be useful for a wide variety of applications.

In this work, the characteristics of polyelectrolyte complexes and films formed from sugar-cane bagasse hemicellulose (xylan) and PEI is analyzed, using different pH values and mass ratios. Initially, both polymers were characterized, and, as they are weak polyelectrolytes, the interaction between them was studied as a function of pH. The size distribution of the complexes was analyzed at two pH values (5.0 and 7.0) and at different mass ratios. These complex suspensions were used to obtain films by casting/evaporation process. Using certain charge ratios, the complex suspension turns into a two phase system (coacervate formation). The characteristics of the films containing a high amount of xylan (from 50 to 90 wt%) were analyzed for both, the coacervate and the whole suspension. Their mechanical properties, thermal stability and water vapor transmission rate were studied. Finally, the thermoplastic behavior of the film containing 50% xylan was verified by printing a coin on the film by hot-compression.

2. Experimental Section

2.1. Xylan Isolation and Characterization

Xylan was alkali extracted from sugar-cane bagasse. Raw material (500 g) was treated in a 14 L cylindrical tumbling rotary reactor at 50 °C, using 40 g NaOH/100 g of bagasse and 25:1 liquor to bagasse ratio, for 180 min. Previously, bagasse was washed for 30 min at 50 °C. Diethylenetriaminepentaacetate (DTPA), 0.2 g/100 g of bagasse, was added as chelating agent. Extracted xylan was precipitated from the liquor using 96% v/v ethanol (1:1 liquor:ethanol volume ratio), and then separated by centrifugation at 1800 g for 15 min, after 15 h of repose. The wet precipitate obtained (with high alcohol content) was reserved in a sealed plastic tube at -4 °C. For its use, xylan was directly taken from the plastic tube. In a previous work,^[25] it was shown that this raw material and the isolation conditions here applied lead to a xylan-rich hetero polysaccharide material of the following composition (expressed as % on dry precipitate): xylose 67, arabinose 18, glucuronic acid 2, acid insoluble lignin 7, soluble lignin 6.

The intrinsic viscosity of xylan was determined using an Ubbelohde-type viscometer (Size 0C) at 25 °C, according to the technique proposed by Koshijima et al.^[26] Xylan was dried in a vacuum oven at 60 °C and then dissolved in cupriethylenediamine solution (0.04 M) to obtain a xylan solution concentration of 0.70 g dL⁻¹. Four dissolutions were prepared by diluting the original one in the same solvent (0.10, 0.23, 0.36, and 0.50 g dL⁻¹). Intrinsic viscosity $[\mu]$ was determined by extrapolating inherent

and relative viscosities to zero concentration. Equation (1) was used to determine the degree of polymerization of xylan (Pn)

$$[\mu] = 2.2 * 10^{-2} * Pn^{-0.72} \quad (1)$$

Xylan is a weak polyelectrolyte, thus its charge density depends on the pH. In this work, xylan/PEI interaction (to obtain PECs) was analyzed at pH 5.0 and 7.0. Therefore, the charge density of xylan was determined at these pHs by polyelectrolyte titration method employing a streaming current charge analyzer (Chemtrac ECA 2100). Xylan was dissolved to obtain a solution of 2.19 × 10⁻⁵ g L⁻¹. Polydiallyldimethylammonium chloride (pDADMAC) (Sigma-Aldrich) solution (diluted to 1.3 × 10⁻³ N) was used as titrant. The ionic strength of both solutions was adjusted to 1100 μS cm⁻¹, using NaCl. The zero value in the streaming current signal was indicative of the colloidal charge neutralization.

2.2. PEI Characterization

A commercial polyethylenimine solution (BASF) was used (27 wt%). Molecular weight fractions of PEI were determined using Amicon Ultra-15 Centrifugal Filter Devices (3, 10, and 100 kDa molecular weight cut off). A 600 ppm PEI solution (15 mL), dissolved in NaCl 10⁻² N and pH 5.0, was spun for 15 min to obtain two fractions. The filtered fraction was reserved, and the retained fraction was diluted up to 15 mL with NaCl 10⁻² N and spun again for 15 min. This latter operation was repeated once. PEI concentration was quantified, in the filtered and in the final retained fractions, using a colorimetric method.^[27] For that, 1 mL of 0.01 M cupric acetate was added to 5 mL of the dilute solution (retained or filtered) and the mixture was vigorously stirred. The absorbance was then measured at a 277 nm wavelength. A solution containing 1 mL of 0.01 M cupric acetate in 5 mL of distilled water was used as a blank. The unknown concentration was determined using a calibration curve (0–100 ppm) obtained taking the original solution as standard.

The content of primary (1°), secondary (2°) and tertiary (3°) amines was determined through ¹³C-NMR analysis (nuclear magnetic resonance) using a 300 MHz Bruker Avance II Spectrometer. For quantification, 100 mg of PEI were dissolved in D₂O and the spectrum was recorded at 25 °C after 12 000 scans. The amine percentages were calculated from signal intensities according to Equation (2)^[12]

$$1^\circ : 2^\circ : 3^\circ = (A_7 + A_8) : [(A_4 + A_5 + A_6) / 2] : [(A_1 + A_2 + A_3) / 3] \quad (2)$$

To determine the charge density of PEI at pH values of PEC preparation and film formation (5.0 and 7.0), polyelectrolyte titration was used. The method employed was the same as the one used for the determination of xylan charge density, but the titrant was potassium polyvinylsulfate (PVSK).

2.3. Xylan/PEI Ionic Interaction

The ionic interaction between xylan and PEI at different pH values (3.0, 4.0, 5.0, 6.0, 7.0, and 8.0) was analyzed by streaming

current measurement (Chemtrac ECA 2100). Furthermore, the streaming current curves were used to estimate the mass ratio corresponding to polyelectrolyte neutralization. A dilute xylan solution (0.3 g L^{-1}) was added using a microburette (in aliquots of 0.2 mL) on 150 mL of dilute PEI solution ($2 \times 10^{-3} \text{ g L}^{-1}$), both in $\text{NaCl } 10^{-2} \text{ N}$, and previously adjusted at the corresponding pH. The potential of the PECs solution was registered after 2 min of each aliquot addition. The charge neutralization was indicated by the zero value of the potential. The solution concentration was chosen according to the operational range of the equipment.

2.4. PECs Preparation and Film Formation

The corresponding mass of xylan was mixed with water (4.0 g L^{-1}), and heated for 10 min in a bath at $100 \text{ }^\circ\text{C}$ until dissolution. This solution was added through a continuous drip to the PEI solution (2.5 g L^{-1}) under magnetic stirring to obtain 250 mg of PECs. Xylan/PEI mass ratios of 50/50, 60/40, 70/30, 80/20, 85/15, and 90/10 were studied. Before mixing them, the pH of each solution was adjusted using HCl (0.1N). Once the PEC solution was prepared, it was cast into a rectangular silicone mold (4.5 cm width; 9.1 cm length; 3.2 cm high) and dried in a fan forced oven at $40 \text{ }^\circ\text{C}$. The final thicknesses of films were $45\text{--}55 \mu\text{m}$.

In previous studies^[9,10,25] it was demonstrated that pH 5.0 was optimal in the case of xylan/chitosan film formation due to the high degree of interaction of these two polyelectrolytes. Considering those results and that there is no difference in the mass ratio at the neutrality at pHs 5.0 and 7.0 (discussed in the Section 3), these two pH values were selected for polyelectrolyte complex preparation and film formation.

In some cases, the formation of a coacervate with a supernatant dilute phase was observed (xylan/PEI mass ratio 80/20 and higher, at pH 7.0; and 85/15 and higher, at pH 5.0). In those situations, the removal of the supernatant after leaving PECs in suspension for one day at room temperature allowed to isolate the coacervate. That phase separation could be advantageous for obtaining films, spending less energy and time in the drying process. Thus, film formation using only the coacervate phase was evaluated. These last films were identified with the mass ratio used and the subscript "coa" (i.e., 85/15_{coa}). In the case of 90/10 at pH 7.0 it was necessary to leave the solution in repose for three days before removing the supernatant.

2.5. Particle Size of PECs

The effect of pH on the particle size distribution of PECs was analyzed by dynamic light scattering (DLS) using Zetasizer Nano ZS90 equipment (Malvern Instruments, UK). Since the objective was to know the size of PEC particles that form the film, pH values 5.0 and 7.0 were evaluated. PEC solutions were prepared following the same procedure as for film formation, and the measurements were done without dilution at $25 \text{ }^\circ\text{C}$, at both pHs. The size was determined using the intensity curve of particle size distribution (PSD). The relative amount of each peak in the distribution was estimated from the volume PSD distribution curve, according to the operating instructions of the equipment. For PECs, the refractive index of water (1.334) was considered,

due to the high water content of the PEC particles.^[28,29] Five measurements were done for each mass ratio. The mean value and the standard deviation are informed.

2.6. Xylan and PEI Quantification in Supernatant

Xylan and PEI were quantified in the supernatants to determine the amount of these polyelectrolytes that is removed when it is separated from the coacervate. For xylan, the phenol/sulfuric acid method was used.^[30] A volume of 1 mL of phenol at 5% (m/v) and 5 mL of concentrated sulfuric acid were added to 1 mL of solution. The mixture was shaken, left at room temperature for 10 min and shaken again. Then, it was placed in a water bath at $25\text{--}30 \text{ }^\circ\text{C}$ for 20 min. Absorbance was spectrophotometrically measured at 480 nm . A calibration curve using xylose as a standard was employed. Determinations were done by triplicate.

PEI was quantified using the colorimetric method explained in Section 2.2.

2.7. Thermal Gravimetric Analysis (TGA)

To characterize their thermal stability, the behavior of 50/50, 85/15, and 85/15_{coa} (pH 7.0) films was analyzed using a thermogravimetric analyzer (TGA/SDTA851e Module – Mettler Toledo). These three mass ratios were chosen to evaluate films of low and high xylan content, with and without phase separation. The measurements were done on 5 mg of conditioned sample ($23 \text{ }^\circ\text{C}$, 50% RH), under a nitrogen stream and using a heating rate of $10 \text{ }^\circ\text{C min}^{-1}$ from room temperature to $900 \text{ }^\circ\text{C}$.

2.8. Mechanical Properties of the Films

Tensile strength and strain at break were determined using an Instron 3344 universal testing machine (Instron, USA), with a load cell of 1000 N , following the ASTM D882 standard test (tensile test for thin plastic sheeting) with some modifications. Before testing, films were conditioned at $23 \text{ }^\circ\text{C}$ and 50% RH for 24 h. Thickness was determined using a micrometer (TMI: Testing Machine Inc.; model N° 46–63) with a precision of $1 \mu\text{m}$. For each mass ratio, at least two films were used to obtain ten specimens of 5.0 mm width, and a length enough to allow an initial testing-grip distance of 22.0 mm . Tests were made at $23 \text{ }^\circ\text{C}$ and 50% RH.

2.9. Dynamic Mechanical Thermal Analysis (DMTA)

Dynamic mechanical properties of 50/50, 85/15, and 85/15_{coa} (pH 7.0) films, conditioned at $23 \text{ }^\circ\text{C}$ and 50% RH, were investigated using a dynamic mechanical analyzer (DMA, Q8000, TA Instrument). A frequency of 1 Hz , a temperature ramp of $5 \text{ }^\circ\text{C min}^{-1}$ between 30 and $250 \text{ }^\circ\text{C}$ and a constant strain tension of 0.1% were employed. The storage modulus (E'), loss modulus (E''), and $\tan \delta$ were obtained as a function of temperature. Glass transition temperature was defined as the point of highest value of $\tan \delta$.

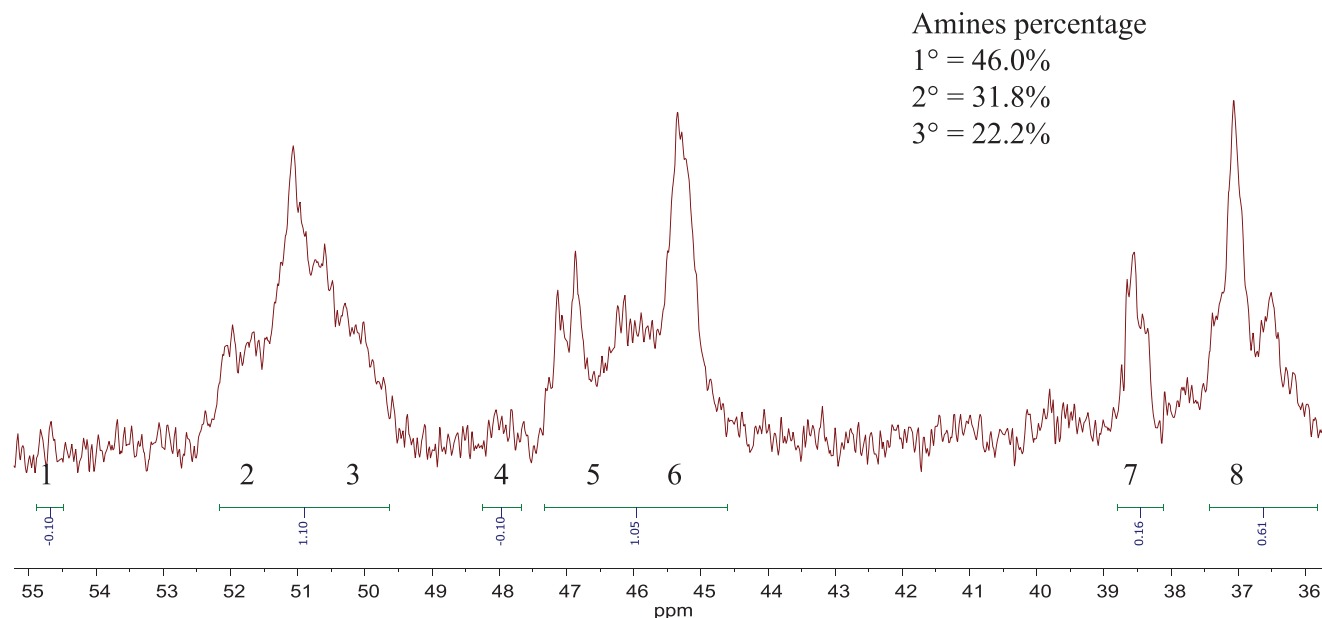


Figure 1. NMR spectra of PEI. Percentages of primary, secondary, and tertiary amines are shown.

2.10. Water Vapor Transmission Rate (WVTR)

The WVTR ($\text{g s}^{-1} \text{m}^{-2}$) of films (50/50, 85/15, and 85/15_{coa}, at pH 7.0) were determined gravimetrically according to ASTM E96-98. Cylindrical cups of polypropylene (7.1 cm diameter, 3.0 cm high) containing 10 mL of distilled water were used. The lids of the cups were perforated with a circle area of 39.6 cm² (*A*) where the films were placed between two o-rings. Device weight was monitored every 30 min for 5 h. Tests were carried out at 23 °C and 50% RH, and WVTR was calculated according to Equation (3). $\Delta m/\Delta t$, was obtained from the linear regression of the weight-time curve. An average of two measurements is reported for each sample

$$\text{WVTR} = (\Delta m/\Delta t) / A \quad (3)$$

2.11. Hot-Compression Molding

To investigate the thermoplastic behavior of 50/50 xylan/PEI film, a hot-compression molding was made at 160 °C, a temperature above the T_g previously determined for the film. For this assay, a coin (24.0 mm diameter) was used to brand the film. 45 μm thick xylan/PEI film was placed over a preheated 4.0 mm thick silicone film backed by a metallic plate for 15 min at 160 °C. After that, the preheated coin was placed on the film and a metallic plate (also preheated) was placed over it. Finally, pressure was applied using a screw clamp. The whole system was maintained in an oven at 160 °C for 15 min. Once out of the oven, the set was cooled down for a few minutes and finally the clamp was opened.

3. Results and Discussion

3.1. Xylan and Polyethylenimine Characterization

The degree of polymerization (P_n) of xylan determined by intrinsic viscosity was 136. The xylan charge density, determined by

polyelectrolyte titration was 1.02 ± 0.11 and 0.76 ± 0.05 meq g⁻¹ of xylan, at pH 7.0 and 5.0, respectively. At pH 7.0, there is a complete ionization of carboxyl groups of the glucuronic acid. There was a 25% reduction in the charge density of xylan, which is associated with the lower ionization of these groups at lower pH.

Figure 1 shows the NMR spectra obtained for PEI. The ratio of the different amino groups that form the polymer was calculated using Equation (2). As can be observed, the PEI used in this work has a high content of primary amines (46%). This indicates that the polymer is highly branched, and this can partly be explained by the presence of low molecular weight compounds formed during polymerization. The values are in agreement with those reported by Pierre and Geckle^[31] for a commercial PEI and by von Harpe et al.^[12] and Kim et al.,^[32] for PEI produced in laboratory.

The different molecular weight (Mw) fractions of the PEI solution are: 17.7% lower than 3 kDa, 21.0% between 3 and 10 kDa, 30.8% between 10 and 100 kDa, and 30.5% with a molecular weight greater than 100 kDa.

The high dispersion of the molecular weight can be attributed to the industrial polymerization process used for the production of this particular PEI (additive for the cellulosic industry), in which the linearity or branching of the polymer is not controlled.

The charge density of PEI was affected by the pH value. Through polyelectrolyte titration, values of 3.29 ± 0.14 and 4.79 ± 0.16 meq g⁻¹ of PEI at pH of 7.0 and 5.0 respectively were found. As expected, these results indicate an increase in PEI amine groups ionization when the pH decreases. Furthermore, it can be observed that the charge density of PEI is markedly higher than the xylan charge density.

3.2. Xylan/PEI Ionic Interaction

Figure 2 shows the potential measurements as a function of the xylan/PEI mass ratio. Deviations from the stoichiometry can be

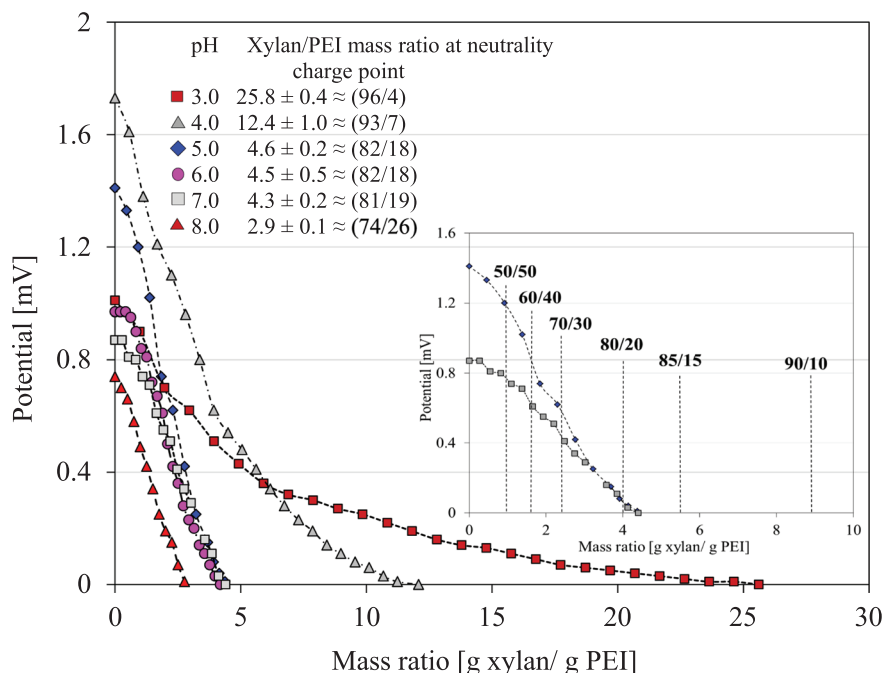


Figure 2. Streaming current titration curves of xylan and PEI at different pH values (3.0, 4.0, 5.0, 6.0, 7.0, and 8.0). The xylan/PEI mass ratios at the neutrality charge point are indicated in brackets, and the different mass ratios selected later to prepare films at pH values 5.0 and 7.0 are shown in the smaller plot.

expected, due to both polyelectrolytes are weak and they have a very different charge density. The figure shows a noticeable effect of the pH value on the ionic interaction between xylan and PEI for pHs: 3.0, 4.0, 5.0, 6.0, 7.0, and 8.0. As the pH of the medium is increased from pH 3.0 to pH 5.0, the amount of xylan required by the PEI to reach the neutrality of the charges is significantly reduced. No significant difference between the mass ratios corresponding to the neutrality charge at pH 5.0, 6.0, and 7.0 is observed. In these ranges of pH values, the mutual masking of the charges on the reacting macromolecules could occur and/or they could be sterically less accessible.

At pH 8.0, the neutrality mass ratio shows a slight decrease due to the complete ionization of xylan and the decrease in PEI ionization.

The stability of PECs decreases near the neutrality of charge. Thus, evaluation of the ionic interaction between these two weak polyelectrolytes could help to predict the coacervation phenomenon.

3.3. Charge Ratio and Particle Size of PECs

Table 1 shows the mass and the charge ratios used for PEC formation. The mass ratio is expressed on a basis of 100 (e.g., 100 mg PECs of 70/30 xylan/PEI mass ratio is composed by 70 mg of xylan and 30 mg of PEI). PEC charge ratio can be calculated for each mass ratio using the respective charge density determined for PEI and xylan by polyelectrolyte titration at the corresponding pH values. Since xylan and PEI have opposite charges, for the example cited before (70/30 xylan/PEI mass ratio), at pH 5.0, there are 27 anionic and 73 cationic in a total of 100 charges.

Table 1. Xylan/PEI mass ratio and charge ratio of PECs at different pH values.

xylan/PEI mass ratio	xylan/PEI charge ratio pH 5.0	xylan/PEI charge ratio pH 7.0
50/50	14/86	24/76
60/40	19/81	32/68
70/30	27/73	42/58
80/20	39/61	55/45
85/15	47/53	64/36
90/10	59/41	74/26

In the case of xylan, at pH 7.0, there is a complete ionization of the glucuronic acid groups, which contribute the anionic charge.^[33] In the case of PEI, it is difficult to quantify the number of repetitive units with charge, due to the high degree of branching. Considering that the total mass of PEC remained constant, regardless of the mass ratio used, charge ratios are given as a percentage of each polyelectrolyte used.

As can be observed, at pH 5.0, the minimum difference in charged groups (positives and negatives) of both polyelectrolytes is found at 85/15 xylan/PEI mass ratio, while at pH 7.0 this minimum is found at 80/20 xylan/PEI mass ratio. These results confirm that it is necessary to be close to the charge neutrality for coacervate formation. These results are in agreement with those obtained by streaming potential measurements (Figure 2), which show the mass ratio corresponding to the stoichiometry charge.

Table 2. Size distribution of PECs at pHs 5.0 and 7.0 for different xylan/PEI mass ratios used.

xylan/PEI mass ratio	pH 5.0		pH 7.0	
	xylan/PEI charge ratio	Size distribution in nm (relative amount %)	xylan/PEI charge ratio	Size distribution in nm (relative amount %)
50/50	14/86	279 ± 34 (47.1%) 4504 ± 424 (52.9%)	24/76	216 ± 33 (49.9%) 4802 ± 320 (50.1%)
60/40	19/81	321 ± 48 (75.0%) 4850 ± 344 (25.0%)	32/68	270 ± 17 (55.8%) 4701 ± 463 (44.2%)
70/30	27/73	177 ± 59 (5.1%) 1548 ± 256 (91.6%) 4957 ± 416 (3.4%)	42/58	283 ± 65 (4.8%) 1214 ± 587 (73.2%) 3954 ± 519 (22.0%)

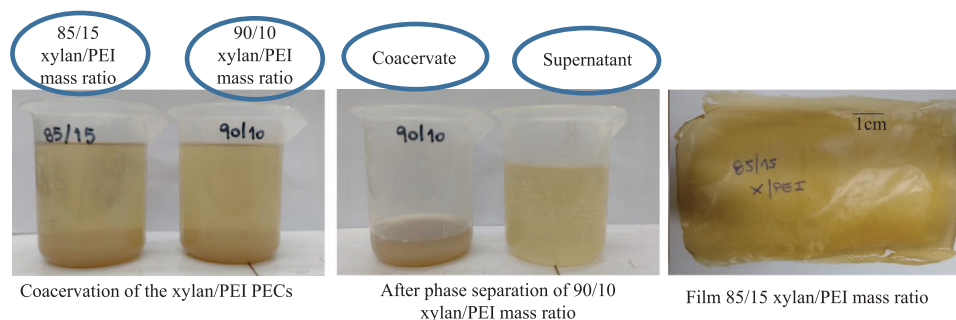


Figure 3. Coacervate and supernatant phase formed for xylan/PEI mass ratio of 85/15 and 90/10 at pH 5.0. At pH 7.0 the same effect was observed. Film formed using the coacervate of the PEC suspension of 85/15 xylan/PEI mass ratio.

Table 2 shows the size of the xylan/PEI PECs prepared at different mass ratios, at pHs 5.0 and 7.0. For each value reported, the respective volume percentage is shown in brackets.

When a relatively high amount of PEI was used (50/50 and 60/40), two size distribution modes were obtained and the value of the lower size was increased as the xylan content was increased. Furthermore, particle sizes at pH 7.0 were lower than at pH 5.0. In these cases, the total colloidal charge was cationic due to the higher ionic charge of PEI compared to that of xylan. Complexes appear to have been stabilized by these charges. Tiya-boonchai et al.,^[34] who evaluated the formation of nanoparticles of PEI and dextran sulfate, claimed that the existence of a sufficient quantity of this cationic polymer acts as a colloidal protective agent and prevents the coalescence of the nanoparticles.

At pH 7.0, PEI, which is the receptor polymer during PECs formation, had a slightly lower ionization degree, and this fact could explain the generation of smaller particles than at pH 5.0.

When a 70/30 xylan/PEI mass ratio was used, which was closer to the charge neutrality point, three size distribution modes were obtained for both pH values. In addition to the low and the high size modes, an intermediate fraction (1548 and 1214 nm at pH 5.0 and 7.0, respectively) was obtained as the main fraction of the size distribution. This could be attributed to the agglomeration of smaller particles, generating a large percentage (over 70%) of particles with higher size. At high xylan content, the particle size of the PECs could not be measured due to the coacervation phenomenon.

3.4. Coacervation Phenomenon

At pH 5.0, when PECs were formed using 85/15 and 90/10 xylan/PEI mass ratios, a coacervate formation (and a supernatant phase) was observed few hours after the suspension had been placed in the oven. Thus, the phase separation prior to oven drying was studied. Figure 3 shows the phase separation after one day of PEC formation at pH 5.0. The same phenomenon was observed when mass ratios of 80/20, 85/15 and 90/10 at pH 7.0 were analyzed. According to Figure 2, the xylan/PEI mass ratio in the neutrality point at pH 5.0 was 82/18, while at pH 7.0 it was 81/19. For low xylan addition (70 wt% or less), in the working range where an excess of positive charge attributed to PEI still exists, a stable colloidal suspension was obtained. Nevertheless, when the xylan content was increased close to the neutrality or to higher mass ratio, there was a decrease in stability and the coacervation process took place. The macroscopic coacervation phenomenon observed during PEC preparation showed in Figure 3, is directly related to the charges ratio shown in Table 1.

In the case of 90/10 xylan/PEI mass ratio at pH 7.0, exists a great excess of negative charges (74/26 charge ratio, shown in Table 1). When PECs are prepared, a coacervate phase is formed due to charge neutralization. It could be assumed that the large excess of negative charges contributed by xylan stabilizes the suspension and makes the coacervation phenomenon difficult. As result, more time is necessary to achieve the phase separation.

Table 3. Initial Xylan/PEI mass and charge ratios, and final ratios after phase separation. The amount of original percentage mass separated with the supernatant and the final composition of the films prepared from the coacervate are also reported.

pH	Initial xylan/PEI ratio		Final xylan and PEI content				
	xylan/PEI mass ratio	xylan/PEI charge ratio	Supernatant phase			Coacervate	
			Xylan (% of initial)	PEI (% of initial)	PECs fraction (% of total initial mass)	xylan/PEI mass ratio	xylan/PEI charge ratio
5	80/20	39/61	—	—	—	80/20	39/61
7	80/20	55/45	13.4%	31.4%	17.0%	83/17	60/40
5	85/15	47/53	9.5%	29.9%	12.6%	88/12	54/46
7	85/15	64/36	19.8%	40.0%	22.8%	88/12	69/31
5	90/10	59/41	11.1%	21.6%	12.2%	91/9	62/38
7	90/10	74/26	27.5%	60.8%	30.9%	94/6	83/17

Figure 3 also shows a film formed using the coacervate of the PECs suspension of 85/15 xylan/PEI mass ratio (initial). All films obtained were similar in appearance, homogeneous, translucent and brownish as can be observed for the film shown in the figure.

3.5. Xylan and PEI Content in Supernatant

When a coacervate was formed at both pH values, a translucent supernatant phase could be separated and its xylan and PEI content could be quantified. Table 3 shows the mass percentage of PEI and xylan quantified in the supernatant and the final mass and charge ratios in the film obtained using only the coacervate. It can be observed that a considerable part of both polymers, perhaps in the form of soluble complexes, remains in solution even though this supernatant appears translucent.

The table shows that in all cases the amount of PEI removed (relative to the total used) was higher than that of xylan, despite the higher presence of this latter component. The large amount of PEI separated could be associated with its high fraction of small molecular weight. Furthermore, the total mass (xylan plus PEI) separated was higher at pH 7.0 than at pH 5.0. Considering the charge ratios shown in Table 1, at pH 7.0 the excess of negative charge is higher than at pH 5.0. A greater amount of stabilized PECs is expected in solution, and they were removed with the supernatant.

For a 90/10 mass ratio, different effects were observed at each pH value. At pH 5.0, PEI had a higher ionization, and the final mass ratio of the film was close to that initially added. At pH 7.0, the amount of each polyelectrolyte quantified in the supernatant was larger.

As mentioned above, for this particular case (pH and mass ratio) a period of three days was needed to obtain a clear phase separation. This indicates that the coacervation and phase separation were less effective in this case.

Total polyelectrolytes separated in the supernatant were between 12.6% and 30.9% of the initial mass, and in all cases the liquid volume removed was about 60%. A considerable reduction of the energy required for film formation, with a small loss of the starting material, was achieved. Separation also allowed removing 60% of the initial salt content, which was corroborated

through conductivity measurements of the initial PECs solution and the supernatant (approximately 1000 $\mu\text{S}/\text{cm}$ for both).

In all cases, the final xylan/PEI mass ratio in the film was slightly higher than the initial one.

3.6. Film TGA

Figure 4a–c shows the results of the thermal gravimetric analysis for xylan/PEI films of 50/50 (where no phase separation was observed), the whole suspension of 85/15 and the coacervate of 85/15_{coa}, at pH 7.0, respectively.

For a 50/50 film, a weight loss of 9% was observed up to 150 °C, assigned to the water absorbed (moisture) in films. Two maximum degradation rates in the differential thermal analysis (DTA) were identified, one at 294.2 °C and the other at 408.5 °C. The decompositions in these regions were associated with xylan and PEI, respectively. De Carvalho et al.^[35] determined a decomposition temperature of 265.1 °C for sugarcane bagasse xylan (with a weight loss of 62.5%) and Shen et al.^[36] demonstrated the complete degradation of PEI between 300 °C and 400 °C. These results are in agreement with those reported in this work.

In the case of 85/15 and 85/15_{coa} the highest degradation occurred between 200 °C and 300 °C, which can be explained by the high content of xylan. Additionally, in the case of 85/15_{coa} there was a small increment in the amount of material decomposed at the temperature range mentioned, which agrees with the increment of xylan/PEI ratio in the coacervate (used to form the film), once the supernatant was removed.

According to these results, xylan/PEI films could be used in different applications, due to their good thermal stability under 200 °C.

3.7. Film Mechanical Properties

3.7.1. Tensile Testing

In Figure 5a,b, mechanical properties (tensile stress and strain at break, respectively) are shown as a function of the xylan mass percentage employed in the formulation, at both pH values. The

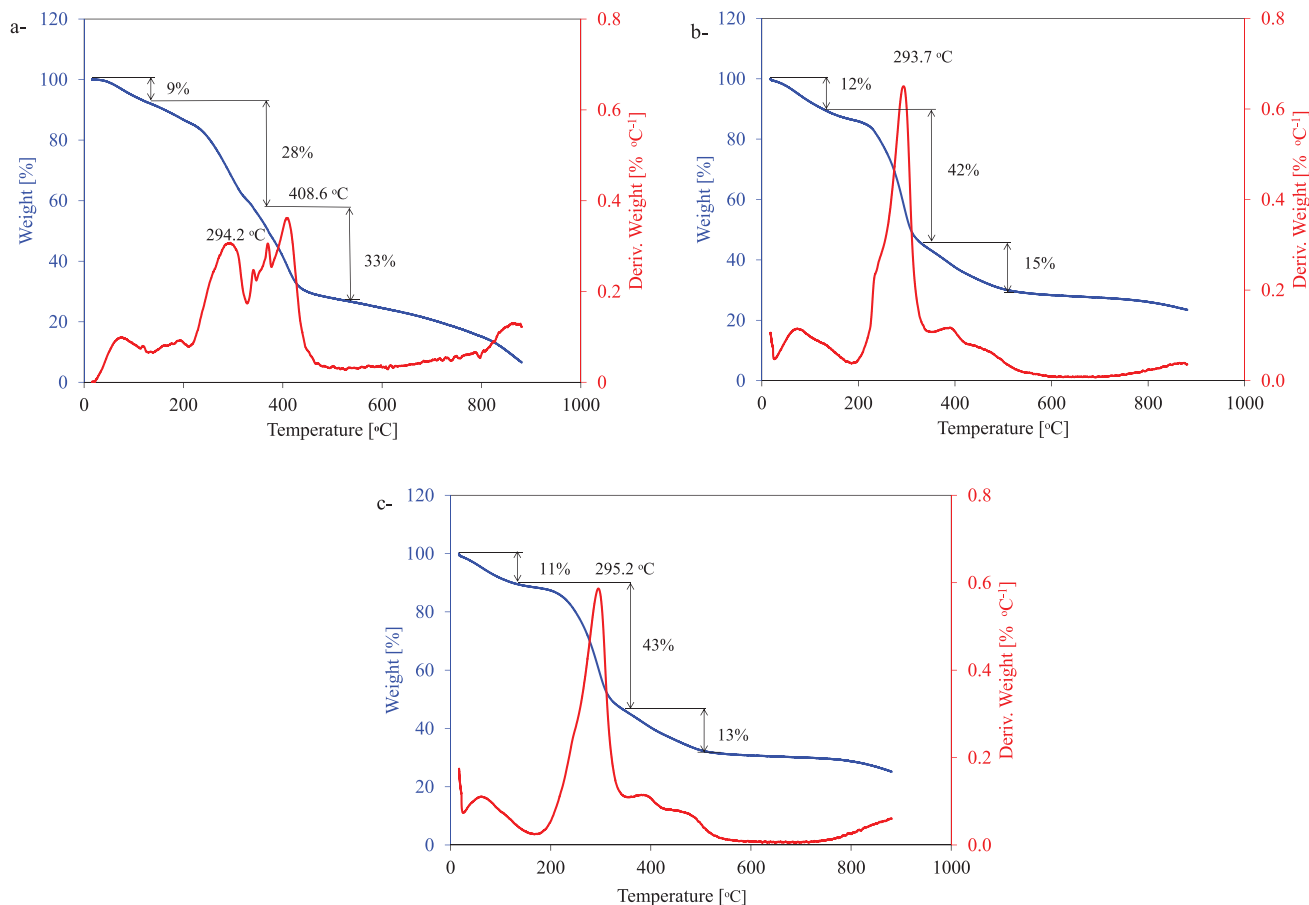


Figure 4. a) TGA and DTA of 50/50 xylan/PEI film, b) TGA and DTA of 85/15 xylan/PEI film, and c) TGA and DTA of 85/15_{coa} xylan/PEI film. Temperature at maximum degradation rate and percentage of material degraded are shown.

mass ratio corresponding to the charge neutrality is indicated for each pH, in plot (a).

At pH 5.0, there was a significantly increase in the stress at break when the xylan/PEI mass ratio increased from 80/20 to 85/15. Despite this small change in the composition, the coacervation of the PECs solution occurred when 85/15 was used, with a consequent phase separation (inside mold) during the drying process. Evidently, the particles association and the final coalescence of PECs were clearly favored, improving the conformation and, consequently, the stress at break. On the other hand, when the phase separation prior to film formation was made, a clear improvement of at least 35% in the stress at break at both pHs was observed. For instance, at pH 5.0 and 85/15 mass ratio, the strength was increased from 18.7 to 25.3 MPa, but the strain at break did not change. This improvement in strength can be ascribed to two reasons: a) the higher xylan/PEI ratio of the coacervate with respect to the whole suspension which was shown in Table 3, and b) the removal of salts that supernatant separation implies. The strain at break was decreased as the xylan content in the films was increased. A higher PEI content value led to a remarkable high strain value, but the stress at break was low.

The strain at break at pH 7.0, showed a similar effect. Additionally, the increment in the stress at break occurred when the mass rate composition changed from 70/30 to 80/20. Although

the charge neutrality point was 81/19, the coacervation started at a lower mass ratio. At this pH, there was no difference in the stress at break between the 90/10_{coa} and 90/10 without supernatant removal. As mentioned before, for this case, phase separation was not very effective, and approximately 31% of the initial PECs was removed (a higher amount than for the rest of conditions). We can consider that under these conditions, the beneficial effects of salt removal and xylan/PEI mass ratio increment were counteracted by the high amount of material removed by the separation of the supernatant.

The highest stress at break of the film was obtained for 85/15_{coa} at pH 7.0 (37.2 MPa), which represents an increase of 61% with respect to 85/15 without supernatant removal.

3.8. DMTA

Figure 6a,b shows the DMTA analysis (storage modulus (E'), loss modulus (E''), and $\tan \delta$) for films prepared with xylan/PEI mass ratio of 50/50, and 85/15 with and without phase separation, respectively, at pH 7.0. For each case, the maximum value of $\tan \delta$ reported was associated with the T_g (glass transition temperature) of the material, and these were 152.3 °C (50/50), 219.8 °C (85/15) and 235.0 °C (85/15_{coa}). It can be clearly observed that

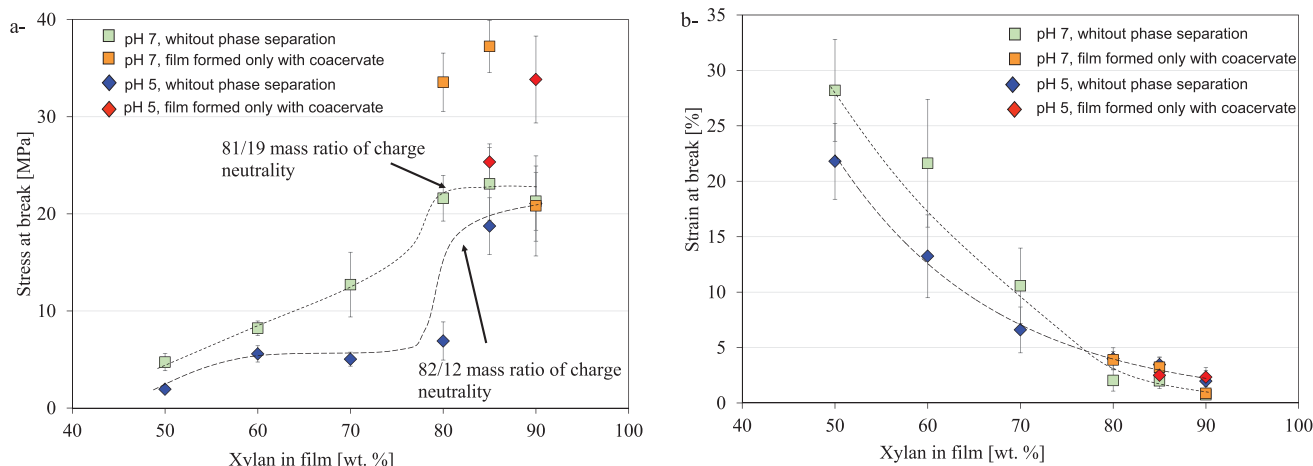


Figure 5. Tensile properties as a function of xylan percentage employed to prepare films at pHs 5.0 and 7.0 using the whole volume or just the coacervate. a) Stress at break (mass ratios corresponding to the charge neutrality are indicated). b) Strain at break.

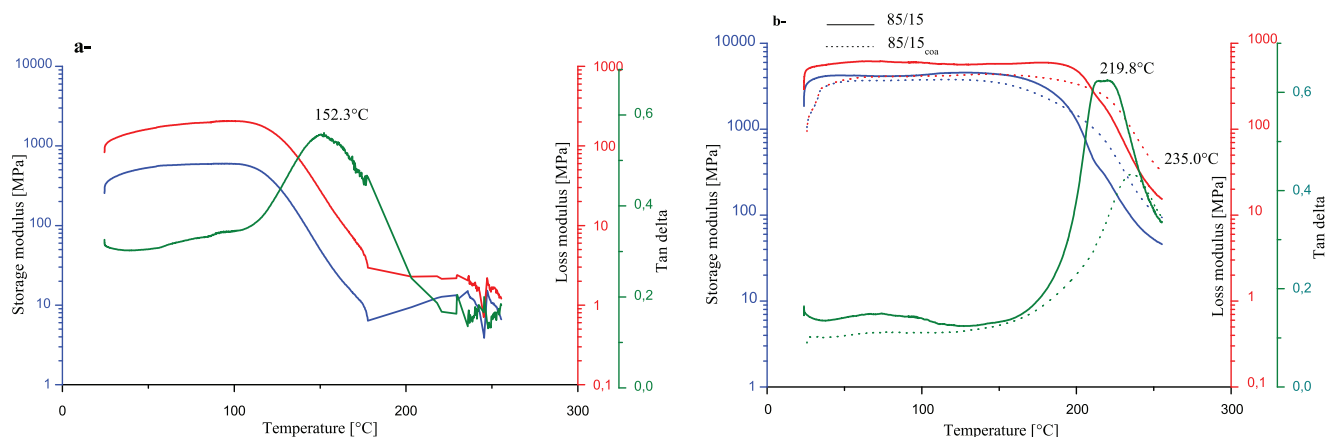


Figure 6. a) DMTA of xylan/PEI 50/50 film and b) DMTA of xylan/PEI 85/15 and 85/15_{coa} films. In both figures T_g is indicated.

T_g increased as the content of xylan increased. When the supernatant was removed in the 85/15 ratio formulation, the final xylan/PEI ratio in the film was 88/12, which could be associated with the small increment of the 85/15_{coa} T_g with respect to the 85/15.

Yang et al.^[37] reported a T_g of -25.6 °C for PEI and de Carvalho et al.^[35] reported a T_g of 121.5 °C for xylan extracted from sugarcane bagasse. Both results were determined by differential scanning calorimetry (DSC). Gröndahl et al.^[38] did not observe any T_g for aspen glucuronoxylan, which indicates that it is not always possible to identify this parameter. In this paper, it is shown that the combination of these two polymers allows to obtain films with acceptable mechanical properties. They can be considered as thermoplastic since both moduli (loss and the storage) are favorably reduced at a temperature that is lower than the thermal decomposition range. This thermoplastic property can be useful for the application of thermo-compression to films in order to give them a desired shape.

A clear difference between the storage modulus (E) of 50/50 and 85/15 films (with and without phase separation) can be noticed. While the former only reached values lower than 700 MPa,

Table 4. Water vapor transmission rate of different biobased xylan films.

Author	Mass ratio and component	WVTR [$10^{-3} \text{ g s}^{-1} \text{ m}^{-2}$]
This work	50/50 xylan/PEI	7.08 ± 0.01
This work	85/15 xylan/PEI	6.71 ± 0.51
This work	85/15 _{coa} xylan/PEI	7.74 ± 0.43
Solier et al. ^[10]	70/30 xylan/chitosan	5.2 ± 0.2
	80/20 xylan/chitosan	5.9 ± 0.2
Schnell et al. ^[40]	70/30 xylan/chitosan	5.9 ± 0.2

the 85/15 showed values of up to 5000 MPa. It is worth mentioning that this higher stiffness of the 85/15 films could be clearly perceived by touch.

3.9. Film WVTR

Table 4 shows the WVTR values obtained for the films formed with xylan/PEI 50/50, 85/15 and 85/15_{coa} mass ratios, at pH 7.0.



Figure 7. Hot-compression molding of the xylan/PEI of 50/50 mass ratio. The coin used to mark that the film is also shown. Image of coin: Copyright 2016, Banco Central de la República Argentina.

Results of xylan/chitosan films found in previous studies, using xylan from different raw materials, are also reported for comparison.

The films analyzed corresponded to a PEC solution with a total positive charge (50/50) and a PEC solution with a total negative charge (85/15) due to the excess of xylan. The values reported for these cases do not differ significantly from each other. They are similar to those found for xylan/chitosan films, and they are within the magnitude order for films formed from polysaccharides.

It can be concluded that the presence of PEI, which is a synthetic polymer, did not affect the WVTR, and this particular characteristic of the films can be attributed mostly to xylan.

Polysaccharide films could find application for fresh food products, such as vegetables, where it is important to avoid dehydration. These materials have good surface adhesion and they have generally good gas barrier properties.^[39] Particularly, the low oxygen permeability of xylan^[40,41] and PEI^[16,37] has been demonstrated. As a result, the useful life of the product can be improved without creating anaerobic conditions unlike lipid-based films.^[42]

3.10. Film Hot-Compression Molding

Figure 7 shows the brand molded into the film and the coin employed to do it. A temperature over the T_g of the film (152.3 °C) was selected. In this figure, it can be observed that all the details of the coin could be marked onto the film. According to TGA and DTA analysis, at 160 °C there is no appreciable degradation of material. For other xylan/PEI mass ratios, a higher temperature would be necessary to mark the film, although a mass loss can be expected due to some degradation. Native arabinoxylan does not flow at temperatures much lower than its degradation temperature.^[11] Nevertheless, the proper combination of this xylan with PEI could be used to obtain thermoplastic films. This possibility represents a great progress in the field of biobased hemicelluloses films. As was mentioned before, all films, irrespective of mass ratio, were similar in appearance. The hot compression molding did not modify the color, transparency and homogeneity of the film.

4. Conclusions

Films can be obtained through the controlled formation of polyelectrolyte complexes (PECs), using xylan from sugar-cane bagasse as a main component, and a low-molecular-weight highly branched polyethyleneimine. Here, it is shown that a wide range of mass ratios can be used.

Charge density of both weak polyelectrolytes is affected by pH. The ionic interaction between these opposite-charge polyelectrolytes showed a neutrality mass ratio similar for pH 5.0 and pH 7.0, which was 82/18 and 81/19, respectively. This interaction is useful to predict the coacervation phenomenon. PEC size is influenced by mass ratio and pH and, for high xylan content, it is possible to separate a coacervate from a diluted liquid phase.

The mechanical properties of the film were strongly dependent on xylan content. The strain at break decreased, while the stress at break increased when the xylan content was increased. For a 50/50 mass ratio, a stress at break of 2 MPa and 25% elongation were obtained, and for a mass ratio of 90/10 a stress at break of 21 MPa and a strain at break of approximately 2%, were obtained for both pH values.

Except for 90/10 at pH 7.0, the phase separation and film formation using only the coacervate clearly improved the stress at break (up to 37 MPa for 85/15_{coa} mass ratio). Approximately 60% of the original volume was separated as supernatant, and thus the same percentage of salts was removed. Furthermore, the energy necessary to obtain the film is reduced. This methodology enhances the industrial scalability of these materials.

The thermoplastic property for a film containing 50% of xylan could be verified. The transition temperature (T_g) increased when the xylan content was increased, from a value of 152 °C, temperature for which thermal degradation does not exist, to 220 °C for which thermal degradation is evidenced. On the other hand, the stiffness, revealed by the storage modulus (E'), was increased ten times when the xylan content was increased from 50% to 85%.

The satisfactory value of water vapor transmission rate was not significantly affected by film composition.

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Conflict of Interest

The authors declare no conflict of interest.

Data Availability Statement

Research data are not shared.

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